



รายงานวิจัยฉบับสมบูรณ์

โครงการ ศักยภาพของโลหะราคาถูกในการทดแทนโลหะมีตระกูลที่บรรจุลงบน
ตัวเร่งปฏิกิริยาประเภทซีโอไลต์สำหรับกระบวนการไพโรไลซิส

รองศาสตราจารย์ ดร. ศิริรัตน์ จิตการคำ และคณะ

มิถุนายน 2559

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วิทยาลัยปิโตรเลียมและปิโตรเคมี

จุฬาลงกรณ์มหาวิทยาลัย

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย และจุฬาลงกรณ์มหาวิทยาลัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกว. และจุฬาลงกรณ์มหาวิทยาลัย ไม่จำเป็นต้องเห็นด้วยเสมอไป)

กิติกรรมประกาศ

คณะผู้วิจัย ซึ่งประกอบไปด้วย ดิฉัน รองศาสตราจารย์ ดร. ศิริรัตน์ จิตการคำ หัวหน้าโครงการ และทีมนิสิตผู้ช่วยวิจัย ขอขอบพระคุณแหล่งทุนสนับสนุนการวิจัยในครั้งนี้ทุกแหล่ง ที่ได้สนับสนุนเงินทุนวิจัยแก่คณะผู้วิจัยในการทำงานวิจัย โดยมี สำนักงานกองทุนสนับสนุนการวิจัย (สกว.) ผู้สนับสนุนทุนพัฒนานักวิจัย (RSA5680021) เรื่อง “ศักยภาพของโลหะราคาถูกในการทดแทนโลหะมีตระกูลที่บรรจุลงบนตัวเร่งปฏิกิริยาประเภทซีโอไลต์สำหรับกระบวนการไพโรไลซิส” เป็นแหล่งทุนหลัก ขอขอบพระคุณ สำนักงานคณะกรรมการการอุดมศึกษา (สกอ.) ศูนย์ความเป็นเลิศแห่งชาติด้านปิโตรเคมีและวัสดุ วิทยาลัยปิโตรเลียมและปิโตรเคมี และจุฬาลงกรณ์มหาวิทยาลัย ซึ่งสนับสนุนทุนวิจัยร่วมและการสนับสนุนในรูปแบบต่างๆ

ดิฉันขอขอบคุณ นิสิตผู้ช่วยวิจัยปริญญาโทและเอกในความดูแลทุกคน ทั้งในอดีตและปัจจุบัน ที่ได้ช่วยเหลือและให้ข้อมูลในเรื่องต่างๆ รวมทั้งให้กำลังใจและกำลังกายในการสนับสนุนการทำงานวิจัยของดิฉันในทุกด้าน โดยเฉพาะนิสิตผู้ช่วยวิจัยในโครงการนี้ ซึ่งมีรายนามดังต่อไปนี้ น.ส. ภาสณิ แสงอารยะกุล นายโยธิน ปิยะวงศ์ภิญโญ นายสกลพัฒน์ พัทธ์ธีรตันโยธิน นายสุทธิพล หมั่นพล นายฤทธิชัย ยุวพรพานิชย์ นายวิศรุตม์ นามโชติ น.ส. สุพัตรา เส่งเอียด น.ส. ศิรินทิพย์ ตรงยงค์ และนายณฐกร รุจิราวรุดิ ที่มีความขยันขันแข็งตั้งใจทำวิจัยภายใต้โครงการฯ และร่วมเขียนผลงานวิจัยตีพิมพ์ ขอขอบคุณคณาจารย์และเจ้าหน้าที่ทุกท่านในวิทยาลัยปิโตรเลียมและปิโตรเคมี ที่มีส่วนได้ช่วยเหลือดิฉันและนิสิตผู้ช่วยวิจัยเป็นอย่างดีเสมอมา

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ในงานวิจัยเรื่องไพโรไลซิสยางรถยนต์หมดสภาพก่อนหน้า คณะวิจัยได้ทำการศึกษาความเฉพาะเจาะจงของตัวเร่งปฏิกิริยาที่ประกอบไปด้วยโลหะมีตระกูล 6 ชนิดบนตัวรองรับ 3 ประเภท ในการผลิตก๊าซ น้ำมัน และสารปิโตรเคมีที่มีมูลค่า ซึ่งการทดลองครั้งนั้นพบว่า โลหะมีตระกูลทุกตัวสามารถเพิ่มการผลิตสารที่มีมูลค่าดังกล่าวได้ แต่เนื่องจากโลหะมีตระกูลเกือบทุกตัวมีราคาค่อนข้างแพง จึงทำให้ไม่คุ้มค่าที่จะนำไปใช้ในโรงงานผลิตน้ำมันจากยางรถยนต์ที่มีขนาดเล็กและปานกลาง ในงานวิจัยนี้ จึงนำโลหะไม่มีตระกูล 5 ชนิด คือ คอปเปอร์ ซิงค์ เหล็ก โคบอลต์ และนิกเกิล มาทดลองใช้บนตัวรองรับประเภทเดียวกัน เพื่อใช้ทดแทนโลหะมีตระกูล การทดลองพบว่า โลหะไม่มีตระกูลเหล่านี้ มีความสามารถ 2 อย่างคล้ายกัน คือช่วยเพิ่มสารปิโตรเคมีในน้ำมันและลดปริมาณกำมะถันในน้ำมันได้คล้ายๆ กัน และสามารถใช้ทดแทนโลหะมีตระกูลได้ในหลายกรณี กล่าวคือ เหล็ก โคบอลต์ และซิงค์มีความโดดเด่นด้านผลิตเนฟธาเบา ซึ่งสามารถใช้ทดแทนโลหะแพลตินัม พัลเลเดียม หรือรูทีเนียมได้ นิกเกิลสามารถลดปริมาณโพลีโรมาติกส์ในน้ำมัน ซึ่งใช้ทดแทนโลหะแพลตินัมหรือรูทีเนียมได้ ในขณะที่คอปเปอร์บนเอชเมอร์สามารถทดแทนโลหะเงิน โรเดียม และรีเนียมในการผลิตก๊าซหุงต้ม โคบอลต์มีความโดดเด่นด้านการผลิตโอเลฟินส์เบาซึ่งสามารถใช้ทดแทนโลหะรูทีเนียม เงิน โรเดียม หรือรีเนียม นอกจากนี้โคบอลต์ยังมีความสามารถในการผลิตมิกซ์ซีโพร ซึ่งคล้ายกับแพลทินัม เงิน หรือโรเดียม โลหะไม่มีตระกูลทุกตัวที่นำมาทดสอบมีความโดดเด่นด้านการผลิตสารปิโตรเคมี ซึ่งสามารถใช้ทดแทนโลหะรูทีเนียม โรเดียมและรีเนียมได้ นอกเหนือไปจากนั้น คอปเปอร์ ซิงค์ นิกเกิล นิกเกิลโมลิบดีนัม และนิกเกิลโมลิบดีนัมซัลไฟด์มีความโดดเด่นด้านการลดสารกำมะถันในน้ำมัน ซึ่งสามารถใช้ทดแทนโลหะโรเดียมหรือเงินได้ ทั้งนี้ พึงระลึกว่าประสิทธิภาพของโลหะต่างๆ ขึ้นอยู่กับตัวรองรับที่ใช้ในปริมาณหนึ่งด้วย

คำหลัก: ตัวเร่งปฏิกิริยา; ยางรถยนต์หมดสภาพ; ไพโรไลซิส; น้ำมันจากยางรถยนต์; สารปิโตรเคมี.

Abstract

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Project Title : Potential of Non-Noble Metals as Substitutes of Noble Metals
Supported on Zeolites as Catalysts for Waste Tire Pyrolysis
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In our previous work on waste tire pyrolysis, the selectivity of various catalysts composed of six noble metals and three types of supports were investigated toward the production of various products such as valuable gases, oils, and some petrochemicals. Back then, it was found that most of noble metal-supported catalysts improved the production of such products. Due to a high price of most of the noble metals, it is difficult in economically applying these catalysts in a small- and medium-scale waste tire-pyrolysis plant. In order to develop a cheaper catalyst, non-noble metals (Cu, Zn, Co, Fe, and Ni) were used in this work as alternative promoters on some zeolites with the aims of producing oil and gaseous products at a similar quantity and quality as using a noble metal catalyst. As a result, the non-noble metals were found to give similar activities among themselves; that are, they can outstandingly produce valuable petrochemicals and remove sulfur in oil. They can also be used to substitute noble-metals in various aspects. Fe, Co, and Zn were outstanding in light naphtha production, which can substitute Pt, Pd, and/or Ru. Ni can reduce poly-aromatics in oil, potentially being able to substitute Pt and/or Ru whereas Cu only on HMOR can substitute Ag, Rh, and/or Re in producing cooking gases. Co can substitute Ru, Ag, Rh, and/or Re for light olefins production, and can substitute Pt, Ag, and/or Rh for producing mixed C4s. All test non-noble metals have outstanding activity on enhancing valuable petrochemicals in oil, which can substitute Ru, Rh, and/or Re. Moreover, Cu, Zn, Ni, NiMo, and NiMoS are dominant on removal of sulfur from oil, which can replace Rh and/or Ag. However, it shall be noted that the activities depended on the supports used as well to some extent.

Keywords: Catalysts; Waste tire; Pyrolysis; Tire-derived oil; Petrochemicals



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Chapter 1

Executive Summary

จากการสำรวจพื้นที่ภาคกลางของประเทศไทยในระยะรัศมี 400 กิโลเมตรจากกรุงเทพฯ พบว่ามีจำนวนยางรถยนต์หมดสภาพถูกทิ้งประมาณ 350,000 คันต่อปี และประมาณ 40% ของยางที่ถูกทิ้งนั้น ไม่พบว่าถูกนำไปใช้ประโยชน์ใดๆ (MCS, 2552; Jitkarnka, S. and Permsantitham, W., 2009) และ 60% ที่เหลือนั้นถูกนำไปใช้เป็นยางรีไซเคิลบ้าง ใช้เป็นเชื้อเพลิงแข็งในโรงงานอุตสาหกรรมและใช้ในภาคการเกษตร ใช้เป็นยางกันกระแทก ใช้เป็นวัตถุดิบในการผลิตรองเท้าและถังขยะ ใช้ในโรงงานไพโรไลซิส และยังมีบางส่วนถูกส่งออกไปขายต่างประเทศอีกด้วย สิ่งที่ยังตามมาคือ องค์กรบางองค์กรในประเทศไทยไม่ถือว่ายางรถยนต์หมดสภาพนั้นเป็น “ขยะ” เพราะมันยังสามารถนำมาใช้ประโยชน์ได้อีกนั่นเอง กระบวนการไพโรไลซิสยางรถยนต์หมดสภาพนั้นได้รับความสนใจในประเทศอย่างกว้างขวางติดต่อกันเป็นระยะเวลาหนึ่งแล้ว โดยหลักการทั่วไป กระบวนการไพโรไลซิสก็คือ กระบวนการที่ใช้ในการย่อยสลายสารต่างๆ ด้วยความร้อนให้มีขนาดโมเลกุลที่เล็กลงในบรรยากาศที่ปราศจากก๊าซออกซิเจนหรือมีออกซิเจนน้อยที่สุด ผลผลิตที่จากกระบวนการไพโรไลซิสนั้นเป็นน้ำมันและก๊าซชนิดต่างๆ และมีของแข็งที่เหลือจากกระบวนการ ซึ่งของแข็งนี้สามารถนำมาผลิตเป็นเป็นคาร์บอนแบล็คเกรดต่ำ หรือใช้เป็นเชื้อเพลิง หรือสามารถนำมาผ่านกระบวนการเพื่อผลิตเป็นถ่านกัมมันต์ได้ (Williams and Brindle, 2003) ส่วนก๊าซที่ได้นั้นประกอบไปด้วยไฮโดรคาร์บอนที่มีคาร์บอน 1-5 ตัวเป็นองค์ประกอบ มีก๊าซไฮโดรเจนในปริมาณที่สูงโดยปริมาตร (Barbooti et al, 2004) และมีก๊าซซัลเฟอร์ไดออกไซด์ในปริมาณที่ต่ำ (Berrueco et al., 2005) ส่วนน้ำมันที่ได้นั้นเป็นสารผสมของไฮโดรคาร์บอนหลายองค์ประกอบ โดยมีสารประกอบอะโรมาติกส์อยู่ในปริมาณที่สูง (Cunliffe and Williams, 1998)

น้ำมันที่ได้จากยางรถยนต์นั้นถูกระบุว่ามีค่าความร้อนสูงถึง 41-44 เมกะจูลต่อกิโลกรัม (Cunliffe and Williams, 1998) นอกเหนือไปจากนั้นคุณลักษณะของมันยังคล้ายคลึงกันในระดับหนึ่งกับปิโตรเลียมแนฟทาที่มีขายในเชิงพาณิชย์ (Benellal et al., 1995) เมื่อน้ำมันถูกใช้ผสมกับน้ำมันดีเซลเพื่อใช้ในเครื่องยนต์ดีเซล พบว่าอัตราส่วนการเติมสูงสุด 70% ยังคงทำให้เครื่องยนต์ทำงานได้ดีอยู่ (Murugan et al., 2009) แต่อย่างไรก็ตามยังมีการปลดปล่อยควัน ไฮโดรคาร์บอน และคาร์บอนมอนอกไซด์ในปริมาณที่สูงอยู่ และยังทำให้เกิดการเกาะตัวของน้ำมันเหนียวที่หัวฉีดและเครื่องยนต์ ซึ่งเชื่อกันว่าเป็นผลมาจากการที่น้ำมันมีสารประกอบอะโรมาติกส์ในปริมาณที่สูง โดยเฉพาะสารประกอบอะโรมาติกส์ประเภทหลายวง (Murugan et al., 2009) นอกเหนือไปจากนั้น ยังมีปริมาณซัลเฟอร์ที่อยู่ในรูปของไฮโอฟินส์ เบโซไฮโอฟินส์ และอนุพันธ์ของทั้งสองอยู่ใน

ปริมาณที่สูงพอสมควร (Williams and Bottrill, 1995; Pakdel et al., 2001) ซึ่งจำกัดการใช้งานในเครื่องยนต์ เพราะเหตุว่าประสิทธิภาพของเครื่องยนต์จะลดต่ำลง และมีการปลดปล่อยซัลเฟอร์ไดออกไซด์ในปริมาณที่สูงอยู่ อย่างไรก็ตามน้ำมันที่ได้จากยางรถยนต์ยังมีสารปิโตรเคมีที่มีประโยชน์เป็นองค์ประกอบ เช่น สารประกอบโมโนอะโรมาติกส์ (เบนซีน โทลูอิน และไซลีนส์) ที่สามารถใช้เป็นสารตั้งต้นในอุตสาหกรรมปิโตรเคมีได้ ส่วนก๊าซที่ได้จากการไพโรไลซิสยางรถยนต์นั้น ยังประกอบไปด้วยก๊าซที่มีความสำคัญในปิโตรเคมีหลายประเภท เช่น เอทิลีน โพรพิลีน หรือแม้แต่ก๊าซหุงต้ม ดังนั้น จึงถือได้ว่ากระบวนการไพโรไลซิสยางรถยนต์หมดสภาพนั้นเป็นกระบวนการทางเลือกอีกทางหนึ่งในการผลิตสารปิโตรเคมีจากแหล่งวัตถุดิบที่ไม่ใช่ปิโตรเลียม

มีบทความทางวิทยาศาสตร์จำนวนมากที่รายงานผลการใช้ตัวเร่งปฏิกิริยาในกระบวนการไพโรไลซิสยางรถยนต์ โดยเฉพาะตัวเร่งปฏิกิริยาประเภทกรด ซึ่งพบว่าน้ำมันที่ได้จากกระบวนการนั้นมีปริมาณและคุณภาพที่ดีขึ้น ก่อนหน้านี้ด้วยเงินทุนวิจัยร่วมที่ได้จากสำนักงานกองทุนสนับสนุนการวิจัยและสำนักงานคณะกรรมการการอุดมศึกษา กลุ่มวิจัยของเราได้ประสบความสำเร็จในการศึกษาผลของโลหะมีตระกูล (Pt, Ru, Rh, Pd, Ag, and Re) บนตัวเร่งหลากหลายประเภท (HBETA, HMOR, HY, KL, SBA-1, MCM-41, and MCM-48) ที่มีต่อปริมาณและธรรมชาติของผลิตภัณฑ์ที่ได้จากกระบวนการไพโรไลซิสยางรถยนต์ ความสามารถของตัวเร่งปฏิกิริยาและผลของตัวเร่งสามารถแยกออกได้เป็น 4 กลุ่ม กล่าวคือ (ก) ผลของตัวรองรับที่มีคุณสมบัติเป็นกรด (ข) ผลของโลหะมีตระกูลบนตัวรองรับที่มีคุณสมบัติเป็นกรด (ค) ผลของโลหะมีตระกูลบนตัวรองรับที่มีคุณสมบัติเป็นเบส และ (ง) ผลของตัวรองรับที่มีรูพรุนระดับมีโซ และอิทธิพลของรูธินีเยม ซึ่งสรุปโดยย่อจากผลการทดลอง พบว่า โลหะมีตระกูลแทบทุกตัว โดยเฉพาะ Pt และ Pd เมื่อบรรจุลงบนซีโอไลท์แล้วพบว่าช่วยผลิตน้ำมันเบาได้มากขึ้น และยังช่วยลดปริมาณสารประกอบโพลาร์อะโรมาติกส์และสารแอสฟัลทีนในน้ำมันได้อีกด้วย ส่วนตัวเร่งปฏิกิริยาประเภทรูธินีเยมนั้น สามารถช่วยเพิ่มผลผลิตของสารโอเลฟินส์ได้อย่างมาก โดยเฉพาะอย่างยิ่งเมื่อบรรจุลงบนตัวรองรับ HMOR และ MCMs ตัวเร่งที่มีโลหะเงินบรรจุอยู่นั้นถูกพบว่ามีศักยภาพในการผลิตก๊าซหุงต้มได้อย่างเฉพาะเจาะจง นอกจากนี้ ยังพบว่าตัวเร่งปฏิกิริยาบางชนิด เช่น ชนิดที่มีโรเดียมและรูธินีเยมบรรจุอยู่นั้น สามารถผลิตสารประกอบโมโนอะโรมาติกส์ในน้ำมันได้อย่างเฉพาะเจาะจงมากกว่าตัวอื่นๆ เป็นต้น อย่างไรก็ตามโลหะมีตระกูลแทบจะทุกตัวนี้มีราคาแพง ทำให้ยากที่จะนำไปใช้ในอุตสาหกรรมขนาดเล็กและกลาง อย่างเช่น โรงงานไพโรไลซิสยางรถยนต์หมดสภาพ เป็นต้น วิธีการหนึ่งที่จะพัฒนาตัวเร่งปฏิกิริยาที่มีราคาถูกลง แต่ยังคงประสิทธิภาพในระดับเดิมไว้นั้นก็คือ การใช้โลหะที่ไม่ใช่โลหะมีตระกูลที่มีศักยภาพใกล้เคียงกัน ซึ่งถึงแม้ว่าอาจจะต้องใช้ในปริมาณที่สูงขึ้นกว่าเดิม แต่ราคาสุทธินั้นอาจจะถูกกว่าการใช้โลหะมีตระกูลในปริมาณน้อยกว่า

ตัวเร่งปฏิกิริยาที่เรียกว่า ตัวเร่งสองหน้าที่ (Bifunctional catalysts) นั้นประกอบไปด้วย ส่วนที่ทำหน้าที่เป็นโลหะ และส่วนที่ทำหน้าที่เป็นตัวเร่งประเภทกรด โลหะที่ใช้ในตัวเร่งปฏิกิริยาประเภทนี้มักมีคุณสมบัติที่ต้องการดังนี้คือ (ก) ไฮโดรจิเนชัน (ข) ไฮโดรจิโนไลซิส หรือการแตกพันธะระหว่างคาร์บอนกับคาร์บอน (ค) คุณสมบัติในการเปิดวงเบนซีน และบางชนิดยังมี (ง) คุณสมบัติในการกำจัดกำมะถันออกจากโมเลกุลของไฮโดรคาร์บอน ซึ่งคุณสมบัติเหล่านี้เองที่ทำให้โลหะมีตระกูลมีประสิทธิภาพในการใช้เป็นตัวเร่งบนตัวรองรับ โดยเฉพาะอย่างยิ่งในการเป็นตัวเร่งปฏิกิริยาในกระบวนการไพโรไลซิส แต่อย่างไรก็ตามข้อเสียของโลหะมีตระกูลนอกเหนือจากในเรื่องของราคาแพงแล้วก็คือ มีความต้านทานต่อสารกำมะถันค่อนข้างต่ำ ทำให้ไม่สามารถที่จะนำมาใช้กับสารป้อนที่มีกำมะถันสูง อย่างยางรถยนต์ได้ โลหะประเภทที่ไม่ใช่โลหะมีตระกูลนั้น ถูกพบว่ามีคุณสมบัติที่คล้ายกับโลหะมีตระกูล แต่มักจะมีความสามารถที่ต่ำกว่าเมื่อเทียบกับโลหะมีตระกูลในปริมาณที่เท่ากัน เช่น นิกเกิลหรือโคบอลต์ ก็ถูกพบว่ามีคุณสมบัติในการไฮโดรจิเนชัน (Pedrosa et al., 2006a; Álvarez-Rodríguez et al., 2008a) ไอโซเมโรเซชัน (Fúnez et al., 2008; Eswaramoorthi et al., 2003), ไฮโดรจิโนไลซิส (Escobar et al., 2008; Kaliya and Kogan, 2005; Pedrosa et al., 2006a) และมีคุณสมบัติในการกำจัดกำมะถันออกจากโมเลกุลของไฮโดรคาร์บอน (Crisafulli et al., 2002; Navarro et al., 2009; Espinosa et al., 2011) ทองแดงถูกพบว่ามีคุณสมบัติในการเปิดวงเบนซีน (Fesi et al., 1999) และช่วยในปฏิกิริยาอีพอกไซด์ได้ (Álvarez-Rodríguez et al., 2008b) แต่อย่างไรก็ตามจะไม่มีผลงานชิ้นใดที่พิมพ์เกี่ยวกับการใช้โลหะที่ไม่ใช่โลหะมีตระกูลเป็นตัวเร่งในปฏิกิริยาไพโรไลซิสยางรถยนต์เลย อีกทั้ง ยังไม่มีใครเคยทดสอบชนิดและปริมาณสารประกอบกำมะถันที่เปลี่ยนไปในน้ำมันเมื่อใช้ตัวเร่งปฏิกิริยาดังกล่าวอีกด้วย ดังนั้น ด้วยเหตุผลข้างต้น โลหะทรานสิชันดังกล่าวจึงน่าจะใช้ทดแทนโลหะมีตระกูลในกระบวนการไพโรไลซิสยางรถยนต์ได้ เพราะมีคุณสมบัติที่ต้องการและจำเป็นต่อการปรับปรุงคุณสมบัติของผลิตภัณฑ์ที่ได้จากการไพโรไลซิสยางรถยนต์ แต่ทั้งนี้จำเป็นต้องมีการทดสอบเพื่อค้นหาว่าโลหะแต่ละชนิดนั้นสามารถใช้ทดแทนโลหะมีตระกูลชนิดใดได้บ้าง และต้องใช้ในปริมาณเท่าใดจึงจะมีคุณสมบัติเทียบเคียงได้ นอกจากนี้ยังต้องทดสอบว่า โลหะนั้นเหมาะที่จะใช้กับสารป้อนที่มีกำมะถันสูง อย่างยางรถยนต์หมดสภาพ และใช้ได้กับน้ำมันที่มีปริมาณอะโรมาติกส์สูงอย่างน้ำมันจากยางรถยนต์หรือไม่ ซึ่งจำเป็นจะต้องมีการวิเคราะห์องค์ประกอบเชิงโมเลกุลของน้ำมันและประเภทของสารประกอบกำมะถันในเชิงลึกด้วย ด้วยหลักการและความคิดดังกล่าว จึงเป็นที่มาของโครงการนี้

วัตถุประสงค์ของโครงการนี้ คือ เพื่อศึกษาความเฉพาะเจาะจงและศักยภาพของโลหะที่ไม่ใช่โลหะมีตระกูลชนิดต่างๆ ในการใช้เป็นตัวเร่งปฏิกิริยาทางเลือก สำหรับกระบวนการไพโรไลซิสยางรถยนต์หมดสภาพ และวิเคราะห์ตัวเร่งดังกล่าวเพื่อศึกษาว่าทำไมตัวเร่งปฏิกิริยาดังกล่าวข้างต้น จึงมีความเฉพาะเจาะจงในการผลิตผลิตภัณฑ์ต่างๆ ได้ และเปรียบเทียบความเฉพาะเจาะจงในการผลิตผลิตภัณฑ์ และ/หรือคุณภาพของผลิตภัณฑ์ ของโลหะดังกล่าวกับโลหะมีตระกูลที่ได้เคยทดสอบไว้แล้ว ในการศึกษาปีแรก ทางคณะผู้ดำเนินการวิจัยได้ทำการวิเคราะห์ผลการศึกษาตัวเร่งประเภทโลหะมีตระกูลจากรายงานครั้งที่แล้ว (ทุนรุ่นกลางฯ) และสังเคราะห์เกณฑ์ในการเปรียบเทียบกับตัวเร่งประเภทโลหะที่ไม่ใช่โลหะมีตระกูลกับโลหะมีตระกูลจากรายงานครั้งก่อน โดยพบว่า จะทำการเปรียบเทียบตัวเร่งปฏิกิริยาทั้งสองชุดในประเด็นดังต่อไปนี้ ความสามารถในการ (1) ผลิตเนฟธาเบา (2) ลดสารโพลีอะโรมาติกส์ในน้ำมัน (3) ผลิตก๊าซโอเลฟินส์เบา (4) ผลิตก๊าซหุงต้ม (5) ผลิตมีกซ์ซีโพร (6) ผลิตสารปิโตรเคมีในน้ำมัน และ (7) ลดสารประกอบกำมะถันในน้ำมันที่ได้จากยางรถยนต์

สำหรับการวิจัยในครั้งนี้ ผู้ดำเนินการวิจัยได้ใช้เครื่องมือวิเคราะห์เครื่องใหม่ ซึ่งก็คือ GC×GC-TOF/MS ในการวิเคราะห์องค์ประกอบในน้ำมันที่ได้จากการไพโรไลซิสยางรถยนต์ใช้แล้ว และการจัดกลุ่มขององค์ประกอบในน้ำมันเป็นกลุ่มๆ อย่างละเอียดตามองค์ประกอบเชิงโมเลกุล เพื่อประโยชน์ในการเปรียบเทียบผลที่ได้จากการใช้ตัวเร่งปฏิกิริยาชนิดต่างๆ อย่างเป็นระบบ โดยพบว่า น้ำมันที่ได้จากยางรถยนต์มีองค์ประกอบของโมเลกุลของสารประกอบไฮโดรคาร์บอนเป็นกลุ่มๆ ดังนี้ (1) สารประกอบไฮโดรคาร์บอนอิ่มตัว (2) โอเลฟินส์ (3) เทอร์พีนส์ (4) โมโนอะโรมาติกส์ (แยกเป็นแบบที่มีหมู่ฟังก์ชันที่อิ่มตัวและไม่อิ่มตัว) (5) ไดอะโรมาติกส์ (6) โพลีอะโรมาติกส์ และ (7) สารประกอบซัลเฟอร์ในน้ำมัน สำหรับทดสอบการใช้ตัวเร่งปฏิกิริยาโลหะไม่มีตระกูล (Non-noble metals) ที่ปกติใช้ในอุตสาหกรรมปิโตรเลียม (regenerated NiMoS/Al₂O₃ และ fresh CoMoS/Al₂O₃) มาทดลองใช้เป็นตัวเร่งปฏิกิริยาในการไพโรไลซิสยางรถยนต์โดยมีจุดประสงค์ในการที่จะทดสอบความสามารถในการ Cracking และการลดกำมะถันไปในคราวเดียวกัน ซึ่งผลการทดสอบพบว่า regenerated NiMoS/Al₂O₃ และ fresh CoMoS/Al₂O₃ สามารถลดกำมะถันในน้ำมันเหลือแค่ 0.60% และ 0.55% (จาก 1.36%) ตามลำดับ ส่วนการทดสอบตัวเร่งชุด NiMo/HBETA และ NiW/HBETA พบว่า สามารถลดกำมะถันในน้ำมันเหลือแค่ 0.82% และ 1.02% (จาก 1.36%) ตามลำดับ นอกจากนี้ ยังได้ทดสอบการใช้ตัวรองรับซีโอไลท์เป็นตัวเร่งปฏิกิริยาในการไพโรไลซิส โดยวิเคราะห์ในประเด็นและตามเกณฑ์และประเด็นต่างๆ ข้างต้น จากผลวิเคราะห์ที่ได้จาก GC×GC-TOF/MS โดยผลที่ได้จากตัวรองรับดังกล่าว นั้น จะถูกนำมาใช้เป็นฐานในการเปรียบเทียบและศึกษาผลที่ได้จากการบรรจุโลหะชนิดต่างๆ

สำหรับการวิจัยในปีต่อๆ มา ผู้วิจัยและคณะ ได้ทำการศึกษาผลของโลหะไม่มีตระกูล 5 ชนิด Cu Zn Fe Co และ Ni ซึ่งพบว่า เนื่องจากโลหะดังกล่าว เป็นโลหะที่มีคุณสมบัติเชิงเคมีคล้ายกัน

เช่น Cu มีคุณสมบัติคล้าย Zn หรือ Fe Co และ Ni ก็เป็นกลุ่มโลหะที่มีคุณสมบัติเชิงเคมีคล้ายกัน จึงพบว่า มีความสามารถในการปรับปรุงคุณภาพของน้ำมันคล้ายกัน สามารถช่วยเพิ่มสารปิโตรเคมี ในน้ำมัน (BTEXs) คล้ายกัน และสามารถลดปริมาณกำมะถันในน้ำมันได้คล้ายๆ กัน แต่แตกต่างกัน ตรงที่ ชนิดและปริมาณผลิตภัณฑ์นั้นต่างกัน โดยทั้งนี้ ขึ้นอยู่กับตัวรองรับที่ใช้อีกด้วย พบว่า คุณสมบัติของตัวรองรับที่ใช้มีผลต่อปริมาณผลิตภัณฑ์ที่ผลิตได้ค่อนข้างมาก แต่ละตัวรองรับ และแต่ละโลหะ ก็มีความโดดเด่นเฉพาะเจาะจงที่แตกต่างกัน ซึ่งสามารถสรุปได้ดังนี้

(ก) Fe, Co, and Zn มีความโดดเด่นด้านผลิตเนฟธาเบา ซึ่งสามารถใช้ทดแทนโลหะ Pt, Pd, and/or Ru ได้

(ข) Ni มีความโดดเด่นด้านลดปริมาณโพลีโรมาติกส์ในน้ำมัน ซึ่งสามารถใช้ทดแทนโลหะ Pt and/or Ru ได้

(ค) Co มีความโดดเด่นด้านการผลิตโอเลฟินส์เบา ซึ่งสามารถใช้ทดแทนโลหะ Ru, Ag, Rh, and/or Re ได้

(ง) Cu บน HMOR และซีโอไลท์เปล่า มีความโดดเด่นด้านการผลิตก๊าซหุงต้ม ซึ่งสามารถใช้ทดแทนโลหะ Ag, Rh, and/or Re ได้

(จ) Co มีความโดดเด่นด้านการผลิตเมทิลซีโพร ซึ่งสามารถใช้ทดแทนโลหะ Pt, Ag, and/or Rh ได้

(ฉ) Fe, Co, Ni, Cu, and Zn มีความโดดเด่นด้านการผลิตสารปิโตรเคมี ซึ่งสามารถใช้ทดแทนโลหะ Ru, Rh, and/or Re ได้

(ช) Cu, Zn, Ni, NiMo, and NiMoS มีความโดดเด่นด้านการลดสารกำมะถันในน้ำมัน ซึ่งสามารถใช้ทดแทนโลหะ Rh and/or Ag ได้

ผู้วิจัยได้ตีพิมพ์ผลงานวิจัยในวารสารต่างประเทศไปแล้วรวมทั้งสิ้น 10 เรื่อง (แบ่งเป็นผลงานในฐาน ISI จำนวน 4 เรื่อง และในฐาน Scopus จำนวน 6 เรื่อง) (เอกสารประกอบ 1 – 10) และนำผลงานไปเสนอในที่ประชุมวิชาการแล้ว รวมทั้งสิ้น 12 เรื่อง (แบ่งเป็นที่ประชุมนานาชาติจำนวน 7 เรื่อง และที่ประชุมระดับชาติจำนวน 5 เรื่อง) หัวหน้าโครงการได้รับรางวัล PTIT Scholar Award (2015 – 2016) จากสถาบันปิโตรเลียมแห่งประเทศไทย และผลงานส่วนหนึ่งถูกนำไปใช้ประโยชน์ในเชิงวิชาการ โดยวุฒิสภา ผ่านคณะกรรมการวิจัยและพัฒนาของวุฒิสภา



Chapter 2

Background and Literature Review

2.1 Introduction to the research problem and its significance

In Central Thailand of around 400 kilometers in radius away from Bangkok, it was estimated that there were around 350,000 tons of waste tires discarded per years, and approximately 40% of them was found unidentified for their uses and utilization (MCS, 2552; Jitkarnka and Permsantitham, W., 2009). The rest 60% of waste tires were used as reclaimed rubber, direct solid fuel in industry and agricultural sectors, bumpers, raw materials for producing shoes and garbage bins, raw materials for pyrolysis, and an exported waste. As a result, to some organizations in Thailand, waste tires are not identified as “Wastes” since they still can be utilized in many ways. Thus, over recent years, tire pyrolysis has attracted renewed significant attention in Thailand countrywide. It essentially involves decomposition of the tire components by exposure to high temperatures in the absence of oxygen. The result is a carbonized char, condensable oil, and a gas fraction. The char can be used as low-grade carbon black, as a solid fuel, or may be upgraded to activated carbon (Williams and Brindle, 2003), whereas the gas contains mainly hydrocarbons (C1- C5), hydrogen with a relative high content (Barbooti *et al.*, 2004), and a low concentration of H₂S (Berruenco *et al.*, 2005). The tire-derived oil is a complex mixture of hydrocarbons with a high amount of aromatics (Cunliffe and Williams, 1998).

The tire-derived oil was reported to have a high calorific value of about 41-44 MJ/kg (Cunliffe and Williams, 1998). In addition, its property is similar, to a certain extent, to that of commercial petroleum naphtha (Benellal *et al.*, 1995). When it was used as a fuel by mixing with a reference fuel in a diesel engine, a reliable operation could be achieved up to 70% of this oil in the blend (Murugan *et al.*, 2009). However, higher smoke, hydrocarbon (HC) and CO emissions were recorded. Also, oil sticking was occasionally found on the nozzle stem and sac. These phenomena were believed to come from the high concentration of aromatics, especially the high concentration of polycyclic HCs (Murugan *et al.*, 2009). In addition, there are considerable amounts of sulfur-containing compounds such as thiophene, benzothiophene, and their derivatives found in the tire-derived oil



(Williams and Bottrill, 1995; Pakdel *et al.*, 2001), consecutively limiting its applications as a direct-usable fuel due to the serious problem of SO₂ emission and a decrease in the efficiency of the engine. Nevertheless, tire-derived oils contain an amount of useful petrochemicals such as mono-aromatics (benzene, toluene, xylenes) that can be used as raw materials in petrochemical industry. Pyrolytic gas from waste tire pyrolysis is also composed of a significant amount of valuable petrochemical gases, for examples, ethylene and propylene, or even cooking gases. Thus, the pyrolysis of waste tires can be considered as an alternative to produce some petrochemicals from a non-petroleum source.

A number of scientific papers reported the uses of catalysts, especially acid catalysts, on waste tire pyrolysis. Higher quantity and quality of tire-derived oil were found in a certain way. Previously, with the mutual supports by TRF and The Commissions on Higher Education, our group has accomplished on the investigation of various noble metal-supported catalysts (Pt, Ru, Rh, Pd, Ag, and Re supported on HBETA, HMOR, HY, KL, SBA-1, MCM-41, and MCM-48) for their influences on the yields and nature of the products obtained from waste tire pyrolysis. The catalyst activity and their effects were classified and reported into four groups; that is, (a) Effects of acid supports, (b) Effects of metals on acid supports, (c) Effects of basic support and metals on basic support, and (d) Effects of mesoporous supports and the roles of rhutenium. The pyrolysis was carried out in a bench-scale autoclave reactor from room temperature to the final temperature of 500°C (for the pyrolysis zone) and 350°C (for the catalytic zone) with the heating rate of 10°C/min in the atmospheric pressure. The results were described in terms of product yield, gas composition and yield, true boiling point curves, petroleum fractions, petrochemical yields, carbon number distribution, and the molecular composition of oils. A number of interesting outcomes were reported. For instances, most of metal-supported catalysts, especially Pt- and Pd-loaded ones, improved light oil production with low contents of polar-aromatics and asphaltene. Ru catalysts selectively produced light olefins, especially when loaded on HMOR and MCMs. Ag-supported catalysts were found promising in producing cooking gases. Moreover, some catalysts such as Rh- and Re-loaded ones selectively produced a high mono-aromatic content in oil. However, most of noble metals have high prices, making difficulties in applying the catalysts in small- and medium-scale waste tire-pyrolysis plants. In order to develop a cheaper catalyst, non-noble metals are taken into



consideration in this work with the aims of producing oil and gaseous products at a similar quantity and quality as using a noble metal-supported catalyst.

2.2 Literature review

Pyrolytic oil is a complex mixture of hydrocarbons (HCs) highly-distributed in naphtha and gas oil ranges (Benellal *et al.*, 1995) with high concentration of aromatics, particularly single-ring aromatic HCs (Cunliffe and Williams, 1998). Yet, their concentration is not high enough to achieve an economical separation process. Moreover, the aromatic property of the tire-derived oil, especially its remarkable content of polycyclic HCs, has limited its application as a direct-usable fuel. This is due to the fact that these compounds together with the sulfur-containing compounds found in the oil (Pakdel *et al.*, 2001) cause a lot of smoke, HC and CO emissions, and also oil sticking on the nozzle stem and sac of diesel engine (Murugan *et al.*, 2009). Williams and Taylor (1993) suggested that the pyrolysis of tire led to the production of ethylene, butadiene..., which could react to form cyclic olefins, followed by dehydrogenation to aromatic compounds. As a result of subsequent associative reaction, the formation of polycyclic aromatics might occur. A poly-aromatic compound, such as phenanthrene, was also formed after the formation of naphthalene, a di-aromatic compound. Moreover, no evidence proving the direct formation of aromatics from cyclization of alkanes was observed. Pyrolytic oil also has a considerable amount of sulfur-containing compounds, such as benzothiophene, thiophene and their derivatives (Williams and Bottrill, 1995; Pakdel *et al.*, 2001). However, the formation of these compounds during pyrolysis is still remained unelucidated.

In petrochemical industry, catalysts have been introduced for reaction improvement and value-added products. In general, catalysts are used to improve the selectivity of desired products. Their physical and chemical properties play an important role in the selectivity of products. Williams and Brindle (2002) studied the catalytic pyrolysis of waste tire using two types of zeolites, Y and ZSM-5, and reported an increase in the concentration of single-ring aromatic hydrocarbons, i.e. benzene, toluene and xylene. Y zeolite produced the higher amount of these aromatics with respect to ZSM-5 due to its lower Si:Al ratio and larger pore size. Later, with the aim for a much higher concentration of certain single-ring aromatic,



Boxiong *et al.* (2007a) used USY and ZSM-5 as catalysts in the pyrolysis of waste tire. The experimental results indicated the high concentrations of benzene, toluene, and xylenes, which could be achieved with USY zeolite. The high concentration of aromatics, particularly poly- and polar-aromatic hydrocarbons (PPAHs), as mentioned earlier, has limited the use of tire-derived oil as fuel. However, this limitation is still remained unsolved. Actually, no study has been found so far aiming at the reduction of PPAHs in this oil. Other families of zeolites such as SAPO (Fan *et al.*, 2005) and mesoporous materials (Miguel *et al.*, 2006; D ng *et al.*, 2009) were also investigated for their activity on waste tire pyrolysis. ZSM-5, beta zeolites, and two meso-structured materials (Al-MCM-41 and Al-SBA-15) were found to give a marked selectivity of aromatic species, particularly toluene, m/p-xylene and benzene (Miguel *et al.*, 2006). The mesostructured catalysts, Al-MCM-41 and Al-SBA-15 exhibited stronger aromatization and benzene alkylation capacity because of their weaker Lewis acid and larger pore size, which provide larger molecules of products.

Bifunctional catalysts comprised of metal and acid functions have been extensively studied for various applications such as the reduction of aromatics in fuel (Lugstein *et al.*, 1999). Whereas the acid function of a support can undergo cracking (β -scission), **noble metals** can catalyze the hydrogenation of the feedstock, making it more reactive for cracking (hydrogenolysis, or C-C bond cleavage) and heteroatoms (i.e. sulfur, oxygen) removal (Ali *et al.*, 2002). For examples, Rh-promoted catalysts were found to have high activity on the hydrogenolysis cleavage and skeletal rearrangement of C-C bonds (Teschner *et al.*, 2002; Jacquin *et al.*, 2003), and Re sulfide was highly active for the hydrodesulfurization (HDS) reactions, in some cases even higher than the classic Mo and W sulfide, either in the unsupported state (Pecoraro and Chianelli, 1981; Lacroix *et al.*, 1989) or supported ones (Ojeda *et al.*, 2005; Nacheff *et al.*, 1987; Okal and Kubicka, 1998). Usually, a high level of aromatic hydrogenation at moderate hydrogen pressures can be achieved with using noble metals-promoted catalysts (Eliche-Quesada *et al.*, 2006a; 2006b; Reddy and Song, 1996; Albertazzi *et al.*, 2003). The intrinsically-high hydrogenation activity can also help reducing steric effects that impede the direct elimination of the sulfur heteroatom in the hydrodesulfurization (HDS) (Pecoraro and Chianelli, 1981). The hydrogenation and ring opening reactions of polycyclic aromatic hydrocarbons has been performed to enhance the quality of diesel oil, the pyrolytic oil products and other oil products by using bifunctional catalysts; for instances, Pd-promoted catalysts (Weitkamp *et al.*, 2001), Pt-promoted catalysts



(Arribas and Martinez, 2002; Santikunaporn *et al.* 2004), and Ru-promoted catalysts (Eliche-Quesada *et al.*, 2006a; 2006b; Gao and Schimidt, 1989; Sajkowski *et al.*, 1990; Wu *et al.*, 1990). Other noble metals which have the similar effect as Pt are Ir, Rh, Ru and Pd, reported by Du *et al.* in 2005. Moreover, noble metals such as Pt have a high activity on the hydroisomerization of light paraffins (Roldan *et al.*, 2005). Although noble metal-promoted catalysts can work effectively, one major limit of noble metals is its low resistance to sulfur poisoning. Interestingly, the sulfur tolerance can be enhanced by modifying the physicochemical characteristics of the metal atoms by (i) using acidic carriers (Barbier *et al.*, 1990), (ii) changing the metal particle size, or (iii) alloying with other metals (Lee and Rhee, 1998). Bimetallic catalysts were found to exhibit superior activity, selectivity, and deactivation resistance than their corresponding monometallic samples (Sinfelt, 1983; Poncet and Bond, 1995). Based on **our previously-funded work**, noble metal-supported catalysts (Pt, Ru, Rh, Pd, Ag, and Re supported on HBETA, HMOR, HY, KL, SBA-1, MCM-41, and MCM-48) were tested for their influences on the yields and nature of the products obtained from waste tire pyrolysis. As a result, most of metal-supported catalysts, especially Pt- and Pd-loaded ones, improved light oil production with low contents of polar-aromatics and asphaltene (Dung *et al.*, 2009). Ru catalysts selectively produced light olefins, especially when loaded on HMOR and MCMs (Dung *et al.*, 2009; 2010). Ag-supported catalysts were found promising in producing cooking gases (Wehathornnavee and Jitkarnka, 2010). Moreover, some catalysts such as Rh- and Re-loaded ones selectively produced a high mono-aromatic content in oil (Pinket and Jitkarnka, 2010; Mahanin and Jitkarnka, 2010).

Besides the low sulfur tolerance, the high price of noble metals limits their applications. **Non-noble metals** were also found to have similar activities as those of noble metals, but they usually have a lower activity when loaded with the same amount on the support. For instances, Ni and Co were found to have hydrogenation activity (Pedrosa *et al.*, 2006a; Álvarez-Rodríguez *et al.*, 2008a), isomerization activity (Fúnez *et al.*, 2008; Eswaramoorthi *et al.*, 2003), hydrogenolysis activity (Escobar *et al.*, 2008; Kaliya and Kogan, 2005; Pedrosa *et al.*, 2006a), and hydrodesulfurization activity with or without co-loading with other promoters (Crisafulli *et al.*, 2002; Navarro *et al.*, 2009; Espinosa *et al.*, 2011). Cu was found to have ring opening activity (Fesi *et al.*, 1999) and reforming activity (Álvarez-Rodríguez *et al.*, 2008b). Fe is widely used in industrial processes such as Fischer – Tropsch synthesis (Pour *et al.*, 2004; Ma *et al.*, 2009) and selective catalytic reduction (SCR) of NO_x (He *et al.*,



2009). Co has also the activities on hydrodesulfurization (Espinosa *et al.*, 2011) as well as Fischer – Tropsch synthesis (Zola *et al.*, 2007; Ngamcharussrivichai *et al.*, 2007), and is usually co-loaded with Fe for promoting the activity (Ma *et al.*, 2009; Tavasoli *et al.*, 2009). Besides their inexpensive prices, non-noble metals in general have higher sulfur tolerance than noble ones. Therefore, together with their activities similar to those of noble metals, non-noble metals mostly in the first row of transition elements are selected in this proposed work in order to investigate their potential on replacing noble metals previously used to the activity and selectivity of waste tire pyrolysis catalysts.

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2.3 Objectives

The objective of this work was to investigate the influences of various non-noble metal -promoted catalysts on the selectivity or yields and nature of the products obtained from waste tire pyrolysis. The goals of the investigation are described as follows;



(a) in order to study the potential of non-noble metal-promoted catalysts as alternative catalysts for waste tire pyrolysis;

(b) in order to compare the activities of the non-noble metal-promoted catalysts with those of the noble metal-promoted ones previously tested by our group (in terms of the nature of products or the quality of products); and

(c) in order to examine whether or not the non-noble metal-promoted catalysts of interest have any other outstanding activity that overcomes that of the noble metal-promoted ones.

However, in terms of “Products”, they mean (i) commercial oils such as gasoline, kerosene, and diesel (gas oil), and/or (ii) commercial gases such as C1 – C4 hydrocarbons, and/or (iii) petrochemicals such as light olefins and aromatics, which can be used as alternative raw materials for petrochemical industry.

2.4 Methodology

(a) Catalyst Preparation

Catalysts were prepared by using the incipient wetness impregnation.

(b) Tire Pyrolysis Experiment

The autoclave reactor and experimental system are shown in Figures 1 and 2, respectively. A tire sample was pyrolyzed in the lower zone of the reactor from room temperature to a final temperature of 500°C with a heating rate of 10°C/min. This pyrolysis zone was kept at the final temperature for 1 hour to ensure the total conversion of tire. The evolved product was carried by a 25 ml/min nitrogen flow to the upper zone controlled at a desired temperature and packed with a catalyst. The influences of catalyst were investigated at this zone. The obtained product was next passed through an ice-salt condensing system containing 3 condensers to separate incondensable compounds from the liquid product. The non-condensable products or gaseous products were passed through the condensers and kept in a Tedlar gas sampling bag. The solid and liquid products were weighed to determine the product distribution. The amount of gas was then determined by mass balance.

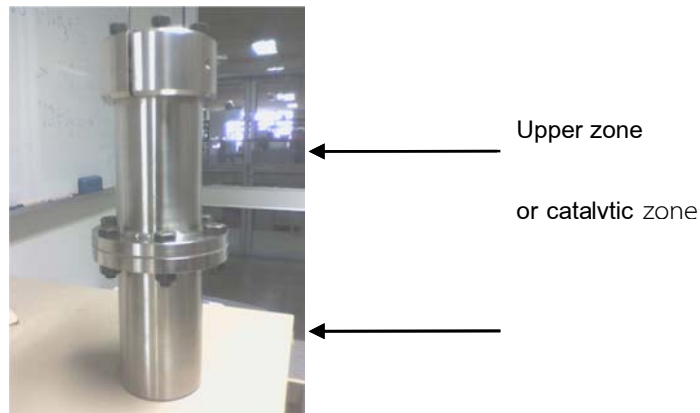


Figure 1 Autoclave reactor used in the experiment.

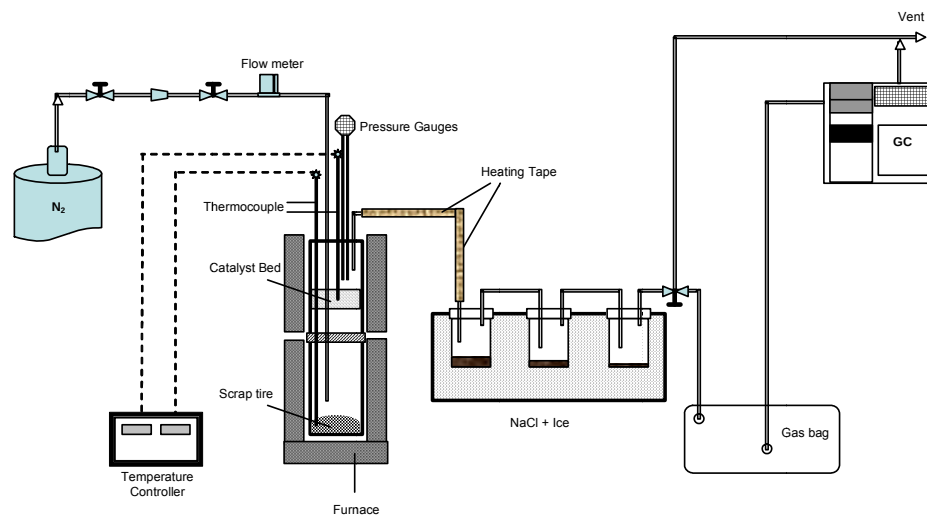


Figure 2 Schematic of the pyrolysis process.

(c) Product Characterization

Pyrolytic gas fraction was analyzed by a gas chromatograph, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30m x 0.32mm i.d. 20 μ m film. FID was used as a detector with He as the carrier gas. The oil product was extracted for maltenes using n-pentane, and the maltene was fractionated by



using a chromatographic column (Sebor *et al.*, 1999), and also analyzed by using Varian CP-3800 Simulated Distillation Gas chromatography (SIMDIST GC), equipped with FID, using a 15 m x 0.25 mm x 0.25 μm , WCOT fused silica capillary, according to ASTM D 2887. The outcome from the SIMDIST-GC was a true boiling point curve of the oil obtained from the waste tire pyrolysis process, which can be cut into petroleum fractions as identified in (Speight, 2002). Sulfur compounds in maltene were also analyzed using an elemental analyzer and a GC-TOF instrument.

(d) Catalyst Characterization

Catalyst characterization was conducted using various techniques such as X-ray Diffraction Spectroscopy (XRD), X-ray Fluorescence Spectroscopy (XRF), Surface Area and Pore Size Analysis, Electron Microscope (SEM/TEM), Temperature-programmed techniques, etc.

2.5 Scope of research

In order to achieve the goals in time, the scope of this work was set as listed below;-

(a) All pyrolysis experiments were subjected to some fixed conditions; that is, they were carried out in a bench-scale autoclave reactor from room temperature to the final temperature of 500°C (for the pyrolysis zone) and 350°C (for the catalytic zone) with the heating rate of 10°C/min in the atmospheric pressure. Other parameters; particle size, holding time, N₂ flow rate, the amount of sample and catalysts were fixed at 8-18 mesh, 90 min, 30 ml/min, 30 g, and 7.5 g, respectively.

(b) At least three supports were used in this work, and they were selected based on the previously-obtained results. More supports may be also selected during the process if considered having potential.

(c) At least four non-noble metals in the first row of transition elements were used in this work, and their activities were compared with those of Pt, Ru, Rh, Pd, Ag, and Re, obtained from the previous work, when loaded on those selected supports.

(d) The percentage of non-noble metal loading may be varied in a range appropriate to individual non-noble metal.



(e) Gaseous and liquid products were analyzed for their compositions, type, and quantity whereas solid products were only analyzed for their quantity. The quality of all types of products was investigated only if the analysis instruments would be possibly available and allowed.

(f) The activities of catalysts were compared as, for examples, naphtha-producing catalysts, cooking gas-producing, and olefins-producing catalysts, etc.



Chapter 3

Analysis of tire-derived oil using GC $\times$ GC – TOF/MS for better identification and grouping of hydrocarbon compounds*

Abstract: A tire-derived oil (TDO) consists of many types of hydrocarbons such as mono-aromatics (MAHs), di-aromatics (DAHs), poly-aromatics (PAHs) and polar-aromatics (PPAHs). Previously, a GC/MS has been used to analyze the components in TDOs, and 38 hydrocarbon species were found and identified. However, the drawback of a regular GC/MS is that it cannot separate the hydrocarbon species with the same retention time because boiling points, vapor pressures and mass spectral fragmentation patterns are indistinguishable. Therefore, hundreds of hydrocarbons in the oil could not be observed and identified due to the overlapped mass spectra. At present, no work has been reported on analysis of a tire-derived oil using Two-Dimensional Gas Chromatography coupled with a Time-of-Flight Mass Spectrometry (GC $\times$ GC / TOF-MS) for hydrocarbon species. The objective of this work was to examine the components in a tire-derived oil, and completely report the results in terms of 2D (contour plot) and 3D (surface plot) plots of total ion chromatograms for outstanding groups of hydrocarbon species such as saturated hydrocarbons (SATs), olefins (OLEs), terpenes (TERs), MAHs, DAHs, PAHs, and PPAHs, including sulfur compounds. Maltenes (liquid fractions without asphaltene) were collected and analyzed by using a SIMDIST GC, and GC $\times$ GC / TOF-MS. As a result, the SATs consists of aliphatic hydrocarbons starting at C13, C14 to C16. The OLEs consists of di-olefins and tri-olefins. The TERs consists of Carene and Limonene. The MAHs is categorized into two groups; that are, (a) mono-aromatics with saturated substituents (MAHs-SS) such as indanes, alkylbenzenes, and tetralins, and (b) mono-aromatics with unsaturated substituents (MAHs-US) such as indenenes and alkenylbenzene. The DAHs consists of naphthalene and alkyl naphthalenes. The PAHs consists of phenanthrene, anthracene, fluorene, and pyrene. Finally, the PPAHs consist of thiophenes, benzothiophenes, and dibenzothiophenes.

Keywords: GC $\times$ GC TOF/MS, tire-derived oil, pyrolysis, hydrocarbon species, grouping, waste tire



1. Introduction

Due to the growth of population and development of transportation in the world, a large number of cars have been increased rapidly resulting in a lot of tires consumed in every year [1]. Waste tires become more serious environmental problem because of non-biodegradable properties. Therefore, waste tire management needs to be implemented. Pyrolysis has been introduced in this decade as a renewable waste tire recycling technology. The products are liquid (e.g., oil), gas (e.g., methane, ethane, ethylene, propane, propylene, H_2 , H_2S , CO , and CO_2), and solid (e.g., char or carbon black). Tire-derived oil (TDO) is a dark brown/black colored, medium viscosity oil with sulphur or aromatic odor. This liquid is very complex, containing more than 100 compounds in majority [2]. Among those, they were saturated hydrocarbons, olefins, and aromatics, for examples. Dai *et al.* used SiO_2/Al_2O_3 liquid column chromatography to separate a TDO, and analyzed by using GC/MS. They reported that the hydrocarbon species in TDOs was 26.77 wt.% alkanes, 42.09 wt.% aromatics, 26.64 wt.% non-hydrocarbon, and 4.05 wt.% asphaltene, and found that the aromatics were the mixture of mono-aromatics, di-aromatics, and poly-aromatics [3]. William and Bottrill used SiO_2/Al_2O_3 liquid column chromatography to separate sulfur-polycyclic aromatic hydrocarbons, and then analyzed by using a normal GC/MS. They found that these compounds were 2-methylthiophene, 3-methylthiophene, 2-ethylthiophene, 2,5-dimethylthiophene, 2,4-dimethylthiophene, 2,3-dimethylthiophene, 3-ethylthiophene, 2-isopropylthiophene, 2-tert-butylthiophene and their derivatives [4]. Pakdel *et al.* studied the production of *dl*-limonene by vacuum pyrolysis of used tire using a normal GC/MS, and found that *dl*-limonene was mixed in alkane, alkene, and poly-aromatics fractions. However, the peaks were not easy to be resolved because they came out nearly at the same retention time and had similar boiling point[5]. Moreover, Lagesgoiti *et al.* characterized the liquid product in TDO by using a normal GC/MS. They found that the chromatograms of poly-aromatics and polar-aromatics were not explicitly separated from one another, and it was



difficult to interpret the results [6]. Boxiong *et al.* revealed hydrocarbon species in TDOs by using a normal GC/MS to investigate the influence of zeolite USY catalyst, and found 38 hydrocarbon species of aromatic hydrocarbons in the light fraction that are the mixtures of saturated hydrocarbons (with aliphatic and branch chain), olefins, naphthenes, and aromatics. They also found that the chromatograms showed some of saturated hydrocarbons and olefins that could not be identified because they evolved at the same retention time[7]. From the literature reviews, several authors used a normal GC/MS, and reported that the chromatograms overlapped and might not bring about accuracy data analysis. In conclusion, it is not easy to resolve overlapped peaks from chromatograms of TDOs using a normal GC/MS; therefore, the separation of a complex mixture of TDOs requires highly-advanced technology with high chromatogram resolution.

Comprehensive 2D gas chromatography with time-of-flight mass spectrometry (GC $\times$ GC- TOF/MS) is a new technique that has high performance to resolve the complexity of compounds. GC $\times$ GC - TOF/MS consisted of two consecutively-connected columns and TOF/MS as a detector. The key to the GC application of comprehensive chromatography analysis was the ability to rapidly pulse segments of effluent from Column 1 to Column 2. The first column (a primary non-polarity column) can separate the components based on carbon number, and it consequently provides the second column (a secondary polar column) with a series of sub-samples containing the same carbon number that can be further separated based on the polarity. The second column does not need to create a large peak capacity because the component from the first column is limited [8]. Time-of-flight (TOF/MS) instrument is able to scan at the high scan rates of ≥ 50 spectra/second. The data can be collected at high rates, which are shown obviously at separated retention time and accurate quantification [9]. After that, the raw data are plotted into two-dimension chromatogram (contour plot) and three-dimension chromatogram (surface plot). In conclusion, this technique can give high resolution of chromatogram and better results than a normal GC/MS. Indeed, GC $\times$ GC -



TOF/MS is equipped with a software that can deconvolute chromatograms for identification as well as accurate quantification [10]. The analysis of an unresolved complex mixture such as oil spill, rich biodegraded crude oil, cigarette smoke, and standard polycyclic aromatics have been well accomplished by using this technique [11-14]. To our knowledge, no work has been done to analyze TDO by using GC $\times$ GC - TOF/MS. The purposes of this study were to reveal hydrocarbon species in TDOs using GC $\times$ GC - TOF/MS, and the LECO ChromaTOF® software was used to classify the obtained data into different groups of hydrocarbons, including sulphur compounds. The hydrocarbon groupings are presented in contour plots, and some abundantly-observed compounds in each group are also identified and reported.

2. Experimental

2.1 *Pyrolysis of waste tire*

Figure 1 displays the experimental diagram. A used passenger tire tread, Bridgestone TURANZA GR-80, was shredded and sieved to a size range of 8-18 mesh. The tire sample was pyrolyzed in the reactor where the temperature was ramped from room temperature to the final temperature of 500°C with the ramping rate of 10 °C min⁻¹, and kept at the final temperature for one hour to ensure the total conversion of tire. A 25 ml min⁻¹ nitrogen was used to purge the reactor before the experiment and to carry the product out of the reactor. The obtained product was passed through the ice-salt condensing system containing two consecutive containers in order to separate the liquid product from incondensable compounds. After the experiment, the solid and liquid were weighed to determine the product distribution. The amount of gas was calculated from mass balance. Only the oil was brought to analysis in this study. It was first dissolved in n-pentane with the ratio of 40:1 (n-pentane:oil) to separate asphaltene. The clear solution after filtration is called maltene.

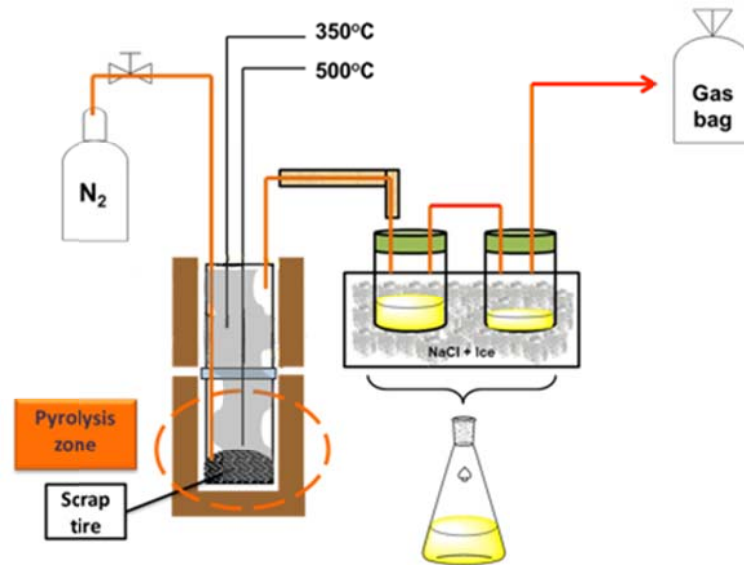


Figure 1 Schematic of pyrolysis experiment

2.2 Analysis using GC × GC – TOF/MS

The GC × GC–TOF/MS system was composed of an Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA), a thermal modulator, and a Pegasus® 4D TOF-MS (LECO, St. Joseph, MI, USA). The GC was installed with two columns: the first column was a non-polar Rtx 5 silms® (30m x 0.25 mm i.d. x 0.25 µm film thickness), and the second column a Rxi®-17 ms (1.10 m x 0.10 mm i.d. x 0.10 µm film thickness). Both columns were made by Thames Restek (Sounderton, UK). The main GC oven was operated from at 50 °C with 2 minute holding at the beginning and then ramped to 310 °C at 5 °C min⁻¹ with 10 minute holding at 310 °C, and the secondary oven was operated at 60 °C held for 2 minutes at the beginning and ramped to 320 °C at 5 °C min⁻¹ with 10 minute holding at the final temperature. One µl of the 10 mg/ml maltenes in carbondisulfide (CS₂) was injected via a spiltless injector at 250 °C using He as the carrier and a constant column flow rate of 1.0 ml/min. The modulator was operated under modulation timing of 4-s cycle time and 0.5-s holding time in the release position. The nitrogen cryogen coolant maintained the temperature of the modulation trap to at least 30



°C. A Pegasus 4D® TOF/MS instrument was used to acquire mass spectral data, using -70 V electron impact ionization. The ion source temperature was set at 250 °C. The detector voltage was set at 1600 V. The transfer line temperature was 250 °C. The mass range collected was from 35 to 500 m/z , with 100 spectra/s transferred to the data station. The data processing was set S/N value of 10, match required to combine 500, and dt that was used to calculate the percentage area. Data were recorded and analyzed using the LECO ChromaTOF® software. The NIST library provided with the instrument was used for spectral searching. The analysis was repeated for 3 times.

3.Result and Discussion

3.1 *Components in tire-derived oils from GC x GC TOF/MS*

One of the advantages of GC x GC – TOF/MS is the power to separate a complex mixture of components, like a tire-derived oil. The two columns were installed; the first column (a primary non-polarity column) can separate the components based on carbon number, and the second column (a secondary polar column) can separate the chemicals that have the same carbon number based on the polarity. Figure 2(a) shows the contour plot of total ion chromatogram (2D TIC) of the maltene. It indicates that the conditions used to analyze the tire-derived oil are satisfied to separate the complex components, which were found in a total of more than 1,500 compounds. As the structural complexity of the components increases, partial overlap between component classes can occur even though they are shown by GC x GC-TOF/MS in the total ion chromatogram. However, the GC x GC – TOF/MS can reveal the separation of components in the overlap chromatograms as seen on the surface plot of total ion chromatogram (3D plot) in Figure 2(b) because the secondary column (the polar column) can separate the components with different polarities, which emerge at the same retention. These components are separated layer by layer as seen in the profile on the contour plot, continuing as the carbon number increases. Subsequently, all hydrocarbon

compounds were identified using the NIST database.

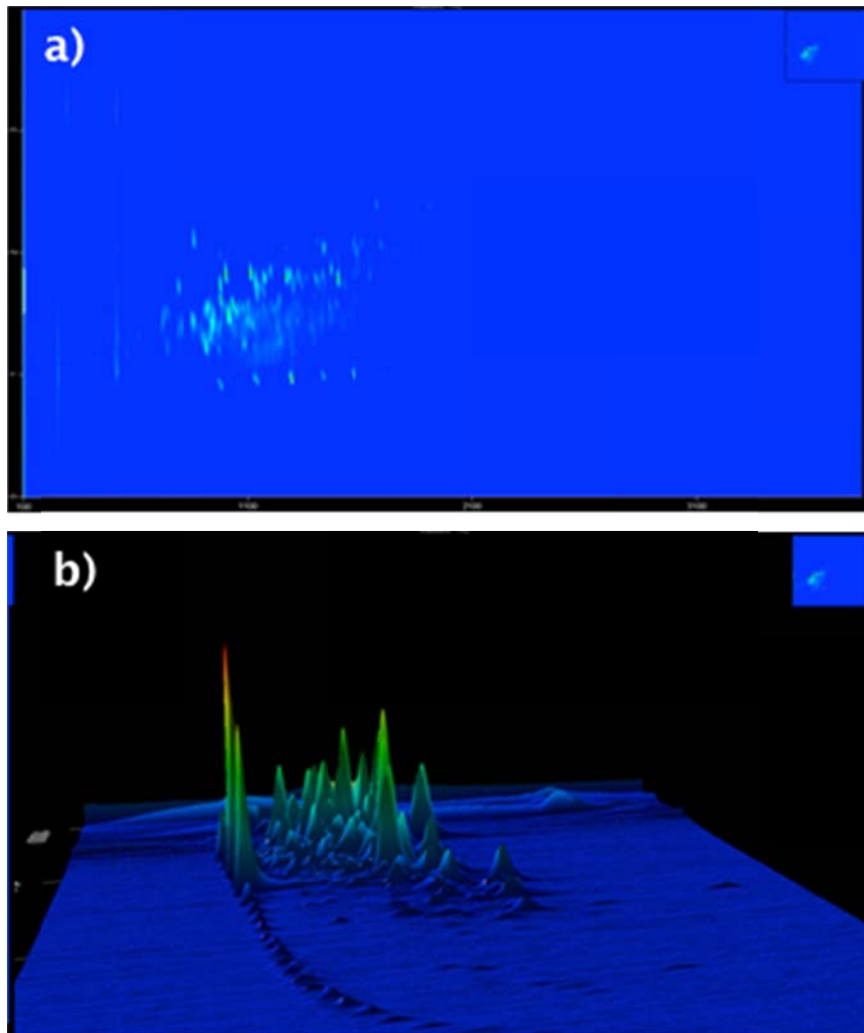


Figure 2 Total ion chromatogram of the maltene :(a) contour plot and (b) surface plot.

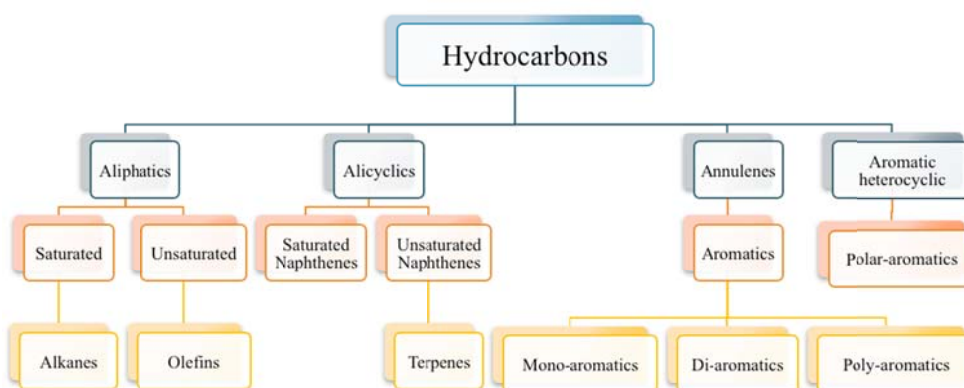
3.2 Grouping of hydrocarbons in TDO using automate LECO

ChromaTOF® software

According to the IUPAC, hydrocarbon species are of different types, depending upon the types of carbon-carbon bonds present in the molecules;

*Pithakratanayothin, S., Jitkamka, S. Proceeding of The 29th International Conference on Solid Waste Technology and Management, Philadelphia, PA U.S.A., March 30-April 2, 2014

therefore, they can be classified into three main categories – (i) aliphatic hydrocarbons, (ii) alicyclic hydrocarbons or naphthene, and (iii) aromatic hydrocarbons are shown in Scheme 1. Aliphatic hydrocarbons classified into two classes: (i) paraffins or saturated hydrocarbons, and (ii) olefins or unsaturated hydrocarbons. Naphthene or alicyclic hydrocarbons are classified into two classes: (i) saturated alicyclic hydrocarbons, and (ii) unsaturated alicyclic hydrocarbons or terpenes. Annulenes are hydrocarbons with alternating single and double bonds, like Benzene which is a six-membered annulene. The aromatic hydrocarbons are classified into four classes: (i) mono-aromatic hydrocarbons (MAHs), (ii) di-aromatic hydrocarbons (DAHs), (iii) poly-aromatic hydrocarbons (PAHs), and (iv) aromatic heterocyclic compounds or so-called polar-aromatic hydrocarbons (PPAHs)[15-21]



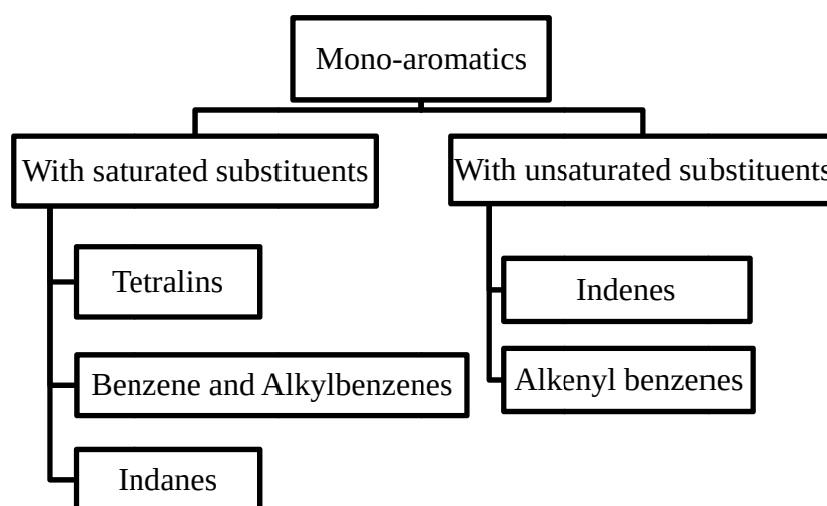
Scheme 1 Classification of hydrocarbons in TDO

The ChromaTOF® software was used to process the raw data to peak table, and succeeded in classification within 180 min. Based on IUPAC, the components are thus categorized into groups according to their chemical structures; namely, mono-aromatics (MAHs), saturated hydrocarbons (SATs), olefins (OLEs), terpenes (TERs), di-aromatics (DAHs), poly-aromatics (PAHs), and polar-aromatics (PPAHs).

However, due to high capability of the GC x GC-TOF/MS, better classification of each group can be done in details as follows.

(a) Mono-aromatics (MAHs)

MAHs are the most valuable group of chemicals in the petrochemical industry. Some of them play an important role as upstream petrochemicals in either polymer or advanced material industries. Two main classes of MAHs are mono-aromatics with saturated substituents (MAHs-SS) and mono-aromatics with unsaturated substituents (MAHs-US) as illustrated in Scheme 2.



Scheme 2 Classification of mono-aromatic group

Scheme 2 describes the classification of mono-aromatics into those with saturated substituents composed of three species that are benzene, alkylbenzenes, indanes, and tetralins, and those with unsaturated substituents of two groups that are indenes and alkenylbenzenes [17, 21]. Some species abundantly found in each class of MAHs and other groups are shown in Table 1. Moreover, the total ion chromatogram of MAHs, which indicates the region of each class based on carbon number, are depicted in Figure 3 for easy identification and view. The peak markers (dots) in Figure 3 locate the classes of MAHs found in the tire-derived oil. The carbon numbers of MAHs include C9, C10, C11, C12, C13, and C14, starting from left

to right, accordingly. The C9 – C14 MAHs present in majority are depicted in Table 2, for examples.

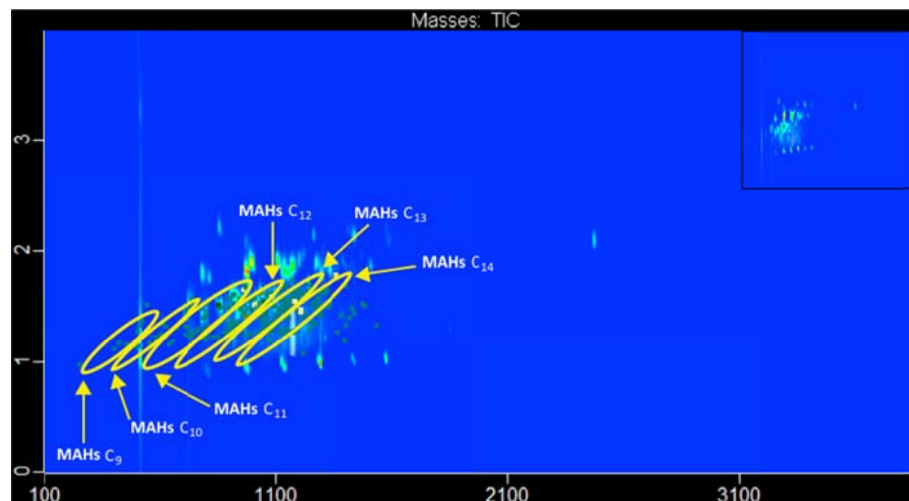
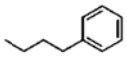
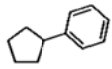
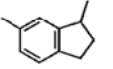
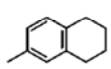
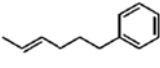
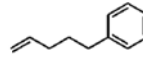
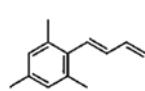
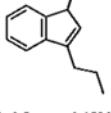
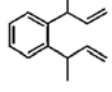
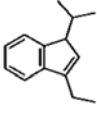


Figure 3 Total ion chromatogram with peak markers of MAHs classified based on carbon number.

(b) *Saturated hydrocarbons (SATs)*

Since SATs are defined as the hydrocarbons with only single bonds of C-C according to the chemical structure [15]. As a result, the compounds in SATs in the TDO are not classified into classes, but rather done based on carbon number. The SATs are found to consist of aliphatic hydrocarbons starting at C13, C14, and C16 as depicted in Figure 4, which shows the classes of SATs found in TDO with peak markers based on carbon number: C13, C14, and C16 from left to right. The examples of hydrocarbons in each carbon number are shown in Table 3.

Table 2 Examples of MAHs found in each carbon number

Carbon number	Hydrocarbon species of MAHs		
9	 1-ethyl-2-methylbenzene	 2,3-dihydro-1H-indene	 1,2,3-trimethylbenzene
10	 1-methyl-2-propylbenzene	 4-methyl-2,3-dihydro-1H-indene	 butylbenzene
11	 cyclopentylbenzene	 1,6-dimethyl-2,3-dihydro-1H-indene	 6-methyl-1,2,3,4-tetrahydronaphthalene
12	 (E)-hex-4-en-1-ylbenzene	 1,1,5-trimethyl-2,3-dihydro-1H-indene	 pent-4-en-1-ylbenzene
13	 1,1-dimethyl-3-vinyl-2,3-dihydro-1H-indene	 (E)-2-(buta-1,3-dien-1-yl)-1,3,5-trimethylbenzene	 1-methyl-3-propyl-1H-indene
14	 1,2-di(but-3-en-2-yl)benzene	 3-ethyl-1-isopropyl-1H-indene	

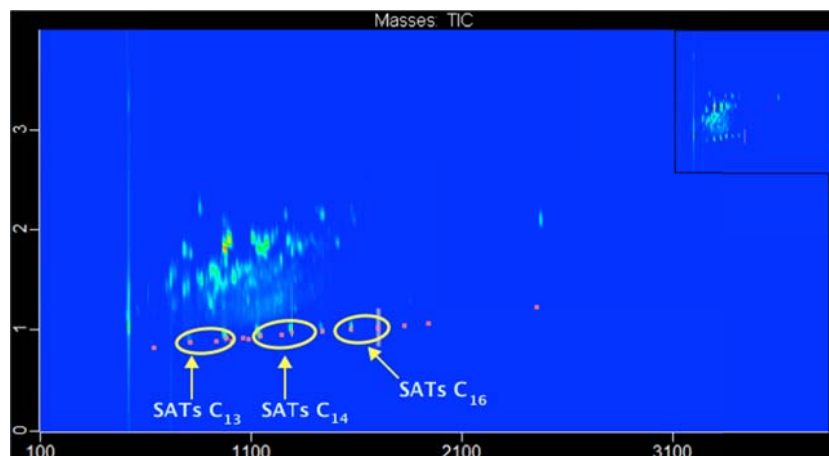
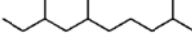
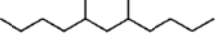
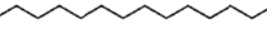
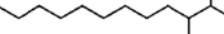
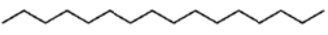


Figure 4 Total ion chromatogram with peak markers of SATs classified based on carbon number.

Table 3 Examples of SATs found in each carbon number

Carbon number	Hydrocarbon species of SATs		
13	 tridecane	 2,6,8-trimethyldecane	 5,7-dimethylundecane
14	 tetradecane	 2,3-dimethyldodecane	 3,8-dimethylundecane
16	 hexadecane		

(c) *Olefins (OLEs)*

The OLEs are hydrocarbons with the carbon-carbon bond and carbon-hydrogen, which has at least one double bond of carbon-carbon present in the chemical structure [16]. As a result, OLEs in the TDO can be classified into two classes: those with straight chain, and those with branching as shown in Table 1. However, based on carbon number, they consist of unsaturated hydrocarbons, also starting at C8, C9, C10, C11, C12 and C13 as grouped in Figure 5 from left to right. The examples of hydrocarbons in each carbon number are shown in Table 4.

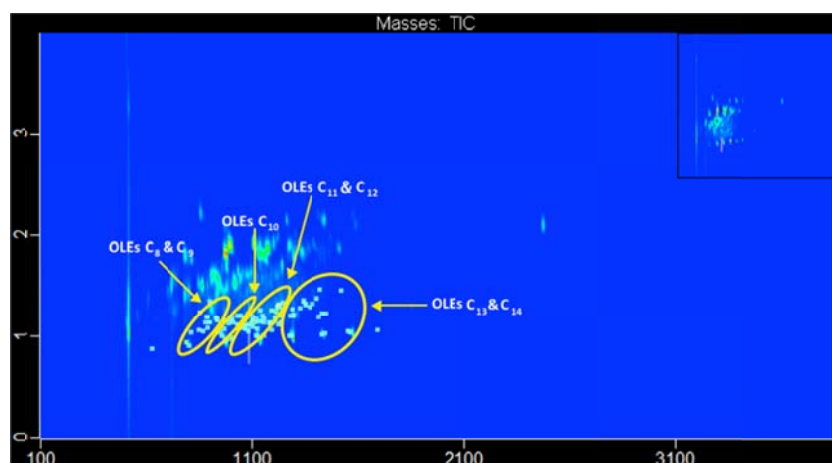
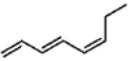
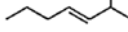
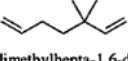
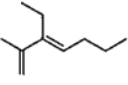
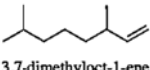
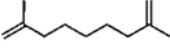
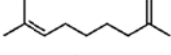
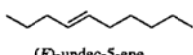
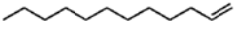
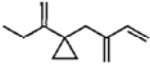
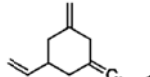
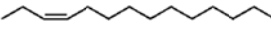
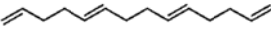


Figure 5 Total ion chromatogram with peak markers of OLEs classified based on carbon number.

Table 4 Examples of OLEs found in each carbon number

Carbon number	Hydrocarbon species of OLEs		
8	 (3E,5Z)-octa-1,3,5-triene	 (2Z,4Z)-3,4-dimethylhexa-2,4-diene	 (E)-2-methylhept-3-ene
9	 3,3-dimethylhepta-1,6-diene	 (E)-non-4-ene	 nona-1,8-diene
10	 (E)-3-ethyl-2-methylhepta-1,3-diene	 3,7-dimethyloct-1-ene	 (2E,8E)-deca-2,8-diene
11	 2,8-dimethylnona-1,8-diene	 2,8-dimethylnona-1,7-diene	 (E)-undec-5-ene
12	 dodec-1-ene	 1-(but-1-en-2-yl)-1-(2-methylenebut-3-en-1-yl)cyclopropane	 1-methylene-3-(prop-1-en-1-ylidene)-5-vinylcyclohexane
13	 (E)-tridec-3-ene	 (Z)-tetradec-3-ene	 (5E,9E)-tetradeca-1,5,9,13-tetraene

(d) Terpenes (TERs)

The classification of TERs is evaluated from the isoprene present in the basic molecular skeleton [22, 23], which are of the two classes, carenes and limonenes, as stated in Table 1. Moreover, TERs in the TDO can also be classified according to carbon number as illustrated in Figure 6. Examples of species in each class of carbon number are shown in Table 5.

(e) Di-aromatics (DAHs)

The DAHs are hydrocarbons containing two benzene rings fused together, which are naphthalene and alkylnaphthenes [17, 21]. As a result, classified according to carbon number, DAHs in TDOs are composed of hydrocarbon species starting at C10 to C14. Figure 7 shows the classes of DAHs found in TDOs with peak markers: C10, C11, C12, C13 and C14 from left to right. Examples of species in each carbon number are shown in Table 6.

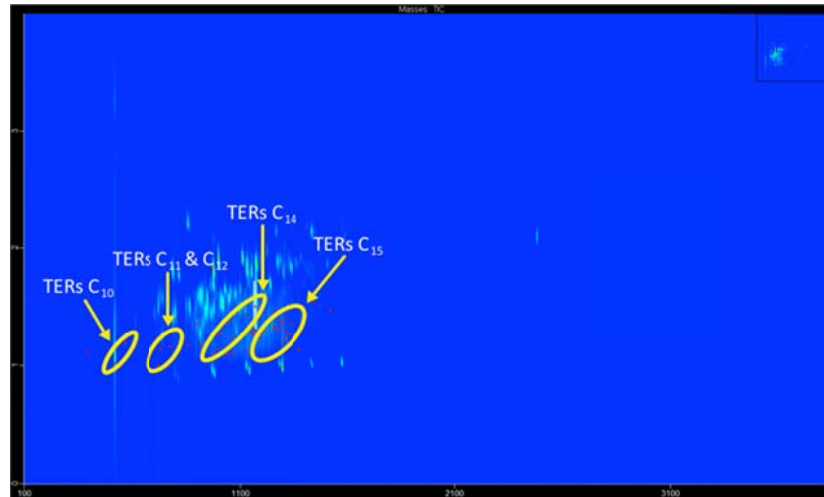
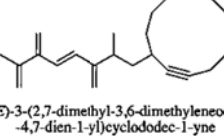
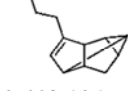
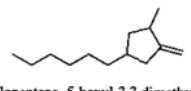
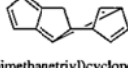


Figure 6 Total ion chromatogram with peak markers of TERs classified based on carbon number.

(f) *Poly-aromatics (PAHs)*

The PAHs contain three or more than two benzene rings fused together, which can be classified into anthracenes, pyrenes, phenanthrenes, and 1,1'-biphenyl. The mostly-found compounds in each class are shown in Table 1. The 1,1'-biphenyl is classified as a poly-aromatic hydrocarbon, although the two benzene rings do not fuse together, but form a new carbon-carbon bond [17, 21]. As a result, PAHs in TDOs contain hydrocarbon species starting at C12, C13, and C14 as shown in Figure 8 from left to right. Examples of species in each carbon number are shown in Table 7.

Table 5 Examples of TERs found in each carbon number

Carbon number	Hydrocarbon species of TERs		
10	 (S)-1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene	 3,7,7-trimethylbicyclo[4.1.0]hept-3-ene	 3-methyl-4-methylenebicyclo[3.2.1]oct-2-ene
11	 2-methyl-7-vinylbicyclo[4.2.0]oct-1-ene		
12	 (E)-3-(2,7-dimethyl-3,6-dimethyleneocta-4,7-dien-1-yl)cyclododec-1-yne		
13	 5-butyl-1,2,3,3a,4,6a-hexahydro-1,2,4-(epimethanetriyl)pentalene	 (Z)-bicyclo[10.1.0]tridec-1-ene	 Cyclopentene, 5-hexyl-3,3-dimethyl-
14	 1H-1,4,8-(epimethanetriyl)cyclopenta[f]azulene		
15	 1,1-dimethyl-4-methylenedecahydro-1H-cyclopropa[e]azulene	 3,8-dimethyl-4-(prop-1-en-2-yl)-1,2,3,3a,4,5,8,8a-octahydroazulene	

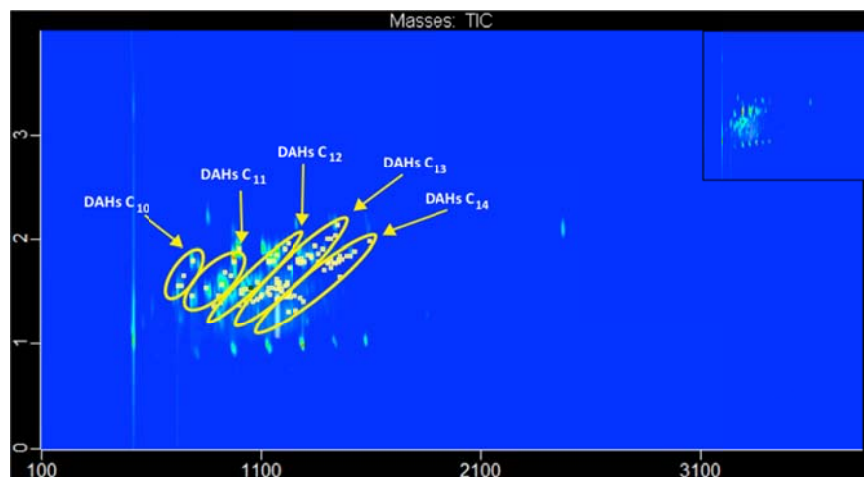
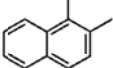
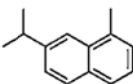
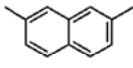
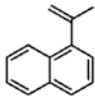
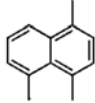
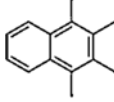
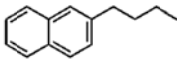


Figure 7 Total ion chromatogram with peak markers of DAHs classified based on carbon number.

Table 6 Examples of majority of DAHs found in each carbon number

Carbon number	Hydrocarbon species of DAHs
10	 naphthalene
11	 1-methylnaphthalene
12	 1,2-dimethylnaphthalene
13	 1-allylnaphthalene
14	 7-isopropyl-1-methylnaphthalene
	 2,7-dimethylnaphthalene
	 1-(prop-1-en-2-yl)naphthalene
	 1,4,5-trimethylnaphthalene
	 1,2,3,4-tetramethylnaphthalene
	 2-butylnaphthalene

(g) Polar-aromatics (PPAHs)

The polar-aromatic hydrocarbons (PPAHs) are aromatic hydrocarbons having at least two atoms of different elements in the benzene ring. For example, benzothiophene is composed of thiophene and benzene fused together. Moreover, when two benzene rings are fused together with thiophene, the compounds are called dibenzothiophenes. As a result, it is found that PPAHs in TDOs can be classified to hydrocarbon classes starting at C9, C10, C11, and C12 as shown in Figure 9 from left to right. Examples of species in each carbon number are shown in Table 8. The polar-aromatics in TDO are mostly sulfur-containing compounds.

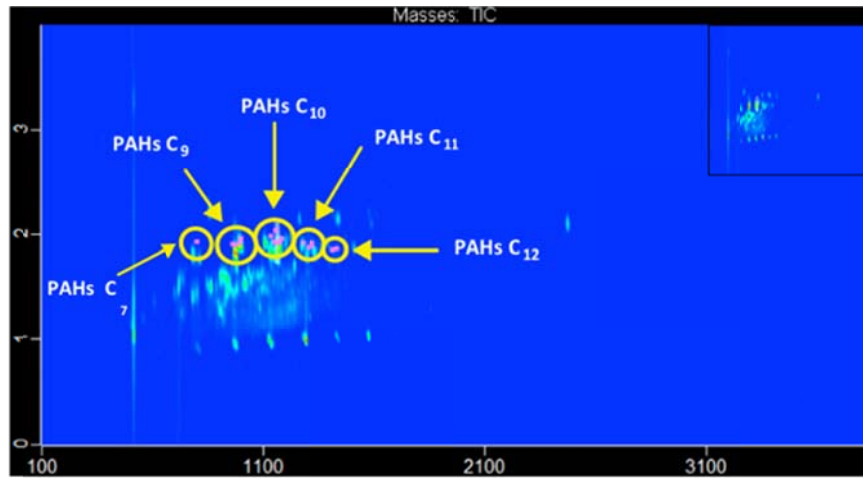
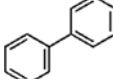
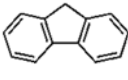
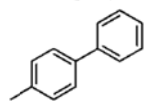
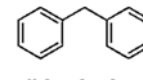
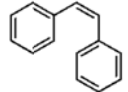
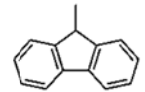
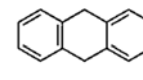


Figure 8 Total ion chromatogram with peak markers of PAHs classified based on carbon number.

Table 7 Examples of PAHs found in each carbon number

Carbon number	Hydrocarbon species of PAHs		
12	 1,2-dihydroacenaphthylene	 1,1'-biphenyl	
13	 9H-fluorene	 4-methyl-1,1'-biphenyl	 diphenylmethane
14	 (Z)-1,2-diphenylethene	 9-methyl-9H-fluorene	 9,10-dihydroanthracene

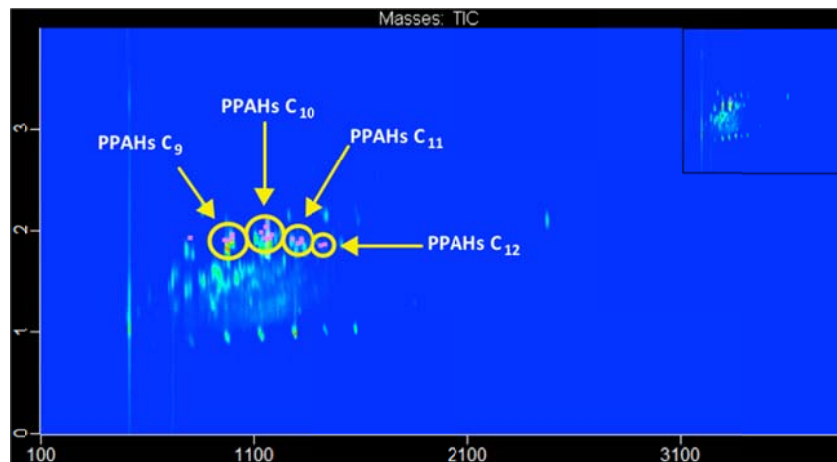


Figure 9 Total ion chromatogram with peak markers of PPAHs classified based on carbon number.

4. Conclusion

It was succeeded to analyze the tire-derived oil by using GC × GC-TOF/MS processed by LECO ChromaTOF® software. The data processing can be done within 180 min. The chromatographic peaks were explicitly resolved. The hydrocarbon species found in the tire-derived oil were more than 1,500 compounds, and can be classified into groups of MAHs, SATs, OLEs, TERs, DAHs, PAHs, and PPAHs including sulphur compounds. As a result, MAHs were categorized into two groups: (a) mono-aromatics with saturated substituents (MAHs-SS) such as indanes, alkylbenzenes, and tetralins, and (b) mono-aromatics with unsaturated substituents (MAHs-US) such as indenenes and alkenylbenzene. The carbon number of SATs ranged between C13 to C16. OLEs were di-olefins and tri-olefins with C8-C14. TERs were classified into 3-carene and d-Limonene found to have carbon numbers in the range of C10-C15. DAHs consisted of naphthalene and alkyl-naphthalenes with C10-C14. PAHs contained phenanthrenes, anthracenes, fluorenes, and pyrenes, with C12-C14. Finally, PPAHs consisted of thiophenes, benzothiophenes, and dibenzothiophenes with C9-C12.

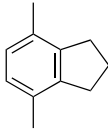
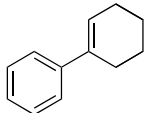
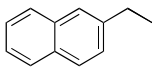
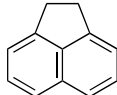
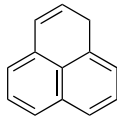
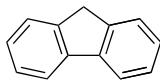


Table 1 Abundantly-found hydrocarbons in tire-derived oils

Group	Carbon number	m/z^a	Assigned compound ^b	
SATs	13	184.219	Tridecane	$\text{CH}_3\left[\text{CH}_2\right]_{11}\text{CH}_3$
	14	198.235	Tetradecane	$\text{CH}_3\left[\text{CH}_2\right]_{12}\text{CH}_3$
	16	226.266	Hexadecane	$\text{CH}_3\left[\text{CH}_2\right]_{14}\text{CH}_3$
OLEs	10	136.125	Isomycorene	
	13	182.203	Tridecene	
	14	196.219	Tetradecene	
TERs	10	136.125	3-Carene	
			d-Limonene	
MAHs	9	118.087	Indane	
	10	132.094	1-ethylIndane	
		134.110	p-Cymene	
	11	144.094	2,3-dimethylIndene	
		146.110	Cyclopentylbenzene	

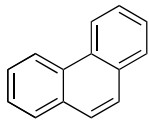
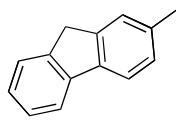
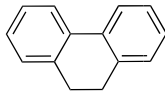
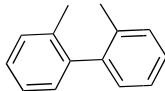
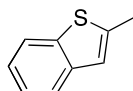
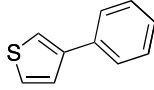
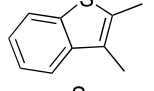
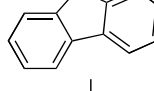
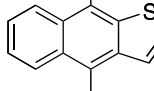
^aPithakratanayothin, S., Jitkarnka, S. Proceeding of The 29th International Conference on Solid Waste Technology and Management, Philadelphia, PA U.S.A., March 30-April 2, 2014



Group	Carbon number	m/z^a	Assigned compound ^b	
MAHs	11	146.110	4,7-dimethyl-2,3-dihydro-1H-Indene	
	12	158.110	Cyclohexenylbenzene	
			1-ethyl-3-methylIndene	
			hexa-2,4-dimethylBenzene	
			Cyclohexylbenzene	
		160.125	5-ethyl-1,2,3,4-Tetrahydroaphthalene	
			4-propyl-2,3-dihydro-1H-indene	
		162.141	Hexylbenzene	
DAHs	12	156.094	2-ethylnaphthalene	
PAHs	12	154.078	1,2-dihydroacenaphthylene	
	13	166.078	1H-phenalene	
			9H-fluorene	

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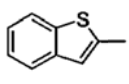
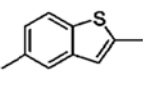
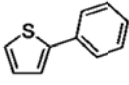
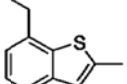
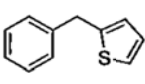
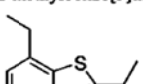
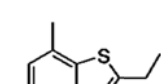


Group	Carbon number	m/z^a	Assigned compound ^b	
PAHs	14	178.078	Phenanthrene	
		180.094	9-methyl-9H-fluorene/	
		182.110	9,10-dihydrophenanthrene	
			2,2-dimethyl-1,1'-biphenyl	
PPAHs	7	126.050	Thiophene, 2-(1-methylethyl)-	
	9	148.035	Benzo[b]thiophene, 2-methyl-	
	10	160.035	Thiophene, 2-phenyl-	
		162.050	Benzo[b]thiophene, 2,5-dimethyl-	
	12	184.035	Dibenzothiophene	
		212.066	Naphtho[2,3-b]thiophene, 4,9-dimethyl-	

#

^aMass peak and ^bAssigned compound are based on the NIST library matches. The criteria used for identification hydrocarbon species are the %area that is higher than 0.1 % and match peaks that are more than 750.

Table 8 Examples of PPAHs found in each carbon number

Carbon number	Hydrocarbon species of PPAHs	
7	 2-isopropylthiophene	
9	 3-methylbenzo[b]thiophene	 2-methylbenzo[b]thiophene
10	 2,5-dimethylbenzo[b]thiophene	 2-phenylthiophene
11	 7-ethyl-2-methylbenzo[b]thiophene	 2-benzylthiophene
12	 2,7-diethylbenzo[b]thiophene	 2-ethyl-5,7-dimethylbenzo[b]thiophene

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Chapter 4

Valuable Petrochemicals, Petroleum Fractions, and Sulfur Compounds in Oils Derived from Waste Tyre Pyrolysis Using Five Commercial Zeolites as Catalysts: Impact of zeolite properties*

Abstract: Valuable petrochemicals such as benzene, toluene, and xylenes have been observed in waste-tyre derived oils, indicating that waste tyre exhibits its potential to be used for an alternative source for sustainably producing petrochemicals. However, without a catalyst, such chemicals cannot be produced in a high amount. Sulfur compounds causing environmental problems and the low quality of oils were also found in tyre-derived oils. In waste tyre pyrolysis, zeolites that have been used very often to improve the quality of oil are HZSM-5 and HY, owing to their cracking and single-ring aromatics-producing abilities. Some other zeolites have been also employed occasionally, but the effects of zeolite properties on the hydrocarbon species and sulfur compounds in oils have not been explained clearly. The objective of this work was therefore to investigate the effects of zeolite properties; that are, acidity/basicity, pore channel structure, pore size, and Si/Al ratio on hydrocarbon species in pyrolysis products, especially valuable C6-C8 petrochemicals and sulfur compounds. The oils were analyzed by using SIMDIST GC for petroleum fractions and using a GCxGC-TOF/MS for valuable petrochemicals and sulfur-containing compounds. The analysis of the results from using five zeolites indicated that, for high production of valuable C6-C8 petrochemicals from waste tyre pyrolysis, a catalyst must: (a) possesses acid sites, rather than basic ones, that have high enough strength for cracking, which can result in high production of naphtha fraction, and (b) have a complex channel structure with a large enough pore size (at least $\sim 7 \text{ \AA}$) that allows molecules to stay inside at a long contact time. In addition, high acid strength is more preferred to high acid density for high production of valuable C6-C8 petrochemicals, but high acid density is more preferred for production of oil with low sulfur content.

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4.1 Introduction

Olefins and aromatic hydrocarbons are important petrochemicals, conventionally derived from petroleum. Light olefins are produced from fluid catalytic cracking unit in oil refineries and steam cracking of natural gas whereas useful aromatic hydrocarbons such as benzene, toluene, and xylenes are derived from petroleum-based naphtha and used as a wide range of raw materials in petrochemical industry. For sustainable future petrochemical industry, various renewable raw materials such as biomass or wastes have gained great attention from society, governments and policy makers since they cannot only replace petroleum-based raw materials (Hancsók et al. 2014) by the time of scarcity, but also the replacement can reduce greenhouse gases (Fiksel et al. 2011). With or without a catalyst, waste tyres (Srogi, 2008) and waste plastics (Sakaki et al. 2014) are also hydrocarbon-based materials, which exhibit potential to be used as an unconventional source for liquid fuel and petrochemical productions. At early stages during 1990s, pyrolytic oil from pyrolysis of waste tyre was examined mostly for uses as fuels, but later it was found to contain valuable hydrocarbons. For examples, Islam et al. (2008) analyzed liquid products from waste motorcycle tyre pyrolysis, and found that pyrolytic oils were complex mixtures, which consisted of aliphatic and aromatic compounds. Pakdel et al. (2001) found dl-limonene in waste tyre-derived oil, and later it was suggested that the pyrolytic oil can be used as chemical feedstocks for aromatic production (Banar et al. 2012). Moreover, pyrolytic oil also contains a considerable amount of sulfur-containing compounds, such as benzothiophene, thiophene and their derivatives (Williams and Bottrill, 1995). However, the formation of these compounds during pyrolysis still remains unelucidated.

In pyrolysis of waste plastics or tyres, an acid catalyst is needed for either accelerating degradation or enhancing product selectivity. Silica-alumina catalyst is the simplest catalyst for these purposes. For instances, in the catalytic degradation of mixed polyethylene and polypropylene using a silica-alumina catalyst, the conversion greatly increased in association with the improve yield of gasoline (Roozbehani et al. 2015). When employed in polystyrene pyrolysis, the catalyst was found to greatly enhance the selectivity of styrene monomer in the product (Moqadam et al. 2015). HZSM-5 is the most frequently employed zeolite in pyrolysis of waste materials; for example, it was found to change product compositions and distribution, depending on the type of plastics and pyrolysis



temperature (Mikulec and Vrbova, 2008). Common zeolites that have been tested in waste tyre pyrolysis are, for examples, HZSM-5, HY, HMOR, and HBETA. Briefly, HZSM-5 with the zigzag 3D channel structure of 5.3×5.6 Å pore size and Y zeolites with also a 3D structure (FAU: faujasite) but pore diameter of 7.4 Å have been frequently employed in pyrolysis in order to investigate the effects of catalysts on the composition of tyre-derive oils (Olazar et al. 2008), especially aromatics (Williams and Brindle, 2003a) and single-rings aromatics (Williams and Brindle, 2003b). William and Brindle (2002) studied the influence of two different pore size catalysts, Y-type zeolite (7.8 Å) and ZSM-5 (5.6 Å), and found that Y-type zeolite with larger pore size and higher surface acidity yielded higher aromatic compounds but lower liquid yields than ZSM-5 catalyst. Later in 2003, they tried to maximize the single ring aromatics from scrap tyres pyrolysis using three types of catalysts (ZSM-5, and two Y-zeolites), and reported that Y zeolite with a lower Si/Al ratio gave a higher yield of all 5 aromatics (benzene, toluene, m/p/o-xylenes, or BTX) than the one with a higher ratio, confirming that higher surface acidity resulted in higher single-ring aromatic production. Moreover, more results from the pyrolysis of waste tyre using USY and ZSM-5 also confirmed the higher concentrations of BTX (Boxiong et al. 2007a) and the lower oil yield achieved by USY zeolite (Boxiong et al. 2007b).

KL zeolite is considered as a basic zeolite with a 1D straight channel structure of 12-membered rings and a pore opening of 7.1 Å in diameter. Recently, KL has been used as a catalyst for waste tyre pyrolysis, and found to enhance mono-aromatics with a significant decrease of di-aromatics and terpenes in the tyre-derived oil (Pithakratanayothin and Jitkarnka, 2014). Additionally, BETA zeolite is a kind of high silica zeolites with a 3D straight channel system and pore size of 7.6×6.4 Å whereas HMOR zeolite is a moderate acidic zeolite that has large pore size with an opening of 6.5×7.0 Å. HMOR zeolite is considered as 1D straight channel structure with 12-membered rings. Dũng et al. (2009) used HBeta and HMOR as the supports for Pt in waste tyre pyrolysis, and found that HBETA exhibited higher activity for polar-aromatic reduction as compared to HMOR, which was ascribed to its higher medium and strong acid site density, smaller particle size and 3D-structure. Furthermore, Muenpol and Jitkarnka (2014) have investigated the effect of pore channel structure on the hydrocarbon compounds and petrochemicals in waste tyre-derived oils using HMOR and HBeta. It was reported that HBeta gave the higher amount of aromatics than HMOR and the lower amounts of olefins and naphthenes than HMOR. It can be explained that the complex pore of HBeta converted more olefins and naphthenes to aromatics inside the pore than the



straight pore of HMOR. In addition, these two zeolites can reduce sulphur in oils, and the species of sulphur were different. Moreover, both HBeta and HMOR catalysts caused the increment in the group of benzothiophenes and the reduction in the group of benzothiazoles.

According to the literature reviews, no study has been intensively focused on the impacts of zeolytic supports properties on the production of useful aromatic petrochemicals (C6 – C8s) and the species of sulfur compounds in waste tyre-derived oil. Thus, in this work, the effects of zeolites properties; that are, acidity or basicity (using HMOR vs KL), pore channel structure (using HMOR vs HBeta), pore size (using HBeta vs HZSM-5), and acid strength or Si/Al ratio (using HY and HBeta) on the production of useful aromatic petrochemicals (C6 – C8s) and the species of sulfur compounds in waste tyre-derived oils were specifically investigated. In analysis, since such valuable petrochemicals mostly are components in naphtha fraction, the activities on cracking, mono-aromatics production, and sulfur removal were emphasized.

4.2 Experimental

4.2.1 Catalyst Preparation and Characterization

KL, HMOR, HBeta, HZSM-5, and HY were obtained from Tosoh Company in Singapore. The properties of the zeolites are tabulated in Table 1. In order to remove impurity from zeolites, KL, HMOR, and, HZSM-5 zeolites were calcined at 500 °C for 3 h with the heating rate of 10 °C/min, and HY was calcined at 500 °C for 3 h with the heating rate of 5 °C/min, while HBeta was calcined at 600 °C for 5 h with 2 °C/min. Calcination procedures were made different because the purchased zeolites were obtained from the manufacturer with different forms of cations. After that, zeolite powders were pelletized, crushed, and sieved into the particle size range of 40-60 mesh.

Table 1 Properties of zeolites

Zeolite	Pore Size (Å)	Channel System	Membered Ring	Si/Al ratio
KL	7.1	1D	12	3
HMOR	6.5×7.0	1D	12	9.5
HBeta	6.4×7.6	3D	12	13.5
HZSM-5	5.3×5.6	3D	10	15
HY	7.4	3D	12	7.5

X-ray diffraction patterns were taken using a Bruker X-ray diffractometer system equipped with a 2.2 kW Cu anode in a long fine focus ceramic X-ray tube for generating a CuK α radiation (1.5405 Å). The detector scanned for the diffractive peaks from the sample as a function of 2θ by starting at the 5° to 100° (2θ) range and a scan speed of 5°(2θ)/min. The specific surface area and pore volume were characterized by using ThermoFinnigan/Sorptomatic1990 equipment. In addition, Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis) was used to determine the amount of coke deposited on spent catalysts. The temperature was ramped to 900 °C with heating rate of 10 °C/min. Moreover, sulfur deposited on a catalyst surface was determined by using LECO®Elemental Analyzer (TruSpec®S).

4.2.2 Pyrolysis of Waste Tyre

The pyrolysis reaction was operated under the process as reported in Dũng et al. (2009). Briefly, there were 2 zones of the pyrolysis reactor, which are catalytic zone (the upper zone) and pyrolytic zone (the lower zone). Firstly, 30 g of the waste tyre (Bridgestone TURANZA GR-80) with sizes in the range of 20-40 mesh was loaded into the lower zone, and 7.5 g of catalyst with pellet size range of 40-60 mesh was loaded to the catalytic zone. Then, the pyrolysis zone was heated with the rate of 10 °C/min from the room temperature to 500 °C. Once reached, the final temperature was kept for 120 min. The temperature of pyrolytic zone was controlled at 350 °C. The flow rate of N₂ was controlled at 30 mL/min, and used as a carrier gas of the pyrolysis products to condensers and a gas sampling bag. These condensers were placed into an ice-salt bath in order to collect the liquid product.



A gas sampling bag collected the incondensable products.

4.2.3 Product Analysis

The liquid products were dissolved in *n*-pentane (40:1 mass ratio of oil/*n*-pentane) to precipitate asphaltene, and then asphaltene was filtered using polyamide membrane (pore size: 0.45µm). After that the maltenes (the obtained oils after asphaltene separation) were analyzed for true boiling point curve and petroleum fractions using a Varian GC-3800 Simulated Distillation Gas Chromatography (SIMDIST-GC) conformed to the ASTM D-2887. Petroleum fractions in maltenes are classified according to boiling point distillation conformed with ASTM D-2887 into five fractions: full range naphtha (< 200 °C), kerosene (200-250 °C), light gas oil (250-300 °C), heavy gas oil (300-370 °C), and long residue (> 370 °C). Moreover, the chemical compositions of maltenes were analyzed using a two-dimensional Gas Chromatography with Time of Flight Mass Spectrometer (GC×GC-TOF/MS) equipped with a non-polar Rtx®-5Sil MS (1.10 m × 0.25 mm ID × 0.25 µm film thickness) and Rxi®-17 MS (1.10 m × 0.10 mm ID × 0.10 µm film thickness) as the first and second columns, respectively. The gas products were analyzed for their compositions using a Gas Chromatography (GC-FID), Agilent Technologies 6890 Network GC system, equipped with HP-PLOT Q column (30 m × 0.32 mm ID × 20 µm film thickness). In addition, an LECO®Elemental Analyzer (TruSpec®S) was also used to analyze the sulfur content in shredded tyre, oil and solid products, while sulfur content in gas products was calculated by mass balance.

4.3 Results and Discussion

The catalyst properties obtained from surface area analyzer of HBeta, HMOR, HZSM-5, HY, and KL zeolites are revealed in Table 2. Powder XRD technique confirmed the crystallinity and the types of the zeolites.

Table 2 Surface and Pore Volume of Catalysts

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Median pore width (Å)
KL	218	0.113	7.08
HMOR	394	0.199	8.42
HBeta	539	0.257	8.35
HZSM-5	545	0.189	5.84
HY	515	0.266	8.37

4.3.1 Overall performance of the zeolites

All batches of pyrolysis runs gave a very similar char yield of around 41 wt. %. The yields of oil and gas products are not significantly different (see **Table 3**) for all zeolites. Using acid zeolites, except HMOR, the production of mixed C₄s is significantly enhanced with the suppression of ethylene and propylene production as illustrated in **Table 4**. Moreover, the full-range naphtha content in oil is also enhanced with the use of all acid zeolites as shown in **Table 5**, indicating their ability in cracking. Additionally, the amounts of overall “valuable petrochemicals” (hereby, focused on benzene, toluene, xylenes, styrene, cyclohexane, and cumene) in maltenes are shown in Table 6. It can be ranked as HBeta (10.8 wt.%) > HMOR (2.32 wt.%) > the non-catalyst case (1.57 wt.%) > KL (0.580 wt.%). Table 7 illustrates sulfur content on spent catalysts and in oils obtained from using all catalysts. In general, the zeolites can reduce sulfur in oils by around 7 – 19.4%. Next, the results obtained from each pair of zeolites were analyzed in order to study the effects of acidity/basicity (HMOR vs KL), pore channel structure (HMOR vs HBeta), pore size (HBeta vs HZSM-5), and Si/Al ratio (HBeta vs HY). Since valuable petrochemicals are mostly aromatic components in naphtha fraction, the performances of the zeolites on cracking, mono-aromatics production, and sulfur removal were focused in analysis. The details are discussed in the next following sections.

Table 3 Yield (wt.%) of products from tyre pyrolysis

Catalyst	Yield (wt.%)			
	Gas	Liquid	Solid	Coke
Non-catalyst	11.6	46.0	42.4	0.00
KL	12.2	43.5	41.5	2.79
HMOR	11.9	43.8	41.6	2.60
HBeta	9.62	43.3	41.6	5.41
HZSM-5	13.2	43.1	41.7	1.90
HY	10.8	42.6	42.2	4.49

Table 4 Composition (wt.%) of gaseous products (H₂-free basis) obtained from using various zeolites in waste tyre pyrolysis

Catalyst	Methane	Ethylene	Ethane	Propylene	Propane	Mixed-C ₄	Mixed-C ₅
Non-catalyst	20.3	9.38	15.9	12.2	9.06	19.6	13.5
KL	19.5	6.70	15.9	12.4	9.13	19.9	16.4
HMOR	18.2	4.73	14.9	10.6	16.7	19.4	15.5
HBeta	14.8	6.31	11.0	11.9	8.98	29.2	17.8
HZSM-5	13.6	5.20	10.7	10.5	19.7	26.5	13.7
HY	18.0	5.94	13.8	10.4	9.87	25.4	16.7

Table 5 Petroleum fraction (wt.%) in tyre-derived oils

Catalysts	Fractions (wt.%) in tyre-derived oil				
	Full range naphtha	Kerosene	Light gas oil	Heavy gas oil	Long residue
Non-catalyst	22.1	23.4	20.1	18.3	16.2
HMOR	31.7	21.5	16.9	17.5	12.5
KL	22.1	27.9	19.2	15.4	15.5
HBeta	38.6	22.0	19.1	10.1	10.4
HZSM-5	28.2	21.5	17.3	18.8	14.3
HY	32.9	20.6	16.8	16.4	13.4

Table 6 Petrochemicals obtained from waste tyre pyrolysis (wt.% in maltene)

Chemicals	Catalysts					
	Non-catalyst	KL	HMOR	HBeta	HZSM-5	HY
Benzene	0.430	0.265	0.124	4.81	-	2.50
Toluene	0.0274	0.00497	0.184	0.917	0.196	2.66
Ethylbenzene	0.833	0.102	0.408	3.31	0.258	0.367
<i>m</i> -Xylene	-	-	0.185	-	0.0981	-
<i>o</i> -Xylene	-	-	-	0.161	-	0.260
<i>p</i> -Xylene	-	-	-	0.129	0.0304	0.376
Styrene	0.189	0.125	1.31	0.320	0.207	0.523
Cyclohexane	0.0239	-		1.05	3.46	0.470
Cumene	0.0660	0.0827	0.105	0.0771	0.0348	0.174
Total	1.57	0.580	2.32	10.8	4.28	7.33

Table 7 Sulfur content on spent catalysts and in oils obtained from using all catalysts

Sample	Sulfur (wt.%)					
	Non-cat.	KL	HMOR	HBeta	HZSM-5	HY
Spent catalyst	-	0.25	0.18	0.41	0.27	0.273
Oil	1.17	1.02	1.08	1.10	1.08	0.943

4.3.2 Comparison between acidic and basic zeolites

The effect of acid properties of zeolites are discussed in this section, which HMOR and KL were chosen for comparison to eliminate the effects of pore size, pore dimension, and pore structure, since both zeolites have the same 1D pore channel structure. It can be observed from **Table 5** that KL does not enhance full range naphtha, but increases kerosene fraction whereas HMOR can increase the amount of full range naphtha to 31.7 wt.% in oil, and also decreases all other heavier fractions. Thus, apparently the acidic zeolite possesses better cracking ability than the basic one.

The chemical components in oils are classified into seven groups: paraffins, olefins, naphthenes, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics, as illustrated in **Fig.1(a)**. The results exhibit that HMOR gives a slightly lower concentration of paraffins, olefins, naphthenes and poly-aromatics than KL. It can be suggested that olefins and naphthenes, produced by thermal cracking, are further converted to aromatics via carbenium ions generated on the acid catalyst via aromatization and Diels-Alder reactions (Meng et al. 2013), which is also confirmed by the reduction of light olefins (ethylene, propylene) in the gas product (see in Table 4). The mono-aromatics content in oil is more greatly enhanced with using HMOR than KL. Therefore, it can possibly explained that the formation of mono-aromatics can occur in two pathways: (a) aromatization of olefins and naphthenes for an acidic catalyst, and (b) ring-opening of poly-aromatics for both acidic and basic zeolites.

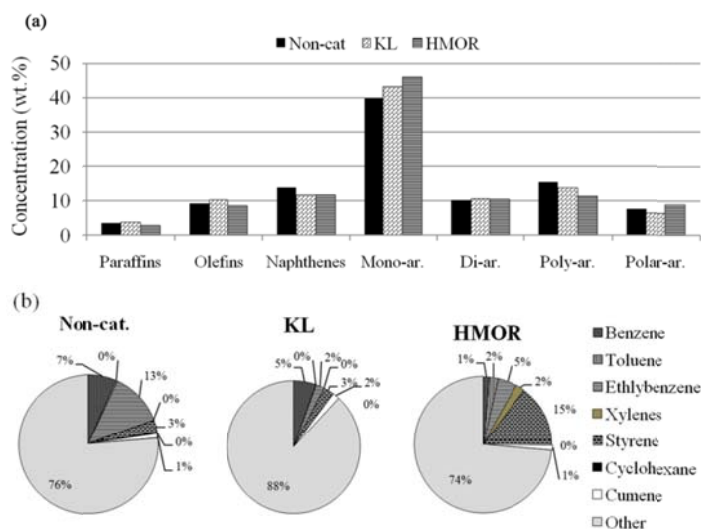
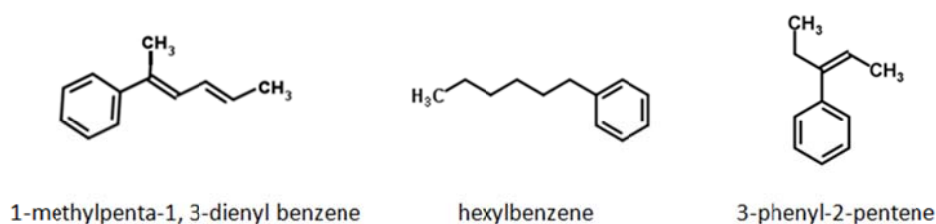


Fig. 1 Compositions in tyre-derived oils obtained from KL and HMOR: (a) molecular composition in maltenes, and (b) valuable petrochemicals in gasoline fractions

Moreover, **Fig.1(b)** shows that HMOR has a potential to produce more total petrochemicals (26 wt.% in gasoline) than KL (12 wt.% in gasoline). HMOR also enhances the amount of styrene with the suppression of ethylbenzene and benzene. Owing to the acid sites on HMOR, styrene might be produced directly from (a) cracking of tyre molecules, (b) dehydrogenation of ethylbenzene, and (c) trans-alkylation reaction of benzene with an olefin, resulting in the increasing of styrene (Sudha et al. 2007). On the other hand, KL increases mono-aromatics production, but does not enhance the formation of total valuable petrochemicals. It can be explained that KL produces mono-aromatics with longer chains; for instance, it was observed that other mono-aromatic species such as 1-methylpenta-1,3-dienyl benzene, hexylbenzene, and 3-phenyl-2-pentene, as depicted below, are significantly enhanced. In conclusion, the acidic zeolite does not only gives a light liquid products, but also gives more valuable hydrocarbons than the basic zeolite.



From Table 7, it can be seen that KL has slightly better sulfur-in-oil removal performance than HMOR, possibly KL is a base that can better adsorb acidic sulfur compounds. Moreover, the sulfur-containing compounds in oils are classified into five groups: thiophenes, benzothiophenes, dibenzothiophenes, benzothiazoles, and a mixture of heteroatom (O and/or N)-containing sulfur compound, or so-called “others” as shown in **Fig.2**. It can be seen that both zeolites decrease benzothiazoles, especially HMOR, and heteroatom-containing sulfur molecules. It can be suggested that the acid sites on HMOR are stronger in attacking the C-N, C=N and C-S bonds in a benzothiazole molecule than the basic sites on KL; thus, benzothiazoles are possibly into hydrocarbons better than KL (a base catalyst). Moreover, benzothiazoles possibly rearrange to form benzothiophenes in the case of KL since the yield of benzothiophenes increases with using KL, but slightly decreases with using HMOR. In summary, the acid zeolite gives better quality of oil, in terms of high petrochemicals content and the ease on further desulfurization, than the base one.

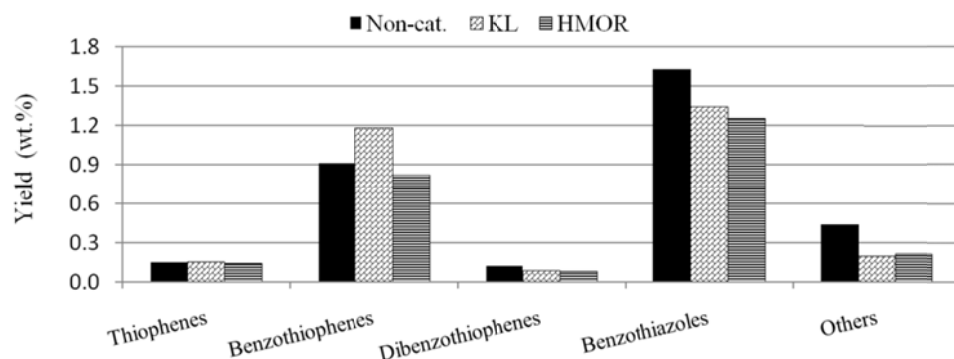


Fig. 2 Yields of sulfur-containing compounds in tyre-derived oils obtained from KL and HMOR.

4.3.3 Comparison between two pore channel structures (1D and 3D) of zeolites

HMOR and HBeta zeolites have different pore channel structures; that are, 1D (HMOR) and 3D (HBeta) with no difference in pore size, which have been used to study the effect of pore channel on pyrolysis products (Muenpol and Jitkarnka, 2014). The results can be summarized and further discussed in more



details as follows. HBeta gives a higher amount of the full range naphtha and then a less amount of heavier fractions than HMOR (**Table 5**). Thus, it can be concluded that using HBeta results in lighter liquid product than using HMOR. It may be also possible that HBeta has a higher acid strength than HMOR (Düng et al. (2009), possibly due to the strain in the more complex 3D channel of HBeta. Moreover, the 3D pore channel allows molecules to stay inside the zeolite channel with a long residence time, and then heavy fractions can be cracked into light fractions more effectively than in the 1D pore channel. Additionally, HBeta gives the higher amount of total aromatics than HMOR, and consequently gives the lower paraffins, olefins, and naphthenes contents than HMOR. It can be explained that aromatic compounds can be formed via Diels-Alder reaction of light olefins to cyclic hydrocarbons, and subsequently aromatics are formed via condensation reaction (Cypres, 1987). The pathway of reactions occurs via carbenium ion generation on an acid site; thus, HBeta with higher acid strength (Düng et al. 2009) can better generate carbenium ions that allow such reactions to occur more easily than HMOR. These are confirmed by the greater decreases in olefins and naphthenes in accordance with the greater increase of total aromatics, especially di-aromatics, in the oil in **Fig. 3(a)**, with using HBeta.

Valuable hydrocarbon compounds in the oils are shown in **Fig. 3(b)**. HBeta can produce petrochemicals of interest in a much higher concentration (61 wt.% in gasoline) in the oil than HMOR (26 wt.% in gasoline). Moreover, HBeta can produce a higher amount of benzene, ethylbenzene, toluene, and cyclohexane than HMOR. Moreover, a small amount of *o*-xylene and *p*-xylene are produced by using HBeta, and *m*-xylene is produced by using HMOR. In addition, the amount of styrene sharply increases with using HMOR, and the amount of cumene is not significantly changed for all cases. It is possible that HBeta, with more complex channel structure that creates slightly higher acid strength (also slightly higher Si/Al ratio) than HMOR, can better catalyze the cyclization reaction of paraffins or olefins to form cyclic hydrocarbons such as cyclohexane, and then convert to benzene via carbenium ion mechanism (Joshi and Thomson, 2005). Moreover, both zeolites may catalyze trans-alkylation reaction of benzene with an olefin to styrene and ethylbenzene (Sudha et al. 2007).

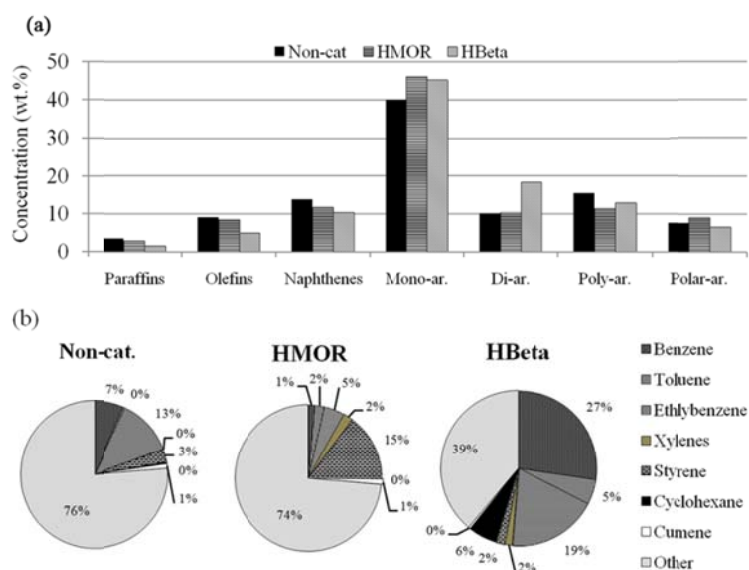
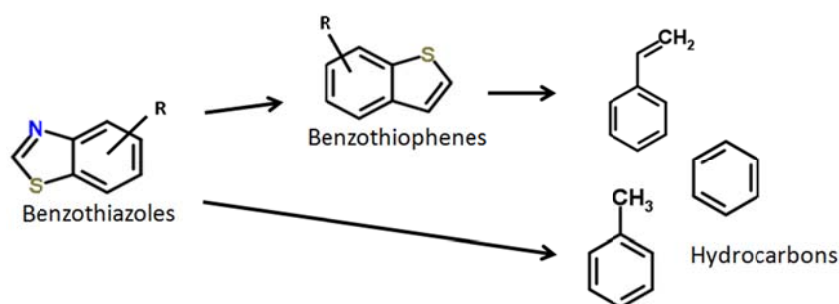


Fig. 3 Compositions in tyre-derived oils obtained from HMOR and HBeta: (a) molecular composition in maltenes, and (b) valuable petrochemicals in gasoline fractions.

Owing to its more complex 3D channel structure, HBeta results in a higher content of coke (**Table 3**) and sulfur compounds (**Table 7**) deposited on the spent catalyst than HMOR. Moreover, sulfur content in oils is reduced with using both catalysts, and HMOR gives slightly lower sulfur content in oils (1.08 wt.%) than HBeta (1.10 wt.%). However, it was found that benzothiophenes dramatically increased with using HBeta, but insignificantly changed with using HMOR (Muenpol and Jitkarnka, 2014). Moreover, benzothiazoles sharply decreased with using both catalysts, whereas the group of heteroatom (O and/or N)-containing sulfur compounds was reduced. It can be suggested that HMOR and HBeta possibly convert benzothiazoles and the others, possibly forming hydrocarbon compounds such as derivative of benzenes, or even non-aromatics, as illustrated below.





Unlike HMOR, HBeta possibly rearranges benzothiazoles to form benzothiophenes inside the zeolite channel. In addition, 3D pore channel of HBeta allows molecules to stay inside its channel with a longer residence time than 1D pore channel of HMOR; thus, resulting in a high amount of benzothiophenes produced by HBeta, but not by HMOR. Moreover, since HMOR gives a less amount of benzothiophenes and dibenzothiophenes than HBeta; thus, it means that the oil obtained from HMOR is easier to be further desulfurized than those from HBeta.

4.3.4 Comparison between two pore sizes of zeolites

For this part, the effect of pore size of zeolite is discussed by comparing the results obtained from using HZSM-5 and HBeta zeolites. Both of them are acidic zeolites with 3D-pore channel. In addition, the Si/Al ratios of these zeolites are not significantly different, but they have a significant difference in pore size; that are, $5.3 \text{ \AA} \times 5.6 \text{ \AA}$ (HZSM-5) and $6.4 \text{ \AA} \times 7.6 \text{ \AA}$ (HBeta). As a result, HBeta exhibits a higher amount of full range naphtha (38.6 wt.%) than HZSM-5 (28.2 wt.%), indicating that the large pore size of HBeta allows a higher amount of molecules to go inside the pore to be cracked than the medium pore size of HZSM-5. **Fig. 4(a)** exhibits that using HBeta gives a higher amount of total aromatics as well as a lower amount of paraffins, olefins, and naphthenes than the non-catalytic pyrolysis. On the other hand, HZSM-5 can reduce the concentration of total aromatics and paraffins with the increase of olefins as compared to the non-catalytic pyrolysis. Moreover, the amount of naphthenes does not significantly change with using HZSM-5. It can be explained that the medium pore size of HZSM-5 that allows a less amount of molecules to go inside the zeolite pore than the large pore of HBeta. Moreover, HZSM-5 has a lower pore volume ($0.1780 \text{ cm}^3/\text{g}$) than HBeta ($0.2570 \text{ cm}^3/\text{g}$); thus, resulting in less chance in transformation of small olefins to cyclic hydrocarbons and aromatic hydrocarbons (Olazar et al. 2008), which is also confirmed by the high content of olefins in the oil in **Fig. 4(a)**. In addition, it can be seen that mono-aromatic hydrocarbons are enhanced with the use of HBeta, but suppressed with the use of HZSM-5. It can be explained that mono-aromatic molecules can pass into the medium pore size of HZSM-5, and then are converted to olefins. That is also the reason why HZSM-5 can a lot less produce valuable petrochemicals (26 wt.% in gasoline), that are mostly mono-aromatics, than HBeta (61 wt.% in gasoline) as depicted in **Fig. 4(b)**.

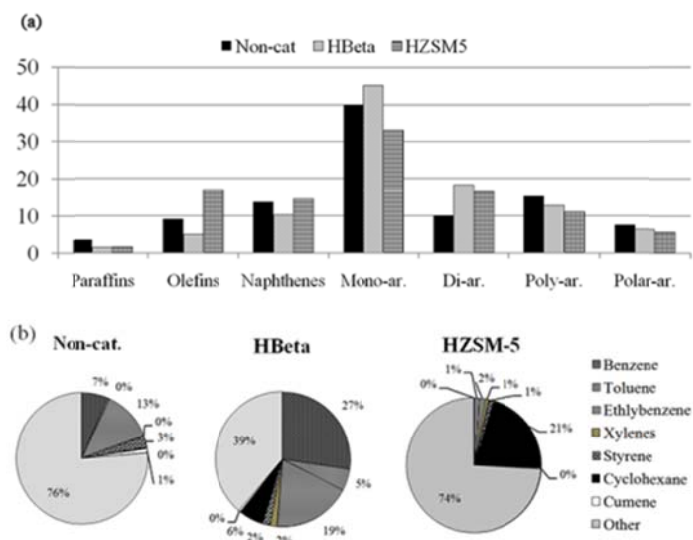


Fig. 4 Compositions in tyre-derived oils obtained from HBeta and HZSM-5: (a) molecular composition in maltenes, and (b) valuable petrochemicals in gasoline fractions.

Among mono-aromatics, HBeta sharply increases the amount of benzene (4.81 wt.% in gasoline) and ethylbenzene (3.31 wt.% in gasoline), and slightly increases toluene whereas HZSM-5 does not produce benzene; however, it gives a high amount of cyclohexane and a small amount of ethylbenzene and toluene. It should be noted that HBeta gives a higher amount of valuable aromatics, such as benzene, ethylbenzene, and toluene, than HZSM-5. These observations agree with Roldán et al. 2004, which reported that the medium pore of HZSM-5 was inactive for the transformations of benzene and xylenes, whereas the larger pore of HBeta was active toward the reactions. It was due to medium pore zeolite that hinders the process through steric restriction in the pore (Roldán et al. 2004).

Moreover, the depositions of coke (Table 3) and sulfur (Table 7) on the spent HZSM-5 are lower than those on the spent HBeta, which is owed to the smaller pore size and pore volume of HZSM-5 (Table 2). HBeta and HZSM-5 slightly reduce sulfur in oils, and the difference in their ability on sulfur removal is not relevant. In addition, Fig. 5 illustrates that the larger pore of HBeta results in a higher amount of large S-compounds (benzothiophenes, dibenzothiophenes, and benzothiazoles) than the smaller pore of HZSM-5. In addition, benzothiazoles sharply decrease with using both catalysts, especially HZSM-5, whereas

benzothiophenes increase with using HBeta and insignificantly change with using HZSM-5. It can be explained that HZSM-5 and HBeta possibly convert benzothiazoles and the other sulfur compounds to hydrocarbon compounds such as benzene derivatives. In addition, the medium pore of HZSM-5 has less capacity to form large compounds, such as benzothiophenes, dibenzothiophenes, and benzothiazoles, than the larger pore of HBeta since these groups of compounds are easier to be desulfurized on HZSM-5 than HBeta, based on the principle described in Cottrell (1958) and García-Cruz et al. (2008).

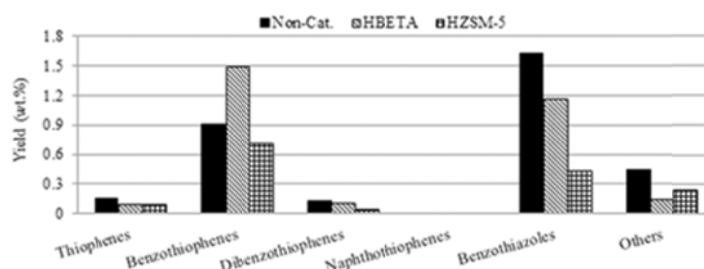


Fig. 5 Yields of sulfur-containing compounds in tyre-derived oils obtained from HBeta and HZSM-5.

4.3.5 Comparison between two Si/Al ratios of Zeolites

With similar pore openings, pore structures, the results obtained from using HBETA (Si/Al=13.5) and HY (Si/Al=7.5) were compared to examine the effects of acid strength and density on the pyrolysis products. As a result, HBeta can more greatly enhance full-range naphtha fraction than HY (Table 5). Responsible by higher acid strength (higher Si/Al ratio), HBeta can produce lighter oil (higher full-range naphtha) than HY with lower acid strength (lower Si/Al ratio) because the higher acid strength can ease carbenium ions generation and lower reaction activation energies (Rigby et al. 1997).

HY and HBeta catalysts increase the formations of mono- and di-aromatics while the other groups (except polar-aromatics in the HY case) are decreased as shown in **Fig. 6(a)**. The results indicate that both catalysts can crack poly-aromatics and/or aromatize paraffins, olefins, and naphthenes to be mono- and di-aromatics. HY produces a slightly higher concentration of total aromatics

than HBeta because HY has higher acid density with slightly higher pore volume and pore diameter, resulting in higher cyclization and aromatization (Olazar et al. 2008). **Fig. 6(b)** depicted that even though HY can produce higher total mono-aromatics in the oil, the valuable mono-aromatics are produced in a lower concentration (55 wt.% in gasoline) than those obtained from HBeta (61 wt.% in gasoline). This observation indicates that the impact of acid strength is more pronounced in producing valuable petrochemicals than that of acid density. HY can produce a high amount of benzene (2.50 wt.%) and toluene (2.66 wt.%) in gasoline, while those of benzene (4.81 wt.%) and ethylbenzene (3.31 wt.%) are sharply produced by HBeta.

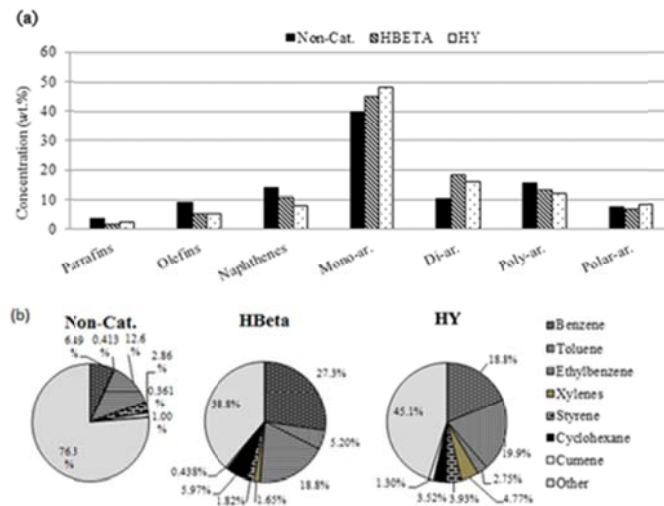


Fig. 6 Compositions in tyre-derived oils obtained from HBeta and HY: (a) molecular composition in maltenes, and (b) valuable petrochemicals in gasoline fractions.

HBeta gives the higher sulfur content in the oil (Table 5) than HY, which indicates that high acid density is need for high sulfur removal ability. Furthermore, **Fig. 6(b)** also shows that HBeta and HY sharply reduce benzothiazoles. However, HY can more greatly reduce benzothiazoles than HBeta, in association with a sharp decrease in benzothiophenes. Thus, it can be concluded that high acid density is more essential for breaking a large number of C-N and C-S bonds in large molecules of benzothiazoles and benzothiophenes than high acid strength.

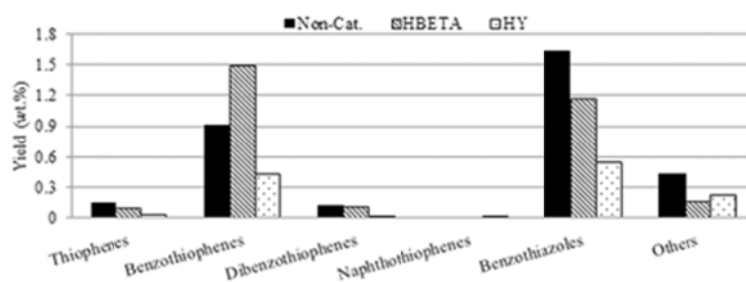


Fig. 7 Yields of sulfur-containing compounds in tyre-derived oils obtained from HBeta and HY.

4.4 Conclusions

To our knowledge, based on literature reviews, not so many types of zeolites have been employed in the catalytic pyrolysis of waste tyre. The most often used zeolites were Y and ZSM-5 zeolites. Furthermore, among articles reporting the uses of zeolites in tyre pyrolysis, only a few groups of researchers, namely Williams's and Boxiong's groups, were found to report the influence of particular Y or ZSM-5 zeolites on the formation of valuable hydrocarbons in tyre-derived oil (Boxiong et al. 2007; Williams and Brindle 2003a). The knowledge on how zeolites affect the production of valuable aromatic hydrocarbons (i.e. benzene, toluene, xylenes, styrene etc.) and the species of sulfur compounds in tyre-derived oil is limited for literature search. Therefore, in this work, five zeolites were used to investigate the effects of zeolite properties; that are, (a) acidity/basicity, (b) pore channel structure, (c) pore size, and (d) Si/Al ratio on hydrocarbon species and sulfur compounds in pyrolysis products. HMOR and KL were employed the effect of acidity/basicity. HMOR (1D pore channel) and HBeta (3D pore channel) were chosen to study the effect of pore channel. With the same 3D channel structure, HBeta ($7.6 \times 6.4 \text{ \AA}$) and HZSM-5 ($5.3 \times 5.6 \text{ \AA}$) were selected to study the effect of pore size. In addition, with 3D channel structures and similar pore size, but different Si/Al ratios, HY and HBeta were also studied the impact of acid strength. The results showed that all of the zeolites can enhance the quality of the oils, petrochemical production, and sulfur removal from oils. Moreover, the amounts of such petrochemicals were also increased when all zeolites (except KL zeolite) were used.



In the work of Boxiong et al. (2007) and Williams and Brindle (2003a), tyre-derived oil was refined for the light fraction ($< 220^{\circ}\text{C}$) prior to analysis using a GC-MS; therefore, the concentrations of valuable aromatics in the light fraction were reported. With the powerful GCxGC-TOF/MS machine employed in this work, the contents of each hydrocarbon species in tyre-derived oils were instead reported without having to refine the oils. The results can be summarized as follows.

(a) The acid catalyst (HMOR) was found to have a higher cracking activity than the basic one (KL), and found to produce greater petrochemicals production (a total of 2.32 % in oil) with more styrene, ethylbenzene, toluene, *m*-xylene, and cumene than KL (a total of 0.580 % in oil). However, KL seems to have better sulfur removing ability (12.8 % removal) than HMOR (7.69 % removal).

(b) The pore channel structures affected the contact time of molecules to stay inside the pore. Owing to higher contact time in the pore, 3D pore channel (HBeta) exhibited a better cracking ability and total petrochemicals production (10.8 % in tyre-derived oil) than 1D pore channel (HMOR) that gave only a total of 2.32 %.

(c) Moreover, pore size was found to control the size of obtained products. The large pore (HBeta) exhibited better cracking ability and total petrochemicals production (10.8 % in oil) than the medium pore (HZSM-5) that yielded 4.28% in oil. Likewise, Williams and Brindle (2003a) compared the activity of ZSM-5 and Y zeolites in waste tyre pyrolysis, and they also made a similar conclusion that the ZSM-5 with a smaller pore size produced less single ring aromatic hydrocarbons in the light fraction ($< 220^{\circ}\text{C}$) of tyre-derived oil than the Y zeolite that have a larger pore size.

(d) Furthermore, with the same pore size and channel structure, HBeta with higher Si/Al ratio can produce lighter oil than HY with lower Si/Al ratio because the higher acid strength of HBeta can provide the higher cracking ability. The valuable mono-aromatics (benzene, toluene, ethylbenzene, xylenes, styrene, cyclohexane and cumene) produced from HY (7.33 % in oil) were lower than HBeta (10.8% in oil), but HY had higher sulfur removal ability (19.4 % removal) than HBeta (5.98% removal). Similarly, Boxiong et al. (2007) compared the activity of ZSM-5 and Y zeolites that had the differences in both pore size and Si/Al ratio in waste tyre pyrolysis, and concluded that the catalyst with a larger pore size and a lower Si/Al



ratio (Y zeolite) was much more effective in production of valuable aromatics (totally 41.25% of benzene, toluene, ethylbenzene, and xylenes in the light fraction) than the ZSM-5 catalyst that yielded a total of 23.82 % in the light fraction (< 220 °C) of oil.

It can be concluded that the use of zeolites increased the value of oil, and also reduced sulfur content in oils for all cases. The sulfur-containing compounds in oils were classified into five groups: thiophenes, benzothiophenes, dibenzothiophenes, benzothiazoles, and a mixture of heteroatom (O and/or N)-containing sulfur compounds. All zeolites were found to decrease benzothiazoles and heteroatom (O and/or N)-containing sulfur compounds. In summary, a catalyst for high production of valuable C6-C8 petrochemicals with low sulfur content from waste tyre pyrolysis must be an acid catalyst, rather than a basic one, preferably with high strength, and have a complex channel structure with a large enough pore size (at least ~7 Å).

4.5 Acknowledgements

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Chapter 5

Cu-doped catalysts and their impacts on tire-derived oil and sulfur removal*

Abstract: Metal-loaded zeolites are potential catalysts for upgrading the quality and quantity of waste tire pyrolysis products. Acquired from metal and zeolite properties, the catalysts can exhibit multi-functions in catalysis, including hydrogenation, dehydrogenation, ring-opening, cracking, and aromatization. Cu is widely used in several applications such as selective hydrogenation of undesired unsaturated hydrocarbons in a mixed-C₄ stream, and sulfur removal from liquid fuels. So, Cu was expected to be a promoter of zeolites for enhancing the quality of tire-derived oil in terms of sulfur removal and the increase in valuable petrochemicals in the oil. Therefore, the effect of Cu-support interaction on tire-derived oils, petrochemicals, and sulfur removal was studied using three types of zeolites (HBETA, HY and HMOR) as supports at a 5 wt% Cu loading. Catalytic pyrolysis of waste tire was operated in a bench reactor, and GCxGC-TOF/MS and SIMDIST-GC instruments were used to analyze the liquid products for chemical compositions and petroleum fractions, respectively. Sulfur in the pyrolysis products was determined by using an S-analyzer, whereas the gas composition was analyzed by using a GC-FID. As a result, all Cu-promoted catalysts can reduce more sulfur content in oils than their pure zeolites; therefore, Cu was found to enhance desulfurization of oils by converting sulfur compounds into thermodynamically-stable forms on Cu. Furthermore, Cu-support interaction highly affected the sulfur removal from oils. Interestingly, it was revealed that valuable petrochemicals highly produced by Cu/HY were benzene, ethylbenzene and cyclohexane whereas Cu/HMOR highly produced benzene, toluene and ethylbenzene. Cu/HBETA highly yielded benzene and ethylbenzene in the oil. It can be observed that benzene and ethylbenzene are common petrochemicals highly produced by the Cu-loaded catalysts.

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5.1 Introduction

Two facts, known to the tire pyrolysis community, about tire-derived gas and oil are: (1) they contain a considerable amount of sulfur compounds, resulting in strong disturbing odors during uses, and (2) regardless of high aromatic contents, they may contain valuable petrochemicals such as light olefins, cooking gas, mixed-C4, limonenes, and C6-8 hydrocarbons. Indeed, sulfur in a whole tire (1.4 wt%) can distribute in each part of tire-derived products in different amounts of total sulfur in the system: 10.6 wt%, 48.8 wt%, and 40.6 wt% in gas, oil, and carbon black, respectively [1]. The gaseous product contains 2.5-5.1 vol% H_2S while the oil and char contain 1.0-1.4 wt% S and 2.3-2.6 wt% S as reported in [2].

Generally, major sulfur species in gas products consist of H_2S , SO_2 , COS and CS_2 [3,4]. Liquid products contain many types of sulfur containing compounds of which the main groups were thiophenes, benzothiazoles, benzothiophenes, dibenzothiophenes, and their alkylated derivatives while minor groups were also found such as naphthothiophenes, benzonaphthothiophenes, and their alkylated derivatives [1,5 – 7]. In the main groups of sulfur containing compounds, main species found in the reports as mentioned above were 2-methylthiophene, 3-methylthiophene, 2,3-dimethylthiophene, 2,5-dimethylthiophene, 2-ethylthiophene, dibenzothiophene, methyl dibenzothiophenes, dimethyldibenzothiophenes and trimethyldibenzothiophenes. In the hydrodesulfurization process, sulfur-polycyclic aromatic hydrocarbons (PASH) can be removed, and petrochemicals can be produced such as toluene and styrene/ethylbenzene via hydrodesulfurization of 4,6-dimethylbenzothiophene [8] and benzothiophene [9], respectively. The reports indicated the potential of C6 – C8 aromatics-containing tire-derived oils because PASH can be desulfurized, and then petrochemicals [8,9] such as toluene, ethylbenzene, and styrene can be formed.

Copper is an interesting metal because it is a non-noble metal, having a low cost for pyrolysis operation. Furthermore, Cu has potential usable properties beneficial to pyrolysis as well. Cu-loaded catalysts can be used in selective hydrogenation that can remove undesired compounds in the process. For example, Cu/ SiO_2 catalyst was used to remove alkynes and butadiene in C4-stream by partial hydrogenation reaction converting into butenes [10]. Copper loading on hydrotalcite, malachite, SiO_2 and Al_2O_3 catalysts were used to convert propyne into propylene at high selectivity and undesired products at low selectivity [11]. Cu



metal was widely used in hydrogenolysis reaction for alcohol production [12,13]. In other applications, Cu(I)-exchanged zeolites (HY, HY- Al_2O_3 , or HBETA) can be used as an adsorbent for thiophene removal from liquid fuels as well [14 – 17]. Villarroel *et al.* [18] used the first row transition metals (Mn, Fe, Co, Ni, Cu and Zn) to promote Mo and W sulfides for sulfur removal of gas-oil containing 2700 ppm of sulfur compounds. They found that at an operating temperature of 325 °C the metal sulfides can generate spillover hydrogen on their surfaces, and then transfer hydrogen atoms to the surface of molybdenum or tungsten sulfides that can enhance hydrodesulfurization activity. Moreover, both quality and quantity of waste tire pyrolysis products can be enhanced by using catalysts. Due to their acid/basic properties and shape selectivity, zeolites were selected to be catalysts for enhancing the desired products.

For the catalytic pyrolysis of waste tire with the properties mentioned above, copper was expected to promote sulfur removal from oil and increase petrochemical products in oil as well. In this work, the effects of Cu doping on tire-derived oils and sulfur removal were studied. Cu was impregnated on several zeolites (HBETA, HY and HMOR), and the Cu-support interaction was examined using H_2 -Temperature Programmed Reduction (TPR). The tire-derived oils were analyzed using a GCxGC-TOF/MS for their chemical composition.

5.2 Experimental

5.2.1 Catalyst Preparation

Three types of zeolites, NH_4 -BETA (Si/Al=13.5), HY (Si/Al=7.5), and HMOR (Si/Al=9.5), purchased from TOSOH Company (Singapore) were calcined in static air at the conditions shown in **Table 1**. The calcination conditions were made different due to the different forms of purchased zeolites. The purchased BETA zeolite was in the NH_4 -BETA form; therefore, it was calcined at 600 °C in order to completely change NH_4^+ to H^+ form. All calcined zeolites were impregnated with an appropriate amount of a copper solution ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) to obtain 5 wt% Cu, dried overnight in an oven at 120 °C, and calcined again at the same calcination conditions. Next, the calcined catalysts were reduced at 600 °C for 2 hr in hydrogen atmosphere. Finally, the catalyst powders were pelletized, crushed and sieved to the pellet sizes in the range of 40-60 mesh.

Table 1 Calcination conditions of fresh zeolites before using as supports

Zeolite	Calcination	Heating Rate	Holding Time at
	Temperature (°C)	(°C/min)	Calcination Temperature (hr)
BETA	600	2	5
Y	500	5	3
MOR	500	5	3

5.2.2 Catalyst Characterization

XRD machine (Rikagu) was used to acquire the XRD patterns of the catalysts using CuK α radiation operated at 40 kV and 30 mA. The angles in the range of 5 - 65° were scanned at a scanning speed of 5°/min. Cu(111), with the highest intensity peak at the 2 θ ~ 43.47°, was used to determine the thickness of Cu clusters on (111) plane, using the following equation:

$$L_{hkl} = k\lambda/\beta\cos\theta$$

where

L is the thickness of a crystallite (Å)

hkl is the diffracting plane (hkl = 111)

λ is the wavelength of Cu K α beam (λ = 1.5418 Å)

β is the peak width (the full width at the half maximum intensity, FWHM)

θ is the angle between the normal on the reflecting plane and the beam

k is a shape factor (k = 0.9)

Surface area and pore volume of catalysts were determined by N₂ physisorption using Thermo Finnigan Sorptomatic 1990 equipment. TPR profiles of catalysts were obtained for determining the metal-support interaction using Thermo Finnigan TPDRO 1100 operated from room temperature to 950 °C with a heating rate of 20 °C/min under 4.99 % H₂/N₂ flow at 20 ml/min.

The amount of coke on spent catalysts was determined by using Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis), TG/DTA. The temperature was ramped up from room temperature to 900 °C with the heating rate of 10 °C/min. The amount of coke was calculated from the weight loss beyond 200 °C since the weight loss occurring below 200 °C was resulted from water or

volatile organic compounds adsorbed on the catalyst surface. Sulfur content on catalyst surface was determined by using LECO®Elemental Analyzer (TruSpec®S), and calculated from the following equation:

$$S_{\text{Spent Cat}} = (W_{\text{Fresh Cat}} + W_{\text{Coke}}) \cdot (\%S_{\text{Spent Cat}}) / 100$$

where

- $S_{\text{Spent Cat}}$ = Weight of sulfur on a spent catalyst surface (g)
 $\%S_{\text{Spent Cat}}$ = Weight percentage of sulfur in spent catalyst
 $W_{\text{Fresh Cat}}$ = Weight of fresh catalyst (g)
 W_{Coke} = Weight of coke in spent catalyst (g)

5.2.3 Pyrolysis of Waste Tire

Since waste tire in general is not a homogeneous material, only the thread of one waste tire (Bridgestone Turanza GR80) was therefore used as a raw material in every batch. Its particle size was controlled in the range of 20-40 mesh. Pyrolysis experiments were conducted using the same pyrolysis station as reported in Dũng and coworkers [19]. The pyrolysis scheme was re-drawn and illustrated in **Fig. 1**. The catalytic pyrolysis of waste tire was operated at atmospheric pressure from room temperature to a temperature of 500 °C (the pyrolysis zone) and 350 °C (the catalytic zone) with a ramp rate of 10 °C/min and a holding time of 90 min after the final temperatures were reached in order to ensure that the tire was decomposed completely. Thirty grams of shredded tire (20-40 mesh) and 7.5 grams of a catalyst (40-60 mesh) were packed in the pyrolysis zone and the catalytic zone, respectively. Nitrogen gas with a flow rate of 30 mL/min was used as a carrier gas. Liquid products were condensed in the condensers immersed in an ice-salt (NaCl) bath, while the gas products were collected by using a gas sampling bag. With the fixed controlled parameters, the impact of Cu-promoted catalysts on tire-derived oil and sulfur removal were investigated. The structure of zeolites and Cu-support interaction were the interested parameters examined in this work.

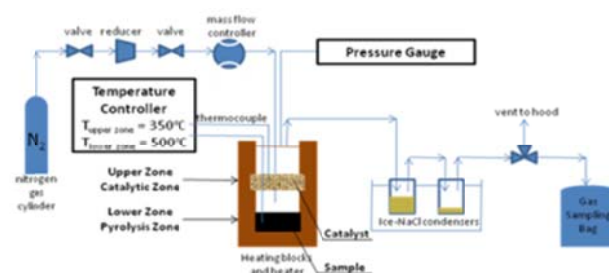


Fig. 1 Pyrolysis diagram.

2.4 Product Analysis

Liquid and solid products were weighed for calculating the product yield. Before analysis, asphaltene was firstly precipitated from the liquid products via mixing with n-pentane in the oil/n-pentane mass ratio of 40:1. After that the precipitated asphaltene was filtered from the solution using a Teflon membrane (0.45 μm) in a vacuum system, and then the maltene solutions were analyzed for the composition by using Gas Chromatography-Mass Spectrometry (GCxGC-TOF/MS). The Agilent gas chromatograph 7890 system consists of a cryogenic modulator and a LECO Pegasus 4D TOF/MS. The 1st column was a non-polar Rtx®-5Sil MS with 30 m x 0.25 mm ID x 0.25 μm film thickness installed in the main oven operated at 50 °C, held for 2 min at the beginning of analysis, then ramped to 310 °C with 5 °C/min, and held at the final temperature for 10 min. The 2nd column was an Rxi®-17 MS with 1.10 m x 0.10 mm ID x 0.10 μm film thickness installed in the second oven started at 60 °C, held for 2 min, then heated to 320 °C with 5 °C/min, and held for 10 min when the final temperature was reached. The modulator timing condition was set at the cycle time of 4 sec and holding time of 0.5 sec in the release position. Nitrogen (UHP) was used as a cryogen coolant set at least -80 °C of the modulation trap temperature. The electron impact ionization of -70 V was applied to provide mass spectral data collected in the range of 35 to 500 m/z with the data transfer of 100 spectra/sec. The ion source and detector voltage were set at 250 °C and 1,600 V, respectively. The transfer line was heated to 250 °C. The LECO ChromaTOF® software was used to record and analyze data, and spectral identification was provided by the NIST library. The accuracy and sensitivity of MS detector were calibrated and tested by using perfluorotributylamine (PFTBA) and hexachlorobenzene (HCB), respectively. Maltene solution samples were prepared from diluting 1 μl of maltene with CS_2 into 2 ml, and analyzed by injection into the



instrument via a splitless injector operated at 250 °C. Helium at the flowrate of 1.0 mL/min was used as the carrier gas.

Furthermore, the true boiling point curves of maltene solutions were also analyzed by using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) conformed to the ASTM-D2887 method. The instrument equipped with FID and WCOT fused silica capillary column (15 m x 0.25 mm x 0.25 μ m). The true boiling point curves were cut into petroleum fractions according to their boiling points; gasoline (<149 °C), kerosene (149-232 °C), gas oil (232-343 °C), light vacuum gas oil (343-371 °C) and heavy vacuum gas oil (>371 °C).

The gas products were analyzed for hydrocarbon species and concentrations by using a GC-FID, Agilent Technologies 6890 Network GC system (HP-PLOT Q column: 20 μ m film thickness and 30 m x 0.32 mm ID). Furthermore, the liquid and solid products were also analyzed for their carbon, hydrogen, nitrogen, and sulfur contents by using a LECO®Elemental Analyzer (TruSpec®CHNS) whereas the sulfur content in gas products was calculated via mass balance.

5.3 Results and Discussion

5.3.1 Catalyst Characterization and Cu-Support Interaction

The XRD patterns of all zeolites and Cu-promoted catalysts are displayed in **Fig. 2**. The results show that the introduction of Cu onto HMOR and HY does not affect zeolite structures. , However, the HBETA support loses some crystallinity after doped with Cu. The peaks of Cu appear at the 2 θ s of $\sim$ 43.47° and 50.67°, and the thickness (L_{111}) of the Cu clusters on the 111 plane, Cu (111), shown in **Table 2** is ranked as follows: Cu/HBETA < Cu/HMOR < Cu/HY. According to the Cu (111) crystallite thickness, the Cu dispersion on the supports can be ranked in the opposite way as Cu/HBETA > Cu/HMOR > Cu/HY. The highest Cu dispersion on HBETA indicates that the catalyst has the strongest Cu-support interaction. Similarly, The TPR profiles of catalysts are illustrated in **Fig. 3**. The profiles indicate the Cu-support interaction of all catalysts in comparison. Stronger metal-support interaction is considered from the peak evolving at a higher temperature [20]. The peaks appear in **Fig. 3** at 477 °C and 377 °C for Cu/HBETA and Cu/HY, respectively, whereas Cu/HMOR gives two reduction peaks at 329 °C and 424 °C. So, it can be

concluded that the interaction between Cu and the supports is ranked in the order: Cu/HBETA > Cu/HMOR > Cu/HY, which corresponds well with that determined from the cluster size, L_{111} using the XRD patterns.

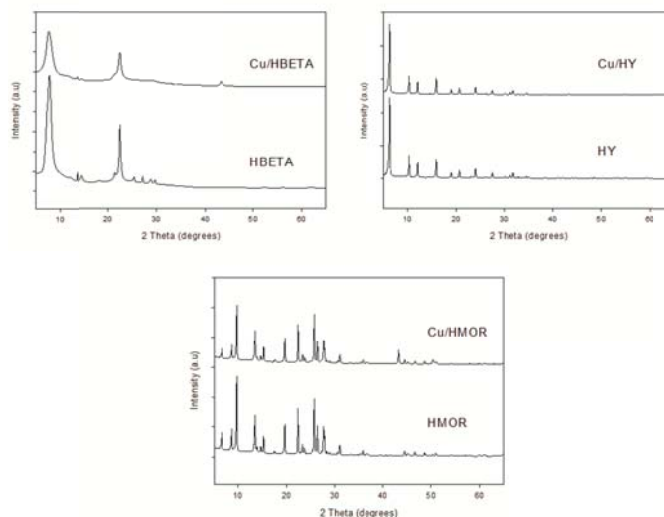


Fig. 2 XRD patterns of Cu-loaded catalysts.

It is noted hereby that the two peaks in the TPR profiles of Cu/HMOR might be resulted from the change in the oxidation state of copper species from Cu^{2+} to Cu^+ for the first peak, and then Cu^+ was further reduced to Cu^0 for the second peak. The changes, if they occur very fast on a support, can only give a peak on the TPR profiles. In our case, Cu/HMOR presents two peaks. Thus, it is possible that the changes from Cu^{2+} to Cu^+ and from Cu^+ to Cu^0 occur more slowly on HMOR than those on the other supports. Moreover, it is also possibly resulted from two different sites of Cu loaded on the HMOR.

Table 2 Thickness of Cu clusters on various supports, L_{111} , ($k = 0.9$ and $\lambda = 0.15418$ nm)

Catalyst	2θ (deg)	β (deg)	L_{111} (Å)
Cu/HBETA	43.2055	0.6062	141
Cu/HY	43.2575	0.2660	523
Cu/HMOR	43.2792	0.1637	322

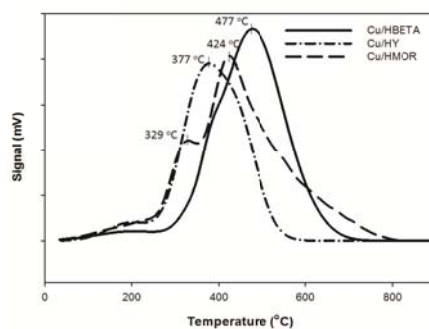


Fig. 3 TPR profiles of Cu-loaded catalysts.

Coke deposited on catalyst surface can be acquired from the TG/DTA profiles (Fig. 4). Types of coke were generally defined into soft and hard cokes (with the weight loss at the temperature range of 200-400 °C [21] and above 400 °C [22], respectively). Soft coke is considered as coke precursors, i.e. aromatics and asphaltenes, whereas hard coke is a refractory one [22] or the polyaromatic coke located in the pore of zeolites. From Fig. 4, all Cu-promoted catalysts produce more hard coke than their corresponding parent zeolites, indicating higher cracking activity than the parent zeolites. The HBETA catalysts with and without Cu produce no soft coke whereas the HY ones slightly produce soft coke. The polyaromatic-type coke can be completely removed from HBETA, Cu/HBETA, HMOR, and Cu/HMOR at 600 °C, but it takes about 650 – 700 °C in order to remove the hard coke from HY and Cu/HY surfaces, possibly due the zigzag channel structure of HY zeolite that retains the coke from being removed easily.

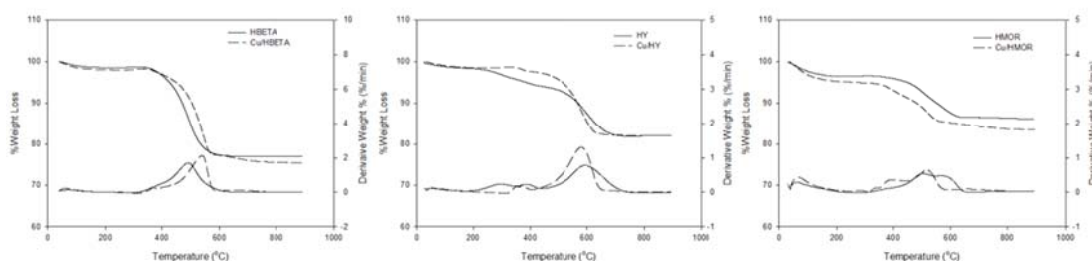


Fig. 4 TG/DTA profiles of spent catalysts.

Moreover, Cu loaded on HBETA and HMOR can produce higher H/C ratio of coke (See Table 3) than the parent zeolites because Cu potentially exhibit hydrogenation ability [21]. However, Cu/HY did not increase H/C ratio of coke as



compared to HY, which might be caused by the poor dispersion of Cu on HY surface, resulting in lower hydrogenation activity as compared to the other Cu-loaded catalysts. The BET specific surface area and pore volume of catalysts are shown in **Table 4**. These results indicate that the introduction of Cu onto all zeolites reduces the specific surface area and pore volume because copper might partially block the pore of zeolites.

Table 3 Elemental composition (wt.%) in coke on the spent catalysts

Catalyst	C	H	N	S	H/C ratio
HBETA	20.0	1.87	2.01	0.411	9.39
HY	16.0	1.59	1.87	0.262	9.90
HMOR	10.3	1.27	2.10	0.143	12.3
Cu/HBETA	18.6	1.78	1.87	1.05	9.61
Cu/HY	15.7	1.10	1.84	1.10	7.05
Cu/HMOR	10.5	1.54	1.91	0.965	14.6

Table 4 BET specific surface area and pore volume of catalysts

Catalyst	BET surface area (m ² /g)	Pore Volume (cm ³ /g)*
HBETA	539	0.257
HY	515	0.266
HMOR	395	0.199
Cu/HBETA	413	0.200
Cu/HY	488	0.256
Cu/HMOR	345	0.180

* Horvath-Kawazoe (H-K) Calculations

5.3.2 Tire-derived Oil

Pyrolysis products can be divided into three types based on their phases; that are gas, liquid, and solid. **Fig. 5** shows that the introduction of 5 wt% Cu onto HBETA (Si/Al = 13.5) and HY (Si/Al = 7.5) zeolites increases the gas production, decreases the liquid yields, and increases the amount of coke as well,

indicating that the introduction of Cu can promote the activity in cracking of zeolites. The increment of coke formation can also indicate that the activities on the catalyst surface are increased when Cu was loaded. Particularly, the product from thermal pyrolysis of waste tire, which is fed to a catalyst bed, contains a considerable amount of aromatic compounds because the tire contains SBR rubber. The high cracking ability of an acid catalyst is likely to drive coke formation on the catalyst; therefore, coke formation is an indicator of high cracking ability.

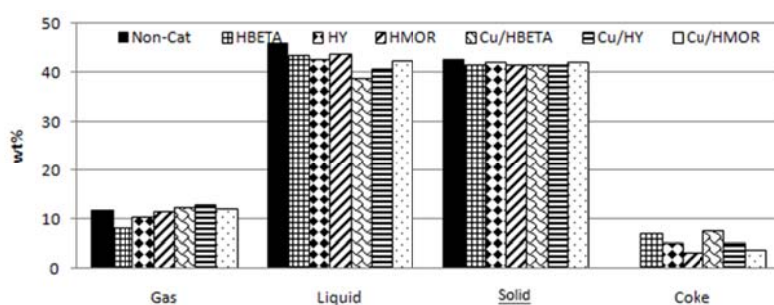


Fig. 5 Product distribution from using Cu-loaded catalysts.

In gas analysis as shown in **Fig. 6**, the gas compositions are slightly changed, indicating that the presence of Cu on the zeolites does not significantly promote any gas species. **Fig. 7** shows the effect of Cu on the zeolites on maltene compositions. In this work, the components of maltenes are divided into 7 groups; that are, paraffins (p), olefins (ole), naphthenes (nap), and monoaromatics (mono), diaromatics (di), polyaromatics (poly) and polar aromatics (polar). Cu on HBETA and HY decreases the concentration of monoaromatics. Furthermore, the concentrations of paraffins, olefins and naphthenes are increased in the Cu/HBETA case while the concentrations of diaromatics and polyaromatics are increased in the Cu/HY case. It can be concluded that Cu/HBETA exhibits hydrogenation and ring-opening activities that convert monoaromatics into paraffins, olefins and naphthenes, while Cu/HY favors aromatization, producing multi-ring aromatics from monoaromatics, olefins and naphthenes because HY support has high acid density. The results indicate that small multi-ring aromatic molecules in Cu/HY are also cracked, which is governed by hydrogenation and ring-opening before breaking more C-C bonds [23] because gasoline is increased in the Cu/HY case as compared with the HY case (**Fig. 8**). So, Cu on both zeolites also promotes hydrogenation and ring-opening activities. The higher acid density and specific surface area of Cu/HY (higher cracking activity) also

cause the lighter hydrocarbon portion (based on boiling points) in maltene than Cu/HBETA.

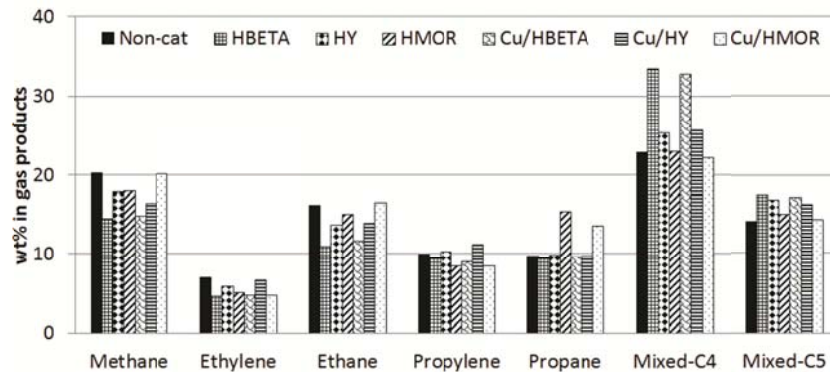


Fig. 6 Compositions in the gaseous products from using Cu-loaded catalysts.

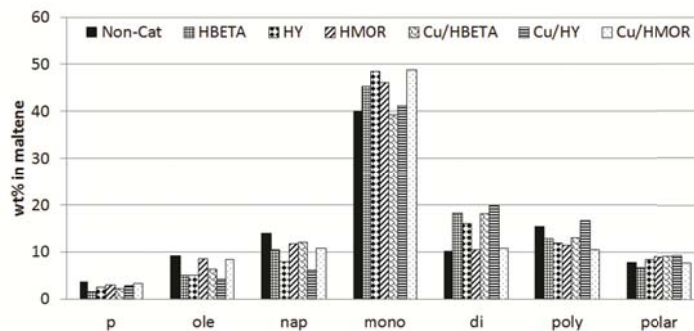


Fig. 7 Maltene compositions (p = paraffins, ole = olefins, nap = naphthenes, mono = monoaromatics, di = diaromatics, poly = polyaromatics, and polar = polar aromatics).

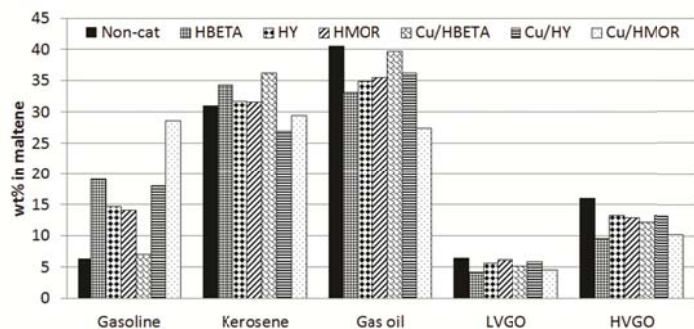


Fig. 8 Petroleum cuts of maltenes using Cu-loaded catalysts.



Copper on HMOR can increase the concentration of monoaromatics in maltene via hydrogenation and ring-opening of polyaromatics, and via aromatization of naphthenes. Furthermore, gasoline is also highly increased because copper promotes cracking activities. As compared between Cu on two zeolites with different pore channel structures (HY with 3 Dimensional pore channel structure and HMOR with 1 Dimensional pore structure), Cu/HMOR produces higher single ring-aromatics content in maltene than Cu/HY because 1D pore channel structure might be proper to monoaromatic production from cracking polyaromatics, while Cu/HY with 3D pore structure favors the productions of multi-ring aromatics because 3D pore channel structure catalyst has too much open space (pore size and architecture) for aromatization, resulting in lower concentration of olefins and higher bulky aromatics in oils [24].

Copper addition can increase gasoline fraction in oils, except Cu on HBETA since Cu/HBETA highly cracks hydrocarbons in the gasoline range to smaller molecules in the gas phase more than the other Cu-loaded catalysts. It can be explained that the strong Cu-HBETA interaction results in low sulfur deposition on the Cu surface that is the active sites for hydrogenation, cracking, and ring-opening. Moreover, the GCxGC-TOF/MS results indicate that the main compositions of oil are aromatics in all petroleum cuts (**Table 5**). So, tire-derived oils are not quite suitable for being used directly as fuels.

Table 5 Composition of each petroleum cuts

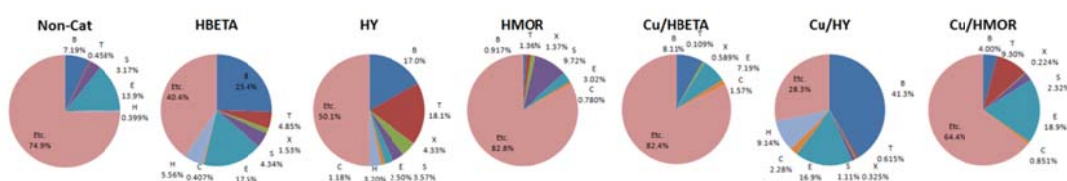
	Gasoline	Kerosene	Gas Oil	LVGO	HVGO
Paraffins	0.00-1.92	0.806-1.69	3.95-11.6	0.00-13.5	0.00-23.9
Olefins	2.69-11.3	4.55-9.04	4.46-9.51	0.00-22.3	-
Naphthenes	7.85-13.8	4.77-13.0	5.12-16.8	0.00-22.0	-
Aromatics	75.5-84.7 [*]	76.3-90.0	65.4-81.1	71.1-100	76.1-100

^{*} 37.5 – 71.9 wt% of monoaromatics in gasoline

**Table 6** Petrochemicals productivity from waste tire pyrolysis

Catalyst	Petrochemical Productivity (kg/ton of tire)
No Catalyst	7.15
HBETA	49.1
HY	31.2
HMOR	10.6
Cu/HBETA	4.74
Cu/HY	52.3
Cu/HMOR	43.0

Petrochemicals in this paper are defined as primary petrochemicals (benzene, toluene and xylenes) and/or intermediates (styrene, ethylbenzene, cumene, and cyclohexane). In tire-derived oil, petrochemicals can be formed two ways: (1) conversion of hydrocarbons, and (2) conversion of sulfur-containing compounds. The petrochemicals productivity and selectivity in gasoline (**Table 6** and **Fig. 9**) are increased when Cu was loaded on HY and HMOR zeolite. It is noted here that B = Benzene, T = Toluene, X = Xylenes, S = Styrene, E = Ethylbenzene, C = Cumene, and H = Cyclohexane. With the same reason, Cu on HBETA highly promotes cracking reaction of small molecules (including these petrochemicals) in the gasoline range, forming gases; so, the selectivity of petrochemicals in the Cu/HBETA case is the lowest among those of all catalytic cases.

**Fig. 9** Selectivity of petrochemicals in gasoline-range products (B = Benzene, T = Toluene, X = Xylenes, S = Styrene, E = Ethylbenzene, C = Cumene, and H = Cyclohexane).

Cu on HY and HMOR reduces the amount of total BTz and ITC yields as compared with pure HY and HMOR cases, indicating that BTz and ITC can be converted into benzene. Furthermore, Cu/HY catalyst promotes benzene,



ethylbenzene and cyclohexane production because Cu/HY might promote hydrogenation and dealkylation of HY. Cu/HMOR catalyst highly produces ethylbenzene, toluene and benzene because Cu/HMOR might increase dealkylation activity.

Even though the amount of sulfur-containing compounds is markedly lower than that of petrochemicals and/or gasoline, the increase of petrochemical production is quite high because Cu-support interaction might strongly affect the petrochemical production. Cu-support interaction can relate to the adsorption of sulfur-containing compounds and desorption of sulfur atoms on the catalyst surface via reacting with hydrogen to form H_2S and/or hydrocarbons to form thiophenes. Desorption of sulfur atoms on the catalyst surface can form the molecular structures, similar to the sulfur-containing compounds that can also re-adsorb and form petrochemicals. Benzothiophenes can be formed from the reaction between H_2S and olefins [25] or from the reaction of two molecules of thiophenes [26].

5.3.3 Sulfur Compounds in Oil and Sulfur Removal

After pyrolysis, 50% of sulfur in waste tire is deposited in char, or carbon black originally existing in the tire, as illustrated in **Fig. 10**. It is suggested that tire, when pyrolyzed in the pyrolysis zone, releases sulfur in the forms that can be adsorbed on the char. The other 50% of sulfur is evolved in the effluents taken by nitrogen used as the carrier gas. Once the effluents come into contact with a catalyst in the catalytic zone, sulfur is distributed into oil and gaseous products, with a little amount that is deposited on the catalyst surface. From **Fig. 10**, it can be seen that, using a zeolite as a catalyst, sulfur is more distributed in the gaseous product than in the oil phase whereas only 2 – 6 % is deposited on the zeolite surfaces. After doping with Cu, it is obvious that less sulfur is distributed in gas and oil, but more sulfur is distributed on the catalyst surfaces, indicating that sulfur is deposited on Cu.



Fig. 10 Overall sulfur distribution.

Table 7 Sulfur content in oil (wt%)

Catalyst	wt% Sulfur in oil	S Removal (%)	S Removal by Cu (%)
No Catalyst	1.22	-	-
HBETA	1.11	9.02	-
HY	0.889	27.1	-
HMOR	0.991	18.8	-
Cu/HBETA	0.764	37.4	28.4
Cu/HY	0.800	34.4	7.3
Cu/HMOR	0.842	31.0	12.2

Table 7 indicates that Cu can promote sulfur removal ability of the supports, especially when loaded on HBETA. The ability on S removal of the Cu-doped catalysts can be ranked in the order: Cu/HBETA > Cu/HY > Cu/HMOR. Therefore, Cu/HBETA seems to be the best catalyst in terms of the activity on sulfur removal from the tire-derived oils. However, considered from the differences on S removal ability of catalysts between with and without Cu, it can be seen that the ability of Cu dopant on S removal can be ranked as Cu on HBETA > Cu on HMOR > Cu on HY at a fixed Cu loading. This observation indicates that Cu-support interaction may affect the S removal ability of Cu.

Sulfur-containing compounds found in oils can be classified into six groups: thiophenes (Th), benzothiophenes (BT), dibenzothiophenes (DBT), naphthothiophenes (NT), benzothiazoles (BTz), and isothiocyanates (ITC) as shown

in Fig. 11. Total Th, BT and DBT yields are decreased in all copper-loaded catalyst cases (Fig. 12) because copper can react with sulfur atoms in the compounds, and can form the thermodynamically stable form such as CuS or Cu₂S. This evidence indicates that the sulfur compounds that Cu dopant can remove are in the groups of thiophenes, benzothiophenes, and dibenzothiophenes.

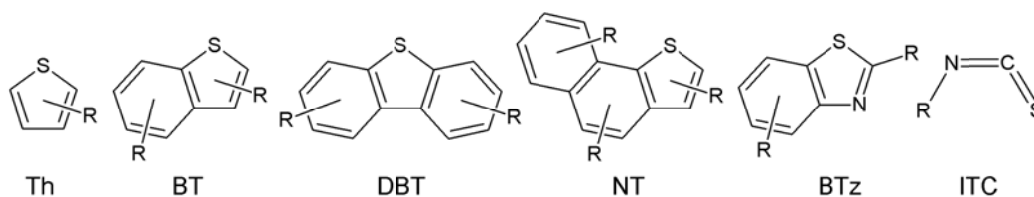


Fig. 11 Major sulfur-containing compounds found in tire-derived oils.

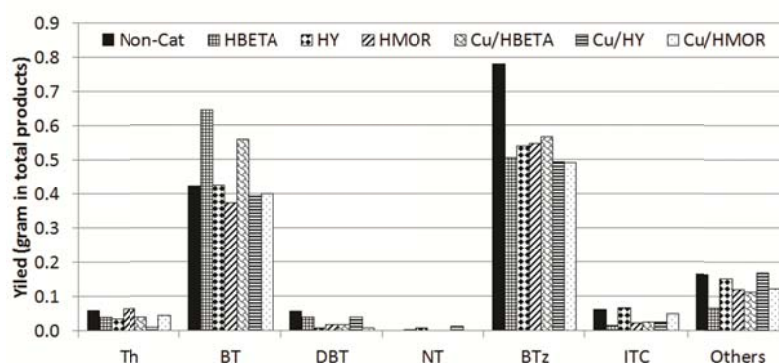


Fig. 12 Sulfur-containing species in maltenes.

Desulfurization can be divided into four steps; (a) the adsorption of an S-compound on a Cu-site, (b) the hydrogenation of the adsorbed S-compound and C-S bond breaking, (c) the desorption of a hydrocarbon and copper sulfide formation, and (d) the removal of S atoms on the surface (surface cleaning). The example of pathways to produce petrochemicals from sulfur-containing compounds is shown in Fig. 13. Sulfur removal ability of Cu doped on the zeolites can be possibly related to the Cu-support interaction. According to the TPR profiles (Fig.3) and the cluster size (L_{111}) of Cu on each support, it has been concluded in Section 3.1 that the Cu-support interaction is ranked as follows: Cu/HBETA > Cu/HMOR > Cu/HY. This is in accordance with the rank in the ability of Cu dopant on S removal (Cu on HBETA > Cu on HMOR > Cu on HY) at a fixed Cu loading.

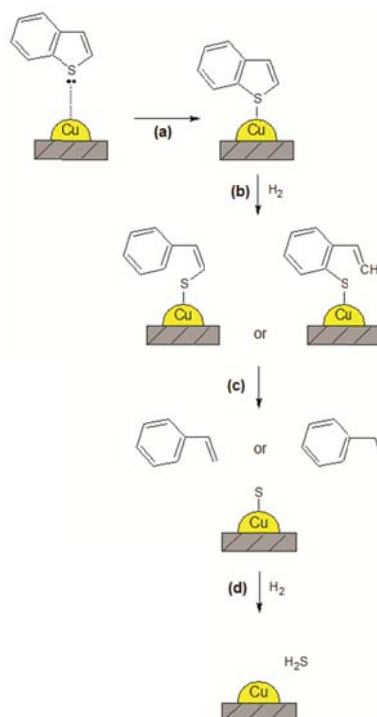


Fig. 13 Sulfur removal pathway of benzothiophene.

Likely, in this work, it can be postulated that high dispersion and strong interaction between Cu and HBETA causes high electron deficiency of the Cu site [27]. Consequently, the high electron-deficient site of Cu prefers to adsorb sulfur, in a sulfur-containing hydrocarbon, that is full of electrons, which creates strong Cu-S interaction and then makes a sulfur-containing adsorbate so unstable that the S-C bond in the molecule can be easily broken. Therefore, in this situation, the release of an S-free hydrocarbon molecule from the Cu/HBETA surface can occur easily, resulting in the lowest sulfur content in oils as compared with the other Cu-loaded catalysts. On the other hand, the interaction between Cu and HY or Cu and HMOR is weaker than that of Cu on HBETA, so they can adsorb a S-compound with lower strength, and a hydrocarbon cannot be easily released.

Since the interaction between Cu and HBETA on Cu/HBETA is the highest among that on the other Cu-doped catalysts, the highest Cu-S bond strength in copper sulfide is created after a hydrocarbon product leaves the surface. Thus, for surface cleaning, it is the most difficult to remove sulfur atoms on the spent Cu/HBETA surface among those of the other spent catalysts [27]. This is



supported by the highest distribution of S on the spent Cu/HBETA catalyst as illustrated in Fig. 10.

5.4 Conclusions

Copper can be used to promote sulfur reduction from tire-derived oils of zeolites because it has sulfur adsorption properties. Sulfur content in oil of the copper-loaded catalysts was 0.764 wt%, 0.800 wt%, and 0.842 wt% in oil for Cu/HBETA, Cu/HY, and Cu/HMOR cases, respectively. The important effects of catalysts on sulfur removal are zeolite properties and Cu-support interaction. The catalysts with strong Cu-support interaction have high ability to adsorb sulfur on their surfaces. The removal of sulfur from sulfur-compounds can also result in the production of petrochemicals because the main species of sulfur-containing compounds have the molecular structures similar to several types of petrochemicals. Furthermore, the tire-derived oils are a potential alternative source for petrochemical production because the oils were composed of the high amount of aromatics, especially monoaromatics. Interestingly, the introduction of copper highly promoted the production of valuable products in oils as well. The results indicated that copper on HY and HMOR zeolites had ability on enhancing the petrochemical productivity. Cu/HY highly produced benzene, ethylbenzene and cyclohexane, Cu/HMOR highly produced benzene, toluene and ethylbenzene, while Cu/HBETA did not promote petrochemical production as compared with HBETA.

5.5 Acknowledgements

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Chapter 6

Effects of Fe supported on zeolites on structures of hydrocarbon compounds and petrochemicals in waste tire-derived pyrolysis oils*

Abstract: Waste tire, a hydrocarbon-based material, exhibits potential to be used for petrochemical production. Valuable chemicals such as benzene, toluene, xylenes, and styrene for instances have been observed in pyrolytic oils. Furthermore, sulfur compounds causing the low quality of oil and the environmental pollutant are also absolutely found. Iron catalysts appear to be economically feasible in catalytic fields. Especially, iron can be used to substitute the noble metal promoters in the pyrolysis of waste tire due to its good activities on hydrogenation and ring opening reactions. This study therefore investigates the effects of iron supported on zeolites (HMOR, HBeta, HZSM-5, and KL) on structures of hydrocarbon compounds and petrochemicals in waste tire-derived oils. Fe-promoted zeolites were prepared by incipient wetness impregnation technique with the fixed amount of Fe at 5 wt.%. The products and catalysts were characterized by using GC, SIMDIST-GC, GCxGC-TOF/MS, elemental analyzer, XRD, and SAA. The results showed that the introduction of 5%Fe on zeolites can enhance the cracking ability of products. Namely, the gas yield increased, at the expense of liquid yield. In addition, light hydrocarbon gases increased in accordance with the reduction of heavier gases. Moreover, the light fractions in oil also increased with using iron-loaded zeolites. Moreover, olefins and naphthenes tended to decrease, but mono-aromatics increased with using all 5%Fe-loaded zeolites. Consequently, the reduction of di- and poly-aromatics was observed for all Fe-promoted catalysts, except 5%Fe/HBeta. Using 5%Fe-loaded zeolites, except 5%Fe/HBeta resulted in the increasing yields of petrochemicals such as benzene, toluene, ethylbenzene, xylenes, and styrene, for examples, in oil. Furthermore, 5%Fe-loaded catalysts resulted in the reduction of sulfur in oil. Dibenzothiophenes and benzothiazoles were the sulfur compounds in oil that decreased with the presence of 5%Fe, except 5%Fe/HZSM-5, whereas benzothiophenes tended to decrease.



6.1 Introduction

Tire is difficult to degrade, and it has a long life; thus, resulting in a large amount of waste tire discarded. Over a half of waste tires go to land fill, resulting in losing a large amount of valuable landfill space. Moreover, the combustion of waste tire releases environmental pollutants. However, tires are hydrocarbon materials which exhibit potential to be used as a source for petrochemical production through waste tire pyrolysis that is an alternative technique to handle waste tire problems. Several researchers reported that products from waste tire pyrolysis can be used as fuels and feedstock for petrochemical production. Aromatics, especially benzene, toluene, xylenes, and ethylbenzene, are important compounds in the production of petrochemicals and plastics. Moreover, styrene and cumene are also widely used in chemical industry. It has been reported that pyrolytic oils can be used as diesel fuel after upgrading such as removing sulfur or blending with commercial fuels [1 – 3]. In addition, the oil which has high sulfur is not permitted to use in vehicle due to the environmental regulations. The source of sulfur in pyrolytic oil is from vulcanization agents and accelerators such as benzothiazole, 2-mercaptobenzothiazole in vulcanization process during tire production [4,5]. In order to reduce sulfur in oil, sulfur removal technology has been developed. García-Cruz et al. [6] reported that small sulfur compounds are easier to be desulfurized than larger sulfur compounds. The activity of sulfur species towards hydrodesulfurization was ranked as thiophenes > benzothiophenes > dibenzothiophenes > 4,6-dimethyldibenzothiophene.

Several researchers used catalysts, especially zeolites, to improve the quality of pyrolytic oil evolved from using several raw materials such as solid wastes [7-9] and biomass [10-12]. Dũng et al. [7] used HMOR zeolite in waste tire pyrolysis. The results showed that introduction of HMOR led to the increasing amounts of gasoline and kerosene and the decreasing amounts of heavy vacuum gas oil due to the good cracking performance of catalyst. They mentioned that HMOR favored to produce gasoline, which was selective to pore size. The pyrolysis of waste tire with using HBeta and KL zeolites were studied by Saeng-arayakul and Jitkarnka [8]. The results showed that using HBeta produced higher gas yield than using KL. Moreover, HBeta zeolite reduced the concentration of heavy liquid fractions (long residues and heavy gas oil) more greatly than KL zeolite. The results demonstrated that long-chain hydrocarbons were more easily cracked by HBeta. Furthermore, both HBeta and KL can reduce the sulfur in oil. Olazar et al. [9] studied the effect of using HZSM-5 catalyst on waste tire pyrolysis. The gas product increased with using HZSM-



5 due to cracking of heavy fractions. Additionally, light olefins which consisted of ethene and propene increased with the use of catalyst. Poly-aromatics in oil products increased with using the catalyst. It was suggested that cyclization, aromatization and condensation reactions occurred inside the pore to form aromatics. The formation of aromatic hydrocarbons and oxygen-containing aromatics (mostly phenolic compounds) was also observed using zeolites in pyrolysis of biomass such as eucalyptus wood [10,11]. Intensive investigation on the effects of zeolites properties on sulfur removal and production of aromatic-type petrochemicals from waste tire pyrolysis has been recently published [12].

Iron catalysts are environment-friendly ones with low toxicity, the usage of iron catalysts are mainly in Fischer-Tropsch (FT) synthesis [13] or selective catalytic reduction (SCR) [14], and appear to be economically feasible in catalytic fields [15]. Pour et al. [14] studied Fischer-Tropsch synthesis catalyzed by pure Fe and Fe supported on ZSM-5. They indicated that the Fe/ZSM-5 catalyst gave a longer chain of hydrocarbons than the pure Fe catalyst because ZSM-5 promoted oligomerization activity, cracking activity, and shape selectivity, followed by aromatization that led to the reduction of light products. Moreover, ZSM-5 improved the quality of gasoline by increasing C_5 - C_{11} hydrocarbons due to the enhancement on secondary chain growth. Fe catalysts supported on HBeta and HZSM-5 zeolites were investigated for selective catalytic reduction (SCR) in order to reduce nitrogen oxide (NO) from the diesel engine [15]. They found that iron loading at 2.5 wt.% gave the high conversion of NO about 97 %. Additionally, Fe/HBeta gave higher activity of SCR than Fe/ZSM-5 due to higher surface area. Besides FT synthesis and SCR, Fe has been used in conversion of biomass-based raw materials, like bio-ethanol, to either olefins [16,17] or liquid hydrocarbons [18]. Fe promoted on HZSM-5 was found to be highly effective even in the presence of water in the feed, and the initial selectivity of C^{3+} olefins and distribution of products were not affected by iron precursors [16,18] and calcination temperature [16]. Moreover, as low as 1% Fe loading can result in a high selectivity of C^{3+} olefins [17]. The high activity of Fe/HZSM-5 catalysts could be possibly resulted from the stronger acidic site than an Al-type acidic site, which is created when Fe is introduced to zeolite framework [19].

Recently, an iron catalyst has been used in waste tire pyrolysis as a substitute for a noble metal catalyst (Ru) [20]. The result showed that the increasing amount of Fe loading on HBeta and HMOR zeolites tended to enhance the cracking ability of liquid to gas products. For liquid products, it was reported that presence



of Fe catalyst led to sharp increase in saturated hydrocarbons in accordance with reduction of poly- and polar-aromatic hydrocarbons. It was attributed to Fe site that had an important role on promotion of hydrogenation and hydrodesulfurization reactions of poly- and polar aromatic hydrocarbons. Moreover, heavy fractions such as heavy gas oil and long residue increased with increasing Fe loading because the secondary reactions, which consist of oligomerization, aromatization and H-transfer, were enhanced on Fe. As observed above, the Fe catalyst had as high activity as the noble metals, Ru and Pd, which can be costly [20].

Currently, no study has been made on the effect of iron-loaded zeolites on the structure and distribution of hydrocarbons in waste tire pyrolysis. The aim of the present study was to investigate effects of iron promotion on zeolites on structures of hydrocarbon compounds and petrochemicals in tire-derived oils. A series of Fe supported zeolites was prepared by incipient wetness impregnation technique loading and the amount of Fe was fixed at 5wt.% for all cases.

6.2 Experimental

6.2.1 Catalyst Preparation

HMOR (Si/Al = 13.5), HBeta (Si/Al = 9.5), KL (Si/Al = 3), and HZSM-5 (Si/Al = 15) were purchased from Tosoh Company in Singapore and Zeolyst International. First, all zeolites were calcined to remove impurity. HMOR, HZSM-5, and KL were calcined at 500 °C for 3 h with the heating rate of 10 °C/min. HBeta was calcined at 600 °C for 5 h with 2 °C/min. Then, each zeolite was loaded with metal, iron(III) chloride hydrate hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), using incipient wetness impregnation technique to obtain 5 wt.% metal-supported catalyst. After that, the catalysts were dried at 100 °C for 3 h, followed by calcination at the same conditions. Next, catalyst powders were pelletized, ground, and sieved to 400-425 μm of particle size. Finally, they were reduced at 800 °C for 2 h with H_2 to convert the iron oxides to metallic Fe.

6.2.2 Catalyst Characterization

Temperature-programmed reduction (TPR) was used to identify the reducibility of the impregnated catalysts and the metal-support interaction. The temperature was ramped from 30 °C to 850 °C with a heating rate of 10 °C/min. X-ray Diffraction (XRD) was used to verify the structure and existence of metal of the catalysts. The detector scanned the peak position from the sample as a function of 2θ by starting at the 5° to 100° (2θ) range and a scan speed of 5°(2θ)/min. XRD

patterns were matched to the standards to identify crystalline phases by smartlab guidance program. The amount of coke on spent catalysts was analyzed by using a Thermogravimetric/Differential Thermal Analysis (TG/DTA). The surface area and pore volume of catalysts were analyzed by using a surface area analyzer (Sorptomatic 1990). Moreover, an elemental analyzer was used to determine sulfur content on spent catalyst.

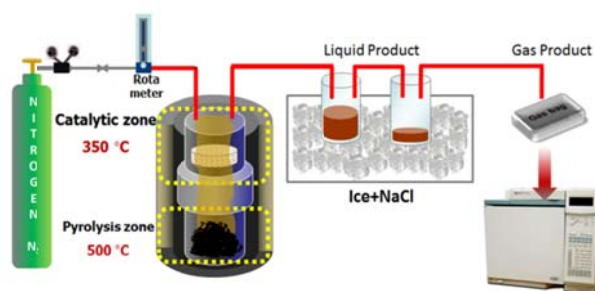


Fig. 1 Experimental setup for pyrolysis experiments.

6.2.3 Pyrolysis of Waste Tire

The ultimate analysis of shredded waste tire samples (Bridgestone TURANZA GR-80) was performed using a LECO® Elemental Analyzer. A ceramic boat filled with nickel boat was added with com-aid and 0.1 gram of each tire sample, and then the ceramic boat was put in the elemental analyzer. The temperature of furnace was next raised from room temperature to 600 °C and held for 15 min in the first step, and then raised again to 1,350 °C in the analyzing step. For a pyrolysis experiment, a 30 g of waste tire was loaded into the lower zone of reactor, operated at 500 °C, and 7.5 g. of a catalyst was loaded to the catalytic zone, operated at 350 °C (the waste tire/catalyst ratio of 4). The experimental setup (see Fig. 1) and the pyrolysis conditions were the same as indicated in our published papers [21,22], which have been achieved from our successive studies [7, 12, 21]. Briefly, the heating rate was controlled at 10 °C/min and then kept for 2 h at the atmospheric pressure. The flow rate of N₂ was controlled at 30 ml/min, which was continuously flown to purge the oxygen out of the pyrolysis system. The obtained product was next passed through condensers in order to collect the liquid product, and subsequently the gas product was kept in a gas sampling bag. The solid and liquid products were weighed to determine the distribution of pyrolysis products.



6.2.4 Product Analysis

Pyrolysis gas was analyzed by using a Gas Chromatography (GC), Agilent Technologies 6890, installed with HP-PLOTQ column: 20 μm film thickness and 30 m $\times$ 0.32 mm ID and equipped with FID detector, using helium as the carrier gas. The oil products were dissolved in *n*-pentane to precipitate asphaltene, and then left for overnight. Subsequently, asphaltene was filtered from the mixture under vacuum using a polyamide membrane with the 0.45 μm of pore size. The solution after asphaltene precipitation is called “maltene”. The true boiling point curves of maltenes were obtained by using a Varian GC-3800 Simulated Distillation Gas Chromatography (SIMDIST-GC) conformed to the ASTM-D2887 method, which were then cut into 5 petroleum fractions; that are, full range naphtha (< 200 $^{\circ}\text{C}$), kerosene (200-250 $^{\circ}\text{C}$), light gas oil (250-300 $^{\circ}\text{C}$), heavy gas oil (300-370 $^{\circ}\text{C}$), and long residue (> 370 $^{\circ}\text{C}$). In addition, the compositions of maltenes were identified by using a LECO[®] 4D Pegasus two-dimensional Gas Chromatography with Time of Flight Mass Spectroscopy (GC $\times$ GC-TOF/MS). Maltene solution samples were prepared from diluting 1 μl of maltene with CS_2 into 2 ml, and injected to the GC installed with two columns. The 1st column was a non-polar Rtx[®]-5Sil MS with 30m $\times$ 0.25mm ID $\times$ 0.25 μm film thickness installed in the main oven operated at 50 $^{\circ}\text{C}$, held for 2 min at the beginning of analysis, then ramped to 310 $^{\circ}\text{C}$ with 5 $^{\circ}\text{C}/\text{min}$, and held at the final temperature for 10 min. The 2nd column was an Rxi[®]-17 MS with 1.10 m $\times$ 0.10 mm ID $\times$ 0.10 μm film thickness installed in the second oven started at 60 $^{\circ}\text{C}$, held for 2 min, then heated to 320 $^{\circ}\text{C}$ with 5 $^{\circ}\text{C}/\text{min}$, and held for 10 min when the final temperature was reached. Other operating conditions such as modulator time, ionization voltage, ion source and detector voltages, and mass spectral data collection were set the same as in [22]. The LECO ChromaTOF[®] software recorded and analyzed data with spectral identification provided by the NIST library. The accuracy and sensitivity of the MS detector were calibrated and tested by using perfluorotributylamine (PFTBA) and hexachlorobenzene (HCB), respectively. Moreover, sulfur content in oils was determined by using a LECO[®] Elemental Analyzer (TruSpec[®]CHNS).

6.3 Results and Discussion

6.3.1 Catalyst Characterization

The TPR profiles of Fe-loaded catalysts are shown in **Fig. 2**. It is found that 5%Fe on HBeta, HZSM-5, HMOR and KL has the reduction peak at 500 °C, 503 °C, 552 °C, and 610 °C, respectively. Therefore, the interaction between Fe and the supports can be ranked in the following order: Fe/KL > Fe/HMOR > Fe/HZSM-5 > Fe/HBeta. **Fig. 3** shows the XRD patterns of Fe-loaded catalysts. It exhibits that the introduction of 5% of Fe on zeolites results in the presence of the metallic Fe peaks at 2θ of 44.6° (110), 65° (200), and 82° (211) in the XRD patterns based on JCPDS 06-0696. The (110) peak was used to calculate the Fe cluster size, L_{110} , using Scherrer's equation;

$$L_{hkl} = \frac{k\lambda}{\beta \cos \theta_o},$$

where λ is the X-ray wavelength of $\text{CuK}\alpha$, which is 1.5406 Å, λ is the peak width (expressed in radian), θ_o is the angle between the beam and the normal on the reflecting plane (expressed in radian), and k is a constant shape factor (often taken as 0.9). Moreover, the other physical properties of fresh catalysts are shown in Table 1. It can be seen that the physical properties of all catalysts are not markedly different, except the surface area.

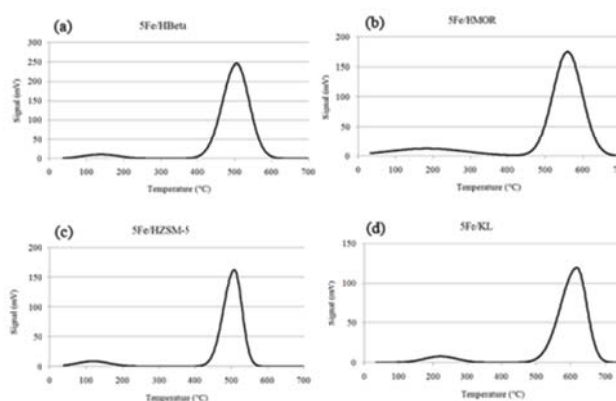


Fig. 2 H_2 -TPR profiles: (a) 5%Fe/HBeta, (b) 5%Fe/HMOR, (c) 5%Fe/HZSM-5, and (d) 5%Fe/KL.

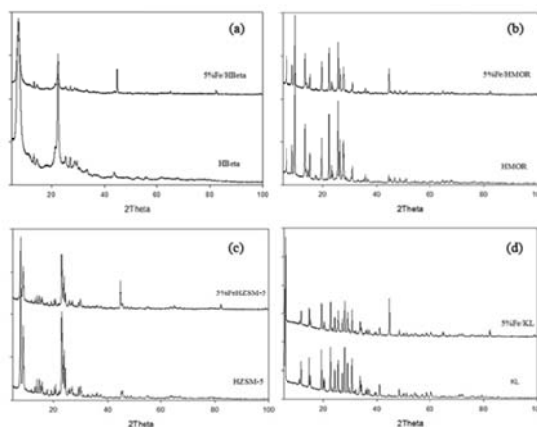


Fig. 3 XRD pattern of (a) 5%Fe/HBeta, (b) 5%Fe/HMOR, (c) 5%Fe/HZSM-5, and (d) 5%Fe/KL.

Table 1 Physical properties of fresh catalysts

Catalyst	BET Surface area	Pore volume*	Maximum pore width*	Median pore width*	Fe cluster size** L ₁₁₀
	(m ² /g)	(cm ³ /g)	(Å)	(Å)	(nm)
HBeta	539	0.257	8.15	8.35	-
HMOR	394	0.199	8.39	8.42	-
HZSM-5	366	0.178	7.77	7.44	-
KL	218	0.113	6.95	7.08	-
5%Fe/HBeta	406	0.234	6.59	8.11	68.4
5%Fe/HMOR	352	0.176	6.50	6.94	60.5
5%Fe/HZSM-5	265	0.131	6.82	6.96	77.6
5%Fe/KL	98.8	0.047	6.62	7.01	80.7

*Calculated from Horvath-Kawazoe method

**Calculated from Scherrer's Equation

6.3.2 Pyrolysis Yield

Waste tire samples with the elemental compositions shown in Table 2 were pyrolyzed using the catalysts, and the distribution of pyrolysis products is illustrated in **Fig. 4**. The yield of char is constant for all cases, indicating that rubbers in the tire samples were totally converted to hydrocarbon products. All parent zeolites results in a slight reduction of the oil yield in accordance with the slight

increase in gas or a high coke deposition on the catalyst as compared to the non-catalyst case. The introduction of 5 wt.% Fe on the zeolites in general does not significantly affect the product distribution. Except Fe/HZSM-5, Fe loading further decreases the oil yield in accordance with increment of gas yield, indicating that Fe enhances the cracking ability, which can be confirmed by a higher deposition of coke that is also observed on Fe/HZSM-5 whereas the coke deposition decreases with 5%Fe loading on the other zeolites. However, the highest coke deposition is observed on the HBeta cases. In addition, the distribution of gaseous products obtained from all catalysts are illustrated **Fig.5**. Briefly, Fe loading enhances the productions of ethylene and propylene, but suppresses those of mixed C4 and C5 hydrocarbons.

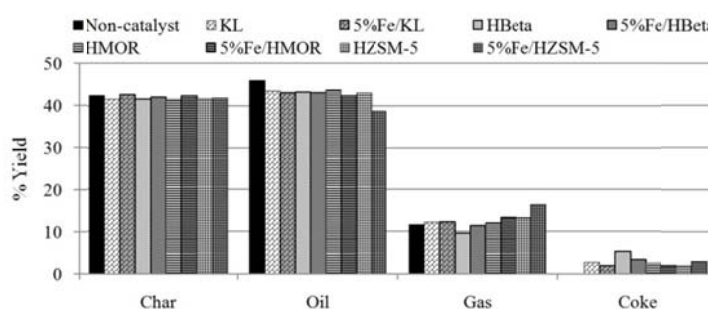


Fig. 4 Yield of pyrolysis products obtained from using the parent zeolites and 5%Fe-promoted catalysts.

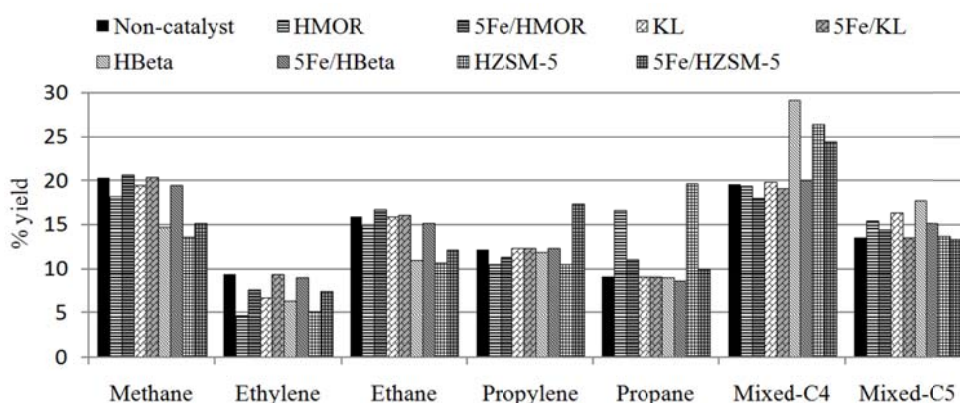


Fig. 5 Gas compositions obtained from using the parent zeolites and 5%Fe-promoted catalysts.

Table 2 Elemental analysis of waste tire samples

Element	% (by weight)
C	81.1 ± 2.85
H	6.81 ± 0.237
S	2.07 ± 0.0279
N	3.71 ± 0.415

6.3.3 Petroleum Fractions

The petroleum fractions, classified into full range naphtha, kerosene, light gas oil, heavy gas oil, and long residue, are revealed in **Fig.6**. The results show that the amount of full range naphtha increases with using the parent zeolites. The effects of zeolites properties have been comprehensively discussed in Muenpol et al., [12]. Furthermore, Fe-loaded catalysts, except 5%Fe/HBeta, markedly enhance the production of full-range naphtha in conjunction with the significant decreases in light gas oil, heavy gas oil, and long residue. It can be concluded that Fe enhances the ability in cracking heavy fractions (especially, light gas oil, heavy gas oil, and long residue) to the lightest full-range naphtha. A tremendous increase in full-range naphtha is obviously observed when Fe is loaded on KL, HMOR, and HZSM-5, but not on HBeta. Since it was observed from the TPR experiments that the interaction between Fe and the three zeolite supports is strong, it can be implied that the strong Fe-support interaction is possibly responsible for the enhanced cracking activity of the catalysts. Similarly, based on Pan et al., (2015), the interaction between Fe and the supports (MOR, ZSM-5, and Beta), which decreases in the same order; Fe/MOR > Fe/ZSM-5 > Fe/Beta, was found responsible for a high adsorption and conversion of NO [23]. Moreover, Fe loading on these zeolites resulted in stronger acidic site and higher acidity, and Fe/MOR was found more acidic than Fe/ZSM-5 and Fe/Beta [24]. Therefore, the enhancement on cracking activity of the catalysts in waste tire pyrolysis could possibly be contributed from strong Fe-support interaction and the enhancement of acidity with Fe loading.

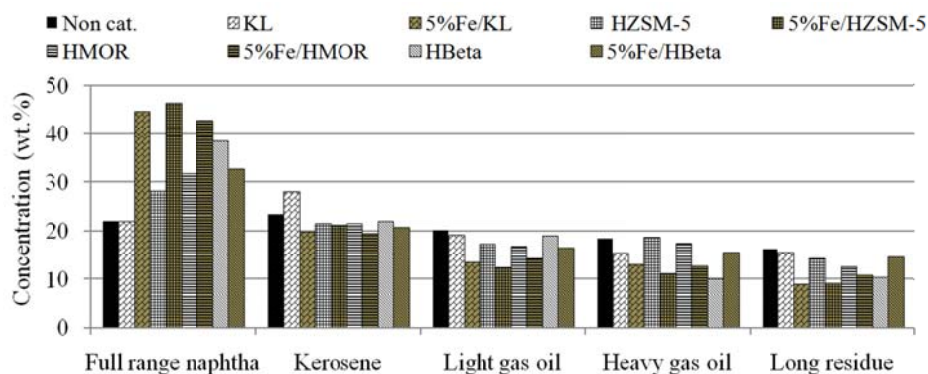


Fig. 6 Petroleum fractions in maltenes obtained from using the parent zeolites and 5%Fe-promoted catalysts.

6.3.4 Petrochemicals in Oils

Components in gasoline (C_5 - C_9), which are classified into paraffins, olefins, naphthenes, and aromatics, are exhibited in **Fig.7**, and the content of petrochemicals in gasoline is shown in **Fig.8**. In general, aromatics are the most abundant species in gasoline, co-existing with a considerable amount of olefins and naphthenes and a trace of paraffins. The parent KL, HMOR, and HBeta do not much alter the distribution of gasoline-range species whereas HZSM-5 significantly enhances the formation of olefins and naphthenes in expense of total aromatics. It can be possibly explained that HZSM-5 has the pore opening window that can selectively fit with the molecular size of gasoline components (C_5 - C_9) whereas the other zeolites have a larger pore opening window. Therefore, the components in this range can be selectively transformed from one to another in the suitable size of HZSM-5's pore. Furthermore, it can be seen that the introduction of Fe-loaded catalysts results in the change of species in gasoline. Especially, naphthenic group is enhanced using Fe/HMOR and Fe/HBeta in expense of olefins or aromatics, indicating that olefins and/or aromatics are transformed to naphthenes. Fe loaded on HZSM-5 and KL increases the aromatic content with the suppression of olefins, possibly via cyclization and then aromatization. It can be stated that Fe seems to drive cyclization of a non-cyclic to a cyclic molecule, either a naphthene or an aromatic, depending on the reactant.

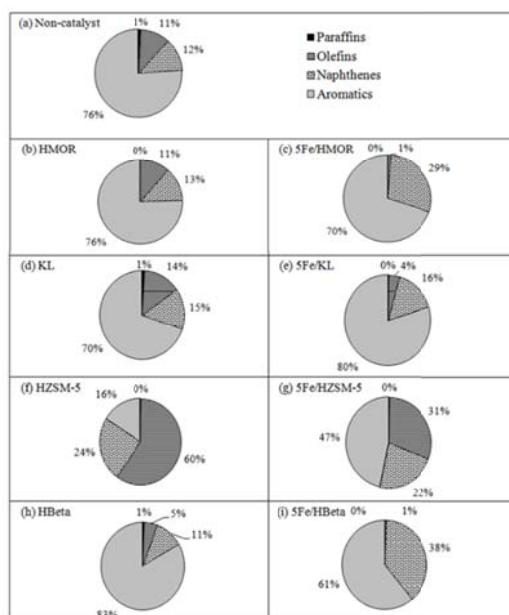


Fig. 7 Components in gasoline (wt.%): (a) the non-catalyst case, (b) HMOR, (c) 5%Fe/HMOR, (d) KL, (e) 5%Fe/KL, (f) HZSM-5, (g) 5%Fe/HZSM-5, (h) HBeta, and (i) 5%Fe/HBeta.

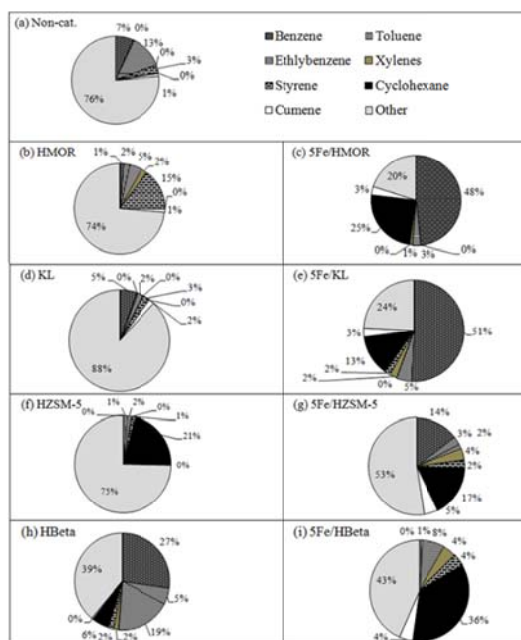


Fig. 8 Petrochemicals (wt.% in gasoline) obtained from (a) the non-catalyst case, (b) HMOR, (c) 5%Fe/HMOR, (d) KL, (e) 5%Fe/KL, (f) HZSM-5, (g) 5%Fe/HZSM-5, (h) HBeta, and (i) 5%Fe/HBeta.



It appears that the tire-derived oils are not suitable for direct use as a fuel in an internal combustion engine due to the high aromatics contents. However, the oils have a potential for use as a feedstock for petrochemicals production since they contain some valuable petrochemicals; that are, benzene, toluene, ethylbenzene, xylenes, styrene, cyclohexane, and cumene. Generally, using the zeolites in tire pyrolysis produces around 12 – 26 wt.% petrochemicals in gasoline, which is not significantly different from the quantity observed in thermal pyrolysis, except the case of using HBeta as a catalyst that gives ~ 60% (**Fig. 8**). Marked increases in petrochemicals production (~ 47 – 80 wt.% in gasoline) are observed with using Fe catalysts, regardless of the zeolite supports, especially 5%Fe/HMOR and 5%Fe/KL, even though Fe/HBeta does not alter the total petrochemicals content significantly. It indicates that Fe promoted on HMOR and KL, that have 1D pore channel, more sharply increases the petrochemicals content in gasoline than on HZSM-5 or HBeta that has a 3D pore channel. In details, 5%Fe loading on HMOR sharply increases benzene and cyclohexane contents whereas the equal loading on KL results in the increase of benzene, cyclohexane and toluene. These observations also support our earlier findings that Fe was found to cyclize olefin to a cyclic or an aromatic compound. Moreover, it is observed that 5%Fe/HZSM-5 produces more amount of benzene than HZSM-5, and 5%Fe/HBeta increases the cyclohexane content in accordance with the reduction of benzene. It can be concluded that 5%Fe loading on KL, HMOR, and HZSM-5 resulted in more valuable products than the parent zeolites. Moreover, the introduction of 5%Fe on KL and HMOR (1D pore channel) enhances the production of valuable hydrocarbons more effectively than on HZSM-5 and HBeta (3D pore channel).

In order to get a clearer picture of how much petrochemicals are produced in the tire-derived oils, Table 3 exhibits the content of petrochemicals in oils (wt.%) obtained from waste tire pyrolysis using pure zeolites; that are, KL, HZSM-5 (HZ), HMOR (HM), and HBeta (HB) and Fe-promoted catalysts. From the results, it can be seen that 5%Fe/HMOR is the best catalyst to produce benzene (14.0 wt.% in oil) and cyclohexane (7.17 wt.% in oil), and HBeta can be used to produce ethylbenzene (3.31 wt.% in oil). On other hand, only a small amount of other petrochemicals; that are, styrene, toluene, cumene, and xylenes, are found in the oils.

Table 3 Petrochemicals content (wt.%) in oils obtained from zeolites and Fe-loaded zeolites

Petrochemical	Petrochemicals content (wt.% in oil)							
	HM	5Fe/HM	HB	5Fe/HB	HZ	5Fe/HZ	KL	5Fe/KL
Benzene	0.12	14.0	4.8	-	-	3.4	0.26	12.7
Toluene	0.18	0.053	0.92	0.095	0.20	0.65	0.005	1.2
Ethylbenzene	0.41	0.83	3.3	0.87	0.26	0.40	0.10	-
<i>m</i> -Xylene	0.18	-	-	-	0.098	0.84	-	0.39
<i>o</i> -Xylene	-	-	0.16	0.23	-	0.01	-	-
<i>p</i> -Xylene	-	0.28	0.13	0.25	0.030	0.044	-	0.21
Styrene	1.3	-	0.32	0.46	0.21	0.60	0.12	0.46
Cyclohexane	-	7.2	1.0	4.1	3.5	4.1	-	3.3
Cumene	0.1	0.88	0.08	0.5	0.03	1.1	0.083	0.68
Total	2.32	23.3	10.8	6.5	4.3	11.2	0.58	18.9

6.3.5 Aromatics in maltenes

The chemical components in maltenes, especially the types of aromatic compounds, can also be illustrated more clearly as shown in **Fig. 9**. It also supports that the concentration of paraffins does not change significantly with using all catalysts, and the concentration of olefins and naphthenes tends to decrease with using Fe-loaded catalysts. It can be explained that olefins and naphthenes may convert to aromatics via Diels-Alder reaction [25,26]. Moreover, mono-aromatics increase significantly with using Fe-loaded catalysts, as compared to the parent zeolites whereas 5%Fe supported on KL, HMOR, and HZSM-5 gives a lower amount of di- and poly-aromatic hydrocarbons than the parent zeolites, but 5%Fe/HBeta gives a higher amount of poly-aromatic hydrocarbons than the parent HBeta. It can be suggested that di- and poly-aromatics convert to mono-aromatics via hydrogenation and ring opening reaction, possibly enhanced by Fe [20,27]. However, the introduction of Fe also results in the reduction of some mono-aromatic species as evidently observed from the GCxGC-TOF/MS results. It can be suggested that these mono-aromatics might be converted to other hydrocarbon compounds or valuable petrochemicals, as observed earlier [12], by hydrogenation and ring opening, also enhanced by Fe. Additionally, polar-aromatic hydrocarbons, that are

the combinations of S, O, and N-containing aromatics, slightly increase with loading Fe on KL, HZSM-5, and HMOR zeolites, but decrease with using Fe supported on HBeta.

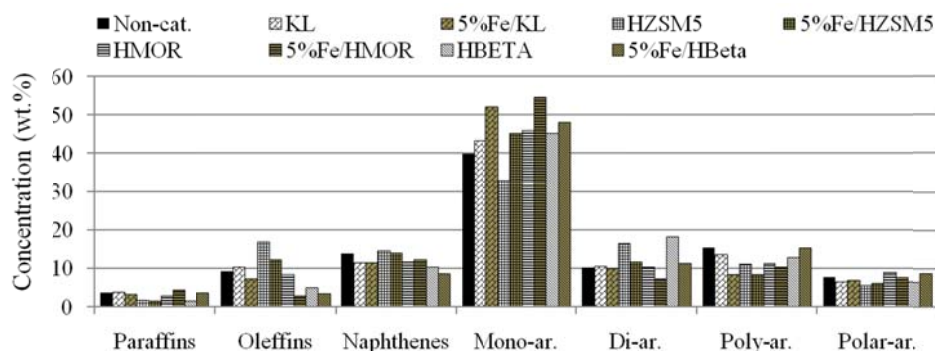


Fig. 9 Concentration of chemical components in maltenes obtained from using the parent zeolites and 5%Fe-promoted catalysts.

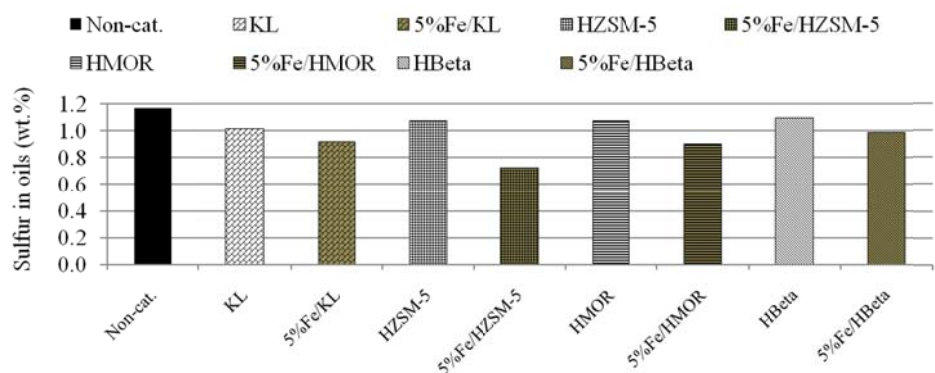


Fig. 10 Sulfur content in oils obtained from using the parent zeolites and 5%Fe-promoted catalysts.

6.3.6 Desulfurization Activity

The sulfur content in pyrolytic oils as exhibited in **Fig.10** is determined by using an elemental analyzer. Originally, it is found that the sulfur content in oil is around 1.17 wt.%. All catalysts result in the reduction of sulfur in oils, as compared to the non-catalytic pyrolysis. In addition, the parent zeolites can reduce sulfur in oil significantly, and Fe-promoted catalysts further reduce sulfur in oils. The lowest sulfur in oils is obtained from using 5%Fe/HZSM-5 (0.73 wt.%), followed by 5%Fe/HMOR (0.91 wt.%), 5%Fe/KL (0.92 wt.%), and then 5%Fe/HBeta (0.99 wt.%). Sulfur removed from the oils is deposited on the spent Fe catalysts as evidently seen from **Fig. 11**. Therefore, it can be concluded that Fe enhances sulfur removal activity.

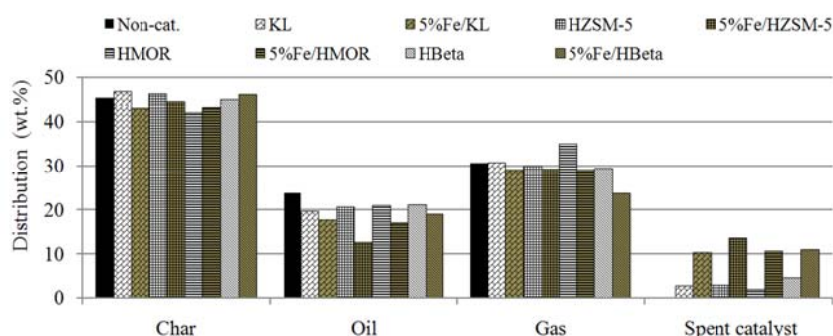


Fig. 11 Overall distribution of sulfur in pyrolysis products obtained from using the parent zeolites and 5%Fe-promoted catalysts.

Fig.12 reveals that the yield of sulfur species in maltenes, which are classified into two groups: (1) sulfur-containing compounds, that consist of thiophenes (Ts), benzothiophenes (BTs), and dibenzothiophenes (DBTs), and (2) heteroatom-containing sulfur compounds, that consist of benzothiazoles (N-containing sulfur compound) and others (N or/and O-containing sulfur compounds). Nitrogen and oxygen are found in oils because nitrogen- and oxygen-containing compounds are used as vulcanization accelerators in rubber production, especially benzothiazoles, which are commonly used in vulcanization process [4,5,28]. The results show that Fe-loaded catalysts tend to decrease the amounts of benzothiophenes and dibenzothiophenes, except 5%Fe/HZMS-5 that increases the amount of BTs, observed with the simultaneously-increasing formations of benzothiazoles and other N or/and O-containing sulfur compounds (see Fig. 11). However, the overall sulfur content in the oils is decreased with Fe loading. From the results, it can be suggested that Fe enhances the C-S bond breaking activity, resulting in the reduction of BTs and DBTs, whereas Fe loaded on HZSM-5 may partially plug the pore opening of HZSM-5, which is the smallest; thus, resulting in the lower activity in reduction of BTs and DBTs. The discussion on the effects of zeolite supports has been previously reported in [12]. However, the increases in benzothiazole content in the oils using Fe-promoted catalysts were also simultaneously observed, which might be explained by two possible reasons: (a) while the C-S bond in the molecules of adsorbed benzothiophenes is broken by an Fe site, the benzothiophenes on the surface are partially attacked and reacted with N-containing compounds, forming benzothiazoles whereas the un-attacked benzothiophenes desorb as S-free products from the surface, leaving sulfur on the

Fe sites of spent catalysts as shown in Fig. 10, and/or (b) other S-containing compounds might adsorb on the Fe sites and then react with N-containing compounds, forming benzothiazoles and other multi-heteroatom containing compounds. Future mechanistic studies are needed to support the explanations.

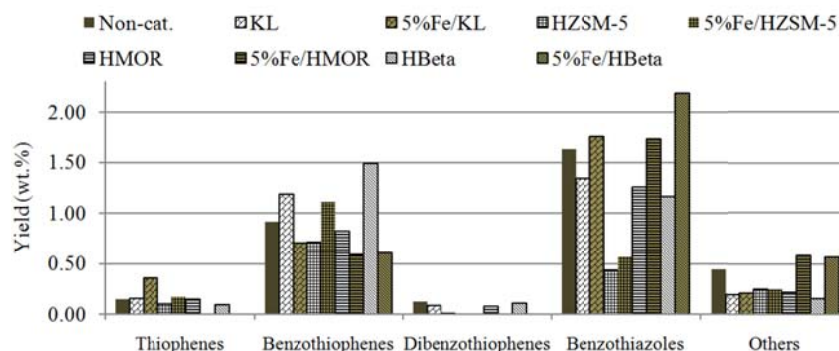


Fig. 12 Yield of sulfur species in maltenes obtained from using the parent zeolites and 5%Fe-promoted catalysts.

6.4 Conclusions

All Fe-promoted catalysts increased the light fraction (full range naphtha) at the expense of the heavier fractions in oil because Fe enhanced the cracking activity of zeolites. Especially, the total petrochemicals in oil were highly increased with using Fe-loaded catalysts, except 5%Fe/HBeta. It can be ranked as 5%Fe/HMOR > 5%Fe/KL > 5%Fe/HZSM-5 > 5%Fe/HBeta. 5%Fe/HMOR appeared to be the best catalyst to produce benzene and cyclohexane. 5%Fe/KL was the best catalyst for toluene production, whereas 5%Fe/HZSM-5 can be used to produce xylenes and cumene. Moreover, sulfur content in oils reduced with using Fe-loaded catalysts, and the lowest sulfur in oil was obtained from using 5%Fe/HZSM-5.

6.5 Acknowledgements

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Chapter 7

Fuels, hydrocarbon compounds and petrochemicals in waste tire-derived pyrolysis oils from using Co-promoted catalysts*

Abstract: Pyrolysis of waste tire is a sustainable way to simultaneously eliminate a large amount of waste tires and recover valuable fuels and chemicals. In tire-derived oil, valuable petrochemicals such as benzene, toluene, xylenes, and styrene have been observed. Furthermore, sulfur compounds causing the low quality of oil and the environmental pollutant are also certainly found. Cobalt has been used in many catalytic reactions such as hydrogenation, isomerization, cracking and desulphurization. In this work, 5 wt.% Co catalysts supported on KL, HBeta, HZSM-5, and HMOR were employed, aiming to simultaneously enhance the production of valuable compounds and suppress the formation of sulfur compounds in tire-derived oil. The pyrolysis products were examined by using GC, SIMDIST-GC, and GCxGC-TOF/MS. The results showed that Co-promoted catalysts increased the light petroleum fractions at the expense of heavier fractions in oils, indicating that Co enhanced the cracking ability. The contents of valuable hydrocarbons in oils such as benzene, cyclohexane, and toluene were significantly enhanced with the presence of Co, except 5%Co/HBeta. The best catalyst for production of valuable petrochemicals was 5%Co/KL, followed by 5%Co/HZSM-5, 5%Co/HMOR, and 5%Co/HBeta, accordingly. In addition, 5%Co/KL can produce the highest amount of benzene, toluene, and p-xylenes whereas 5%Co/HZSM-5 exhibited the potential for o-xylene and p-xylene production. 5%Co/HMOR was dominant for production cyclohexane. In addition, using Co-loaded catalysts resulted in the reduction of sulfur contents in oils, suggesting that Co has ability to break C-S bonds of sulfur compounds in tire-derived oil. The lowest sulfur content in oil was obtained from using 5%Co/KL (0.850 wt. %). Moreover, the types of sulfur species in oils were changed significantly with the presence of Co as well. For instance, all Co-loaded catalysts tended to decrease the contents of benzothiophenes and dibenzothiophenes in tire-derived oil. It can be concluded that Co-promoted catalysts can produce light tire-derived oils, and they have the ability to simultaneously enhance the production of valuable hydrocarbons and reduce the sulfur content in oil.



In order to improve the performances of zeolites, metals can be employed as promoters. Non-noble metals that exhibit good performances and low cost are interesting for the pyrolysis process. Non-noble metals such as Cu [7, 18], Fe [8], Ni [19,20], and NiMo [21] were employed instead of noble metals, for instances, Pt [22], Ru [23,24], and Pd [19,25]. Cobalt is a non-noble metal with a high availability, and known to be a good adsorbent or catalyst, especially in Fischer-Tropsch



synthesis [26-29] and sulfur removal [30-32]. Supported Co catalysts gave a high yield of paraffinic hydrocarbons [26] and a lower olefin selectivity in Fischer-Tropsch synthesis, attributed to a high hydrogen concentration on the catalyst surface and the re-adsorption of olefins on the surface that led to secondary hydrogenation [27], and resulted in high molecular weight hydrocarbons [28]. Cobalt is also well known to be a part of sulfur-removal adsorbents [30], sulfur-oxidizing catalysts [31], and hydrotreating catalysts [32]. Additionally, supports also appear to influence the performance of cobalt promoter. Yang et al. [29] compared the products obtained from Co/SiO₂, Co/SiO₂-ZSM-5(physical mixture), and a capsule catalyst of Co/SiO₂ covered by ZSM-5 zeolite as Fischer-Tropsch catalysts. The result showed that Co/SiO₂-ZSM-5 gave the narrower carbon number distribution in the range of C3-C7, compared to Co/SiO₂, because ZSM-5 zeolite helped to reduce heavy fractions to lighter ones by the enhancement of isomerization and the cracking ability of zeolite. Since Co can enhance hydrogenation and sulfur removal, together with the cracking ability of a support, Co was expected to improve the quality of tire pyrolysis oil, remove sulfur from the oil, and enhance the formation of some valuable compounds in the oil. Therefore, the aim of this study was to investigate the effects of cobalt supported on zeolites (KL, HMOR, HBeta, and HZSM-5) on structure of hydrocarbon compounds, fuels, and petrochemicals in tire-derived oils. A series of Co supported zeolites was prepared by incipient wetness impregnation technique loading, and employed as catalysts in waste tire pyrolysis.

7.2 Experimental

7.2.1 Catalyst Preparation and Characterization

All zeolites (KL, HMOR, HBeta, and HZSM-5) were obtained from Tosoh Company in Singapore and Zeolyst International. In order to remove impurity from zeolite, HMOR and HZSM-5 zeolites were calcined at 500 °C for 3 h with the heating rate of 10 °C/min. HBeta was calcined at 600 °C for 5 h with 2 °C/min, and KL was calcined at 500 °C for 3 h at 10 °C/min. Then, Co was loaded on the zeolite using incipient wetness impregnation technique. Cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O) solution was dropped on a zeolite, and the amount of Co was fixed at 5 wt.%. After that, the catalysts were dried at 100 °C for 3 h in an oven, and then calcined again at the same conditions. Finally, they were reduced at 600 °C for 2 h with H₂ prior to uses. X-ray Diffraction (XRD) technique was used to verify the metallic form of the catalysts. X-ray diffraction patterns were taken by using a Bruker X-ray diffractometer system (D8 Advance) equipped with a 2.2 kW Cu anode



in a long fine focus ceramic X-ray tube for generating a $\text{CuK}\alpha$ radiation ($1.5405 \text{ \AA}$). The detector scanned the peak position from the samples as a function of 2θ by starting at the 5° to 100° (2θ) range and a scan speed of 5° (2θ)/min. H_2 -Temperature-programmed reduction (TPR) was used to identify the reducibility of the impregnated catalysts and the metal-support interaction. The temperature was ramped from 30 to 850°C with a heating rate of $10^\circ\text{C}/\text{min}$. Surface area (BET) was determined by using Sorptomatic equipment. Moreover, Thermogravimetric/Differential Thermal Analysis (TG/DTA) machine was used to determine coke deposited on spent catalysts. In addition, an elemental analyzer was used to determine sulfur content on spent catalyst.

7.2.3 Pyrolysis Experiment

The same shredded waste tire samples (Bridgestone TURANZA GR-80) with the same ultimate analysis reported in [8] was used in all pyrolysis experiments. The pyrolysis experiments were also conducted using the same pyrolysis system as described in [8,17]. Briefly, there were 2 zones of the pyrolysis reactor: that are, the catalytic zone (the upper zone) and pyrolytic zone (the lower zone). Firstly, 30 g of the waste tire with sizes in the range of 20-40 mesh was loaded into the lower zone, and 7.5 g of pellet catalyst was loaded to the catalytic zone. Then, the pyrolysis was heated with the rate of $10^\circ\text{C}/\text{min}$ from the room temperature to 500°C , and then kept for 120 min at the atmospheric pressure. The temperature of pyrolytic zone was controlled at 350°C . The flow rate of N_2 was controlled at 30 ml/min, continuously flown to purge the oxygen out of the system prior to pyrolysis and subsequently for carrying the pyrolysis products to condensers and a gas sampling bag. These condensers were placed into an ice bath in order to collect the liquid product. A gas sampling bag collected the incondensable products. The liquid product was dissolve in *n*-pentane to separate asphaltene by using a polyamide membrane (pore size = $0.45 \mu\text{m}$). Then, true boiling point curve and petroleum fractions were determined by using a Simulated Distillation Gas Chromatography (SIMDIST-GC) conformed to ASTM D-2887. Finally, the composition of a maltene was analyzed by using a comprehensive two-dimensional Gas Chromatography with Time of Flight Mass Spectrometer (GCxGC-TOF/MS). The gas products were analyzed for compositions by using a Gas Chromatography (GC-FID). In addition, an elemental analyzer was used to determine the sulfur content in solid products and spent catalysts.

7.3 Results and discussion

7.3.1 Catalyst Characterization

The XRD patterns of Co-loaded catalysts are shown in **Fig. 1**. It exhibits that the introduction of 5 wt.% of cobalt should result in the presence of new peaks that belong to metallic Co in the XRD patterns of all catalysts; however, the low amount of cobalt only gives the low intensity of Co peaks at 2θ of 44° , 51° , and 55° . TPR profiles of Co-loaded catalysts are shown in **Fig. 2**. The results indicate that reduction peak exhibits at 429°C (Co/HMOR), 458°C (Co/HBeta), 485°C (Co/HZSM-5), and 535°C (Co/KL). The ease in reducing cobalt on the supports can be ranked as Co/HMOR > Co/HBeta > Co/HZSM-5 > Co/KL. The physical properties of the catalysts are shown in **Table 1**.

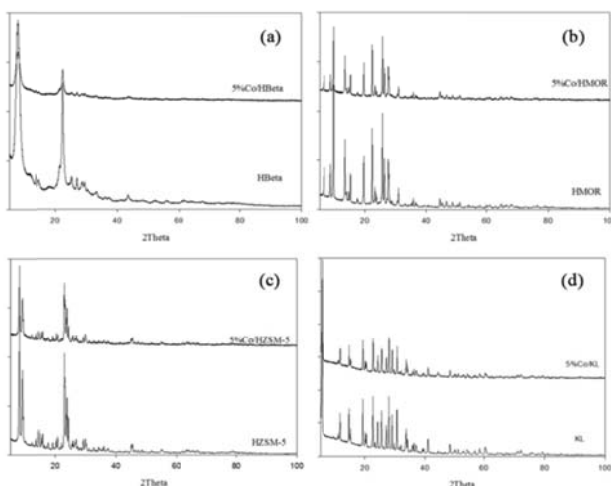


Fig. 1 XRD patterns of all catalysts.

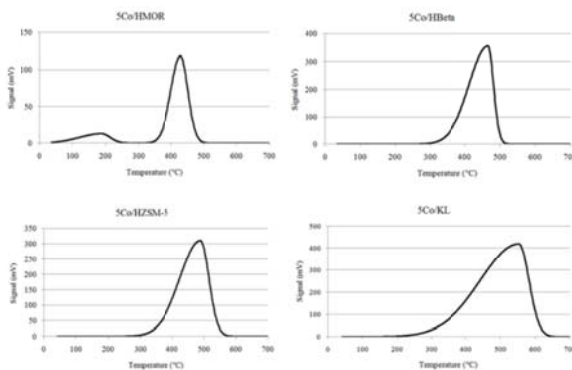


Fig. 2 H_2 -TPR profiles of Co-promoted catalysts.

**Table 1** Catalyst properties obtained from surface area analyzer

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Maximum pore width (Å)	Median pore width (Å)
HBeta	539.3	0.2570	8.148	8.351
HMOR	394.3	0.1990	8.392	8.422
HZSM-5	366.3	0.1780	7.774	7.443
KL	218.0	0.1130	6.954	7.078
5%Co/HBeta	434.2	0.2422	7.137	7.277
5%Co/HMOR	361.8	0.1821	7.553	7.421
5%Co/HZSM-5	310.3	0.2245	5.907	6.188
5%Co/KL	114.1	0.0570	6.426	6.275

7.3.2 Pyrolysis Yield

The distribution of pyrolysis products is shown in **Fig. 3**. The results show that using zeolites, which are KL, HMOR, and HZSM-5, except HBeta, results in the reduction of oil in accordance with the increment of gas and coke as compared to the non-catalytic pyrolysis. Moreover, the char yield is not significantly different. The introduction of cobalt strongly affects the yield of pyrolysis products. 5%Co supported on KL, HBeta, HMOR, and HZSM-5 zeolites further decreases the oil yield in accordance with the increment of gas and char, except 5%Co/HMOR. In addition, **Fig. 4** illustrates gas compositions obtained from using pure zeolites (HBeta, HMOR, HZSM-5, and KL) and 5%Co supported on those zeolites. It can be seen that using 5%Co-loaded zeolites results in the increment of methane, ethylene, ethane, and propylene, with the decreases of propane, mixed-C₄, and mixed-C₅ as compared to using the parent zeolites. It can be suggested that light hydrocarbon gases increase with the presence of Co. It indicates that the presence of Co enhances the cracking ability, which converts the heavy hydrocarbon gases to lighter hydrocarbon gases.

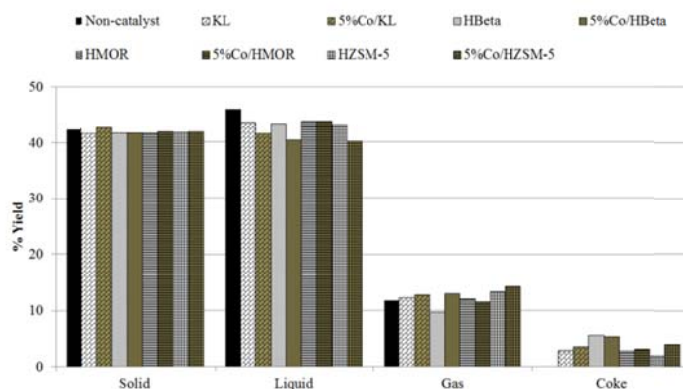


Fig. 3 Yield of pyrolysis obtained from using parent zeolites and 5%Co-promoted catalysts.

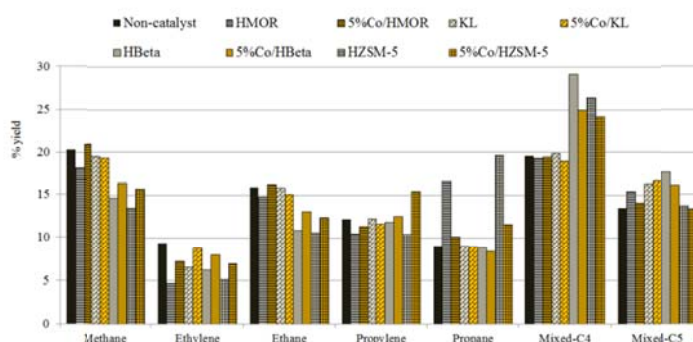


Fig. 4 Gas compositions obtained from the parent zeolites and Co-promoted catalysts.

7.3.3 Petroleum Fractions

Fig. 5 illustrates the petroleum fractions in maltenes; that are, full range naphtha (< 200 °C), kerosene (200-250 °C), light gas oil (250-300 °C), heavy gas oil (300-370 °C), and long residue (> 370 °C). The results exhibit that full range naphtha increases with using the parent zeolites (KL, HZSM-5, HMOR, and HBeta). Furthermore, all Co-loaded zeolites, except 5%Co/HBeta, results in further increment of full range naphtha. It can be seen that Co highly influences on the petroleum fractions; namely, using Co-loaded catalysts cause the increment of light fraction (full range naphtha) in consequence with the reduction of the heavier fractions. In addition, kerosene tends to decrease with Co loaded on KL, HMOR, and HBeta zeolites, but it slightly increases with 5%Co/HZSM-5. All Co-loaded catalysts suppress the amount of light gas oil. Heavy gas oil and long residue decrease with

using 5%Co supported on KL, HZSM-5, and HMOR. According to the results, it can be suggested that the increment of full range naphtha caused by cracking ability, which is enhanced by Co that converts kerosene, light gas oil, heavy gas oil, and long residue to full range naphtha.

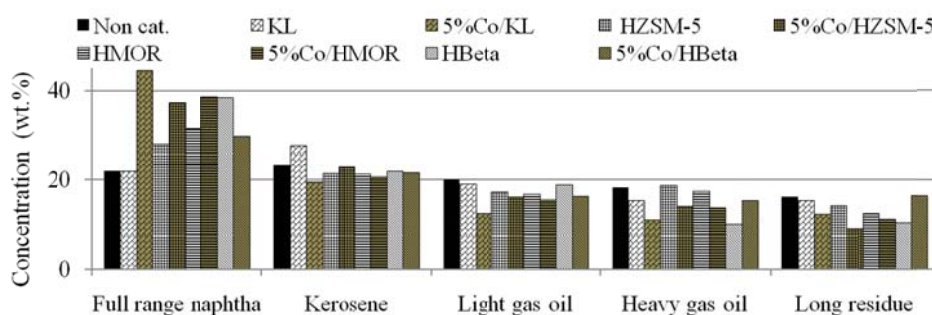


Fig. 5 Petroleum fraction in maltenes obtained from the parent zeolites and 5%Co-promoted catalysts.

5%Co supported on HBeta, which has a large pore size and 3D pore channel, gives a higher amount of heavy gas oil and long residue than HBeta. It can be explained that introduction of Co on HBeta might promote the secondary reaction of Co, such as oligomerization, to form heavy fractions such as heavy gas oil [28]. The components in gasoline classified into paraffins, olefins, naphthenes, and aromatics, are illustrated in **Fig. 6**. The results exhibit that aromatics are the most abundant species with using 5%Co supported on KL, HZSM-5, and HBeta, whereas a high amount olefins are produced with using 5%Co/HMOR.

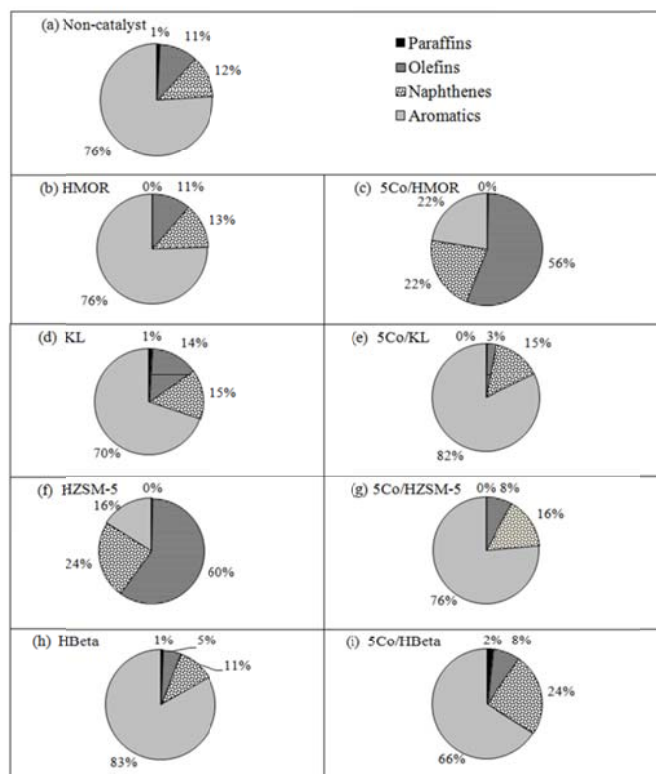


Fig. 6 Components in gasoline (wt.%): (a) the non-catalyst case, (b) HMOR, (c) 5%Co/HMOR, (d) KL, (e) 5%Co/KL, (f) HZSM-5, (g) 5%Co/HZSM-5, (h) HBeta, and (i) 5%Co/HBeta.

7.3.4 Petrochemicals in Oils

A high content of aromatics and olefins in oil can cause a high amount of smoke and gum formation in motor, respectively. Thus, pyrolytic oils are not suitable for a direct use in an engine. However, it can be used as a feedstock for petrochemical production since the valuable hydrocarbons, which are benzene, toluene, ethylbenzene, xylenes, styrene, cyclohexane, and cumene, are found as shown in **Fig. 7**. The results show that the introduction of Co enhances petrochemical production, except 5%Co/HBeta. The introduction of 5%Co on HMOR highly increases the production of cyclohexane whereas loading 5%Co on KL enhances the amounts of benzene, toluene, and cyclohexane. 5%Co/HZSM-5 increases the production of benzene and xylenes, whereas using 5%Co/HBeta decreases the production of all petrochemicals. It may be explained that 5%Co/HBeta can enhance the production of heavy compounds as mentioned before in **Fig. 5**; thus, resulting in the decrease of petrochemicals. Moreover, it can

be concluded that the oils obtained from the introduction of 5%Co on KL, HMOR, and HZSM-5 are more valuable than those obtained from the parent zeolites.

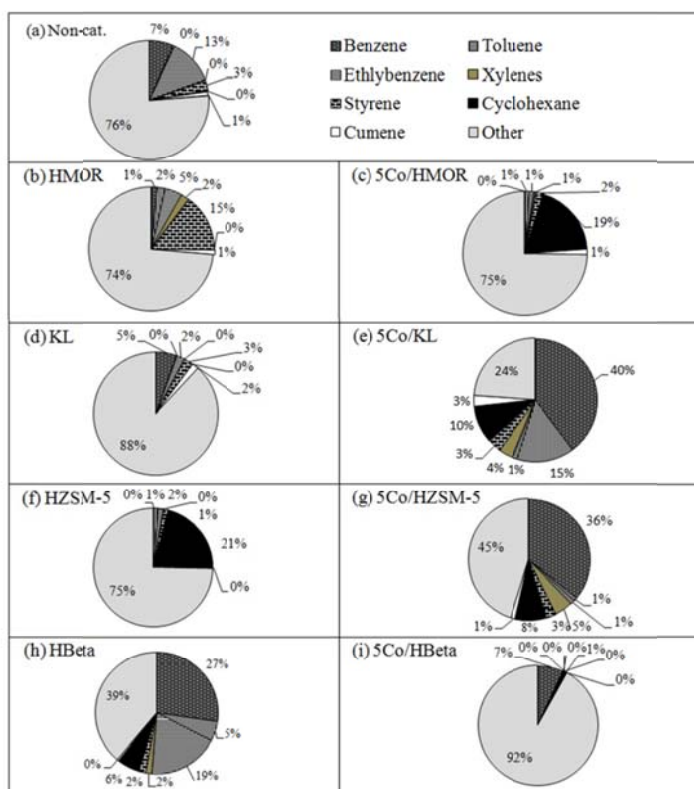


Fig. 7 Petrochemicals (wt.% in gasoline) obtained from (a) the non-catalyst case, (b) HMOR, (c) 5%Co/HMOR, (d) KL, (e) 5%Co/KL, (f) HZSM-5, (g) 5%CO/HZSM-5, (h) HBeta, and (i) 5%CO/HBeta.

The yields of petrochemicals in oils obtained from using the parent zeolites and 5%Co-promoted catalysts are shown in **Table 2**. From the results, it can be suggested that 5%Co/KL is the best catalyst to produce benzene (9.99 wt.%), toluene (3.79 wt.%), *m*-xylene (0.994 wt.%), and cumene (0.717 wt.%). 5%Co/HZSM-5 can be used to produce cyclohexane (3.78 wt.%). The highest amount of styrene (1.31 wt.%) and ethylbenzene (0.408 wt.%) are produced by using HMOR.

It can be seen that loading Co on KL and HMOR, which have a large pore size and 1D pore channel, results in the sharp increment of petrochemical production. Loading Co on HZSM-5 and HBeta, which have 3D pore channel, changes petrochemical production differently. Namely, 5%Co on HBeta results in a



sharp decrease of petrochemical production whereas 5%Co/HZSM-5 produces about 1.5 times higher amount of petrochemicals than HZSM-5. It can be concluded that 1D pore channel possibly enhances the activity of Co on producing petrochemicals more effectively than 3D pore channel. HBeta, which has 3D pore channel and large pore size, possibly allows the molecules to go inside with longer contact time than 1D channel; thus, resulting in the production of heavy compound via secondary reaction such as oligomerization, enhanced by Co [28]. In addition, for Co/HZSM-5, HZSM-5 that has 3D channel and medium pore size allows the molecules to go inside the pore with a longer contact time than 1D channel, but the medium pore size of HZSM-5 may inhibit the formation of heavy compounds as compared with the large pore size of HBeta.

Table 2 Valuable hydrocarbon compounds (wt.% in oils) obtained from zeolites (HMOR, HBeta, HZSM-5, and KL) and Co-loaded zeolites

Petrochemicals	wt.% in oil							
	HM	5Co/HM	HB	5Co/HB	HZ	5Co/HZ	KL	5Co/KL
Benzene	0.124	-	4.81	0.284	-	4.21	0.265	9.99
Toluene	0.184	0.197	0.917	0.005	0.196	0.108	0.00497	3.79
Ethylbenzene	0.408	0.280	3.31	0.004	0.258	0.132	0.102	0.311
m-Xylene	0.185	-	-	-	0.098	-	-	0.994
o-Xylene	-	-	0.161	-	-	0.123	-	-
p-Xylene	-	0.0831	0.129	-	0.0304	0.451	-	-
Styrene	1.31	0.396	0.320	-	0.207	0.313	0.125	0.891
Cyclohexane	-	3.78	1.05	0.0394	3.46	0.972	-	2.43
Cumene	0.105	0.280	0.077	-	0.0348	0.144	0.0827	0.717
Total	2.32	5.01	10.8	0.332	4.28	6.45	0.580	19.1

7.3.5 Liquid Components

The components in maltenes, which consist of paraffins, olefins, naphthenes, mono-aromatic, di-aromatic, poly-aromatic, and polar-aromatic hydrocarbons are shown in **Fig. 8**. The results show that maltenes contain a small amount of paraffins (> 4 wt.%). 5%Co supported on KL and HZSM-5 results in the reduction of olefins and naphthenes whereas total aromatics are increased.

Moreover, it is found that 5%Co on KL and HZSM-5 enhances the amount of mono-aromatics in accordance with the decreases of di- and poly-aromatics. It indicates that Co causes the reduction of di- and poly-aromatics, which convert to mono-aromatics, via saturation aromatic ring and open the hydrocarbon ring by hydrogenation [33].

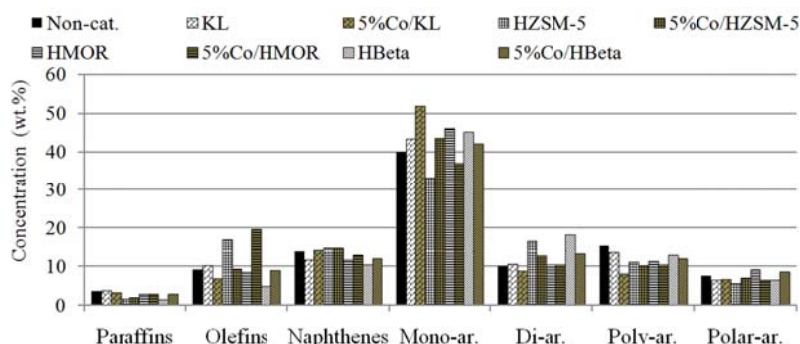


Fig. 8 Concentration of chemical components in maltenes obtained from the parent zeolites and 5%Co-promoted catalysts.

In addition, 5%Co promoted on HMOR and HBeta enhances the amount of olefins and naphthenes. The results show that mono-, di-, and poly-aromatics decrease with using 5%Co/HMOR and 5%Co/HBeta. It can be explained that the presence of Co can enhance hydrogenation and ring opening activity, which further converts mono-aromatics to olefins and naphthenes. Polar-aromatics, which are the heteroatom (S, O, and N)-containing aromatics, slightly increase with the use of 5%Co-promoted catalysts, except 5%Co/HMOR.

Moreover, the species of mono-aromatics are changed differently, and the reduction of some mono-aromatic species with using Co-loaded catalysts is shown in **Tables 3 – 6** (in **Supplementary Materials**). For instance, 5%Co on HMOR suppresses the amount of styrene and 1-cyclopenten-1-yl-benzene. 5%Co/KL decreases the amount of (1-methylpenta-1,3-dienyl)-benzene and 3-phenyl-2-pentene. In addition, 5%Co/HZSM-5 produces a less amount of 2-methyl-1,2-dihydronaphthalene and 1,1,5-trimethyl-indane. It indicates that these mono-aromatics species might be converted to petrochemicals by hydrogenation and ring opening enhanced by Co as depicted in **Fig. 9**. This is well consistent with the increment of petrochemicals; that are, cyclohexane using 5%Co/HMOR, benzene, toluene and cyclohexane using 5%Co/KL, and benzene and xylenes using 5%Co/HZSM-5, as mentioned before in **Table 2**.

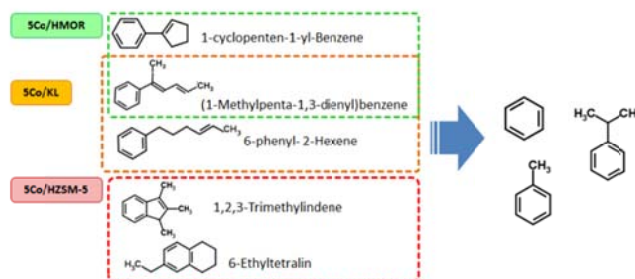


Fig. 9 Postulated transformation of some hydrocarbon molecules into petrochemicals

7.3.6 Desulfurization Activity

Sulfur distribution in pyrolysis products is shown in Fig. 10. The results show that sulfur is mostly distributed in char with no significant difference for all cases. 5%Co supported on zeolites shifts the sulfur distribution to the spent catalyst. In addition, 5%Co supported on KL, HBeta and HZSM-5 results in the insignificant difference of sulfur distribution in gas whereas 5%Co/HMOR slightly decreases sulfur distribution in gas. Moreover, the sulfur contents in oils are shown in Fig. 11a. The results show that 5% Co supported on all zeolites exhibits the reduction of sulfur contents in oils. It can be suggested that Co has ability to break C-S bond. In addition, the lowest sulfur content in oils is obtained from 5% Co/KL (0.850 wt.%).

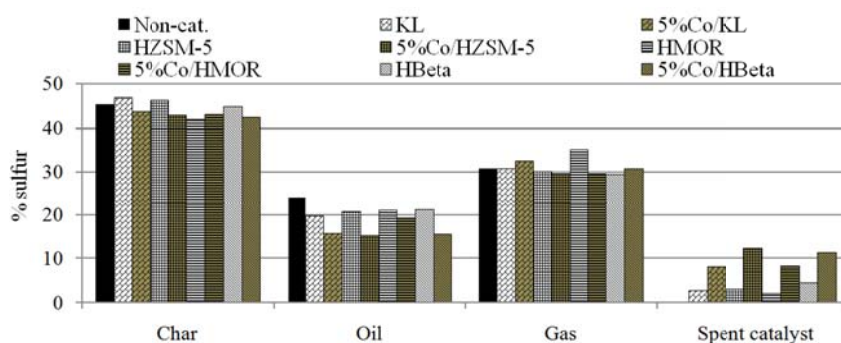


Fig. 10 Postulated transformation of some hydrocarbon molecules into petrochemicals

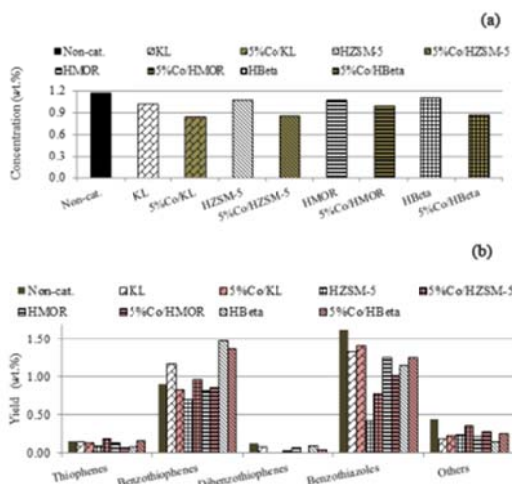


Fig. 11 Sulfur contents in oils (a) and Yield of sulfur species in maltenes (b) obtained from the parent zeolites and 5%Co-promoted catalysts.

Fig. 11b illustrated the yield of sulfur species in oils, which are classified into two groups: (1) sulfur-containing compounds, which consist of thiophenes (Ts), benzothiophenes (BTs), and dibenzothiophenes (DBTs), and (2) heteroatom-containing sulfur compounds, which consist of benzothiazoles (N-containing sulfur compound) and others (N or/and O-containing sulfur compound). The presence of benzothiazoles in oil can be explained that these compounds is used in tire production as a vulcanization accelerator [10,34,35]. It can be seen that that Co-loaded catalysts tends to decrease sulfur-containing compounds (BTs and DBTs), except 5%Co/HZMS-5. 5%Co on HZSM-5 increases the amount BTs. From the results, it can be suggested that Co enhances the C-S bond breaking activity, resulting in the reduction of BTs and DBTs, whereas Co loading on HZSM-5 causes the lowest surface area and pore volume; thus, it might result in the decreasing activity in reducing of BTs and DBTs. Moreover, Co-loaded catalysts tend to increase the heteroatom-containing sulfur compounds.

7.4. Conclusions

The introduction of Co supported on KL, HMOR, HZSM-5 and HBeta catalysts enhanced the cracking ability of heavy products to lighter products. The petrochemicals in oils sharply increased with using Co-loaded catalysts, except 5%Co/HBeta. The best catalyst for production of valuable petrochemicals was 5%Co/KL, followed by 5%Co/HZSM-5, 5%Co/HMOR-5, and 5%Co/HBeta,



accordingly. In addition, 5%Co/KL can produce the highest amount of benzene, toluene, and *p*-xylene. 5%Co/HZSM-5 exhibited the potential for *o*-xylene and *p*-xylene production. 5%Co/HMOR showed an activity for production cyclohexane. Moreover, sulfur in oils was reduced with using Co-loaded catalysts, and the lowest sulfur in oil was obtained from 5%Co/KL.

7.5 Acknowledgements

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Chapter 8

Impacts of Nickel supported on Different Zeolites on Waste Tire-derived Oil and Formation of Some Petrochemicals*

Abstract: Waste tire-derived oils commonly contain the considerable valuable aromatics such as benzene, toluene, ethylbenzene, toluene, xylenes and etc., but they also contain a significantly-high amount of sulfur compounds, which cause a low quality of pyrolytic oil. Ni is a cheap metal, which exhibits hydrogenation/ dehydrogenation and ring-opening like a noble metal, and widely used as promoter in desulfurization of fuels. In this work, Ni was expected to be a catalyst promoter of zeolites for reduction of sulfur content in oil and enhancement of petrochemical formation in oil. Therefore, the effect of 5 wt% nickel loading on different four type zeolites (HZSM-5, HMOR, HY, HBETA) on the sulfur removal and quality of waste-tire derived oil was studied. The results show that the incorporations of nickel on all zeolites significantly reduced sulfur contents in oil. However, the quality of waste tire-derived oil did not only depend on the nickel promoter, but also strongly depended on zeolite supports. The introduction of nickel on HZSM-5 zeolite, which possesses a smaller pore size than HBETA zeolites, provided a lighter oil with higher proportion of gasoline and kerosene than Ni/HBETA catalyst, and produced a higher amounts of valuable aromatic such as ethylbenzene, toluene, cumene, and mixed-xylenes than Ni/HBETA catalyst. Moreover, the addition of nickel on HMOR zeolite, which possesses a 1D zeolite channel structure, also provided a lighter oil with a high proportion of gasoline and kerosene than the Ni-loaded on HBETA (3D zeolite channel structure), and exhibited a better petrochemical production with a higher concentrations of ethylbenzene, toluene, cumene and styrene in maltene. On the other hand, Ni/HBETA provided the lower sulfur content in oil than Ni/HMOR catalyst, but the sulfur removal ability by nickel species on HMOR was higher than nickel species on HBETA zeolite. Furthermore, the introduction of nickel on HY zeolite provided the heavier oil with higher proportion of gas oil, LVGO and HVGO and lower proportion of petrochemical than Ni/HBETA zeolite whereas the sulfur removal of nickel species on the HBETA support with higher acid strength was better than on the HY support.

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8.1 Introduction

In recent decades, pyrolysis of waste tire is the useful process that can recovery valuable chemicals from waste tire and eliminate the environmental impacts from disposal of waste tire. Among the waste tire-derived products, waste tire-derived oils have received more attention since their properties are quite similar to those of commercial diesel and heating oil. Petrochemicals can be classified into olefins and aromatics, and utilized as a raw material in manufacturing of plastics, solvents, detergents, synthetic rubber, cosmetic products and pharmaceuticals. From past to present, petrochemicals such as ethylene, propylene, butadiene and BTEX are mainly produced via cracking of naphtha and ethane derived from crude oil and natural gas [1]. However, the production of petrochemicals via petroleum and natural gas is not sustainable since the petroleum and natural gas resources continuously decrease. As a result, several alternative processes for production of petrochemical by utilization of methane, coal, biomass and waste tire have attracted a great attention. Among these alternative processes, waste tire pyrolysis is considered as an effective process since it can eliminate waste tire problems by breaking up the tire molecules into valuable chemicals or fuel. Moreover, several studies reported that tire-derived oils contain a considerable concentration of valuable aromatics such as benzene, toluene, ethylbenzene, styrene, xylenes and etc. [2] and [3]. However, the major drawback is the relatively high concentrations of sulfur and nitrogen, which vary in the range of 0.5-3 wt%, depending on the pyrolysis system and catalysts [4]. They contain a great amount of sulfur since the sulfur is an additive in vulcanization process. Acidic zeolites such as HBETA, HMOR, HY, HZSM-5 have been proven to be able to reduce sulfur content in oil and enhance the quality of tire-derived oil. Dung *et al.* [5] stated that HMOR increased the concentration of mono-aromatics in oil, whereas the polycyclic aromatics, especially polar-aromatics significantly decreased. In addition, HMOR also increased the naphtha fraction in oil, whereas the heavy fraction drastically decreased. HBETA and HY zeolites increase naphtha and kerosene fractions, whereas the heavier fraction slightly decreased [6]. Thus, these studies indicate that different zeolites provide different product distribution because each zeolite has unique properties. In particular, HZSM-5 zeolite is commonly used as a catalyst in the petrochemical industry due to its pore size, strong acidity and strong resistance to deactivation. Boxiong *et al.* [7] found that the HZSM-5 enhanced the production of benzene, toluene and xylenes. The high acid strength of zeolite is favorable for production of



valuable aromatics, but the high acid density is favorable for sulfur removal from oil. The pore size of zeolite plays an important role in governing the molecular size of products. The large pore size of HBETA provided better cracking activity and petrochemical formation in oil than the HZSM-5 zeolite with medium pore size. The 3D pore channel structure of HBETA zeolite provided a higher cracking activity and petrochemical productivity than 1D pore channel structure of HMOR due to the longer contact time of molecules in the pore. A zeolite support with a sufficiently pore size ($\sim 7 \text{ \AA}$) with 3D complex channel structure was suggested for producing a high quality of oil with a high formation of petrochemicals [8].

Bi-functional catalysts have also been tested in waste tire pyrolysis, and provided the interesting results. Recently, Cu doped on HBETA, HY and HMOR zeolites significantly reduced the sulfur content in oil by 31.0- 37.4 %, respectively and also enhanced the petrochemical formation in oil [9]. Nickel is favorable to hydrogenation/dehydrogenation reactions, or promotes aromatization and cracking reactions [10]. For example, Ni over hierarchical ZSM-5 and Beta zeolites enhanced the production of gas and gasoline from hydroreforming of polyethylene-derived thermal cracking oil. In addition Ni/HZSM-5 catalyst can promote the transformation of olefins into aromatics and iso-paraffins [11]. Another common application of nickel-based catalyst is desulfurization. The sulphur removal efficiency increased with the increase of nickel loading on SBA-15 in adsorptive desulfurization of diesel [12]. In addition, Rodriguez-Castellón *et al.* [13] revealed that nickel supported on zirconium-doped mesoporous silica promoted the hydrogenation and ring-opening of tetralin.

In our earlier work, Ni promoted on HBeta zeolite at various percentages of loading (0 – 20 wt.%) was investigated for its effect on waste tire pyrolysis products, and it was found that a higher % loading of Ni enhanced olefins yield in gaseous product, but the yield of olefins dropped slightly at the highest % Ni loading (20%). The high amount of Ni loaded catalyst produces the higher concentration of light and heavy gas oil, but suppressed the kerosene content [14]. Later, the catalytic pyrolysis of waste tire was performed over Ni catalyst supported on HZSM-5 zeolite [15]. It was found that Ni doping significantly enhanced the yields of ethylbenzene, toluene, mixed-xylenes, and cumene in oil, and enhanced the overall petrochemical productivity. Since the properties of zeolite supports also contributed to the catalyst abilities as previously reported in our study [8], the introduction of Ni on different zeolite supports could also result in different impacts. In this work, nickel was therefore loaded at a fixed 5 wt.% on different



zeolites; that are, HBETA, HMOR, HY and HZSM-5, aiming to investigate the activity of Ni on reduction of the sulfur in tire-derived oil and on the enhancement of formation of valuable petrochemicals in oils when promoted on zeolites with different properties. The effect of nickel loading on each pair of zeolites [8] was discussed mainly on chemical species in waste tire-derived oil and sulfur removing ability.

8.2 Experimental

8.2.1 Catalyst preparation

The commercial zeolites selected in this research were purchased from TOSOH Corporation (Singapore); HBETA (931HOA, Si/Al = 14, H-form), HMOR (640HOA, Si/Al = 9, H-form), HY (360HUA, Si/Al=7.5, H-form) and HZSM-5 (840NHA, Si/Al =20, NH₄-form). Prior to activity testing and metal impregnation, HMOR, HY, and HZSM-5 were calcined in standing air at 500 °C for 3 h (Ramping rate of 10 °C/min). HBETA was calcined in standing air at 650 °C for 2 h (Ramping rate of 2 °C/min). The calcination conditions were made different due to the different forms of the purchased zeolites. For instance, the purchased BETA zeolite was in the NH₄-BETA form; therefore, it was calcined at 600 °C in order to completely convert NH₄⁺ to H⁺ form [5,9]. Ni-loaded zeolites were prepared using incipient wetness impregnation of (NiNO₃)₂·6H₂O until 5 wt% metal loading based on the mass of catalysts. The catalysts were then dried overnight at 105 °C, and calcined at same conditions. The catalyst powders were pelletized, crushed and sieved to 40-60 mesh of particle sizes. The catalysts were activated by reduction under hydrogen flow (30 mL/min) at 600 °C for 2 h (heating rate 10 °C/min).

8.2.2 Catalyst Characterization

The catalyst samples were characterized by different physicochemical characterization methods. X-Ray diffraction (CuK α radiation), carried out in a Rikagu SmartLab X-Ray Diffractometer, was used to identify the crystallinity of catalysts. XRD patterns were recorded in the 5-65 ° (2 θ) range using a scan speed of 10° (2 θ)/min. The surface area and pore volume of catalysts were measured using N₂ adsorption-desorption isotherms with Thermo Finnigan Sorptomatic 1990 instrument. The amount of coke deposition on the spent catalysts was measured by thermogravimetric/differential thermal analysis (TG/DTA), carrier out under flowing of nitrogen (10 mL/min) and oxygen (20 mL/min) on a Perkin Elmer/Pyris

Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA). The sample were heated up from room temperature to 900 °C with ramping rate of 10 °C/min. CHNS analyzer was used to determine the sulfur and nitrogen content on spent catalyst using LECO®Elemental Analyzer.

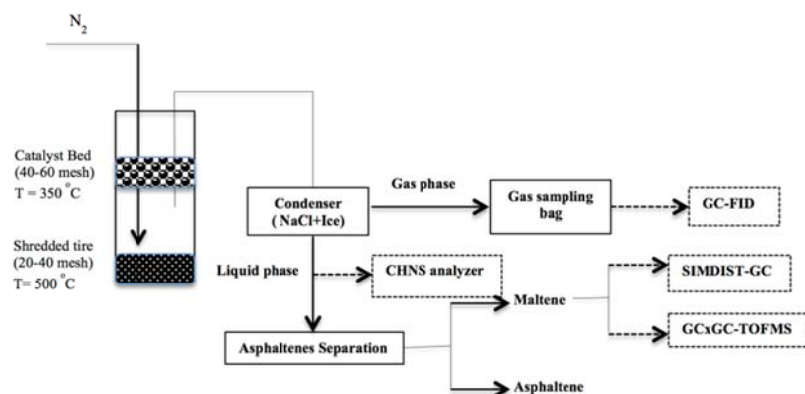


Fig. 1 Schematic of waste tire pyrolysis system for collection and analysis of products.

8.2.3 Waste tire pyrolysis

Only the thread of one waste tire (Bridgestone Turanza GR80) was used as a raw material in every batch in order to prevent the impacts from variation of the components in the feed. The analysis of the same model of tire tread was reported in our previous papers [5,16]. Nevertheless, the ultimate analysis of shredded waste tire samples was performed using a LECO® Elemental Analyzer. A 0.1 gram of the tire sample was put in the elemental analyzer, and next the temperature of furnace was raised from room temperature to 600 °C and held for 15 min in the first step, and then raised again to 1,350 °C in the analyzing step. The schematic pyrolysis system is displayed in **Fig.1**. Firstly, 30 g of shredded tire (20-40 mesh) was pyrolyzed in the lower zone of the reactor at 500 °C under atmospheric pressure. The pyrolysis products were carried by 30 ml/min of nitrogen flow to the catalytic bed filled with 7.5 g of catalyst and heated to 350 °C. After the temperatures of lower and upper zones reached to the desired one, the temperature of two zones was kept at desired temperature for 2 h. The resulting products were separated into gas and liquid fraction by condensers (ice-salt condensing system). Gas product was collected in Tedlar PVF bag.



8.2.4 Product Analysis

Liquid and solid products were weighed to determine the product yield. The gas yield was determined by mass balance. The gaseous products were analyzed by GC, Agilent Technologies 6890 equipped with HP-PLOT Q column (300 mm x 0.32 mmID and 20 μm film thickness) and FID detector. The liquid products were dissolved in n-pentane (mass ratio of n-pentane/oil =40:1) to precipitate asphaltene. Asphaltene was filtered by using a polyamide membrane (0.45 μm). The maltene solutions were then analyzed by Comprehensive Two-Dimension Gas Chromatography (Agilent Technologies 7890) with Time-of-Flight Mass Spectrometer (LECO, Pegasus® 4D TOF/MS equipped with the 1st GC column was a non-polar Rtx®-5Sil MS (30 m x 0.25mmID x0.25 μm) and the 2nd GC column was an Rxi®-17MS(1.790m x 0.1mmID x0.1 μm). The primary column was held up at 50 °C for 2 min, and then heated up to 310 °C with a ramping rate of 5 °C/min. After the final temperature was reached, it was held at 310 °C until the analysis was finished. The temperature of secondary column was held at 60 °C for 2 min, and then ramped up to 320 °C with the ramping rate of 5 °C/min. After reached, the final temperature of column was held at 320 °C until the analysis was finished. The simulated true boiling point curves were determined by using a Varian GC-3800 simulated distillation gas chromatography equipped with FID detector and a 15m x 0.25 mm x 0.25 μm WCOT fused silica capillary column. The petroleum fractions were cut based on their boiling point ranges according to the ASTM D2887; gasoline (<149 °C), kerosene (149-232 °C), gas oil (232-343 °C), light vacuum gas oil (343-371 °C) and heavy vacuum gas oil (>371 °C). Moreover, sulfur and nitrogen content in tire-derived oil and char were determine by LECO®Elemental Analyzer (TruSpec®CHNS). Furthermore, sulfur content in the gas products was determined from mass balance.

8.3 Results and discussion

8.3.1 Catalyst characterization

The XRD patterns of the HBETA, HMOR, HY, HZSM-5 zeolites and the supported Ni catalysts are displayed in **Fig. 2**. Both impregnated catalysts and parent zeolites clearly display the characteristic XRD patterns of BEA, FAU, MOR and MFI structure. Therefore, the introduction of nickel on zeolites seems not to destroy the zeolite structure, but slightly affects the zeolite crystallinity. The characteristic peaks of metallic nickel are present at $\sim 44.5^\circ$ and $\sim 51.8^\circ$.

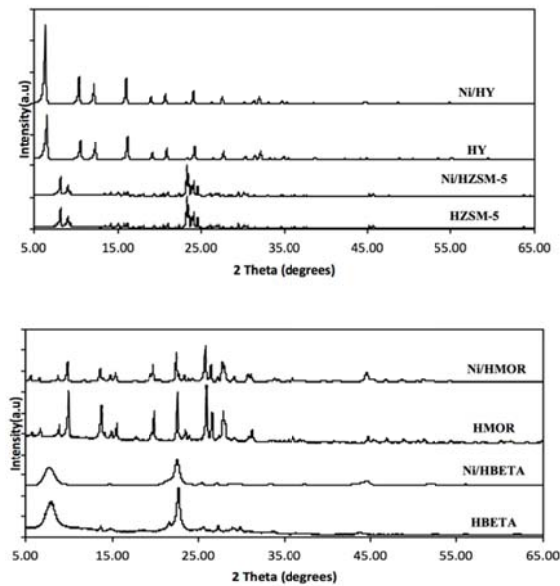


Fig. 2 XRD patterns of zeolites and impregnated catalysts.

Table 1 BET specific area and pore volume of catalysts.

Catalyst	Surface Area (m^2/g)	Micropore Volume (cm^3/g)
HBETA	559	0.280
HMOR	395	0.199
HY	546	0.277
HZSM-5	365	0.178
Ni/HBETA	466	0.215
Ni/HMOR	308	0.158
Ni/HY	537	0.264
Ni/HZSM-5	290	0.142

From Table 1, the decreases in BET surface area and micropore volume clearly indicate that Ni cluster might be located inside the zeolite pore, and partially block the zeolite channel [17]. In addition, some metallic nickels may undergo sintering during the reduction of nickel oxide and then move to external surface of catalyst [10].

8.3.2 Pyrolysis yields

Elemental analysis of waste tire samples revealed that the tire tread samples contained 81.1 ± 2.85 wt.% C, 6.81 ± 0.237 wt.% H, 2.07 ± 0.0279 wt.% S, and 3.71 ± 0.415 wt.% N. These tire samples were then used in pyrolysis experiments. As a result, the pyrolysis product distribution from using parent zeolites and impregnated catalysts are displayed in **Fig. 3**. It can be seen that when catalysts are used, the liquid and gas yields are suppressed while the coke formation over spent catalysts significantly increases. The reduction of liquid yield when catalysts are used in waste tire pyrolysis indicates that catalysts promote cracking activity of pyrolysis liquid. Nickel-modified catalysts are more effective than the parent zeolites since they give higher gas yields and lower liquid yields. Coke formations over spent the nickel modified catalysts is higher than that on parent zeolites since the incorporation of metallic nickel on zeolites increase surface activity and hydrogen transfer, which favors for coke formation.

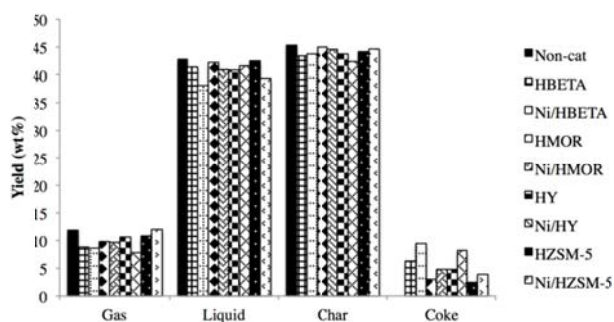


Fig. 3 Effect of nickel based catalysts on pyrolysis yields.

8.3.3 Effect of Ni Loading on Zeolites with Different Pore Sizes

Similarly classified as 3D channel structured possessing zeolites, HBETA has the pore size of 6.4×7.6 Å and HZSM-5 a smaller pore size of 5.3×5.6 Å. The effect of Ni loading was investigated on two supports with different pore sizes, HZSM-5 and HBETA zeolites. **Fig. 4a** and **4b** illustrate the concentration of petroleum fractions in maltenes and maltene compositions, respectively. The results indicate that the incorporation of nickel on HZSM-5 zeolite strongly enhances the gasoline and kerosene, whereas the gas oil, LVGO and HVGO reduce, indicating that the nickel species on HZSM-5 strongly promote cracking activity of HZSM-5 catalyst. Moreover, Ni/HZSM-5 strongly enhances the formation of mono-aromatic, whereas the formation of olefins, naphthenes, di-, poly-, and polar-

aromatics reduced. These results indicate that the addition of nickel on HZSM-5 promote the transformation of multi-ring aromatics to mono-aromatics and aromatization of naphthenes and olefins to mono-aromatics. Significant differences are observed on the petroleum fractions and maltene composition with Ni doped on HBETA zeolite. The results show that the gasoline fraction drastically reduces, whereas the kerosene, gas oil, LVGO fractions clearly increase. This result indicates that the incorporation of nickel on HBETA strongly promotes the formation of heavier fraction in maltene. A similar effect of the addition of nickel on the maltene composition is also observed on HBETA. The formations of naphthenes and mono-aromatics significantly decrease, whereas the formations of di-, poly-, and polar-aromatics are drastically increased. It is reasonable to conclude that Ni species on HBETA strongly promote the formation of heavier fractions, especially polycyclic aromatics via the secondary reactions (oligomerization, cyclization, aromatization, etc) of naphthenes and mono-aromatics.

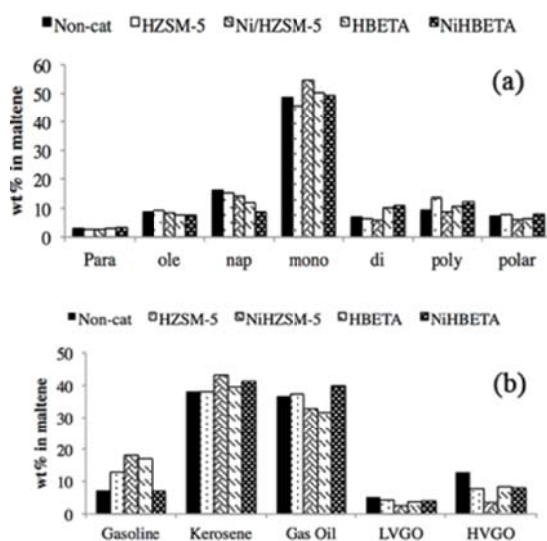


Fig. 4 (a) Concentration of each chemical group, and (b) Petroleum fractions in maltenes using Ni-loaded on HBETA and HZSM-5 zeolites.

The different catalytic behaviors of Ni species on HZSM-5 and HBETA zeolites associate with different characteristics of the supports. HBETA and HZSM-5 zeolites have 3D pore channel with close Si/Al ratios. Therefore, the major difference of two acidic supports is pore size, the pore size of HZSM-5 is $5.3 \text{ \AA} \times 5.6 \text{ \AA}$ and pore size of HBETA is $6.4 \text{ \AA} \times 7.6 \text{ \AA}$. Thus, HBETA zeolite has larger pore size

than HZSM-5 zeolite, so its pore size provides a higher probability of formation of larger hydrocarbons than the smaller pore size of HZSM-5. Generally, cracking is the main reaction in the catalytic pyrolysis of waste tire. However, the secondary reactions also occur simultaneously, depending on the catalyst properties. Hence, the addition of nickel on supports with a large pore size provides a higher probability of undergoing of hydrocarbons via secondary reactions resulting in the high production of multi-ring aromatics. Therefore, the formation of heavy fractions is favorable with the presence of Ni/HBETA catalyst. **Table 2** provides the information about the sulfur contents in oil. In all cases, the sulfur contents in oil significantly decrease by the addition of nickel species to the zeolites. The sulfur in tire samples of around 2.07 ± 0.0279 wt.% is distributed into products and catalysts as shown in **Fig. 5a**. It can be observed that Ni-doped catalysts result in a higher sulfur distribution on the spent catalysts than that obtained from the parent zeolites.

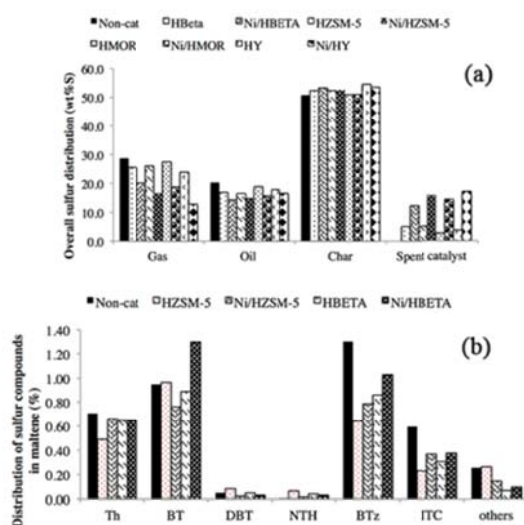


Fig.5 (a) Overall sulfur distribution on in waste tire pyrolysis products and spent catalysts, and (b) Distribution of sulfur compounds obtained from Ni/HBETA and Ni/HZSM-5.

**Table 2.** Sulfur content in oils obtained from Ni/HBETA and Ni/HZSM-5.

Catalyst	Non-catalytic	HBETA	HZSM-5*	Ni/HBETA	Ni/HZSM-5*
Sulfur content in oil (wt%)	0.96	0.83	0.78	0.75	0.68
Sulfur reduction (%)	Base	14.1	18.8	21.6	29.2

*As reported in [15]

These results indicate that sulfur compounds favorably adsorb on the nickel site. Generally, Ni has strong molecular orbital, which can attract sulfur atom from sulfur compounds. The sulfur compounds can donate the electron density to Ni, and further form a bond with Ni. Once favorably forming a bond with Ni, further desulfurization depends on the interaction of nickel with the support and available hydrogen in pyrolysis system. Desulfurization activity of Ni can be also prohibited by coke formation on the Ni sites of catalyst, which also affects to sulfur removal since the Ni site is less available for adsorption of sulfur compounds, causing the highly- competitive adsorption between hydrocarbons and sulfur compounds. The sites of nickel might be reduced when adsorbed hydrocarbons have undergone hydrogen transfer reaction, leading to coke formation. From the **Fig. 3**, it can be clearly seen that the coke formation on Ni/HBETA catalyst is roughly twice as much as that formed on the Ni/HZSM-5. Therefore, sulfur content in oil produced from Ni/HBETA is higher than that produced by Ni/HZSM-5 catalysts since the nickel sites are more highly covered by coke, resulting in the reduction of desulfurization activity.

Moreover, sulfur contents in oil might be affected by different pore size of zeolites as well. Previously, it was found that Ni/HZSM-5 reduced sulphur contents in tyre-derived oil by 29.2% [15]. It can be clearly seen that the addition of nickel on HBETA slightly results in the higher sulfur content than that obtained from Ni/HZSM-5 catalyst [15] (see also **Table 2**). The large pore size of HBETA zeolite allows a higher amount of sulfur-containing compounds to go inside the pore, and then some of sulfur-containing compounds can be desulfurized. Some molecules of sulfur-containing compounds such as thiophene can also be transformed to benzothiophene via undergoing hydrogen transfer reaction with available olefins, followed by cyclization and dehydrogenation [9]. Moreover, some free sulfur molecules, which are formed from cracking of tire, are very active, so they can react



with olefins and mono-aromatics to formed thiophenic compounds [5]. From **Fig. 5b**, it can be clearly seen that sulfur atoms are more distributed in the forms of benzothiophenes when using Ni/HBETA as a catalyst. This evidence confirms that the higher amount of benzothiophene is preferably formed in large pore size of zeolite, leading to the increment of sulfur content in the oil.

Table 3. Dominant di-and polyaromatics in maltene obtained from Ni/HBETA and Ni/HZSM-5.

Hydrocarbons	wt% in Maltene			
	HBETA	Ni/HBETA	HZSM-5	Ni/HZSM-5
2-Methyl biphenyl	0.00	0.63	0.46	0.00
4,4'-Dimethyl biphenyl	0.45	0.89	0.45	0.05
4-Isopropyl biphenyl	0.35	0.55	0.40	0.31
Naphthalene	0.36	0.06	0.38	0.28
1-methyl naphthalene	0.99	0.68	0.42	0.03
1,3-dimethyl naphthalene	1.24	0.92	0.71	0.15
1-ethyl naphthalene	1.14	1.93	0.93	0.96
7-isopropyl-1methylnaphthalene	0.51	0.86	0.10	0.15

Regarding the petrochemical contents in oil, the incorporation of nickel on HBETA zeolite significantly suppresses the formation of ethylbenzene, toluene, cumene, styrene and mixed-xylenes (see **Fig. 6**), whereas di- and polyaromatics such as 7-isopropyl-1-methylnaphthalene, 1-ethylnaphthalene and 2-methylbiphenyl significantly increase (see **Table 3**). This can be explained that these di-and polyaromatics can be formed by combination of valuable small aromatics. It is well known that the pore size of a zeolite governs the molecular size of products, so the molecular size of products cannot be larger than the pore size of a zeolite, unless they are formed at the external surface of a zeolite. Therefore, the addition of nickel on a large pore of HBETA provides a higher possibility of forming of multi-ring aromatics than Ni doped HZSM-5, resulting in the higher amount of di- and poly- and polar- aromatics in maltene.

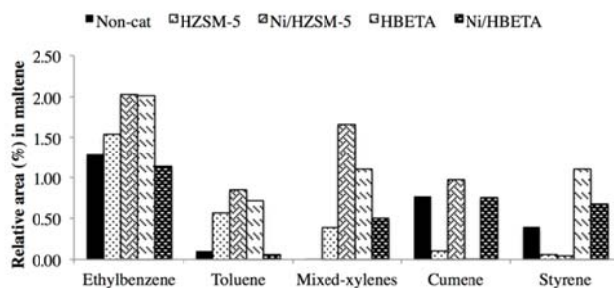


Fig. 6 Petrochemicals in maltenes obtained from Ni/HBETA and Ni/HZSM-5.

A different behavior is observed with the Ni/HZSM-5 catalyst. In this case, the formation of ethylbenzene, toluene, cumene and mixed-xylenes increase, whereas the concentrations of di-, and polyaromatics such as 2-methylbiphenyl, 4,4'-dimethylbiphenyl, naphthalene, 1,3-dimethylnaphthalene, and 1-methylnaphthalene decrease. Therefore, the introduction of Ni on HZSM-5 might promote the transformation of these di- and polyaromatics to valuable aromatics such as ethylbenzene, toluene, mixed-xylene and etc. If the carbon-carbon scission takes place at the position between two benzene rings of 2-methylbiphenyl, the obtained products are benzene and toluene as displayed in **Scheme 1** in Fig.7. However, the concentration of benzene has been not found to increase, so it might possibly convert to other hydrocarbon because the radical benzene ring is very active to react with other hydrocarbons.

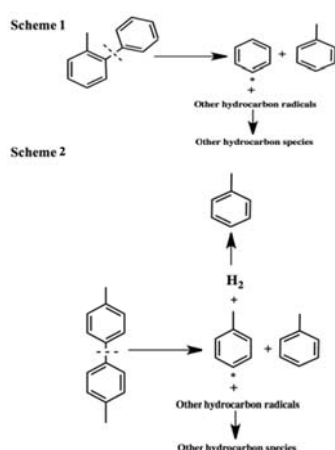


Fig. 7 Possible reaction pathways for transformation of 2-methylbiphenyl and 4,4'-Dimethylbiphenyl to valuable aromatics by Ni/HZSM-5.

In addition, two molecules of toluene can be formed via these steps as shown in **Scheme 2** in **Fig.7**. First, the carbon-carbon scission take places at the position between the two benzene rings of 4,4'-dimethylbiphenyl, resulting in toluene and a radical of benzene derivative of toluene. If the toluene radical reacts with hydrogen, toluene can be formed. However, this radical of toluene is very active, it can react with other hydrocarbons to form other hydrocarbon species as well. Furthermore, di-aromatics such as naphthalene, 1,3-dimethylnaphthalene, and 1-methylnaphthalene can be also transformed to valuable aromatics via two steps. One rings of naphthalene, 1,3-dimethylnaphthalene and 1-methylnaphthalene are firstly hydrogenated at a nickel site to form tetralinic species [18] and [19]. Second, the naphthenic ring of tetralinic species are cracked to formed valuable petrochemicals as displayed in **Fig.8** [18-20].

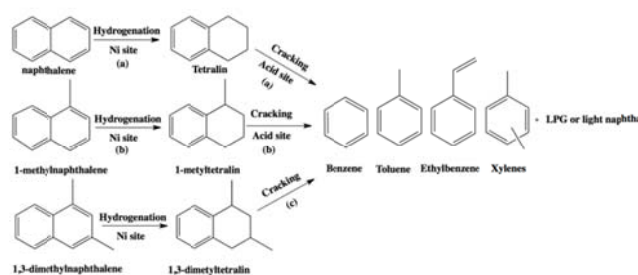


Fig. 8 Possible reaction pathways of naphthalene, 1-methylnaphthalene and 1,3-dimethylnaphthalene by Ni/HZSM-5 adapted from Kim et al., [18] (a), Park et al., [19] (b), and Bredael and Vinh, [20] (c).

8.3.4 Effect of Nickel Loading on Zeolites with Different Channel Structures

With an almost equal pore size, HBETA with 3D pore channel structure and HMOR with 1D pore channel structure were used as the supports for investigating the effect of Ni loading on different pore channel structures. The oil produced by Ni/HMOR is lighter than that produced by Ni/HBETA since the composition of oil contains a higher amount of gasoline and kerosene and a lower amount of gas oil, LVGO and HVGO (see **Fig. 9a**). In addition, the introduction of nickel on HMOR strongly enhances the formation of mono-aromatics and olefins, whereas the formation of di-, poly-, polar-aromatics and naphthenes reduces (see **Fig. 9b**). These results clearly indicate that nickel species on HMOR zeolite promote

the formation of mono-aromatics and olefins together with suppression of di-, poly-, and polar-aromatics and aromatization of naphthenes. In the opposite, the Ni/HBETA catalyst enhances the formation of heavy components, with a significant increment of di-, poly- and polar-aromatics. Ni doping on HMOR and HBETA zeolites promotes aromatization activity of catalysts; Ni doped on HMOR favors the aromatization of naphthenes, forming mono-aromatics, whereas Ni doped on HBETA favor the aromatization of naphthenes and olefins, forming multi-ring aromatics. This is probably a result of the different pore channel structures of zeolites. HMOR zeolite possesses a 1D channel structure, which allows a hydrocarbon molecule can further react with other hydrocarbons at a shorter time than the 3D channel structure of HBETA zeolite. In a 3D channel structure, intermediate hydrocarbons formed from previously-cracked molecules diffuse along the zeolite channel, and then might be combined with other hydrocarbons at nickel sites at a longer contact time, leading to the high formation of multi-ring aromatics. Therefore, the long residence time in a zeolite channel provides a higher possibility of multi-ring aromatics formation.

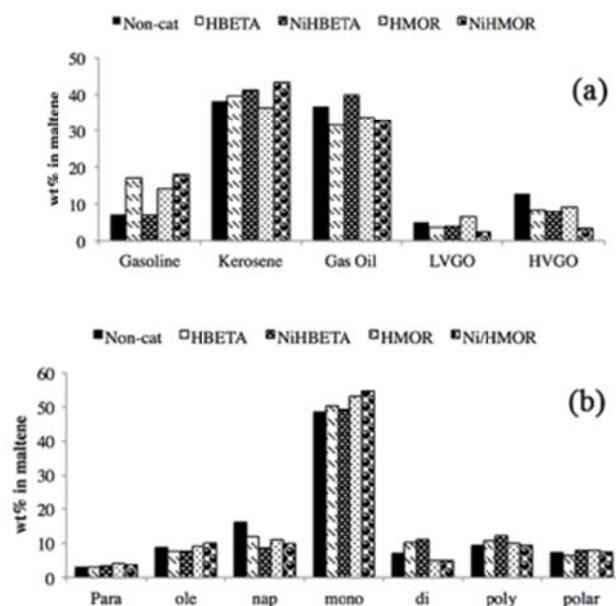


Fig. 9 (a) Petroleum fractions, and (b) Concentration of each chemical group in maltenes using Ni/HBETA and Ni/HMOR catalysts.

**Table 4** Sulfur content in oil obtained from Ni/HBETA and Ni/HMOR catalysts.

Catalyst	Non-catalytic	HBETA	HMOR	Ni/HBETA	Ni/HMOR
Sulfur content in oil (wt%)	0.96	0.83	0.9	0.75	0.78
Sulfur reduction (%)	Base	14.1	5.8	21.6	19.1
Sulfur reduction by Ni (%)	-	Base	Base	9.64	13.3

Table 4 illustrates the sulfur content in oils obtained from Ni/HBETA, Ni/HMOR catalysts and parent zeolites. HBETA zeolite with a 3D channel structure provides a lower amount of sulfur content in oil than that produced by HMOR zeolite since the complex channel structure of HBETA allows the sulfur compounds to stay inside the zeolite channel for a longer residence time, resulting in the higher possibility of desulfurization of sulfur compounds. In addition, the introduction of Ni on both zeolites clearly reduced the sulfur content in oil. The sulfur content in oil obtained from Ni/HBETA is slightly lower than that obtained from Ni/HMOR catalysts. This clearly indicates that the nickel located on 3D zeolite channel provides better desulfurization activity since the sulfur compounds can stay longer in zeolite channel, and then are desulfurized at nickel site more effectively than 1D zeolite channel. Regarding the sulfur reduction by Ni species, the addition of Ni on HMOR zeolite give a better sulfur reduction than that obtained from the Ni/HBETA catalyst. This can be explained that the coke formation on the spent Ni/HBETA is higher than on Ni/HMOR, resulting in the reduction of available Ni sites, which directly affects the desulfurization activity of catalysts since the desulfurization of sulfur compounds mainly take places on the Ni site. **Fig. 10a** displays that benzothiophene (BT) significantly reduces when Ni is doped on HMOR, but sharply increases for Ni/HBETA zeolite. This clearly indicates that the incorporation of Ni on 3D zeolite channel does not only promote sulfur removal from sulfur – containing compounds, but also the interaction of sulfur compounds with other hydrocarbons. The longer residence time of hydrocarbons or sulfur-containing compounds in the channel can provide a higher interaction of hydrocarbons and free sulfur atom, which are directly evolved from cracking of tire molecules.

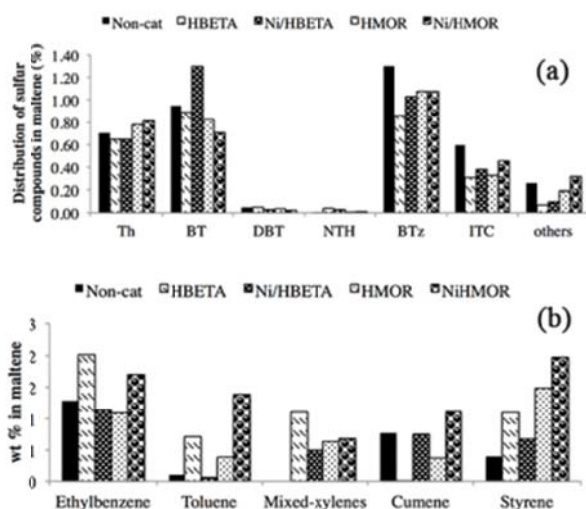


Fig. 10 (a) Distribution of sulfur compounds, and (b) Petrochemicals in maltenes using Ni/HBETA and Ni/HMOR catalysts.

Regarding the petrochemical species in maltene, nickel doping on HBETA zeolite significantly decreases the formation of ethylbenzene, toluene, styrene and mixed-xylenes (see **Fig. 10b**). On the other hand, it was found that the concentrations of 2-methyl biphenyl and fluorene in oil clearly increase with using Ni/HBETA catalyst (see **Table 5**). Therefore, the Ni loading in 3D zeolite channel might promote the interaction of any valuable aromatics as mentioned above to multi-ring aromatics such as 2-methylbiphenyl, fluorene and etc.

Table 5. Dominant polyaromatics species in maltenes obtained from Ni/HBETA and Ni/HMOR catalysts

Hydrocarbons	wt% in Maltene			
	HBETA	Ni/HBETA	HMOR	Ni/HMOR
2-methylbiphenyl	1.18	1.49	1.38	1.24
2-ethylbiphenyl	1.32	1.12	1.15	0.65
Fluorene	0.14	0.26	0.12	0.10

On the other hand, using Ni/HMOR, the formation of ethylbenzene, toluene, cumene and styrene significantly increases, whereas the concentration of polyaromatics in maltene decreases. Simultaneously, it is also found that the

concentration of 2-ethylbiphenyl and 4-methylbiphenyl slightly decreases (see **Table 5**), and these two polyaromatics can be transformed to ethylbenzene and toluene as illustrated in **Fig. 11**. Therefore, the introduction of nickel on HMOR zeolite might promote cleavage of biphenyl compounds. Ethylbenzene and benzene can be directly formed via carbon-carbon scission at the position between two benzene rings of 2-ethylbiphenyl. However, it was found that the concentration of benzene in maltene is extremely lower than that of ethylbenzene, so the benzene radical might react with other hydrocarbon radicals to form other hydrocarbon species as displayed in **Scheme 1**. Toluene and benzene can be directly formed via carbon-carbon scission at the position between two benzene rings of 4-methylbiphenyl as displayed in **Scheme 2**, but benzene might also be converted to other hydrocarbons because benzene with radical is very active to react with other hydrocarbons molecules (see **Fig. 10b**).

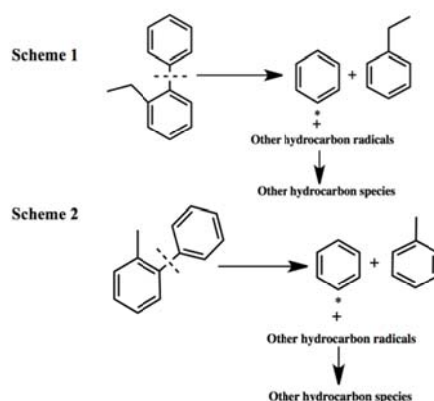


Fig. 11 Possible reaction pathways for transformation of 2-ethylbiphenyl, 4-methylbiphenyl to valuable aromatics promoted by Ni/HMOR.

In summary, the effect of zeolite channel structure is one of important factors, which should be considered in selecting a catalyst for enhancement of oil quality and petrochemical production from pyrolysis of waste tire. The introduction of nickel on a zeolite with 1D channel structure is better than on a zeolite with a 3D channel structure in terms of petrochemical formation and quality of oil. Therefore, it can be suggested that for the enhancement of oil quality and petrochemical production by using Ni is not recommended as a promoter, a zeolite that has a complex channel structure since the combination of complex 3D zeolite channel and Ni species do not only promote cracking activity of catalyst, but



also promote the secondary reactions (oligomerization, cyclization, aromatization and etc.), leading to the high formation of heavy hydrocarbons. Moreover, Ni catalysts normally promote the high formation of coke on the nickel sites, so the combination of nickel with 3D channel structure promoted the higher coke formation than the nickel supported on a zeolite with 1D channel structure since the hydrocarbons, which can stay inside in the 3D channel with a long residence time, easily undergo aromatization and combination reactions, forming coke on the catalyst. The high formation of coke on catalyst strongly decreases the catalytic activity, leading the rapid deactivation of catalyst.

8.3.5 Effect of Nickel Loading on Zeolites with Different Acid Densities

The effect of Ni loading was investigated on two zeolites with different acid densities. With a similar pore size, HBETA ($6.4 \times 7.6 \text{ \AA}$) with the Si/Al ratio of 14 was used in comparison with HY ($7.4 \text{ \AA}$) with the Si/Al ratio of 7.5. Similarly, the introduction of nickel on HBETA and HY zeolites favorably produces the heavier oils with a high proportion of di-, poly-, and polar-aromatics as compared to the parent zeolites. However, the oil produced from Ni/HY catalyst slightly is heavier than the one produced from Ni/HBETA catalyst. Moreover, it is clearly seen that the amounts of di-, poly- and polar-aromatics in the oil obtained from Ni/HY catalyst are higher than those produced by Ni/HBETA catalyst. This can be suggested that nickel species on these two acidic zeolites might promote the combination of lighter hydrocarbons (naphthene, olefins, mono-aromatics) to form multi-ring aromatics. The increment of heavy hydrocarbons might associate with the acidity of catalyst and coke formation on the catalyst. Generally, nickel promotes the hydrogen transfer reactions, leading to the formation of hydrocarbons with various C/H ratios, which can act as a coke precursor. Moreover, the introduction of nickel on a zeolite with a higher acid density (lower Si/Al ratio), for this case, can drive a higher formation of heavy hydrocarbon, especially multi-ring aromatics than the parent zeolite since the high acid density of zeolite promotes cyclization and aromatization activity of catalyst, resulting in reduction of olefins and naphthenes in the maltene (see **Fig. 12a**). Furthermore, the high coke formation on the spent catalysts is a clear indicator that the introduction of nickel with HBETA and HY zeolites provides a higher cracking activity than the parent zeolites. However, the higher cracking activity obtained with nickel promoter does not result in the formation of lighter hydrocarbons, but the higher amount of heavier hydrocarbons



was formed. Therefore, the high catalytic activity usually associates with coke formation on the catalyst. The high coke formation over nickel-based catalysts might reduce the active sites, which is favorable for cracking of hydrocarbons. Therefore, it can be concluded that the introduction of nickel on HY zeolite with a higher acid density promotes the higher formation of di-, poly-, and polar-aromatics than those obtained from the Ni/HBETA catalyst, resulting in the higher proportions of gas oil, LVGO and HVGO (see Fig. 12b).

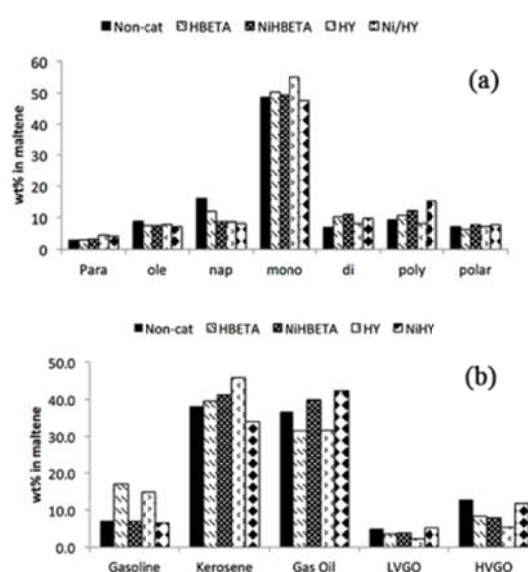


Fig. 12 (a) Concentration of each chemical group, and (b) Petroleum fractions in maltene using Ni/HBETA and Ni/HY catalysts.

Table 6 Sulfur content in oils obtained from Ni/HBETA and Ni/HY catalysts.

Catalyst	Non-catalytic	HBETA	HY	Ni/HBETA	Ni/HY
Sulfur content in oil (wt%)	0.96	0.83	0.88	0.75	0.8
Sulfur reduction (%)	Base	14.1	8.4	21.6	16.5

Furthermore, the introduction of nickel on HBETA and HY zeolites causes a higher reduction of sulfur content in oil than those obtained from the

parent zeolites (see Table 6). Apparently, the Ni/HBETA catalyst produces the oil with a lower sulfur contents than the Ni/HY catalyst.

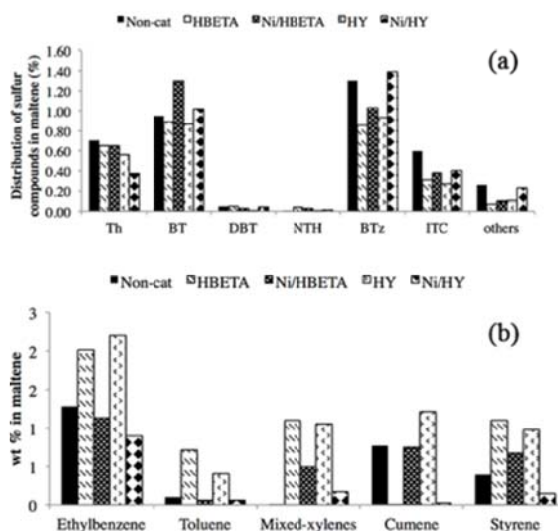


Fig. 13 (a) Distribution of sulfur-containing compounds, and (b) Petrochemicals in maltenes obtained from Ni/HBETA and Ni/HY catalysts.

These results indicate that the introduction of nickel on a zeolite with higher acid strength (higher Si/Al ratio) slightly results in a lower sulfur content in oil since the competition adsorption between other hydrocarbons and sulfur compounds occurs on nickel sites. Moreover, the high content of total aromatics are produced from Ni/HY than from Ni/HBETA. Therefore, the higher amount of aromatics might be adsorbed on the nickel sites of HY zeolite, resulting in the reduction of desulfurization activity of nickel species on HY zeolite. Moreover, the aromatic adsorptions have less influence on the desulfurization activity of catalysts with higher acidity [21]. **Fig. 13a** displays that thiophenes decrease with using Ni/HY as a catalyst, but not Ni/HBETA. These results indicate that high acid density of HY zeolite favorably breaks the C-S bond of thiophene. Moreover, the other sulfur species slightly increase with the presence of nickel on HBETA and HY zeolite. It can be explained that the introduction of nickel on these two zeolites might reduce the active sites of HBETA and HY zeolites, which favorably breaks C-S and C-N bonds of sulfur-containing compounds. Generally, the first step of the sulfur removal from of sulfur-containing compounds is adsorption of sulfur atom on nickel sites. The Ni/HBETA and Ni/HY catalysts generate a high amount of coke on the catalyst,



especially on the nickel sites, so the available nickel sites, which is favorable for removal of sulfur-containing compounds, are reduced when the coke formation and competitive adsorption of aromatics hydrocarbons take place on the nickel sites.

Regarding the petrochemical species in maltenes, nickel species on HBETA and HY zeolites significantly decrease the formation of ethylbenzene, toluene, styrene and mixed-xylenes (see Fig. 19). On the other hand, it is also found that the concentrations of 2-methylbiphenyl, 2-ethylbiphenyl and 4-isopropylbiphenyl significantly increase with the addition of nickel on the HY zeolite, and the concentrations of 7-Isopropyl-1-methylnaphthalene, 2-methylbiphenyl and 2-ethylbiphenyl also increase with using the Ni/HBETA catalyst (see Table 8).

Table 8 Dominant di- and polyaromatics in maltenes obtained from Ni/HBETA and Ni/HY catalysts.

Hydrocarbons	wt % in Maltene			
	HBETA	Ni/HBETA	HY	Ni/HY
2-methyl biphenyl	1.18	1.49	1.13	1.92
4-Isopropyl biphenyl	0.35	0.55	0.20	0.49
2-ethylbiphenyl	1.32	1.12	1.05	1.56
7-isopropyl-1-methylnaphthalene	0.51	0.86	0.34	0.35

This can be explained that some of petrochemicals and other mono-aromatics, naphthenes and olefins might be converted to these polyaromatics. The amounts of these polyaromatics depend on the acid density and acid strength of the two zeolites since the two supports have quite similar pore size and 3D pore channel structure. Therefore, it can be concluded that the introduction of nickel on a zeolite with high acid density such as HY, promotes the higher formation of polyaromatics such as methylbiphenyl, ethylbiphenyl, isopropylbiphenyl and etc. The introduction of nickel on HBETA zeolite, which exhibits a higher acid strength promote the formation of the polyaromatics as well, but the high acid density is more effective for enhancement of multi-ring aromatic formation.

8.4 Conclusions

The effect of nickel promoter loaded on different zeolites; that are HBETA, HZSM-5, HMOR, and HY, were studied. The result showed that all Ni doped catalysts enhanced the aromatic formation and sulfur removal from oil. However, the



catalytic behaviors of nickel promotion strongly depended on zeolite properties. The pore size of zeolite supports was found to govern the size of hydrocarbons products and sulfur removing ability of Ni catalysts. The incorporation of Ni on a HZSM-5 with a smaller pore size produced the lighter oil with higher proportion of gasoline, kerosene and valuable petrochemicals than the Ni/HBETA. Moreover, Ni/HZSM-5 provide the oil with a lower sulfur content than the Ni/HBETA due to lower coke formation and a lower possibility of forming of large hydrocarbons and sulfur-containing compounds. The channel structure of zeolite supports was found to govern the hydrocarbon products and sulfur removing ability of Ni catalyst due to the effect of residence time of hydrocarbons in the pore. The introduction of Ni on HMOR zeolite with 1D channel structure produced the slightly higher sulfur oil with a higher proportion of gasoline, kerosene and valuable petrochemicals than Ni loaded on HBETA zeolite (3D channel structure) due to lower coke formation and a shorter contact time of hydrocarbons. The acid density of zeolite supports was found to promote the formation of heavy aromatics and control the sulfur removing ability of Ni catalysts. The incorporation of nickel on HY zeolite with a higher acid density (lower Si/Al ratio) produced the higher sulfur oil the with a higher proportion of gas oil, LVGO and HVGO, but a lower amount of valuable petrochemicals due to higher competition adsorption of hydrocarbons and sulfur-containing compounds on Ni sites. In conclusion, for the enhancement of oil quality and petrochemical production, Ni is not recommended as a promoter on a zeolite that has a complex channel structure and a large pore size since the introduction of Ni on this kind of supports promoted the formation of heavy hydrocarbons and reduced the sulfur removing ability of Ni catalyst. Therefore, for the production of the waste tire-derived oil with high petrochemicals and low sulfur contents by using Ni promoter, the zeolite supports must have a suitable pore size of around 5.5-7 Å and 1D channel structure that allows hydrocarbons and sulfur compounds can stay inside at enough contact time to form valuable petrochemical and to remove sulfur compounds.

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Chapter 9

NiMo/HBETA as Catalysts with Dual Functions Beneficial to Waste Tire Pyrolysis*

Abstract: The world is running out of petroleum with the increasing demand in the fuel consumption. Oil from waste tires is one of interesting fuels to be developed, and pyrolysis is one of the suitable processes to utilize these waste tires. In the pyrolytic oil from waste tires, sulfur compounds are largely present in the form of polar-aromatics such as thiophene, benzothiophene, and dibenzothiophene, which can cause poisoning of the active sites on the catalyst. Moreover, if sulfur-containing oils are used as fuels, SO_2 that is a pollutant can be produced during combustion. In our previous work, Ni/HBETA was proven to be a potential waste tire pyrolysis catalyst; thus, since NiMo is one of good desulfurization catalyst, it was also expected to have both pyrolysis and sulfur removal activities beneficial to waste tire pyrolysis. The purposes of this work were to study the cracking ability as well as the desulfurization ability of NiMo loaded on HBETA catalyst for tire pyrolysis, and to study the change of sulfur compounds when the compositions of the bimetallic catalysts are varied. The results showed that 5%Ni with 20%Mo catalyst had both good cracking and desulfurization abilities. The pyrolytic oil obtained from the catalyst had lower polar-aromatic and sulfur contents than those from the other catalysts. It was mainly composed of full-range naphtha which had large amounts of saturated hydrocarbons and mono-aromatics. Moreover, the sulfur compounds in the pyrolytic oils were analyzed by GC-MS (TOF). It was found that sulfur compounds were mainly in the kerosene range (C_{10} – C_{13}) such as benzo[b]thiophene, 2,7-dimethyl, benzo[b]thiophene, 2-ethyl-7-methyl- and dibenzothiophene.

9.1 Introduction

The increases in petroleum demand and price have driven the world to seek for alternative fuels. Waste tires discarded in a gigantic quantity are an adequate supply for producing oil substitute through pyrolysis process. Waste tire pyrolysis is the thermal degradation of waste tire in the absence of the oxygen. Three products; pyrolytic gas, oil, and char (Chang, 1996) can be obtained. Pyrolytic oil can be used



directly as a chemical feedstock or fuel oil substitute. In the pyrolytic oil from waste tires, sulfur compounds are largely present in the form of polar-aromatics such as thiophene, benzothiophene, and dibenzothiophene (Pakdel et al., 2001), which can cause poisoning of the active sites of a catalyst. Moreover, if fuels contain sulfur, SO_2 that is a pollutant is produced during combustion. With this reason, many countries limit the amount of sulfur content in transportation fuels. Therefore, not only are the cracking of heavy hydrocarbons to light hydrocarbons as well as hydrogenation and ring-opening needed, but hydrodesulfurization is also important in the pyrolysis process. There were many researchers that used catalysts to improve the quality and quantity of the pyrolytic products. Bifunctional catalysts (metals supported on zeolites) become interesting to order to improve the efficiency of catalytic pyrolysis. Noble metals supported on acidic zeolite were used to optimize the high value products because noble metals can promote hydrogenation and ring opening (Du et al., 2005). For examples, Pt/HBETA showed good ability for polar-aromatic reduction, leading to a decreasing amount of sulfur in the pyrolytic oil (Düng et al., 2009). With the high prices of the noble metals, some of non-noble metals were used instead of noble metals. Saeae et al. (2012) found that Ni loaded on HBETA zeolite increased the cracking ability of HBETA in tire pyrolysis because it increased the gas yield with a consequent decrease in the oil yield. They also found that the sulfur content in oil was further reduced by using Ni/HBETA catalyst. Ni/HBETA also increased the quality of the pyrolytic oil by decreasing long residue and then increasing the full range naphtha. They found that some of non-noble metals can be used to substitute noble metals when used in a higher amount. Moreover, bimetallic catalysts, such as NiMo, NiW, CoMo, and CoW (Mo and W as second metals doped to Ni and Co) supported on Al_2O_3 are normally used in hydrodesulfurization process (Torres-Mancera et al., 2005). Therefore, in this work, Mo was chosen as a second metal promoter on Ni/HBETA since the pyrolysis of waste tire requires both cracking and desulfurization functions of the catalyst. The purposes of this work were, therefore, to study the cracking ability as well as the desulfurization ability of modified Ni/HBETA catalysts (bimetallic NiMo) in tire pyrolysis, and to study the change of sulfur compounds when the compositions of the bimetallic catalysts were varied. Ni was fixed at 5 wt%, whereas the loading of Mo was varied to 10 and 20 wt%. Types and amounts of sulfur compounds in the oil were also studied.



9.2 Experimental

9.2.1 Catalyst Preparation

The zeolite, which is HBETA ($\text{Si}/\text{Al} = 13.5$) obtained from Tosoh Company in Singapore, was calcined at $600\text{ }^{\circ}\text{C}$ for 5 h with a heating rate of $2\text{ }^{\circ}\text{C}/\text{min}$. To prepare the bimetallic catalysts, NiMo/HBETA, appropriate amounts of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot \text{H}_2\text{O}$) were loaded on the HBETA zeolite by incipient wetness impregnation technique. The composition of bimetallic catalysts was varied as 10 and 20 wt% of Mo with the fixed amount of Ni at 5 wt%. After that, the samples were dried at $110\text{ }^{\circ}\text{C}$ for 3 h in an oven, and calcined at $500\text{ }^{\circ}\text{C}$ for 3 h with the heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$ and further reduced at $800\text{ }^{\circ}\text{C}$ for 1 h to obtain the catalysts in the bimetallic form.

9.2.2 Catalyst Characterization

X-ray Diffraction (XRD) was used to verify the metallic form of catalysts. X-ray diffraction (XRD) patterns were taken by using a Bruker X-ray diffractometer system (D8 Advance) equipped with a 2.2 kW Cu anode long fine focus ceramic X-ray tube for generating a $\text{CuK}\alpha$ radiation ($1.5405\text{ \AA}$). The detector scans the peak position from the sample as a function of 2θ by starting at the 10° to 60° (2θ) range and a scan speed of 0.02° (2θ)/0.6 second. The XRD patterns were matched to the standards to identify crystalline phases. Temperature-programmed reduction (TPR) was used to identify the reducibility of the impregnated catalysts and the metal-metal interaction. The TPR experiments were conducted from $30\text{ }^{\circ}\text{C}$ to $850\text{ }^{\circ}\text{C}$.

9.2.3 Pyrolysis Experiment

There are 2 zones of pyrolysis reactor; that are, catalytic zone (the upper zone) and pyrolytic zone (the lower zone). The pyrolysis experiments were conducted according to the procedure in D ng et al. (2009). First, 30 g of the waste tire with sizes in the range of 8-18 mesh was loaded into the lower zone with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ from the room temperature to final temperature. The final temperature of this zone was controlled at $500\text{ }^{\circ}\text{C}$ and then kept for 90 minutes at the atmospheric pressure. In the catalytic zone of the reactor, 7.5 g of pellet catalyst was loaded and controlled at $350\text{ }^{\circ}\text{C}$. N_2 flow rate was controlled at 30



ml/min for purging the oxygen out of the system prior to pyrolysis and subsequently for carrying the pyrolysis product through two condensers and then to a gas sampling bag. These condensers were placed into the ice bath in order to collect the condensable products (pyrolytic oils). The gas sampling bag collected the non-condensable products (pyrolytic gases). Non-decomposable components of the tires were collected as pyrolytic chars.

9.2.4 Product Analysis

Pyrolytic gases were analyzed by using a Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm ID and 20 μ m film thicknesses. A detector was FID type using He as the carrier gas. Pyrolytic oil was separated into asphaltene (n-pentane insoluble) and maltene (n-pentane soluble), and then the maltene solution was fractionated using specific solvents (Šebor et al., 1999) into 5 fractions, which are saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics and polar-aromatics in a liquid chromatography column. The liquid fraction was analyzed using a Varian CP-3800 stimulated distillation gas chromatograph (SIMDIST GC) equipped with an FID, according to the ASTM D2887 method. Each fraction was classified according to its boiling point range, which are full range naphtha (< 200 °C), kerosene (200-250 °C), light gas oil (250-300 °C), heavy gas oil (300-370 °C) and long residue (> 370°C). The sulfur compounds in the pyrolytic oil were determined using a Gas Chromatography equipped with a mass spectrometry of Time of Flight type (GC-TOF).

9.3 Results and Discussion

9.3.1 Characterization

Figure 1 illustrates XRD and TPR obtained from the modified Ni/HBETA catalysts. The XRD confirms that the bimetallic NiMo clusters (+ and 0) are formed on the zeolite. The TPR profile of 5Ni20Mo/HBETA catalysts show a strong Ni-Mo interaction peak whereas that of the 10% Mo doping shows two strong interaction peaks. The strong interaction is believed to be responsible for the cracking and desulfurization abilities of 5Ni20Mo/HBETA catalyst.

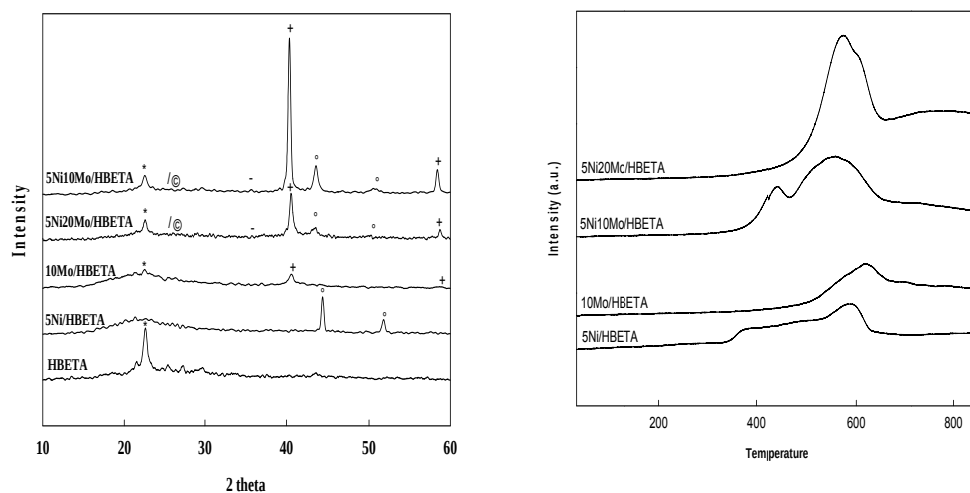
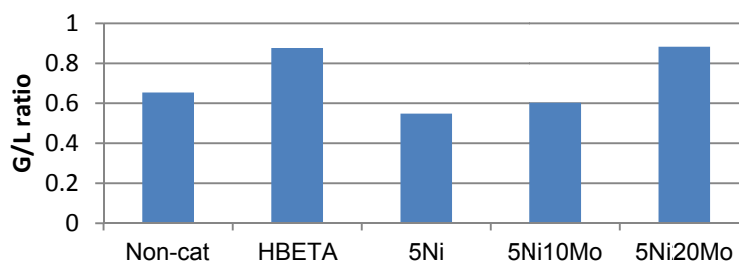


Figure 1: XRD (left) and TPR (right) obtained from modified Ni/HBETA catalysts in comparison with 10Mo/HBETA.

9.3.2 Cracking ability

The results exhibit the qualities and quantities of the pyrolytic products from the Mo-doped Ni/HBETA catalysts. The product distribution can be shown by the ratio of gas to liquid in Figure 2. The solid product remains constant at about 40 wt%.



- * 5Ni = 5 wt% Ni on HBETA
- ** 5Ni10Mo = 5 wt% Ni- and 10 wt% Mo- loaded HBETA
- *** 5Ni20Mo = 5 wt% Ni- and 20 wt% Mo- loaded HBETA

Figure 2: G/L ratio obtained from modified Ni/HBETA catalysts.



Figure 2 shows the ratio between gas and liquid obtained from the modified Ni/HBETA catalysts as compared to that of pure HBETA zeolite and the non-catalytic case or non-cat (thermal pyrolysis). The higher G/L ratio gave the higher the cracking ability because the heavy molecules can be cracked into lighter molecules over the acid sites of the catalysts. For the 5Ni/HBETA catalyst, the reduction of the G/L ratio can be resulted from the interaction between the metal and the support. However, with using the bimetallic catalysts (NiMo), the G/L ratio increases with the increase of the amount of the Mo loading, which indicates that, the modified Ni/HBETA catalysts (5Ni10Mo/HBETA and 5Ni20Mo/HBETA) can increase the cracking ability from the monometallic 5Ni/HBETA catalyst. 5Ni20Mo/HBETA has the highest cracking ability among the others because it had the highest G/L ratio (0.88). Nevertheless, although Mo can enhance the cracking ability of the Ni/HBETA catalyst, the bimetallic catalysts still have the same cracking ability as the parent HBETA zeolite. Therefore, the doping of Mo to Ni/HBETA catalyst helps maintain the cracking activity of the parent zeolite.

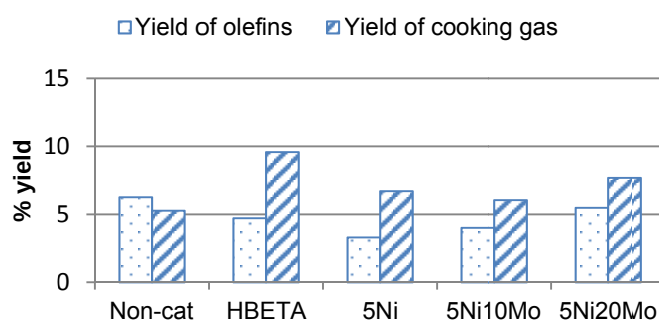


Figure 3: Yield of olefins and cooking gas obtained from pyrolysis with modified Ni/HBETA catalysts.

Non-condensable gases are composed of gases in the range of C_1 - C_5 . Some of these gases are valuable petrochemical products such as olefins (ethylene and propylene), and cooking gas (propane mixed with mixed C_4). Figure 3 show the yield of these petrochemical gases obtained from modified Ni/HBETA catalysts. The results indicate that the non-catalytic case gives 6.25 and 5.27 wt% yield of olefins and cooking gas, respectively. With using the catalysts, the yields of olefins decrease in accordance with the increase in the yield of cooking gases. 5Ni/BETA gives the lowest yield of olefins; however, when the modified Ni/HBETA catalysts are used, the yields of olefins increase significantly. The yield of olefins increases with the



increasing contents of Mo. The pure HBETA gives the highest yield of cooking gas (9.6%) among the other catalysts; including the non-catalytic case. 5Ni/HBETA gives about 6.7 wt% yield of cooking gas. 5Ni10Mo/HBETA does not increase the yield of cooking gas whereas using 5Ni20Mo/HBETA increases the yield of cooking gas significantly. This can be concluded that although the bimetallic catalysts, especially 5Ni20Mo/HBETA, do not enhance the cracking ability, they can increase the yield of the valuable gases.

9.3.3 Quality of the pyrolytic oil

After asphaltene was separated from the liquid products of waste tire pyrolysis, the maltene solutions were separated into 5 fractions; saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics and polar-aromatics, as shown in Figure 4, by using liquid column chromatography (Šebor et al., 1999). These 5 fractions were analyzed by using a SIMDIST-GC for the true boiling point curves that later were cut to the petroleum fractions; naphtha (< 200 °C), kerosene (200-250 °C), light gas oil (250-300 °C), heavy gas oil (300-370 °C), and long residue (> 370 °C)..

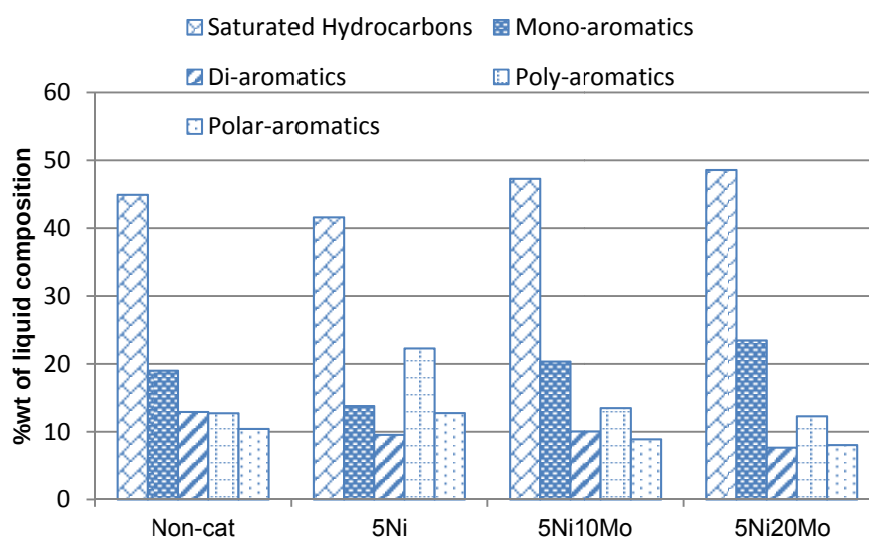


Figure 4: Chemical compositions in maltenes from using modified Ni/HBETA catalysts



Figure 4 indicates the chemical compositions in maltenes from various catalysts. With using 5Ni/HBETA, the light components (saturated hydrocarbons and mono-aromatics) decrease in conjunction with the increase in the heavy components (poly- and polar-aromatics). However, when the bimetallic catalysts (NiMo on HBETA) are used, saturated hydrocarbons and mono-aromatics increase dramatically in the same trend; resulting in the consequently decreases in poly- and polar-aromatics, which indicates the good abilities in cracking and ring-opening of the large aromatic molecules. The NiMo/HBETA catalyst, especially 5Ni20Mo/HBETA, gives the highest concentration of saturated hydrocarbons and mono-aromatics, which are about 48.6% and 23.5% by weight. It can be concluded that the modification of Ni/HBETA catalyst with Mo can increase the qualities of the pyrolytic oils because it can help to convert the heavy components such as poly- and polar aromatics to the lighter components (saturated hydrocarbons and mono-aromatics with a lower average carbon number) as compared with the non-catalytic case. Figure 5 shows the petroleum fractions in maltenes obtained from using modified Ni/HBETA catalysts. It can be seen that using the 5Ni/HBETA catalyst can increase the amount of full range naphtha. The results show that the bimetallic NiMo catalysts are likely to produce the light oils since 5Ni20Mo/HBETA gives the highest amount of the full range naphtha while 5Ni10Mo/HBETA gives the highest amount of kerosene. It can be seen that the higher the loading of the second metal (Mo), the higher full range naphtha is obtained. In addition, pure HBETA produces the heavier oils than all other catalysts. Therefore, it can be concluded that the promotion of Mo in the Ni/HBETA catalyst can improve the quality of oil.

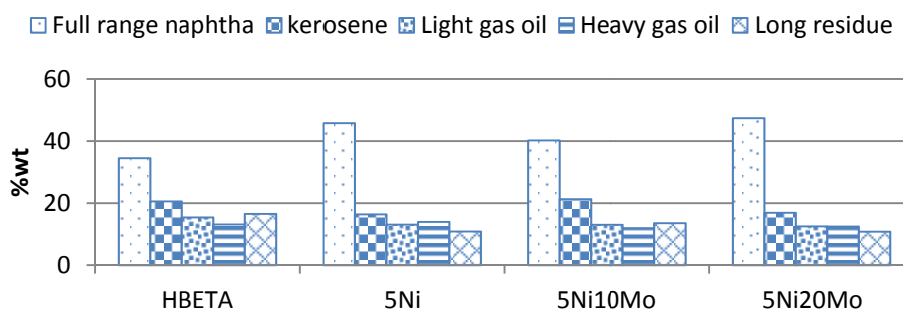


Figure 5: Petroleum fractions in maltenes obtained from using modified Ni/HBETA catalysts

9.3.4 Desulfurization ability

The sulfur contents in pyrolytic oil and sulfur deposition on spent catalysts were determined by a CHNS analyser, and the sulfur compounds in the pyrolytic oils were analyzed by GC-MS (TOF).

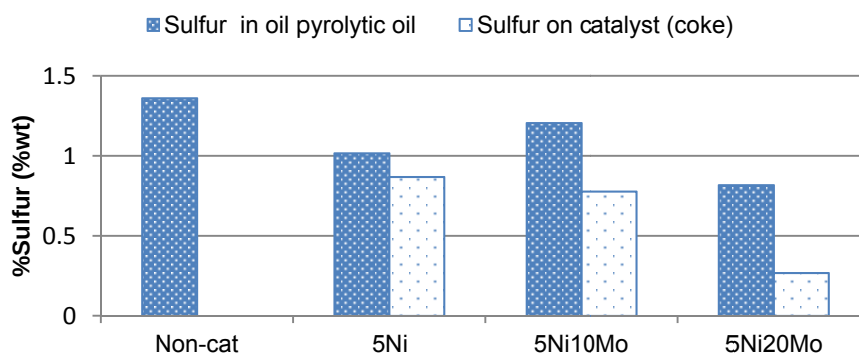


Figure 6: Sulfur contents (%wt) on spent catalysts and in the pyrolytic oils obtained from modified Ni/HBETA catalysts

Figure 6 shows the presence of sulfur contents obtained from the modified Ni/HBETA catalysts. The sulfur content in pyrolytic oil is about 1.36 %wt when none of the catalyst used. 5Ni/HBETA and all of modified Ni/HBETA catalysts show good hydrodesulfurization ability because they can reduce the sulfur content in the pyrolytic oil. When 5Ni/HBETA is used, it can reduce the sulfur content in the pyrolytic oil to 1.02 wt%, and sulfur content on the spent catalyst (coke) is reduced to 0.87 wt%. Using 5Ni10Mo/HBETA, the sulfur content in the pyrolytic oils increases in conjunction with the decrease in sulfur content on the spent catalyst, whereas 5Ni20Mo/HBETA gives the lowest sulfur contents in the pyrolytic oil (0.82 wt%) and the lowest sulfur contents on the spent catalysts (0.27 wt%) among all others. 5Ni20Mo/HBETA is a good catalyst for the sulfur reduction as indicated by the lowest sulfur contents in oil. This can be suggested that 5Ni20Mo/HBETA can breakdown the C-S bonds due to the hydrodesulfurization activity. Moreover, it can be concluded that 5Ni20Mo/HBETA catalyst can produce high quality of oil that contains low sulfur content.

The sulfur compounds in the pyrolytic oils were analyzed by GC-MS (TOF). The sulfur compounds in the oil obtained from 5Ni20Mo/HBETA are mainly in the range



of C₅-C₉, such as thiophene, 2-(1-methylethyl)-, benzo[b]thiophene, 4-methyl and benzo[b]thiophene whereas the sulfur compounds from the non-catalytic case are mainly in the range of C₁₀-C₁₃, such as benzo[b]thiophene, 2,7-dimethyl, benzo[b]thiophene, 2-ethyl-7-methyl- and dibenzothiophene.

9.4 Conclusions

The effects of modified Ni/HBETA catalysts on the quantity and quality of pyrolysis products were investigated. The results showed that the modification of Ni/HBETA catalyst with both 10% and 20%wt of Mo can increase the quality of pyrolytic oil, which contained a high amount saturated hydrocarbons and light petroleum fractions. Moreover, 5Ni20Mo/HBETA also had a good desulfurization ability because it gave the lowest sulfur contents in oil (0.82 wt%).

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Chapter 10

An Attempt on Using a Regenerated Commercial NiMoS/Al₂O₃ as a Catalyst for Waste Tire Pyrolysis*

Abstract: A used commercial sulfided NiMoS/Al₂O₃ catalyst from the hydrodesulfurization unit of a refinery in Thailand was employed as a catalyst for waste tire pyrolysis since it contains both acid and metal sulfide functions that could potentially benefit cracking and sulfur removal simultaneously. It was regenerated prior to use in a catalytic zone operated at 350 °C of the pyrolysis reactor. As a result, as compared to the non-catalytic case, the catalyst gave less long residue with a higher amount of full range naphtha in the tire-derived oil that contained a higher amount of mono-aromatics. Moreover, the oil contained less amount of polar-aromatics as well as less sulfur content. Furthermore, the oils were analyzed for sulfur species by using GC-TOF. The results showed that the oil obtained from sulfided NiMoS/Al₂O₃ had a higher amount of sulfur-containing molecules in the range of gasoline than the non-catalytic oil. Most of the sulfur-containing molecules found in gasoline, kerosene and gas oil ranges were benzothiophene derivatives such as 3-methylbenzothiophene (C₉H₈S), benzo[b]thiophene, 2,5-dimethyl- (C₁₀H₁₀S), and dibenzothiophene derivatives such as naphtho[2,3-b]thiophene, 4,9-dimethyl- (C₁₄H₁₂S).

10.1 Introduction

Tire pyrolysis has been generally known as a feasible and economical method because it allows the valuable substances to be recovered. The products are regined in three main phases comprised of char, oil and gas, which have different applications. Char can be used as a blending, carbon black, or converted to activated carbon. The derived oil can be the source of chemicals in chemical industry since it contains a high concentration of benzene, toluene, xylene and other aromatic derivatives. It is also added to petroleum refinery feedstock due to the gross calorific value of about 40.0 MJ/kg similarly to light fuel oils (Cunliffe and Williams, 1998). The gas products are mainly composed of light hydrocarbons such as olefins and C₁-C₄ paraffins that are also useful as a fuel. Due to the vulcanization of tire, large network between sulfidic crosslinks and rubber chains are formed, which can be monosulfidic (-S-), disulfidic (-S-S-) and polysulfidic (-S-S_x-S-) (Bilgili et



al., 2001). The release of sulfur from the tire structure during pyrolysis affects to the quality of oil products. In consequence, it is expected to be removed to obtain the light oil with less sulfur. Therefore, the cracking and desulfurization abilities of a pyrolysis catalyst are needed simultaneously. A hydrodesulfurization (HDS) catalyst is a commercial catalyst used for removing sulfur compounds from oils to produce the clean fuel. After the regular operation, the activity of the catalyst continuously decreases; however, the spent catalyst can be regenerated for reuse. In exclusive of the economic benefit, a spent commercial NiMoS/Al₂O₃ catalyst has the potential to be used as a tire pyrolysis catalyst because it has both acid and metal sulfide functions that can simultaneously promote the ability of cracking and desulfurization. H₂ required in desulfurization reaction can be supplied from cracking of waste tire. However, the activity on removal of sulfur-containing compounds during pyrolysis is highly acquired from the commercial HDS catalyst. It has been reported that the hydrogenation ability of NiMo sulfide catalyst resulted in high activity in HDS of 4,6-di-methyl-dibenzothiophene (Kim et al., 2003). From the work of Rodríguez-Castellón et al. (2008), a presulfided Ni₅-Mo₁₁ catalyst (using 90/10 % of N₂ /H₂S at atmospheric pressure) gave the highest dibenzothiophene (DBT) conversion at 3.0 MPa and 300-340 °C as compared to the conventional sulfided Co(Ni)Mo(W) catalyst. They also concluded that Ni-promoted catalysts had greater performance than Co-promoted catalysts at high temperatures because of high hydrogenation ability, similar to the result of Li-hua et al. (2011), They found that the sulfided catalyst containing 18% of Mo and 4% of Ni showed high HDS activity, hydrogenation selectivity, and favored the hydrogenation of phenyl ring in the DBT molecule due to the high stacking number of MoS₂ which is the active site facilitating the adsorption of sulfur-containing reactants and desorption of hydrogen sulfide products (Villarroel et al., 2008). Since a regenerated NiMoS/Al₂O₃ catalyst is comprised of acid (Al₂O₃) and metal sulfide (NiMoS), the objective of this work was to investigate the ability of the catalyst in waste tire pyrolysis and desulfurization, aiming to improve the quality and quantity of pyrolysis oil that have a lower sulfur level. Sulfur species and sulfur distribution in products are also reported in this work.

10.2 Experiment

10.2.1 Material and Preparation

A regenerated commercial NiMoS/Al₂O₃ obtained from a refinery in Thailand was first screened for the clean pellets, then crushed, and sieved into the



size range of 400-425 μm by using 40-60 mesh sizes of sieves. To prepare a waste tire sample, the side wall of a used tire sample, Bridgestone TURANZA GR-80, was scraped and then sieved into a particle size range of 8-18 mesh.

10.2.2 Pyrolysis Process

The tire sample was pyrolyzed in the lower zone (thermal pyrolysis zone) of reactor from room temperature to the final temperature of 500 $^{\circ}\text{C}$ with the heating rate of 10 $^{\circ}\text{C}/\text{min}$, and then the pyrolytic effluent with ~30 vol% H_2 (Aylón et al., 2007) carried by nitrogen flow to the upper zone packed with a catalyst. The catalytic zone was controlled at 350 $^{\circ}\text{C}$. The system was held for 90 mins to ensure the complete conversion of tire. The tire pyrolysis experiments were performed according to the procedure written in Dũng et al. (2009). The product effluent carried by nitrogen was condensed to liquid products by using ice-salt condensers. The incondensable product was passed to the condensers and collected by a gas sampling bag.

10.2.3 Catalyst characterization

The element composition of a catalyst sample was characterized by X-ray fluorescence spectrometry (XRF). Thermo Finnigan/Sorptomatic 1990 was used to determine the specific surface area and total pore volume of the catalyst using Brunauer-Emmet-Teller (BET) method. The sample was out-gassed at 150 $^{\circ}\text{C}$, overnight, to primarily clean up the impurity, and then was in a helium environment at 300 $^{\circ}\text{C}$ for 4 hours prior to the adsorption of nitrogen gas. The acidity of catalyst was analyzed by Temperature Programmed Desorption of isopropylamine (IPA-TPD) via manual injection. 0.05 g of sample was firstly purged by He flow to eliminate the moisture until no peak of water was observed. The IPA-TPD was conducted from room temperature to 800 $^{\circ}\text{C}$ with a heating rate of 20 $^{\circ}\text{C}/\text{min}$ under the He flow. The desorption of isopropylamine ($m/e = 44$), ammonia ($m/e = 17$) and propylene ($m/e = 41$) were detected by a mass spectrometer (Kresnawahjuesa et al., 2000 and Farneth and Gorte, 1995). Moreover, the used catalyst was also characterized by LECO[®] Elemental Analyzer, TruSpec[®] S at the furnace temperature of 1,350 $^{\circ}\text{C}$ to determine the amount of sulfur in the catalyst. The amount of coke on the spent catalyst was analyzed by Thermogravimetric/Differential Thermal Analysis (TG/DTA), heated from room temperature to 700 $^{\circ}\text{C}$ (10 $^{\circ}\text{C}/\text{min}$) with oxygen gas (50 mL/min).

10.2.4 Product analysis

The liquid and solid products were weighed to determine the product distribution. The amount of gas was then determined by mass balance. An



incondensable product in the gas sampling bag was analyzed by using a Gas Chromatograph (GC), Agilent Technologies 6890 Network system, using HP-PLOT Q column with FID detector with He as a carrier gas. Asphaltene was first separated from the liquid products by dissolving in n-pentane with the ratio of 1:40 (oil : n-pentane). Saturated hydrocarbons, mono-, di-, poly- and polar-aromatics were fractionated from the obtained maltenes by specific solvents (Šebor et al., 1999) using liquid adsorption chromatography, then further analyzed for the true boiling point curves (TBPs) by using a Varian CP-3800 stimulated distillation gas chromatography (SIMDIST GC), equipped with an FID according to the ASTM D2887 method. The TBPs of liquid hydrocarbons were cut to petroleum fractions, which are full range naphtha (<200 °C), kerosene (200–250 °C), light gas oil (250–300 °C), heavy gas oil (300–370 °C), and long residue (>370 °C). The oils were also analysed for the sulfur content by using elemental analysis (LECO, US). Finally, a Gas Chromatograph-Mass Spectrometer (Time of Flight), GC-MS (TOF), with 2D dimension mode was used to identify sulfur-containing compounds in the oil by using helium and nitrogen as a carrier and cooling gas, respectively.

10.3 Results and Discussion

10.3.1 Effect of spent NiMoS/Al₂O₃ to catalytic pyrolysis of waste tire

The results of pyrolysis with and without the catalyst including the product yield, liquid composition, petroleum cuts and light gas yield are given Figure 1. The results from product yield in Figure 1A indicate that the spent NiMoS/Al₂O₃ decreases the yield of liquid products from ~42 wt% to ~32 wt% in accordance with the increasing amount of gas products and coke formation while the solid yield remains constant. It means that using a catalyst promotes the decomposition of tire-derived product evolved from the thermal pyrolysis zone, resulting in a higher amount of lighter product (gases) that indicates high reaction activity of the catalyst. It is not surprised that coke is formed on the spent catalyst. The amount of coke per gram of the catalyst is also shown in Table 1. Figure 1B presents the chemical composition in the maltene fractions. It is observed that the spent NiMoS/Al₂O₃ catalyst can reduce polar-aromatics, but it shows low performance in poly-aromatics reduction, resulted in the shortage of saturated hydrocarbons. The remarkable result is found on the increase in mono-aromatics in the catalytic case. The TBP of maltene oil was cut into petroleum fractions that are shown in Figure 1C. The amount of the lightest fraction, full range naphtha, is

increased from the expense of heavy fractions in the experiment using spent NiMoS/Al₂O₃ catalyst. Nevertheless, the minor decrease of gas oils and long residue is possibly due to the mild acidity of Al₂O₃ support. It is interesting that using the spent NiMoS/Al₂O₃ shows high selectivity in alkane gas products (Figure 1D), possibly because of the hydrogenation ability (Li-hua et al., 2011, Rodríguez-Castellón et al., 2008 and Kim et al., 2003). It is known that an alkane is a saturated hydrocarbon, so alkane was easily formed by hydrogenation. Hence, the spent NiMoS/Al₂O₃ is a good catalyst for producing light alkane gas products from waste tire pyrolysis if compared with the non-catalytic experiment.

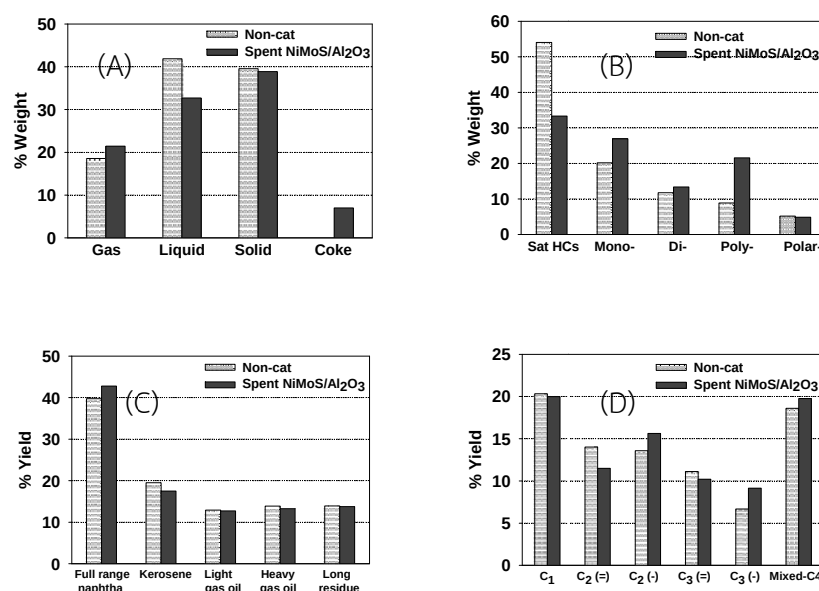


Figure 1: Effects of spent NiMoS/Al₂O₃ on the pyrolysis products: (A) product distribution, (B) liquid composition, (C) petroleum cuts, and (D) light gas yield.

The shift of pyrolysis products from using the spent NiMoS/Al₂O₃ catalyst can be explained by IPA-TPD results. The TPD profiles in Figure 2 present the MS signal of isopropylamine (m/e = 44), ammonia (m/e = 17) and propylene (m/e = 41) from mass spectrometer. The maximum desorption of unreacted isopropylamine was observed at 120 °C, associated to weak acid sites on the surface of the spent NiMoS/Al₂O₃ catalyst while the maximum desorptions of propylene and ammonia around 300-400 °C represent brønsted acid sites due to the fact that isopropylamine is decomposed on brønsted acid sites (not Lewis acid

sites), producing propylene and ammonia. The catalyst has both weak and brønsted acid sites; however, weak acid sites are dominant, meaning that the catalyst has mild acidity or less amount of strong brønsted acid sites. It can be explained that the slight changes on heavy to light products are caused by the mild cracking ability of the spent NiMoS/Al₂O₃ acid catalyst.

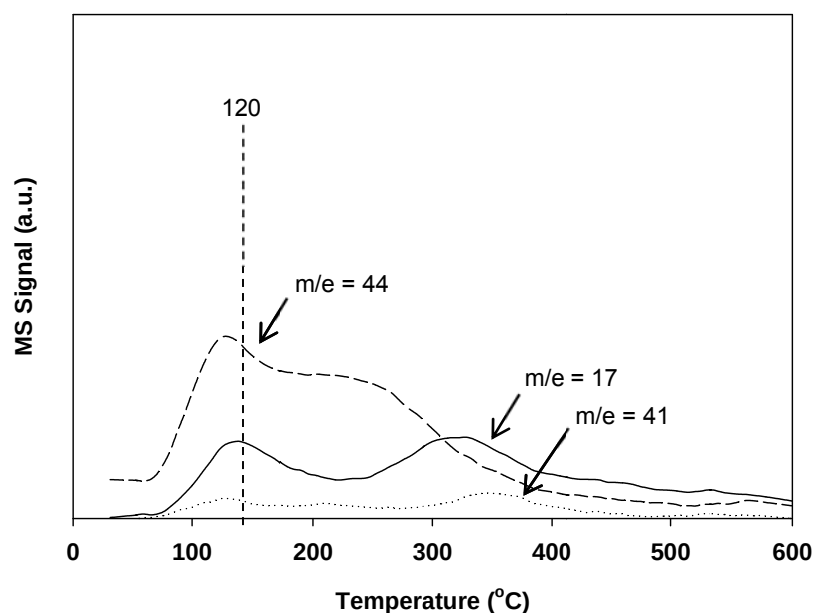


Figure 2: IPA-TPD profiles of isopropylamine ($m/e = 44$) desorption, ammonia ($m/e = 17$) and propylene ($m/e = 41$) formations on the spent NiMoS/Al₂O₃ catalyst.

It is possible that the reactions occur mostly in the pore of catalyst, so it can be suggested that coke is formed in the pore of acid catalyst. The physical properties of catalyst and the amount of coke in the used catalyst are shown in Table 1.

Table 1: Physical properties of spent NiMoS/Al₂O₃ and the amount of coke in the used catalyst

Catalyst	Specific surface area (m ² /g)	Pore specific volume (cm ³ /g)	Median pore width (Å)	Coke (g/g cat)
NiMoS/Al ₂ O ₃	198.75	0.42	8.86	0.36

10.3.2 Sulfur removal ability

The sulfur contents in pyrolysis oil obtained from the elemental analyzer are given in Figure 3A. A high amount of sulfur content was found in the non-catalytic case; however, it can be reduced from 1.36 to 0.60 wt% by using the catalyst. The disappearance of the sulfur in oil occurs in conjunction with a higher distribution of sulfur in the gas product and the used catalyst as indicated by the sulfur balance (Figure 3B). The high amount of sulfur in the gas fraction is possibly in the form of H_2S (Lin et al., 1997). It has been reported that H_2S can be adsorbed on the active site catalyst (Sidhpuria et al., 2008), resulting in a high deposition of sulfur on the spent catalyst. By using the GC-MS (TOF), the distribution of sulfur in light petroleum cuts illustrated in Figure 3C indicates that the spent $NiMoS/Al_2O_3$ catalyst can change the high distribution of sulfur, which is formerly in kerosene ($C_{10}-C_{13}$) and gas oil ($C_{14}-C_{20}$), to in gasoline (C_5-C_9). It can be concluded that the catalyst had the ability in both cracking and desulfurization simultaneously.

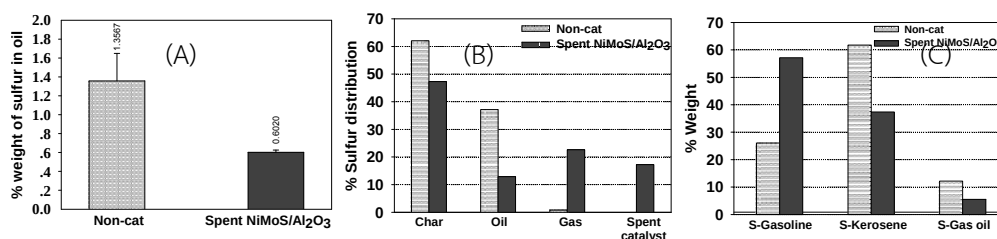


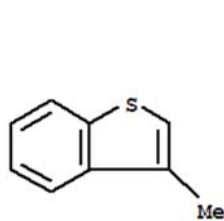
Figure 3: Effect of spent $NiMoS/Al_2O_3$ on the sulfur contents: (A) sulfur in oil, (B) sulfur distribution in products, and (C) petroleum cuts.

Table 2 shows the prominent C, H, S-containing molecules in each petroleum cuts. It is observed that sulfur species obtained in the highest amount from the non-catalytic case are benzo[b]thiophene, 2,7-dimethyl- in kerosene ($C_{10}-C_{13}$) fraction whereas those observed from the spent $NiMoS/Al_2O_3$ case is 3-methylbenzothiophene in gasoline fraction (C_5-C_9), which contains less number of alkyl groups than the non-catalytic case as shown in Figure 4. Most of the sulfur-containing molecules found in gasoline, kerosene and gas oil ranges are benzothiophene derivatives such as 3-methylbenzothiophene (C_9H_8S), benzo[b]thiophene, 2,5-dimethyl- ($C_{10}H_{10}S$), and dibenzothiophene derivatives such as naphtho[2,3-b]thiophene, 4,9-dimethyl- ($C_{14}H_{12}S$). However, the sulfur species found the most in this study are benzothiophene derivatives, which is different from Williams and Bottrill (1995) who found dibenzothiophene derivatives in majority.

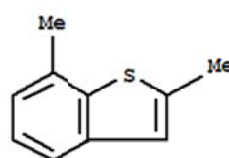
Table 2: Prominent C, H, S-containing molecules found in gasoline (C₅-C₉), kerosene (C₁₀-C₁₃) and gas oil (C₁₄-C₂₀) ranges of the oil

Petroleum cuts	Compounds	Formula	Area (%) [*]	
			Non-cat.	Cat.
Gasoline	Thiophene, 2-ethyl-5-methyl-	C ₇ H ₁₀ S	-	0.0523
	Thiophene, 3-(1,1-dimethylethyl)-	C ₈ H ₁₂ S	-	0.0470
	Benzo[b]thiophene	C ₈ H ₆ S	0.0283	0.0613
	3-Methylbenzothiophene ^I	C ₉ H ₈ S	0.0499	0.1657
Kerosene	Benzo[b]thiophene, 2,7-dimethyl- ^{II}	C ₁₀ H ₁₀ S	0.1138	0.0279
	5-Ethylbenzo[b]thiophene	C ₁₀ H ₁₀ S	0.0137	0.0529
	Benzo[b]thiophene, 2,5-dimethyl-	C ₁₀ H ₁₀ S	0.0409	0.0897
	Benzo[b]thiophene, 7-ethyl-2-methyl-	C ₁₁ H ₁₂ S	0.0077	0.0547
Gas oil	2,8-Dimethyldibenzo(b,d)thiophene	C ₁₄ H ₁₂ S	0.0062	0.0059
	3,7-Dimethyldibenzothiophene	C ₁₄ H ₁₂ S	0.0091	0.0067
	Naphtho[2,3-b]thiophene, 4,9-dimethyl-	C ₁₄ H ₁₂ S	-	0.0140

^{*}% Area of C,H,S-containing molecules in maltene fraction determined by GC-MS (TOF)



(I)



(II)

Figure 4: Examples of sulfur-containing compounds found in pyrolysis oils.

10.4 Conclusions

The roles of a commercial hydrodesulfurization catalyst in the catalytic pyrolysis of waste tire and sulfur removal was proven in this study. The spent



commercial NiMoS/Al₂O₃ catalyst can reduce the amount of sulfur in oil from 1.36 to 0.60 wt%, and can help cracking waste tire to lighter products. Nevertheless, the cracking activity was not considerably high due to its mild acidity. Therefore, it can be concluded that the spent HDS catalyst can be used as a catalyst for the waste tire pyrolysis since it can produce the better quality of pyrolysis oil containing a lower sulfur level because of its acid and sulfide functions.

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Chapter 11

Acid Density, Zn-Support Interaction, and Their Impacts on Light Fractions, Petrochemicals Production, and Sulfur Removal from Tire-Derived Pyrolysis Oil*

Abstract: Over the past decades, many metals have been studied as promoters of zeolites for improving quality and quantity of pyrolysis products. Several research articles focused on the production of valuable products (fuels and petrochemical feedstock) and oil quality upgrading (the reduction of total aromatic content, the increment of saturated hydrocarbons, and sulfur reduction). Zinc is a metal that has been used in light alkane aromatization as catalysts, sulfur removal as adsorbents, and sintering resistance as promoters, for instances. For waste tire pyrolysis, zinc was thus expected to be a promoter of zeolites for production of petrochemical feedstock with a high content of commercially valuable mono-aromatics. Furthermore, sulfur content in tire-derived oils was expected to reduce as well. This work therefore studied the effects of zinc promoter, surface acidity, and Zn-support interaction (Zn on HBETA, HY, and HMOR) on tire-derived oil, petrochemicals and sulfur removal. The results showed that zinc promoted gas yields and the production of small molecules in oils, indicating that zinc promoted cracking activity of zeolites. Furthermore, zinc was found to enhance the catalyst stability since zinc-promoted catalysts, except Zn/HY, generated a lower amount of coke than their pure zeolites. Moreover, the promoted catalysts increased the concentrations of paraffins and mono-aromatics in conjunction with the decreases in other aromatic groups, indicating that zinc can promote hydrogenation, ring-opening and aromatization activities. Furthermore, sulfur content in oils was decreased in all zinc-supported catalysts, especially those in the groups of thiophenes, benzothiophenes, dibenzothiophenes and naphthothiophenes, indicating the sulfur removing activity of Zn promoter. The ability of sulfur removal from oils strongly depended on acid density of catalysts. Furthermore, it was found that Zn loaded on HBETA, HY and HMOR zeolites can produce high selectivity of cumene and ethylbenzene in gasoline. Moreover, Zn/HBETA highly produced cyclohexane while the other zinc-loaded catalysts also highly produced styrene.



11.1 Introduction

Pyrolysis of waste tire is an effective method for recovering the hydrocarbon substances that can be produced in forms of gas and liquid products. In terms of product applications, tire-derived oils have a potential to serve as liquid fuels and petrochemical feedstock. Several researchers studied the improvement of pyrolysis oil quality by enhancing light oil yields, petrochemical yields, and removing sulfur content. For examples, Qu, *et al.* [1] studied the catalytic co-pyrolysis of waste tire with lubricant base oil (LBO) using ZSM-5. They found that LBO can enhance the degradation rate of waste tire, and increase the amount of light oils as well. Dung *et al.* [2] studied the use of ITQ-21 as additives of HMOR zeolite in waste tire pyrolysis process. They found that the additives can promote kerosene and mono-aromatic productions. Furthermore, benzene, toluene and xylenes were also produced from the pyrolysis of waste tire using USY, Y and ZSM-5 as catalysts [3,4]. However, the oils contain a high amount of sulfur because sulfur is an essential ingredient in tire production. So, the quality of tire-derived oils must be improved before the uses. The sulfur species in tire-derived oils were reported by William and Brottill [5]. They revealed that the sulfur-polycyclic aromatic hydrocarbon (PASH) species were benzothiophene, dibenzothiophene and their derivatives. These species are found in crude oil as well. So, the hydrotreating processes for petroleum-based oil can be also applicable for tire-derived oils. Several articles reported that the hydrodesulfurization of sulfur-containing compounds can produce valuable petrochemicals such as toluene, ethylbenzene, and styrene [6,7] as co-products as well. The concentration of petrochemicals in tire-derived oils can be also improved via hydrodesulfurization. Since only a little quantity of valuable C6-C8 petrochemicals can be produced via thermal pyrolysis, the enhancement of C6-C8 compounds in tire-derived oil via desulfurization can be significant although there exists only a little amount of sulfur compounds in it (~1.4 wt%).

Recently, our group has accomplished in using non-noble metals; that are, Cu [8,9], Fe [10], and Ni [11, 12] as promoters on various zeolite supports for the catalytic pyrolysis of waste tire. Although the zeolites themselves were able to enhance the qualities of oil [13], all non-noble metals were found to promote sulfur removal from tire-derived oil, especially Cu that enhanced desulfurization of oils by converting sulfur compounds into thermodynamically-stable forms on Cu [9]. Cu-support interaction highly affected the sulfur removal from oils. Moreover, the non-noble metals can enhance the production of light fractions and petrochemicals



such as benzene, toluene, ethylbenzene, xylenes, and styrene in tire-derived oils. Marked increases in petrochemicals production ($\sim 47 - 80$ wt.% in gasoline) were observed with using Fe catalysts, regardless of the zeolite supports, especially when 5%Fe/HMOR and 5%Fe/KL were employed [11]. Furthermore, for Ni catalysts, the acid density of zeolite supports was found to promote the formation of heavy aromatics and control the sulfur removing ability [13].

Zinc is a metal used as promoters for catalysts in many applications because it has several outstanding properties. For examples, zinc-loaded catalysts were used as aromatization catalysts for a light alkane feed stream [14,15]. Zinc-exchanged zeolites were used to remove sulfur-containing compounds from liquid fuels [16–19]. Furthermore, ZnO can limit the H_2S poisoning of copper by forming ZnS that is more strongly favored thermodynamically than the Cu_2S form at 500 K [20]. Twigg and Spencer [21] studied the deactivation of copper-loaded catalysts for hydrogenation reactions. They found that zinc can be used as a promoter of copper in the catalyst fields for improvement of stabilities (sulfur resistance, thermal sintering, etc.). For the waste tire pyrolysis, zinc is therefore a remarkable metal for use as a promoter of zeolites since it might improve quality of tire-derived oils in the terms of sulfur reduction, and simultaneously promote mono-aromatic formation as valuable petrochemicals.

Hence, this work studied on the influences of acidity and zinc-support interaction on sulfur removal from tire-derived oil. The quality of oils was also examined in terms of chemical species, petroleum fractions, and petrochemicals in oils. Zinc was loaded at 5 wt% on three types of supports (HBETA, HY and HMOR zeolites) using impregnation method. Pyrolysis oils were analyzed to determine their compositions and petroleum cuts by using GCxGC-TOF/MS and SIMDIST-GC, respectively. Gas products were analyzed their compositions by using GC-FID. All three pyrolysis products (gas, oil and char) and spent catalysts were analyzed and/or calculated sulfur distribution by using S-analyzer.

11.2 Experimental

11.2.1 Catalyst Preparation



Commercial zeolites, NH_4 -BETA ($\text{Si}/\text{Al} = 13.5$), HY ($\text{Si}/\text{Al} = 7.5$) and HMOR ($\text{Si}/\text{Al} = 9.5$), supplied by TOSOH Company (Singapore) were calcined in stagnant air at the following conditions. NH_4 -BETA was calcined to 600 °C with the ramping rate of 2 °C /min from room temperature with holding at the final temperature for 5 hrs. HY and HMOR were calcined to 500 °C with the ramping rate of 5 °C /min from room temperature with holding at the final temperature for 3 hrs. The calcined zeolites were subsequently impregnated with an appropriate amount of a zinc solution ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) to achieve the zinc loading of 5 wt%, dried overnight in an oven at 120 °C, and calcined again at the same calcination conditions. The calcined catalysts were then reduced at 500 °C for 2 hours in hydrogen environment. Finally, all catalysts were pelletized, crushed, and sieved into a particle size of 40-60 mesh.

11.2.2 Catalyst Characterization

The XRD patterns of catalysts were obtained from XRD machine (Rikagu) using $\text{CuK}\alpha$ radiation operated at 40 kV and 30 mA. The scanned angle was started from 5° to 65° with a scanning speed of 5°/min. Thermo Finnigan TPDRO 1100 machine performed under 4.99 % H_2/N_2 flow at 20 mL/min with a heating rate of 20 °C/min from room temperature to 950 °C was used to obtain temperature-programmed reduction (TPR) profiles in order to determine Cu-support interaction. The ammonia-temperature programmed desorption (NH_3 -TPD) profiles were obtained from the same instrument operated under 10.03% NH_3/He flow at 10 mL/min and room temperature for the adsorption step and under 99.999% N_2 flow at 10 mL/min with a heating of 10 °C/min from room temperature to 950 °C from the desorption step. XPS spectra were obtained by using an AXIS ULTRADLD (Kratos) to determine metal species on the catalysts. The system was equipped with a monochromatic Al X-ray source and a hemispherical analyzer. The spectrometer was operated at the pass energy of 160 eV and 40 eV to acquire wide scan and core level spectra, respectively. All peaks were calibrated from referring C1s spectra (Binding energy = 284.6 eV). The amount of metal loading on zeolites was determined by using Atomic Absorption Spectrometer (Varian, SpecterAA 300 model) ULTRADLD. A sample was digested with an acid solution (1 conc. HCl: 1 conc. HF: 1 conc. H_2O) to a solution of the metal element. Thermo Finnigan Sorptomatic 1990 equipment was used to determine BET surface area and pore



volume of catalysts by N_2 physical adsorption. Thermogravimetric/Differential Thermal Analysis, TG/DTA (Perkin Elmer/Pyris Diamond), was used to determine the amount of coke deposited on spent catalysts with the heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ from room temperature to $900\text{ }^{\circ}\text{C}$. Sulfur content on catalyst surface was acquired from LECO®Elemental Analyzer (TruSpec®S).

11.2.3 Pyrolysis of Waste Tire

Pyrolysis apparatus was the same as the work published by our group [8-13,22]. The reactor was divided into two zones; the lower zone (pyrolysis zone) was loaded with 30 grams of shredded tire (20-40 mesh), and the upper zone (catalytic zone) was loaded with 7.5 grams of a catalyst. Two zones were heated from room temperature to $500\text{ }^{\circ}\text{C}$ and $300\text{ }^{\circ}\text{C}$ with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ at atmospheric pressure, respectively, and the final temperatures were held at the target temperatures for 2 hr. High purity nitrogen was used as a carrier gas. The condensable products or oils were collected in the condensers immersed in an ice-salt (NaCl) bath. A gas sampling bag was used to collect uncondensable products or gas products, while solid products or chars remained in the bottom of the reactor.

The gas yields was calculated from mass balance, which equals to initial weight of tire abstracted by the liquid and solid yields, and the amount of coke on the catalyst surface determined from the TG/DTA instrument. Before analysis of oil products, asphaltene was first precipitated via mixing the oils with n-pentane in the oil/n-pentane mass ratio of 40:1 for 18 hr. A Teflon membrane ($0.45\text{ }\mu\text{m}$) was used to filter the precipitated asphaltene. GCxGC-TOF/MS apparatus equipped an Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA), a Pegasus® 4D TOF/MS (LECO, St. Joseph, MI, USA) and a thermal modulator was used to analyzed oil compositions. The instrument was operated by the cooperation of two GC columns (Thames Restek, Sounderton, UK). The 1st GC column was a non-polar Rtx®-5Sil MS, $30\text{ m} \times 0.25\text{ mm ID} \times 0.25\text{ }\mu\text{m}$ film thickness. The 2nd GC column was an Rxi®-17 MS, $1.10\text{ m} \times 0.10\text{ mm ID} \times 0.10\text{ }\mu\text{m}$ film thickness. Maltene solution samples were prepared by diluting $1\text{ }\mu\text{L}$ of maltene with CS_2 into 2 mL , and analyzed by injection into the instrument via a splitless injector operated at $250\text{ }^{\circ}\text{C}$ using $1.0\text{ mL}/\text{min}$ of helium as a carrier gas. Moreover, a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) conformed to the ASTM-D2887 method



was used to determine the true boiling point curves of maltene solutions. The equipment was installed with FID and WCOT fused silica capillary column, 15 m $\times$ 0.25 mm $\times$ 0.25 μ m. The true boiling point curves were next cut into petroleum fractions according to their boiling points; gasoline (<149 $^{\circ}$ C), kerosene (149-232 $^{\circ}$ C), gas oil (232-343 $^{\circ}$ C), light vacuum gas oil (343-371 $^{\circ}$ C) and heavy vacuum gas oil (>371 $^{\circ}$ C). A GC-FID, Agilent Technologies 6890 Network GC system (HP-PLOT Q column: 20 μ m film thickness and 30 m $\times$ 0.32 mm ID) was used to determine the compositions and concentrations of the gas products. Furthermore, sulfur contents in the liquid and solid products were also determined by using a LECO®Elemental Analyzer (TruSpec®S) whereas the sulfur content in gas products was calculated via mass balance.

11.3 Results and Discussion

11.3.1 Catalyst Characterization

The XRD patterns of zinc-promoted catalysts and their pure supports are shown in **Fig. 1**. Obviously, it can be observed that the presence of zinc on zeolites does not destroy zeolite structure. The 2θ s of 36.5 $^{\circ}$, 39.1 $^{\circ}$, 43.5 $^{\circ}$ and 54.6 $^{\circ}$ are the characteristic peaks of Zn^0 , and the 2θ s of 31.8 $^{\circ}$, 34.3 $^{\circ}$, 36.5 $^{\circ}$, 47.6 $^{\circ}$ and 57.2 $^{\circ}$ are those of ZnO. However, the characteristic peaks of zinc species cannot be clearly seen since might be highly dispersed on their supports. **Table 1** shows the surface area and pore volume of all catalysts. The introduction of zinc onto zeolites decreases both pore volume and BET specific surface area because zinc might partially block the pore of zeolites. The amounts of zinc loading and zinc species in each catalyst are shown in **Table 2**.

Table 1 BET surface area and pore volume of catalysts

Catalyst	BET surface area (m ² /g)	Pore Volume (cm ³ /g)*
HBETA	539	0.257
HY	515	0.266
HMOR	395	0.199
Zn/HBETA	492	0.233
Zn/HY	515	0.259
Zn/HMOR	380	0.185

* Horvath-Kawazoe (H-K) Calculations

Table 2 Zinc content and species in catalysts

Catalyst	Zinc Content in Catalyst (wt%)*	Zinc Specie (wt%)/ Binding Energy (eV)**	
		Zn ⁰	ZnO
Zn/HBETA	3.61	82.2/ 1021.5	17.8/ 1023.3
Zn/HY	3.04	90.4/ 1021.3	9.60/ 1022.4
Zn/HMOR	2.92	92.0/ 1021.3	7.96/ 1023.0

* from Atomic Absorption Spectroscopy (AAS)

** from X-Ray Photoelectron Spectroscopy (XPS)

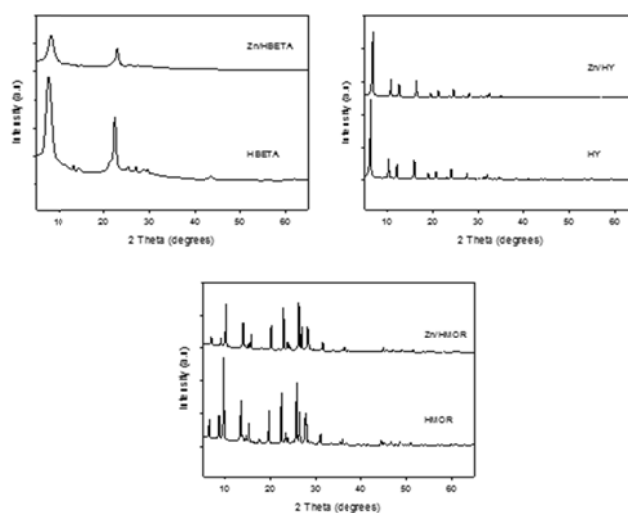


Fig. 1 XRD patterns of Zn-loaded catalysts.

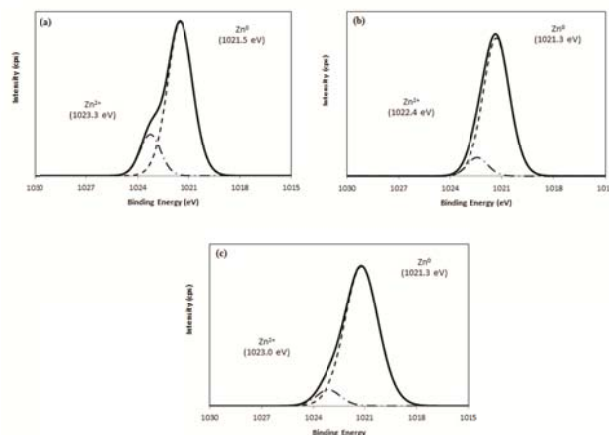


Fig. 2 Zn 2p_{3/2} XPS spectra of zinc-loaded catalysts; (a) Zn/HBETA, (b) Zn/HY, and (c) Zn/HMOR.

In **Fig. 2**, the Zn 2p_{3/2} XPS spectra illustrate the contribution from both Zn⁰ and ZnO at the binding energies of 1021.3 – 1021.5 eV [23] and 1022.4 – 1023.3 eV, respectively [24]. The spectra indicate that zinc species found on the catalysts are composed of a high amount of metallic Zn (82.2 wt%, 90.4 wt%, and 92.0 wt% for Zn/HBETA, Zn/HY, and Zn/HMOR, respectively) with a low amount of ZnO (17.8 wt%, 9.60 wt%, and 7.96 wt% for Zn/HBETA, Zn/HY, and Zn/HMOR, respectively). TPR profiles in **Fig.3** shows that the reduction temperatures of zinc oxide on HBETA, HMOR, and HY are 748 °C, 636 °C, and 596 °C, respectively, consequently indicating that the Zn-support interaction can be ranked as Zn/HBETA > Zn/HMOR > Zn/HY. However, after reduction, only 3% Zn was found left all supports, using XRF. It can be explained that the melting point of metallic zinc is around 419.5 °C [25], while the reduction temperatures of zinc-loaded catalysts are much higher than the melting point (as observed from the TPR profiles in **Fig. 3**). However, the catalysts can be reduced at 500 °C as confirmed by XPS due to the Zn-support interaction and the dispersion of Zn clusters on the support. However, the metal loading of ~3 wt% observed on all Zn-loaded catalysts, instead of the expected 5 wt% is attributed to the partial vaporization of Zn from the surfaces during the reduction. **Fig. 4** shows surface acidity of the catalysts which the acidity of Zn/HBETA and Zn/HMOR is quite similar, and they are higher than that of Zn/HY.

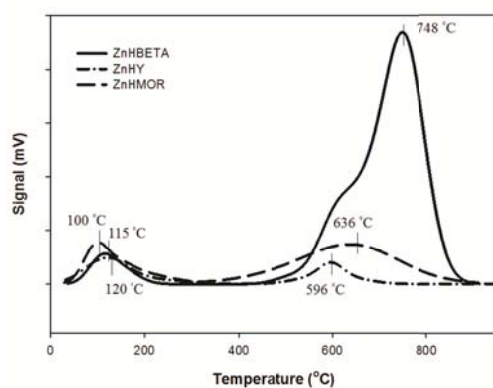


Fig. 3 TPR profiles of Zn-loaded catalysts.

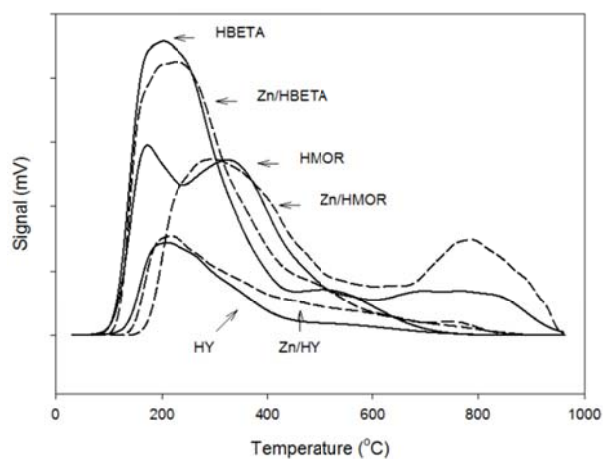


Fig. 4 NH₃-TPD profiles of Zn-loaded catalysts.

Table 3 Desorption temperatures from NH₃-TPD profiles

	T ₁ (°C)	T ₂ (°C)	T ₃ (°C)
HBETA	202	505	-
HY	209	-	-
HMOR	172	324	765
Zn/HBETA	229	490	744
Zn/HY	216	-	-
Zn/HMOR	295	-	786

11.3.2 Product Distribution

All zinc-loaded catalysts slightly increase gas production, and decrease liquid yields with an extent of coke formation and a constant solid yield as shown in **Fig. 5**. It indicates that zinc slightly promotes the cracking activity of zeolites. Surprisingly, all zinc-promoted catalysts (except Zn/HY) reduce the amount of coke on the catalyst surfaces.

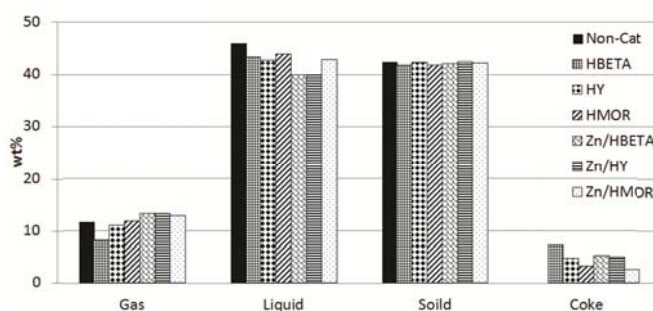


Fig. 5 Product distribution using Zn-loaded catalysts.

11.3.3 Acid Density and Its Influence on Sulfur Removal and Zn-Support Interaction

Hydrodesulfurization can occur via four steps; (a) S-compound adsorption on a Zn-site, (b) the adsorbed S-compound hydrogenation and C-S bond cleavage, (c) the S-free hydrocarbon desorption and zinc sulfide formation, and (d) the sulfur removal from the catalyst surface (surface cleaning). **Fig. 6** and **Table 4** show that the introduction of zinc on the zeolites can improve the sulfur removal from pyrolysis oils. Since Zn can well interact with Brönsted and Lewis acid sites (or surface acidity) on the zeolite supports (**Fig. 7**), the acid sites thus promote the electron deficiency of zinc [26,27], resulting in higher adsorption strength between Zn and a sulfur-containing hydrocarbon, the easier C-S bond cleavage, and then the better S removal from the hydrocarbon. The sulfur removal ability of zinc depends on the acid density, represented the amount of ammonia adsorbed on the catalyst surface as seen in **Fig. 4**. Furthermore, the metal-support interaction also affects the surface cleaning ability of Zn-loaded catalysts. The TPR profiles and binding energies of zinc-loaded catalysts (**Fig. 3** and **Table 2**, respectively) can indicate the Zn-support interaction of the zinc-loaded catalysts. It can be seen that the reduction temperature and Zn 2p_{3/2} binding energies (both Zn⁰ and ZnO) of Zn/HBETA are the

highest, followed by those of Zn/HMOR and Zn/HY, indicating that the highest electron-deficient and strongest metal-support interaction catalyst is Zn/HBETA, followed by Zn/HMOR and then Zn/HY. The results agree with the report of Du *et al.* [26] that the sulfur tolerance can be improved by decreasing the sulfur-metal strength; thus, increasing the electron-deficient metal sites. Even though Zn/HBETA has higher electron-deficient than the others, it is not the catalyst reducing the highest amount of sulfur in the oil. Because zinc has dehydrogenation ability [14,15], resulting in coke resistance improved by zinc addition. So, the amount of sulfur deposited on the catalyst surface in the form of coke is also affected from the presence of zinc. However, Zn/HY does not reduce the amount of coke unlike Zn/HBETA and Zn/HMOR, resulting in the highest sulfur deposition occurring on the Zn/HY surface, and the lowest sulfur content in the oil, followed by Zn/HBETA and then Zn/HMOR as seen in **Fig. 5** and **Table 4**. Zn/HY with the lowest metal-support interaction can create the weakest Zn-S bonds, resulting in the highest surface cleaning ability. However, it is difficult for the surface cleaning to occur because the Zn-S bond strength is so strong [28], resulting in the higher desulfurization activity than the surface cleaning activity. In this work, the Zn/HY catalyst appears to be the best catalyst among all tested catalysts for sulfur removal from tire-derived oils.

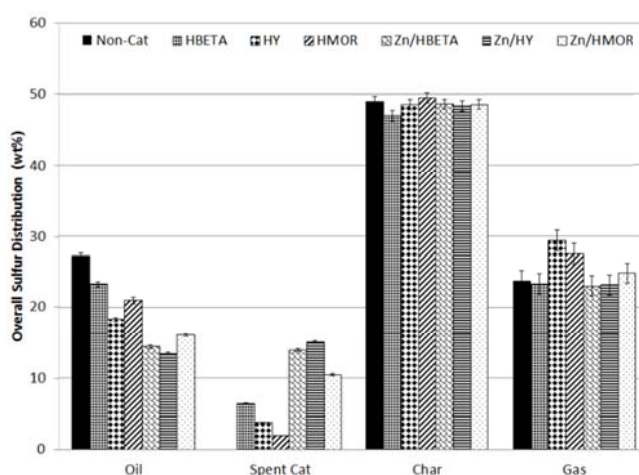


Fig. 6 Overall sulfur distribution using Zn-loaded catalysts.

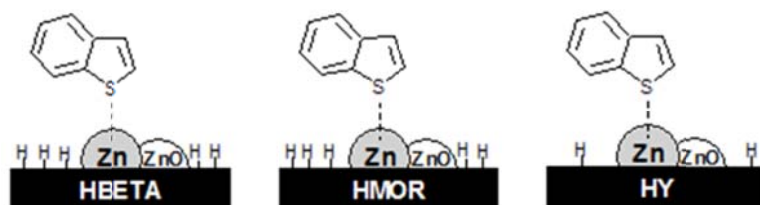


Fig. 7 Surface species on Zn-loaded catalysts and sulfur adsorption.

Table 4 Sulfur content in oil (wt%)

Catalyst	Sulfur Content in oil (wt%)
No Catalyst	1.22±0.0404
HBETA	1.11±0.0200
HY	0.889±0.0253
HMOR	0.991±0.0608
Zn/HBETA	0.748±0.0215
Zn/HY	0.695±0.0111
Zn/HMOR	0.778±0.0165

* S in Tire = 2.066 wt%

Sulfur-containing compounds in oils can be classified into six groups: thiophenes (Th), benzothiophenes (BT), dibenzothiophenes (DBT), naphthothiophenes (NT), benzothiazoles (BTz), and isothiocyanates (ITC) as shown in Fig. 8. Fig. 9 shows that Th, DBT and NT are totally reduced when zinc was loaded on all types of the zeolites because zinc can react with sulfur atoms in sulfur-containing compounds, and form thermodynamically stable ZnS [20,21]. Furthermore, BT is highly reduced in all Zn-loaded catalyst cases as compared with pure zeolite cases. It can be concluded that zinc can promote sulfur removal activity of zeolites.

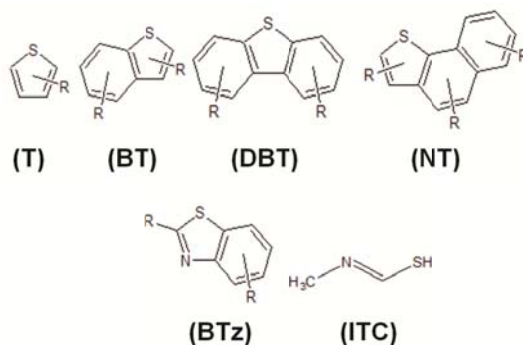


Fig. 8 Major sulfur-containing compounds in tire-derived oils.

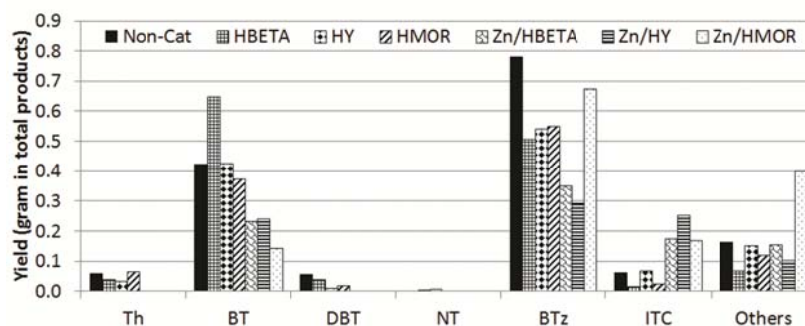


Fig. 9 Yield of sulfur-containing species.

11.3.4 Effect of Zinc-loaded Catalysts on Tire-derived Oils

Fig. 10 shows that zinc can promote cracking activity of zeolites, resulting in the increment of gasoline fraction. Moreover, all petroleum cuts are mainly composed of aromatics (Table 5), indicating that the tire-derived oils are not suitable for direct use as fuels. However, Fig. 11 shows that all zinc-loaded catalysts highly produce ethylbenzene and cumene. The catalysts (except Zn/HBETA) also highly produce styrene, while cyclohexane is highly produced by Zn/HBETA. However, the productivity of petrochemicals (Table 6) is reduced when zinc was loaded on the zeolites, except the Zn/HMOR case.

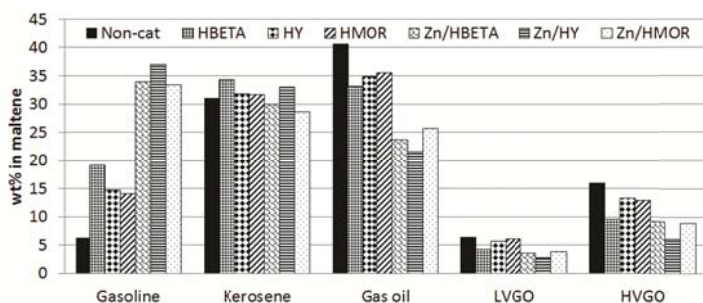


Fig. 10 Petroleum cuts of maltenes using zinc-loaded catalysts.

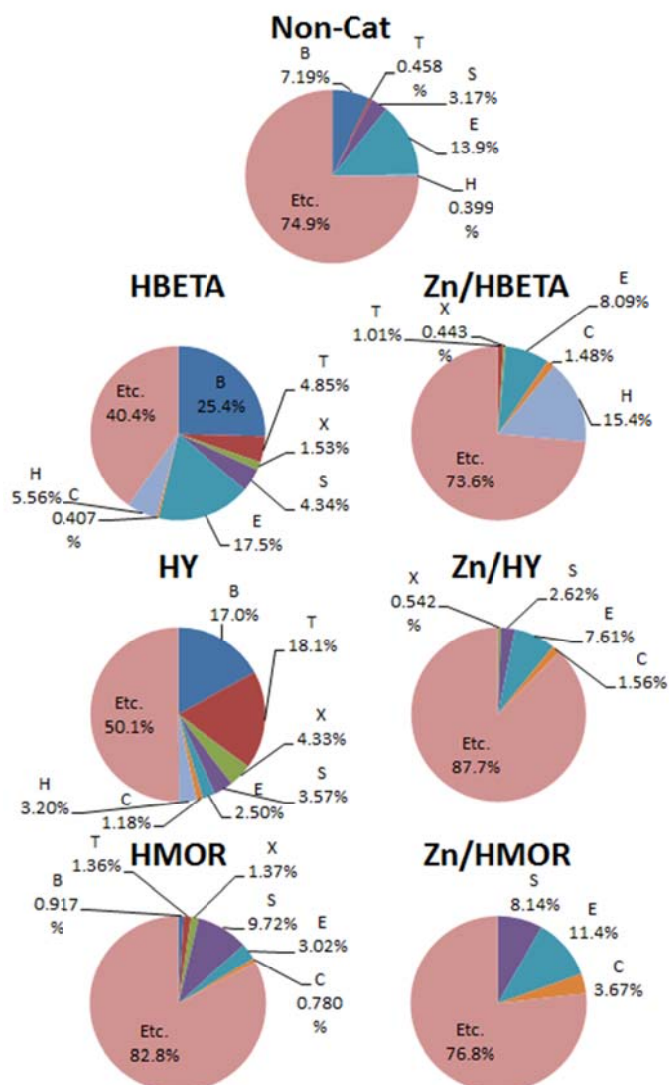


Fig. 11 Selectivity of petrochemicals in gasoline-range products.

**Table 5** Chemical composition in each petroleum cuts

	Gasoline	Kerosene	Gas Oil	LVGO	HVGO
Paraffins	0.00-26.1	0.468-1.66	3.95-23.6	0.00-13.5	0.00-32.6.
Olefins	0.445-11.3	0.254-9.04	0.00-9.51	0.00-22.3	-
Naphthenes	3.77-39.1	1.86-13.0	0.00-16.8	0.00-22.0	-
Aromatics	60.0-96.2 [*]	76.3-96.2	65.4-80.9	71.1-100	67.4-100

^{*} 37.5 – 77.4 wt% of mono-aromatics in gasoline**Table 6** Petrochemicals productivity from waste tire pyrolysis

Catalyst	Petrochemical Productivity (kg/ton of tire)
No Catalyst	7.15
HBETA	52.1
HY	33.6
HMOR	11.1
Zn/HBETA	41.0
Zn/HY	20.9
Zn/HMOR	35.5

11.4 Conclusions

This work studied the effect of Zn-promoted catalysts on tire-derived oil, petrochemicals and sulfur removal by loading the metal on three types of supports with different Si/Al ratios (HY, HMOR, and HBETA with Si/Al = 7.5, 9.5, and 13.5, respectively). The acid density, metal-support interaction, and coke-resistance ability of Zn-promoted catalyst exhibits an important role on sulfur removal from pyrolysis oils. Sulfur content in oils was ranked in the order of: Zn/HY (0.694 wt%) < Zn/HBETA (0.748 wt%) < Zn/HMOR (0.778 wt%). All Zn-loaded catalysts can produce a high selectivity of cumene and ethylbenzene in gasoline. Moreover, Zn/HBETA highly produced cyclohexane while the other zinc-loaded catalysts also highly produced styrene.



11.5 Acknowledgements

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Chapter 12

Discussion and Conclusions: Comparison with noble metals

12.1 Summary of Previous Work: Selectivity of Noble metal-supported Catalysts

In the previous work supported by TRF, various noble metals (Pt, Ru, Rh, Pd, Ag, and Re) were loaded on acid supports (HBETA, HMOR, and HY) and tested for their activity and selectivity of pyrolysis products. The results were also product yield, gas composition and yield, true boiling point curves, petroleum fractions, petrochemical yields, carbon number distribution, and the molecular composition of oil.

(a) Pt-loaded catalysts

With Pt loading the curves shift to the lower boiling points, meaning that all Pt catalysts give lighter oil than all unloaded zeolites. The fraction of naphtha in the maltenes is increased by almost 10% (for HBETA case), 28% (for HMOR case), and 20% (for HY case). Pt/HMOR as the best catalyst among all Pt-loaded catalysts gives about 68% naphtha, 20% kerosene, 6% light gas oil, 5% heavy gas oil, and 1% long residue in the oil. It seems that Pt loading can convert saturated HCs, di-, and polar-aromatics to mono-aromatics. Pt/HY gives some similar results; that is, it decreases saturated HCs and poly-aromatics with the increase of mono-aromatics, indicating that poly-aromatics are converted to mono-aromatics. Pt/HMOR that gives the oil with the highest amount of naphtha further increases the saturated HCs and mono-aromatics in association with the reduction in all types of aromatics. It means that Pt/HMOR not only gives the highest quantity of naphtha, but also it produces naphtha with the highest quality. The introduction of Pt on the zeolites led to a further decrease in the content of polar-aromatics, and the lowest polar-aromatic content was observed when Pt/HBETA catalyst was used. Finally, the formation of polar-aromatics involving the interaction with accessible olefins was proposed and discussed on both cases of with and without Pt catalysts.

(b) Pd-loaded catalysts

All Pd catalysts gave lighter oil than all unloaded zeolites. The lightest oil was obtained from the case when HY was used as the support with Pd



loading, unlike the Pt cases in which the lightest oil was obtained when Pt was loaded on HMOR. The lightness of the oils is again contributed from the increase in naphtha in the oils when all Pd-loaded catalysts are introduced. Pd/HY as the best catalyst among all Pd-loaded catalysts gives about 68% naphtha, 23% kerosene, 5% light gas oil, 1% heavy gas oil, and 3% long residue in the oil, which is even better than Pt/HMOR (the best one among Pt-loaded catalysts). Moreover, similar to all Pt-loaded catalysts, one thing all Pd-loaded catalysts have in common is that they increase mono-aromatic content in the tire-derived oil. However, its effect is not as pronounced as that of Pt, and the pathways seem to be different from those of Pt. Instead, it appears that Pd can change saturated HCs and poly-aromatics to mono- and di-aromatic compounds, possibly via hydrocracking, isomerization, and hydrogenation activities (without ROP activity) of Pd whereas Pt can produce mono-aromatics and some saturated HCs from aromatic compounds, especially poly- and polar-aromatics, via its greater ring-opening activity. Finally, the incipient wetness impregnation was found to be more superior than the ion-exchange method for the preparation of Pd/HBETA.

(c) Ru-loaded catalysts

As compared with the corresponding zeolites, all Ru-loaded catalysts improved the olefins productions. Ru/HMOR was superior in the production of light olefins, so, it showed the highest production of light olefins. All Ru catalysts, except Ru/HBETA, gave lighter oil than all unloaded corresponding zeolites. The fraction of naphtha in the maltenes was increased by almost 24% (for HMOR case), and 17% (for HY case). Ru/HMOR as the best catalyst among all Ru-loaded catalysts gave about 74% naphtha, 13% kerosene, 5% light gas oil, 4% heavy gas oil, and 4% long residue in the oil, which was even better than Pt/HMOR; the best among all Pt-loaded catalysts. Furthermore, all Ru-loaded catalysts decreased poly-aromatics with the significant increase in mono- and di-aromatics in the oil. Among Ru-catalysts, Ru/HMOR gave some distinguished results as it also gave the distinguishable composition of gas product; that is, it increased saturated HCs whereas the other two Ru-catalysts decreased them, indicating that poly-aromatics were not only converted to mono- and di-aromatics, but also saturated HCs. Both Ru/HMOR and Pt/HMOR not only gave the highest quantity of naphtha, but also it produced naphtha with the highest quality. In summary, Ru/HMOR can improve the light olefins production in association with the lightest oil with the best quality. With its capability, Ru was further investigated for its role on light olefins and light



oil production. The conclusions are discussed in Section 8.4.

(d) Ag-loaded catalysts

Similar to Pd, Pt, and Ru, Ag seems to further increase methane, ethylene, ethane, propylene, and propane from what is produced by the corresponding zeolites. The gas profiles of Ag-loaded catalysts tend to be similar to those of Ru-loaded catalysts. Additionally, the concentration of mixed- C₄s significantly increased, leading to the sharp increases in the mixed C₄s yield. The yields of all other light gases (up to C₄s) were greatly improved when Ag-loaded catalysts were used, especially Ag/HBETA due to its great increase in the gas yield. Ag loaded on all tested zeolites, therefore, further increased light olefins, cooking gas, and mixed C₄s productions as compared to the pure zeolite cases, which appears to be one of the two unique characteristics of the Ag-loaded catalysts. Ag/HMOR catalyst showed the highest performance since it gives the highest amount of cooking gas (at an apparently-high amount of propane with a considerable amount of C₄ hydrocarbons). However, unlike noble metals, all Ag catalysts seemed to give heavier oils than the unloaded catalysts. Nevertheless, another unique characteristic of the Ag catalysts is that they enhance the sulfur removal from oils. Pyrolytic oil obtained from using no catalyst contained about 1.38% of sulfur. The use of pure zeolites dramatically decreased the amount of sulfur in the oil products as compared to the non-catalytic case. All unloaded zeolites decreased sulfur concentration from 1.38% to 0.95%. All Ag-loaded zeolites further decreased sulfur in the oil. For example, Ag/HMOR catalyst showed a high performance in sulfur removal capacity. It can decrease from 1.38 wt% to 0.75 wt% of sulfur as compared to the non-catalytic case.

(e) Rh-loaded catalysts

Apart from Ru and Ag, Rh metal appears to be one of the outstanding gas producing catalysts for tire pyrolysis. Similar to Pt/HY, the highest gas yield is obtained when Rh/HY is used as catalyst. The gas profiles of Rh-loaded catalysts were similar to those of Ru- and Ag-loaded catalysts. Two distinguished observations from using Rh-loaded catalysts were that they greatly increased methane and propylene contents and yields. The yields of all other light gases (up to C₄s) were greatly improved when Rh-loaded catalysts were used, which was also found similar to Ag-loaded catalysts. Moreover, Rh/HY appears to the most



outstanding one among the Rh-loaded catalysts. Moreover, for oil production, Rh/HY gave the most distinctive results; that is, it was the only one among all Rh-loaded catalysts that enhanced the naphtha production as well as the gas production. Like Ag catalysts, Rh catalysts behaved differently among themselves, depending on which zeolite was used as the support. However, one distinguished outcome that all Rh-loaded catalysts gave in common was that they improved mono-aromatic content greatly to almost 20% in oils, and this distinctive outcome has not been found so far with using other metals loaded on the same parent zeolites. In fact, Rh loaded on all tested zeolites further increased light olefins and mono-aromatic productions as compared to the parent zeolites. For instance, Rh/HY increased about twice as much light olefins production as HY zeolite alone can, and it gives the highest olefins among all Rh-loaded catalysts. Outstanding activity of Rh catalysts is the sulfur removal ability. The Rh catalysts gave as low as 0.75 – 0.86% S in oil.

(f) Re-loaded catalysts

All Re-loaded catalysts can improve the gas yield by 2% (from HMOR's) to 10% (from HY's) in the expense of the decreases in oil yields in the similar proportions. Re seems to be the least active catalyst for cracking in general regardless of the type of support. The gas profiles of Re-loaded catalysts were somewhat similar to those of Ru-, Ag- and Rh-loaded catalysts. Similar to Rh catalysts, two distinguished observations from using Re-loaded catalysts were that they significantly increased methane and propylene contents and yields, but not as much as those of Rh-loaded catalysts. Similar to Ag and Rh catalysts, all Re catalysts, except Re/HY, seemed to give heavier oils. Both Re/HBETA and Re/HMOR decreased the light petroleum fractions (full range naphtha) whereas the kerosene fraction was increased for all Re-loaded catalysts, which was in this case similar to those of Ag-loaded catalysts. It seems that the naphtha and light gas oil are converted to kerosene fraction. Re/HBETA and Re/HY also appeared to follow the same explanation. Like Rh/HY, Re/HY moreover gave the most distinctive results; that is, it was the only one among all Re-loaded catalysts that enhanced the naphtha production but not as much as Rh/HY. Also, similar to Ag and Rh catalysts, Re catalysts behaved differently, depending on which zeolite was used as the support. Furthermore, Re-loaded catalysts decreased saturated HCs and then increased mono-aromatics and polar-aromatics, which are the distinguished outcomes found similar to those of all Rh-loaded catalysts. Re-loaded catalysts,

however, improve mono-aromatic content greatly to around 17-18% in oils, which is slightly less than Rh-loaded catalysts. These distinctive outcomes of Re- and Rh-loaded catalysts have not been found so far with using other metals loaded on the same parent zeolites. Since Re tends to be a selective catalyst for aromatization, it is a rational explanation of why mono-aromatics or other aromatics can be enhanced by Re loading.

12.2 Comparison of non-noble catalysts with noble ones

Based the current findings discussed in Chapters 4 - 11, the activity of a non-noble promoted catalyst tested in this work can be comparable with that of noble-promoted one(s), previously tested under the TRF support, in various issues as listed in **Table 1**. The non-noble metal-promoted catalysts listed in the table therefore can be used to substitute the noble-metal promoted catalysts in each particular comparison item.

Table 1 Summary of metals with comparable activity

#	Comparison items	Metals with comparable activity	
		Noble metals	Non-noble metals
1	Light naphtha production	Pt, Pd, and/or Ru	Fe, Co, Zn
2	Poly-aromatic reduction	Pt and/or Ru	Ni*
3	Light olefins production	Ru, Ag, Rh, and/or Re	Co
4	LPG production	Ag, Rh, and/or Re	Pure zeolites, Cu**
5	Mixed C4s production	Pt, Ag, and/or Rh	Co
6	Mono-aromatics production (BTEx or petrochemicals)	Ru, Rh, and/or Re	Fe, Co, Ni, Cu, Zn
7	Sulfur reduction from oil	Rh, Ag	Cu, Zn, Ni, NiMo, NiMoS

*depending on the support

**Only Cu/HMOR

It is worth being noted hereby that the outstanding activities of non-noble metal-promoted catalysts that overcome those of the noble metal ones are the



mono-aromatics or petrochemicals production, and sulfur removal ability. All tested non-noble metal catalysts can outstandingly enhance petrochemicals formation in the tire-derived oil. Zn is the best catalyst to reduce sulfur in oil (0.695 – 0.78% S). Moreover, Cu is the second best non-noble metal that can remove sulfur from the oil to the extent as high as what the Rh catalysts can do (around 0.75 – 0.86% S in oil, depending on the support). However, the sulfided form of metals, such as NiMoS, can further suppress the sulfur content in oil to the extent as low as 0.6%.



Chapter 13

Outputs

1. ผลงานวิจัยที่ตีพิมพ์ในวารสารวิชาการระดับนานาชาติ

ผลงานตีพิมพ์ในฐาน ISI

1.1 Suttipong Muenpol, Ritthichai Yuwapornpanit, and **Sirirat Jitkarnka***, “Valuable Petrochemicals, Petroleum Fractions, and Sulfur Compounds in Oils Derived from Waste Tyre Pyrolysis Using Five Commercial Zeolites as Catalysts: Impact of zeolite properties”, Clean Technologies and Environmental Policy, **17** (2015) 1149-1159. IF (2014) = 1.934 (เอกสารประกอบ 1)

1.2 Ritthichai Yuwapornpanit and **Sirirat Jitkarnka***, “Cu-doped catalysts and their impacts on tire-derived oil and sulfur removal”, Journal of Analytical and Applied Pyrolysis, **111** (2015) 200-208. IF (2015) = 3.652 (เอกสารประกอบ 2)

1.3 Suttipong Muenpol and **Sirirat Jitkarnka***, “Effects of Fe supported on zeolites on structures of hydrocarbon compounds and petrochemicals in waste tire-derived pyrolysis oils”, Journal of Analytical and Applied Pyrolysis, **117** (2016) 147–156. IF (2015) = 3.652 (เอกสารประกอบ 3)

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ผลงานตีพิมพ์ในฐาน Scopus

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2. การไปเสนอผลงานในที่ประชุมวิชาการ

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3. รางวัลที่ได้รับและการนำผลงานไปใช้ประโยชน์

รางวัลที่ได้รับ

ดิฉันได้รับรางวัล PTIT Scholar Award ประจำปี 2558 – 2559 จากสถาบันปิโตรเลียมแห่งประเทศไทย

(ดูรายละเอียดของรางวัล: <http://www.ptit.org/index.php/About.Award/PTIT-Awards>) (เอกสารประกอบ 11)

การนำผลงานไปใช้ประโยชน์

วิทยานิพนธ์ระดับปริญญาโทของนิสิตในที่ปรึกษาภายใต้โครงการฯ ซึ่งก็คือ นางสาว ภาสณิ แสงอารยะกุล เรื่อง “กัมมะถันในน้ำมันจากยางรถยนต์หมดสภาพและตัวเร่งปฏิกิริยาสำหรับลดกัมมะถัน” ผ่านการคัดเลือกตามโครงการคัดเลือกวิทยานิพนธ์ระดับปริญญาโทและระดับปริญญาเอก เพื่อสนับสนุนข้อมูลทางวิชาการให้แก่วุฒิสภา ประจำปี 2556 โดยดิฉันในฐานะอาจารย์ที่ปรึกษาวิทยานิพนธ์ ซึ่งเป็นหัวหน้าโครงการฯ ก็ได้รับเกียรติบัตรจากคณะกรรมการวิจัยและพัฒนาของวุฒิสภา ประกาศเกียรติคุณเมื่อวันที่ 20 พฤษภาคม 2557 ที่วุฒิสภา (เอกสารประกอบ 12)





Valuable petrochemicals, petroleum fractions, and sulfur compounds in oils derived from waste tyre pyrolysis using five commercial zeolites as catalysts: impact of zeolite properties

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Abstract Valuable petrochemicals such as benzene, toluene, and xylenes have been observed in waste tyre-derived oils, indicating that waste tyre exhibits its potential to be used for an alternative source for sustainably producing petrochemicals. However, without a catalyst, such chemicals cannot be produced in a high amount. Sulfur compounds causing environmental problems and the low quality of oils were also found in tyre-derived oils. In waste tyre pyrolysis, zeolites that have been used very often to improve the quality of oil are HZSM-5 and HY, owing to their cracking and single-ring aromatics-producing abilities. Some other zeolites have been also employed occasionally, but the effects of zeolite properties on the hydrocarbon species and sulfur compounds in oils have not been explained clearly. The objective of this work was therefore to investigate the effects of zeolite properties, that are, acidity/basicity, pore channel structure, pore size, and Si/Al ratio on hydrocarbon species in pyrolysis products, especially valuable C6–C8 petrochemicals and sulfur compounds. The oils were analyzed using SIMDIST-GC for petroleum fractions and using a GC × GC–TOF/MS for valuable petrochemicals and sulfur-containing compounds. The analysis of the results from using five zeolites indicated that, for high production of valuable C6–C8 petrochemicals from waste tyre pyrolysis, a catalyst must (a) possess acid sites, rather than basic ones,

that have high enough strength for cracking, which can result in high production of naphtha fraction and (b) have a complex channel structure with a large enough pore size (at least ~ 7 Å) that allows molecules to stay inside at a long contact time. In addition, high acid strength is more preferred to high acid density for high production of valuable C6–C8 petrochemicals, but high acid density is more preferred for production of oil with low sulfur content.

Keywords Pyrolysis · Zeolite · Waste tyre · Hydrocarbon · Petrochemicals

Introduction

Olefins and aromatic hydrocarbons are important petrochemicals, conventionally derived from petroleum. Light olefins are produced from fluid catalytic cracking unit in oil refineries and steam cracking of natural gas, whereas useful aromatic hydrocarbons such as benzene, toluene, and xylenes are derived from petroleum-based naphtha and used as a wide range of raw materials in petrochemical industry. For sustainable future petrochemical industry, various renewable raw materials such as biomass or wastes have gained great intention from society, governments, and policy makers since they cannot only replace petroleum-based raw materials (Hancsók et al. 2014) by the time of scarcity, but also the replacement can reduce greenhouse gasses (Fiksel et al. 2011). With or without a catalyst, waste tyres (Srogi 2008) and waste plastics (Sakaki et al. 2014) are also hydrocarbon-based materials, which exhibit potential to be used as an unconventional source for liquid fuel and petrochemical productions. At early stages during 1990s, pyrolytic oil from pyrolysis of waste tyre was examined mostly for uses as fuels, but later it was found to contain valuable

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hydrocarbons. For example, Islam et al. (2008) analyzed liquid products from waste motorcycle tyre pyrolysis and found that pyrolytic oils were complex mixtures, which consisted of aliphatic and aromatic compounds. Pakdel et al. (2001) found dl-limonene in waste tyre-derived oil, and later it was suggested that the pyrolytic oil can be used as chemical feedstocks for aromatic production (Banar et al. 2012). Moreover, pyrolytic oil also contains a considerable amount of sulfur-containing compounds, such as benzothiophene, thiophene, and their derivatives (Williams and Bottrill 1995). However, the formation of these compounds during pyrolysis still remains unelucidated.

In pyrolysis of waste plastics or tyres, an acid catalyst is needed for either accelerating degradation or enhancing product selectivity. Silica–alumina catalyst is the simplest catalyst for these purposes. For instance, in the catalytic degradation of mixed polyethylene and polypropylene using a silica–alumina catalyst, the conversion greatly increased in association with the improved yield of gasoline (Roozbehani et al. 2015). When employed in polystyrene pyrolysis, the catalyst was found to greatly enhance the selectivity of styrene monomer in the product (Moqadam et al. 2015). HZSM-5 is the most frequently employed zeolite in pyrolysis of waste materials; for example, it was found to change product compositions and distribution, depending on the type of plastics and pyrolysis temperature (Mikulec and Vrbova 2008). Common zeolites that have been tested in waste tyre pyrolysis are, for example, HZSM-5, HY, HMOR, and HBETA. Briefly, HZSM-5 with the zigzag 3D channel structure of 5.3×5.6 Å pore size and Y zeolites with also a 3D structure (FAU: faujasite) but pore diameter of 7.4 Å have been frequently employed in pyrolysis in order to investigate the effects of catalysts on the composition of tyre-derived oils (Olazar et al. 2008), especially aromatics (Williams and Brindle 2003a) and single-ring aromatics (Williams and Brindle 2003b). Williams and Brindle (2002) studied the influence of two different pore size catalysts, Y-type zeolite (7.8 Å) and ZSM-5 (5.6 Å), and found that Y-type zeolite with larger pore size and higher surface acidity yielded higher aromatic compounds but lower liquid yields than ZSM-5 catalyst. Later in 2003, they tried to maximize the single-ring aromatics from scrap tyres pyrolysis using three types of catalysts (ZSM-5 and two Y zeolites) and reported that Y zeolite with a lower Si/Al ratio gave a higher yield of all five aromatics (benzene, toluene, *m/p/o*-xylenes, or BTX) than the one with a higher ratio, confirming that higher surface acidity resulted in higher single-ring aromatic production. Moreover, more results from the pyrolysis of waste tyre using USY and ZSM-5 also confirmed the higher concentrations of BTX (Boxiong et al. 2007a) and the lower oil yield achieved by USY zeolite (Boxiong et al. 2007b).

KL zeolite is considered as a basic zeolite with a 1D straight-channel structure of 12-membered rings and a pore

opening of 7.1 Å in diameter. Recently, KL has been used as a catalyst for waste tyre pyrolysis and found to enhance mono-aromatics with a significant decrease of di-aromatics and terpenes in the tyre-derived oil (Pithakratanayothin and Jitkarnka 2014). Additionally, BETA zeolite is a kind of high-silica zeolites with a 3D straight-channel system and a pore size of 7.6×6.4 Å, whereas HMOR zeolite is a moderate acidic zeolite that has large pore size with an opening of 6.5×7.0 Å. HMOR zeolite is considered as 1D straight-channel structure with 12-membered rings. Dũng et al. (2009) used HBeta and HMOR as the supports for Pt in waste tyre pyrolysis and found that HBeta exhibited higher activity for polar-aromatic reduction as compared to HMOR, which was ascribed to its higher medium and strong acid site density, smaller particle size, and 3D-structure. Furthermore, Muenpol and Jitkarnka (2014) have investigated the effect of pore channel structure on the hydrocarbon compounds and petrochemicals in waste tyre-derived oils using HMOR and HBeta. It was reported that HBeta gave the higher amount of aromatics than HMOR and the lower amounts of olefins and naphthenes than HMOR. It can be explained that the complex pore of HBeta converted more olefins and naphthenes to aromatics inside the pore than the straight pore of HMOR. In addition, these two zeolites can reduce sulfur in oils, and the species of sulfur were different. Moreover, both HBeta and HMOR catalysts caused the increment in the group of benzothiophenes and the reduction in the group of benzothiazoles.

According to the literature reviews, no study has been intensively focused on the impacts of zeolytic support properties on the production of useful aromatic petrochemicals (C6–C8s) and the species of sulfur compounds in waste tyre-derived oil. Thus, in this work, the effects of zeolites properties, that are, acidity or basicity (using HMOR vs. KL), pore channel structure (using HMOR vs. HBeta), pore size (using HBeta vs. HZSM-5), and acid strength or Si/Al ratio (using HY and HBeta) on the production of useful aromatic petrochemicals (C6–C8s) and the species of sulfur compounds in waste tyre-derived oils were specifically investigated. In analysis, since such valuable petrochemicals mostly are components in naphtha fraction, the activities on cracking, mono-aromatics production, and sulfur removal were emphasized.

Experimental

Catalyst preparation and characterization

KL, HMOR, HBeta, HZSM-5, and HY were obtained from Tosoh Company in Singapore. The properties of the zeolites are tabulated in Table 1. In order to remove impurity

from zeolites, KL, HMOR, and HZSM-5 zeolites were calcined at 500 °C for 3 h with the heating rate of 10 °C/min, and HY was calcined at 500 °C for 3 h with the heating rate of 5 °C/min, while HBeta was calcined at 600 °C for 5 h with 2 °C/min. Calcination procedures were made different because the purchased zeolites were obtained from the manufacturer with different forms of cations. After that, zeolite powders were pelletized, crushed, and sieved into the particle size range of 40–60 mesh.

X-ray diffraction patterns were taken using a Bruker X-ray diffractometer system equipped with a 2.2 kW Cu anode in a long fine focus ceramic X-ray tube for generating a CuK α radiation (1.5405 Å). The detector scanned for the diffractive peaks from the sample as a function of 2θ by starting at the 5°–100° (2θ) range and a scan speed of 5°(2θ)/min. The specific surface area and pore volume were characterized using Thermo Finnigan/Sorptomatic 1990 equipment. In addition, Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis) was used to determine the amount of coke deposited on spent catalysts. The temperature was ramped to 900 °C with a heating rate of 10 °C/min. Moreover, sulfur deposited on a catalyst surface was determined using LECO®Elemental Analyzer (TruSpec®S).

Pyrolysis of waste tyre

The pyrolysis reaction was operated under the process as reported in Dũng et al. (2009). Briefly, there were 2 zones of the pyrolysis reactor, which are catalytic zone (the upper zone) and pyrolytic zone (the lower zone). Firstly, 30 g of the waste tyre (Bridgestone TURANZA GR-80) with sizes in the range of 20–40 mesh was loaded into the lower zone, and 7.5 g of catalyst with a pellet size range of 40–60 mesh was loaded to the catalytic zone. Then, the pyrolysis zone was heated with the rate of 10 °C/min from room temperature to 500 °C. Once reached, the final temperature was kept for 120 min. The temperature of pyrolytic zone was controlled at 350 °C. The flow rate of N₂ was controlled at 30 ml/min and used as a carrier gas of the pyrolysis products to condensers and a gas sampling bag. These condensers were placed into an ice–salt bath in order to collect the liquid product. A gas sampling bag collected the incondensable products.

Product analysis

The liquid products were dissolved in *n*-pentane (40:1 mass ratio of oil/*n*-pentane) to precipitate asphaltene, and then asphaltene was filtered using polyamide membrane (pore size: 0.45 μ m). After that, the maltenes (the obtained oils after asphaltene separation) were analyzed for true boiling point curve and petroleum fractions using a Varian GC-3800 Simulated Distillation Gas Chromatography (SIM-DIST-GC) conformed to the ASTM D-2887. Petroleum fractions in maltenes are classified according to boiling point distillation conformed with ASTM D-2887 into five fractions: full-range naphtha (<200 °C), kerosene (200–250 °C), light gas oil (250–300 °C), heavy gas oil (300–370 °C), and long residue (>370 °C). Moreover, the chemical compositions of maltenes were analyzed using a two-dimensional Gas Chromatography with Time of Flight Mass Spectrometer (GC $\times$ GC-TOF/MS) equipped with a non-polar Rtx®-5Sil MS (1.10 m $\times$ 0.25 mm ID $\times$ 0.25 μ m film thickness) and Rxi®-17 MS (1.10 m $\times$ 0.10 mm ID $\times$ 0.10 μ m film thickness) as the first and second columns, respectively. The gas products were analyzed for their compositions using a Gas Chromatography (GC-FID), Agilent Technologies 6890 Network GC system, equipped with HP-PLOT Q column (30 m $\times$ 0.32 mm ID $\times$ 20 μ m film thickness). In addition, an LECO®Elemental Analyzer (TruSpec®S) was also used to analyze the sulfur content in shredded tyre, oil, and solid products, while sulfur content in gas products was calculated by mass balance.

Results and discussion

The catalyst properties obtained from surface area analyzer of HBeta, HMOR, HZSM-5, HY, and KL zeolites are revealed in Table 2. Powder XRD technique confirmed the crystallinity and the types of the zeolites.

Overall performance of the zeolites

All batches of pyrolysis runs gave a very similar char yield of around 41 wt%. The yields of oil and gas products are

Table 1 Properties of zeolites

Zeolite	Pore size (Å)	Channel system	Membered ring	Si/Al ratio
KL	7.1	1D	12	3
HMOR	6.5 $\times$ 7.0	1D	12	9.5
HBeta	6.4 $\times$ 7.6	3D	12	13.5
HZSM-5	5.3 $\times$ 5.6	3D	10	15
HY	7.4	3D	12	7.5

not significantly different (see Table 3) for all zeolites. Using acid zeolites, except HMOR, the production of mixed C4s is significantly enhanced with the suppression of ethylene and propylene production as illustrated in Table 4. Moreover, the full-range naphtha content in oil is also enhanced with the use of all acid zeolites as shown in Table 5, indicating their ability in cracking. Additionally, the amounts of overall “valuable petrochemicals” (hereby, focused on benzene, toluene, xylenes, styrene, cyclohexane, and cumene) in maltenes are shown in Table 6. It can be ranked as HBeta (10.8 wt%) > HMOR (2.32 wt%) > the non-catalyst case (1.57 wt%) > KL (0.580 wt%). Table 7 lists the sulfur content on spent catalysts and in oils obtained from using all catalysts. In general, the zeolites can reduce sulfur in oils by around 7–19.4 %. Next, the results obtained from each pair of zeolites were analyzed in order to study the effects of acidity/basicity (HMOR vs. KL), pore channel structure (HMOR vs. HBeta), pore size (HBeta vs. HZSM-5), and Si/Al ratio (HBeta vs. HY). Since valuable petrochemicals are mostly aromatic components in naphtha fraction, the performances of the zeolites on cracking, mono-aromatics production, and sulfur removal were focused in analysis. The details are discussed in the next following sections.

Comparison between acidic and basic zeolites

The effects of acid properties of zeolites are discussed in this section, which HMOR and KL were chosen for comparison to eliminate the effects of pore size, pore dimension, and pore structure, since both zeolites have the same 1D pore channel structure. It can be observed from Table 5 that KL does not enhance full-range naphtha but increases kerosene fraction, whereas HMOR can increase the amount of full-range naphtha to 31.7 wt% in oil, and also decreases all other heavier fractions. Thus, apparently the acidic zeolite possesses better cracking ability than the basic one.

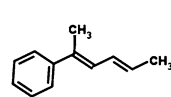
The chemical components in oils are classified into seven groups: paraffins, olefins, naphthenes, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics, as illustrated in Fig. 1a. The results exhibit that HMOR gives a slightly lower concentration of paraffins, olefins, naphthenes, and poly-aromatics than KL. It can be

Table 3 Yield (wt%) of products from tyre pyrolysis

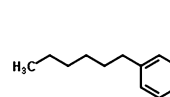
Catalyst	Yield (wt%)			
	Gas	Liquid	Solid	Coke
Non-catalyst	11.6	46.0	42.4	0.00
KL	12.2	43.5	41.5	2.79
HMOR	11.9	43.8	41.6	2.60
HBeta	9.62	43.3	41.6	5.41
HZSM-5	13.2	43.1	41.7	1.90
HY	10.8	42.6	42.2	4.49

suggested that olefins and naphthenes, produced by thermal cracking, are further converted to aromatics via carbenium ions generated on the acid catalyst via aromatization and Diels–Alder reactions (Meng et al. 2013), which is also confirmed by the reduction of light olefins (ethylene and propylene) in the gas product (see Table 4). The mono-aromatics content in oil is more greatly enhanced with using HMOR than KL. Therefore, it can possibly be explained that the formation of mono-aromatics can occur in two pathways: (a) aromatization of olefins and naphthenes for an acidic catalyst and (b) ring opening of poly-aromatics for both acidic and basic zeolites.

Moreover, Fig. 1b shows that HMOR has the potential to produce more total petrochemicals (26 wt% in gasoline) than KL (12 wt% in gasoline). HMOR also enhances the amount of styrene with the suppression of ethylbenzene and benzene. Owing to the acid sites on HMOR, styrene might be produced directly from (a) cracking of tyre molecules, (b) dehydrogenation of ethylbenzene, and (c) trans-alkylation reaction of benzene with an olefin, resulting in the increasing of styrene (Sudha et al. 2007). On the other hand, KL increases mono-aromatics production, but does not enhance the formation of total valuable petrochemicals. It can be explained that KL produces mono-aromatics with longer chains; for instance, it was observed that other mono-aromatic species such as 1-methylpenta-1,3-dienyl benzene, hexylbenzene, and 3-phenyl-2-pentene, as depicted below, are significantly enhanced. In conclusion, the acidic zeolite does not only give light liquid products, but also gives more valuable hydrocarbons than the basic zeolite.



1-methylpenta-1, 3-dienyl benzene



hexylbenzene



3-phenyl-2-pentene

Table 2 Surface and pore volume of catalysts

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Median pore width (Å)
KL	218	0.113	7.08
HMOR	394	0.199	8.42
HBeta	539	0.257	8.35
HZSM-5	545	0.189	5.84
HY	515	0.266	8.37

From Table 7, it can be seen that KL has slightly better sulfur-in-oil removal performance than HMOR, and possibly KL is a base that can better adsorb acidic sulfur compounds. Moreover, the sulfur-containing compounds in

Table 4 Composition (wt%) of gaseous products (H₂-free basis) obtained from using various zeolites in waste tyre pyrolysis

Catalyst	Methane	Ethylene	Ethane	Propylene	Propane	Mixed-C ₄	Mixed-C ₅
Non-catalyst	20.3	9.38	15.9	12.2	9.06	19.6	13.5
KL	19.5	6.70	15.9	12.4	9.13	19.9	16.4
HMOR	18.2	4.73	14.9	10.6	16.7	19.4	15.5
HBeta	14.8	6.31	11.0	11.9	8.98	29.2	17.8
HZSM-5	13.6	5.20	10.7	10.5	19.7	26.5	13.7
HY	18.0	5.94	13.8	10.4	9.87	25.4	16.7

Table 5 Petroleum fraction (wt%) in tyre-derived oils

Catalysts	Fractions (wt%) in tyre-derived oil				
	Full-range naphtha	Kerosene	Light gas oil	Heavy gas oil	Long residue
Non-catalyst	22.1	23.4	20.1	18.3	16.2
HMOR	31.7	21.5	16.9	17.5	12.5
KL	22.1	27.9	19.2	15.4	15.5
HBeta	38.6	22.0	19.1	10.1	10.4
HZSM-5	28.2	21.5	17.3	18.8	14.3
HY	32.9	20.6	16.8	16.4	13.4

Table 6 Petrochemicals obtained from waste tyre pyrolysis (wt% in maltene)

Chemicals	Catalysts					
	Non-catalyst	KL	HMOR	HBeta	HZSM-5	HY
Benzene	0.430	0.265	0.124	4.81	–	2.50
Toluene	0.0274	0.00497	0.184	0.917	0.196	2.66
Ethylbenzene	0.833	0.102	0.408	3.31	0.258	0.367
<i>m</i> -Xylene	–	–	0.185	–	0.0981	–
<i>o</i> -Xylene	–	–	–	0.161	–	0.260
<i>p</i> -Xylene	–	–	–	0.129	0.0304	0.376
Styrene	0.189	0.125	1.31	0.320	0.207	0.523
Cyclohexane	0.0239	–	–	1.05	3.46	0.470
Cumene	0.0660	0.0827	0.105	0.0771	0.0348	0.174
Total	1.57	0.580	2.32	10.8	4.28	7.33

Table 7 Sulfur content on spent catalysts and in oils obtained from using all catalysts

Sample	Sulfur (wt%)					
	Non-cat.	KL	HMOR	HBeta	HZSM-5	HY
Spent catalyst	–	0.25	0.18	0.41	0.27	0.273
Oil	1.17	1.02	1.08	1.10	1.08	0.943

oils are classified into five groups: thiophenes, benzothiophenes, dibenzothiophenes, benzothiazoles, and a mixture of heteroatom (O and/or N)-containing sulfur compound, or so-called “others” as shown in Fig. 2. It can be seen that both zeolites decrease benzothiazoles, especially HMOR, and heteroatom-containing sulfur molecules. It can be suggested that the acid sites on HMOR (H⁺) are stronger in

attacking the C–N, C=N, and C–S bonds in a benzothiazole molecule than the base sites on KL (K⁺) thus, benzothiazoles are possibly into hydrocarbons better than KL (a base catalyst). Moreover, benzothiazoles possibly rearrange to form benzothiophenes in the case of KL since the yield of benzothiophenes increases with using KL, but slightly decreases with using HMOR. In summary, the acid zeolite gives better quality of oil, in terms of high petrochemicals content and the ease on further desulfurization, than the base one.

Comparison between two pore channel structures (1D and 3D) of zeolites

HMOR and HBeta zeolites have different pore channel structures, that are, 1D (HMOR) and 3D (HBeta) with no difference in pore size, which have been used to study the

Fig. 1 Compositions in tyre-derived oils obtained from KL and HMOR: **a** molecular composition in maltenes and **b** valuable petrochemicals in gasoline fractions

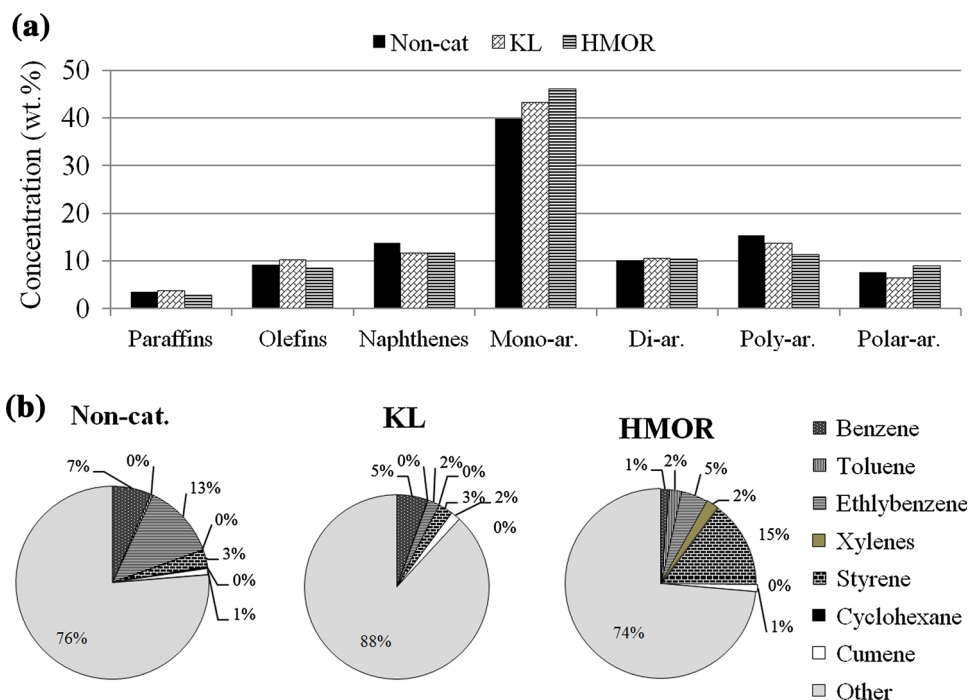
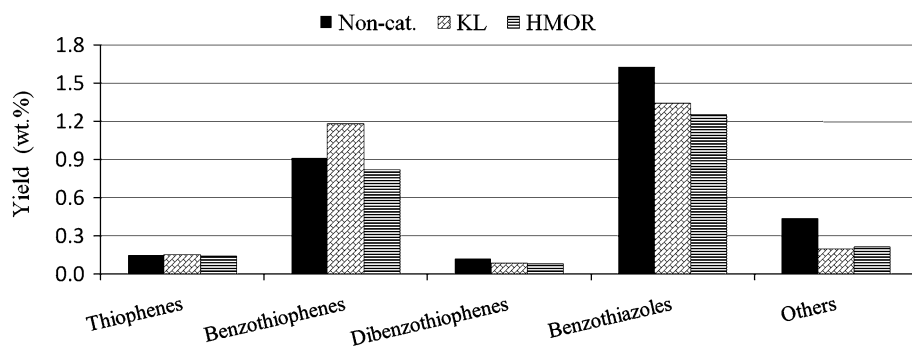


Fig. 2 Yields of sulfur-containing compounds in tyre-derived oils obtained from KL and HMOR



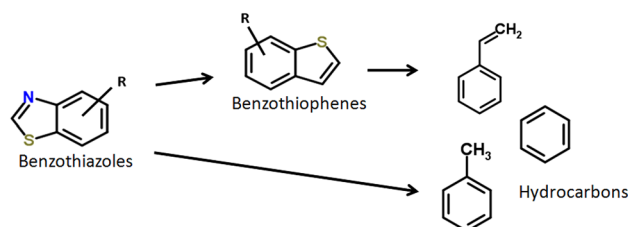
effect of pore channel on pyrolysis products (Muenpol and Jitkarnka 2014). The results can be summarized and further discussed in more detail as follows. HBeta gives a higher amount of the full-range naphtha and then a less amount of heavier fractions than HMOR (Table 5). Thus, it can be concluded that using HBeta results in lighter liquid product than using HMOR. It may be also possible that HBeta has a higher acid strength than HMOR (Düng et al. (2009), possibly due to the strain in the more complex 3D channel of HBeta. Moreover, the 3D pore channel allows molecules to stay inside the zeolite channel with a long residence time, and then heavy fractions can be cracked into light fractions more effectively than in the 1D pore channel. Additionally, HBeta gives the higher amount of total aromatics than HMOR and consequently gives the lower paraffins, olefins, and naphthenes contents than HMOR. It can be explained that aromatic compounds can be formed via Diels–Alder reaction of light olefins to cyclic

hydrocarbons, and subsequently aromatics are formed via condensation reaction (Cypres 1987). The pathway of reactions occurs via carbenium ion generation on an acid site; thus, HBeta with higher acid strength (Düng et al. 2009) can better generate carbenium ions that allow such reactions to occur more easily than HMOR. These are confirmed by the greater decreases in olefins and naphthenes in accordance with the greater increase of total aromatics, especially di-aromatics, in the oil in Fig. 3a, with using HBeta.

Valuable hydrocarbon compounds in the oils are shown in Fig. 3b. HBeta can produce petrochemicals of interest in a much higher concentration (61 wt% in gasoline) in the oil than HMOR (26 wt% in gasoline). Moreover, HBeta can produce a higher amount of benzene, ethylbenzene, toluene, and cyclohexane than HMOR. Moreover, a small amount of *o*-xylene and *p*-xylene are produced using HBeta, and *m*-xylene is produced using

HMOR. In addition, the amount of styrene sharply increases with using HMOR, and the amount of cumene is not significantly changed for all cases. It is possible that HBeta, with more complex channel structure that creates slightly higher acid strength (also slightly higher Si/Al ratio) than HMOR, can better catalyze the cyclization reaction of paraffins or olefins to form cyclic hydrocarbons such as cyclohexane and then convert to benzene via carbenium ion mechanism (Joshi and Thomson 2005). Moreover, both zeolites may catalyze trans-alkylation reaction of benzene with an olefin to styrene and ethylbenzene (Sudha et al. 2007).

Owing to its more complex 3D channel structure, HBeta results in a higher content of coke (Table 3) and sulfur compounds (Table 7) deposited on the spent catalyst than HMOR. Moreover, sulfur content in oils is reduced with using both catalysts, and HMOR gives slightly lower sulfur content in oils (1.08 wt%) than HBeta (1.10 wt%). However, it was found that benzothiophenes dramatically increased with using HBeta but insignificantly changed with using HMOR (Muenpol and Jitkarnka 2014). Moreover, benzothiazoles sharply decreased with using both catalysts, whereas the group of heteroatom (O and/or N)-containing sulfur compounds was reduced. It can be suggested that HMOR and HBeta possibly convert benzothiazoles and the others, possibly forming hydrocarbon compounds such as derivative of benzenes, or even non-aromatics, as illustrated below.

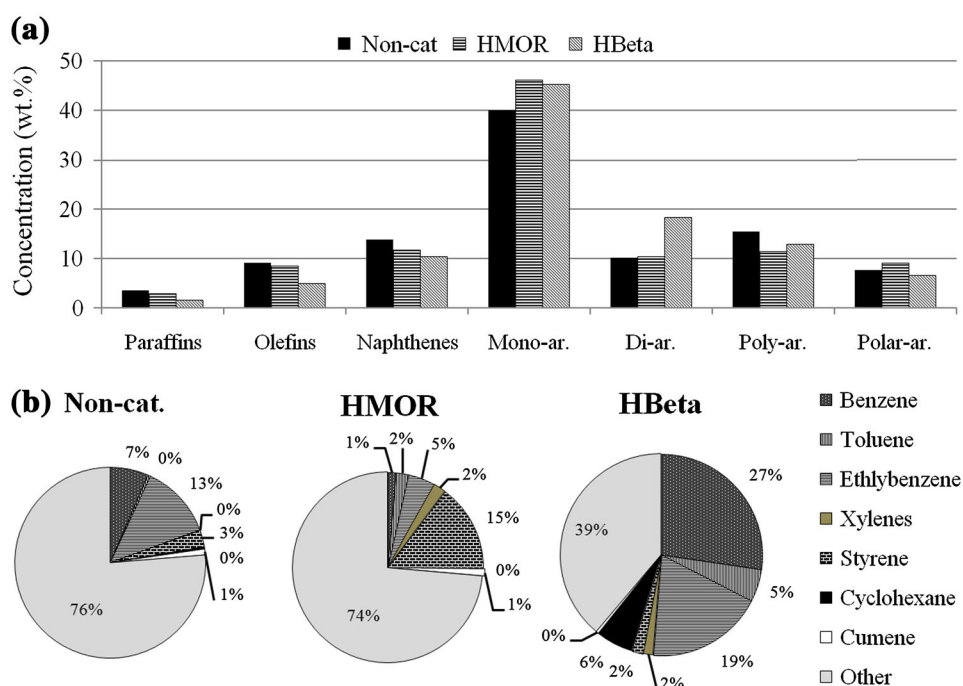


Unlike HMOR, HBeta possibly rearranges benzothiazoles to form benzothiophenes inside the zeolite channel. In addition, 3D pore channel of HBeta allows molecules to stay inside its channel with a longer residence time than 1D pore channel of HMOR, thus resulting in a high amount of benzothiophenes produced by HBeta, but not by HMOR. Moreover, since HMOR gives a less amount of benzothiophenes and dibenzothiophenes than HBeta, thus it means that the oil obtained from HMOR is easier to be further desulfurized than those from HBeta.

Comparison between two pore sizes of zeolites

For this part, the effect of pore size of zeolite is discussed by comparing the results obtained from using HZSM-5 and HBeta zeolites. Both of them are acidic zeolites with 3D pore channel. In addition, the Si/Al ratios of these zeolites are not significantly different, but they have a significant

Fig. 3 Compositions in tyre-derived oils obtained from HMOR and HBeta: **a** molecular composition in maltenes and **b** valuable petrochemicals in gasoline fractions



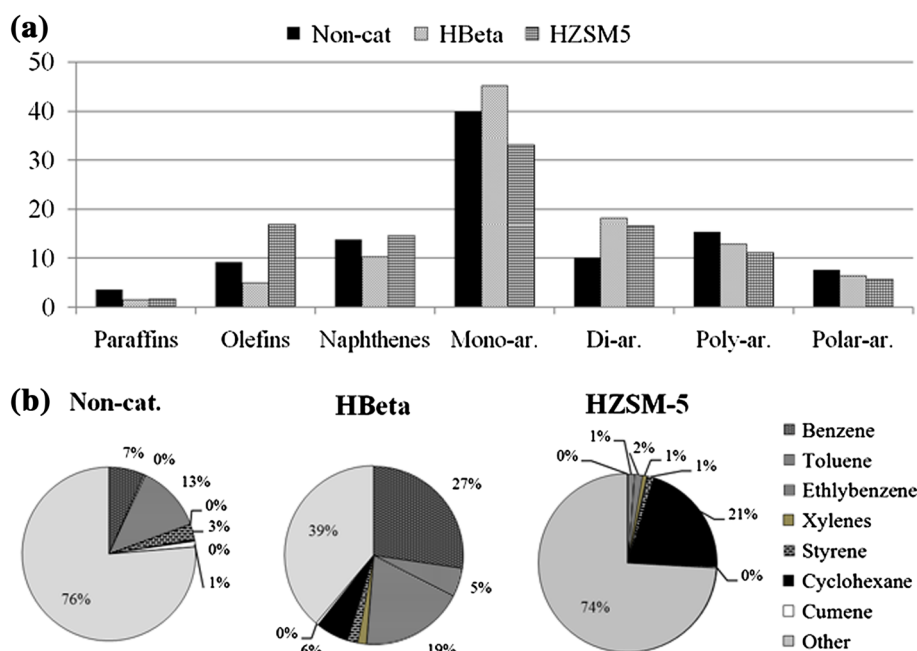
difference in pore size, that are, $5.3 \text{ \AA} \times 5.6 \text{ \AA}$ (HZSM-5) and $6.4 \text{ \AA} \times 7.6 \text{ \AA}$ (HBeta). As a result, HBeta exhibits a higher amount of full-range naphtha (38.6 wt%) than HZSM-5 (28.2 wt%), indicating that the large pore size of HBeta allows a higher amount of molecules to go inside the pore to be cracked than the medium pore size of HZSM-5. Figure 4a exhibits that using HBeta gives a higher amount of total aromatics as well as a lower amount of paraffins, olefins, and naphthenes than the non-catalytic pyrolysis. On the other hand, HZSM-5 can reduce the concentration of total aromatics and paraffins with the increase of olefins as compared to the non-catalytic pyrolysis. Moreover, the amount of naphthenes does not significantly change with using HZSM-5. It can be explained that the medium pore size of HZSM-5 allows a less amount of molecules to go inside the zeolite pore than the large pore of HBeta. Moreover, HZSM-5 has a lower pore volume ($0.1780 \text{ cm}^3/\text{g}$) than HBeta ($0.2570 \text{ cm}^3/\text{g}$), thus resulting in less chance in transformation of small olefins to cyclic hydrocarbons and aromatic hydrocarbons (Olazar et al. 2008), which is also confirmed by the high content of olefins in the oil in Fig. 4a. In addition, it can be seen that mono-aromatic hydrocarbons are enhanced with the use of HBeta, but suppressed with the use of HZSM-5. It can be explained that mono-aromatic molecules can pass into the medium pore size of HZSM-5 and then are converted to olefins. That is also the reason why HZSM-5 can a lot less produce valuable petrochemicals (26 wt% in gasoline), that are mostly mono-aromatics, than HBeta (61 wt% in gasoline) as depicted in Fig. 4b.

Among mono-aromatics, HBeta sharply increases the amount of benzene (4.81 wt% in gasoline) and

ethylbenzene (3.31 wt% in gasoline) and slightly increases toluene, whereas HZSM-5 does not produce benzene; however, it gives a high amount of cyclohexane and a small amount of ethylbenzene and toluene. It should be noted that HBeta gives a higher amount of valuable aromatics, such as benzene, ethylbenzene, and toluene, than HZSM-5. These observations agree with Roldán et al. (2004), who reported that the medium pore of HZSM-5 was inactive for the transformations of benzene and xylenes, whereas the larger pore of HBeta was active toward the reactions. It was due to medium pore zeolite that hinders the process through steric restriction in the pore (Roldán et al. 2004).

Moreover, the depositions of coke (Table 3) and sulfur (Table 7) on the spent HZSM-5 are lower than those on the spent HBeta, which is owed to the smaller pore size and pore volume of HZSM-5 (Table 2). HBeta and HZSM-5 slightly reduce sulfur in oils, and the difference in their ability on sulfur removal is not relevant. In addition, Fig. 5 illustrates that the larger pore of HBeta results in a higher amount of large S-compounds (benzothiophenes, dibenzothiophenes, and benzothiazoles) than the smaller pore of HZSM-5. In addition, benzothiazoles sharply decrease with using both catalysts, especially HZSM-5, whereas benzothiophenes increase with using HBeta and insignificantly change with using HZSM-5. It can be explained that HZSM-5 and HBeta possibly convert benzothiazoles and the other sulfur compounds to hydrocarbon compounds such as benzene derivatives. In addition, the medium pore of HZSM-5 has less capacity to form large compounds, such as benzothiophenes, dibenzothiophenes, and benzothiazoles, than the larger pore of HBeta since these

Fig. 4 Compositions in tyre-derived oils obtained from HBeta and HZSM-5: **a** molecular composition in maltenes and **b** valuable petrochemicals in gasoline fractions



groups of compounds are easier to be desulfurized on HZSM-5 than HBeta, based on the principle described in Cottrell (1958) and García-Cruz et al. (2008).

Comparison between two Si/Al ratios of Zeolites

With similar pore openings and pore structures, the results obtained from using HBETA (Si/Al = 13.5) and HY (Si/Al = 7.5) were compared to examine the effects of acid strength and density on the pyrolysis products. As a result, HBeta can more greatly enhance full-range naphtha fraction than HY (Table 5). Responsible by higher acid strength (higher Si/Al ratio), HBeta can produce lighter oil (higher full-range naphtha) than HY with lower acid strength (lower Si/Al ratio) because the higher acid strength can ease carbenium ions generation and lower reaction activation energies (Rigby and Frash 1997).

HY and HBeta catalysts increase the formations of mono- and di-aromatics, while the other groups (except polar-aromatics in the HY case) are decreased as shown in Fig. 6a. The results indicate that both catalysts can crack poly-aromatics and/or aromatize paraffins, olefins, and naphthenes to be mono- and di-aromatics. HY produces a slightly higher concentration of total aromatics than HBeta because HY has higher acid density with slightly higher pore volume and pore diameter, resulting in higher cyclization and aromatization (Olazar et al. 2008). Figure 6b depicted that even though HY can produce higher total mono-aromatics in the oil, the valuable mono-aromatics are produced in a lower concentration (55 wt% in gasoline) than those obtained from HBeta (61 wt% in gasoline). This observation indicates that the impact of acid strength is more pronounced in producing valuable petrochemicals than that of acid density. HY can produce a high amount of benzene (2.50 wt%) and toluene (2.66 wt%) in gasoline, while those of benzene (4.81 wt%) and ethylbenzene (3.31 wt%) are sharply produced by HBeta.

HBeta gives the higher sulfur content in the oil (Table 7) than HY, which indicates that high acid density is needed for high sulfur removal ability. Furthermore, Fig. 6b also shows that HBeta and HY sharply reduce benzothiazoles. However,

HY can more greatly reduce benzothiazoles than HBeta, in association with a sharp decrease in benzothiophenes. Thus, it can be concluded that high acid density is more essential for breaking a large number of C–N and C–S bonds in large molecules of benzothiazoles and benzothiophenes than high acid strength (Fig. 7).

Conclusions

To our knowledge, based on literature reviews, not so many types of zeolites have been employed in the catalytic pyrolysis of waste tyre. The most often used zeolites were Y and ZSM-5 zeolites. Furthermore, among articles reporting the uses of zeolites in tyre pyrolysis, only a few groups of researchers, namely Williams's and Boxiong's groups, were found to report the influence of particular Y or ZSM-5 zeolites on the formation of valuable hydrocarbons in tyre-derived oil (Boxiong et al. 2007a, b; Williams and Brindle 2003a). The knowledge on how zeolites affect the production of valuable aromatic hydrocarbons (i.e., benzene, toluene, xylenes, styrene, etc.) and the species of sulfur compounds in tyre-derived oil is limited for literature search. Therefore, in this work, five zeolites were used to investigate the effects of zeolite properties, that are, (a) acidity/basicity, (b) pore channel structure, (c) pore size, and (d) Si/Al ratio on hydrocarbon species and sulfur compounds in pyrolysis products. HMOR and KL were employed to study the effect of acidity/basicity. HMOR (1D pore channel) and HBeta (3D pore channel) were chosen to study the effect of pore channel. With the same 3D channel structure, HBeta ($7.6 \times 6.4 \text{ \AA}$) and HZSM-5 ($5.3 \times 5.6 \text{ \AA}$) were selected to study the effect of pore size. In addition, with 3D channel structures and similar pore size, but different Si/Al ratios, HY and HBeta were employed to study the impact of acid strength. The results showed that all of the zeolites can enhance the quality of the oils, petrochemical production, and sulfur removal from oils. Moreover, the amounts of such petrochemicals also increased when all zeolites (except KL zeolite) were used.

Fig. 5 Yields of sulfur-containing compounds in tyre-derived oils obtained from HBeta and HZSM-5

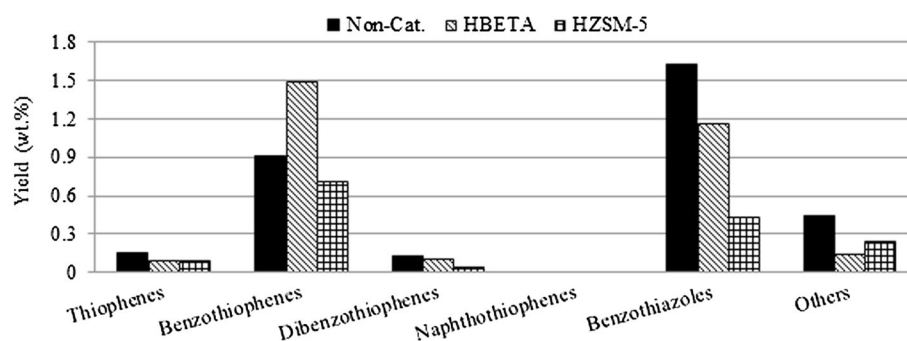


Fig. 6 Compositions in tyre-derived oils obtained from HBeta and HY: **a** molecular composition in maltenes and **b** valuable petrochemicals in gasoline fractions

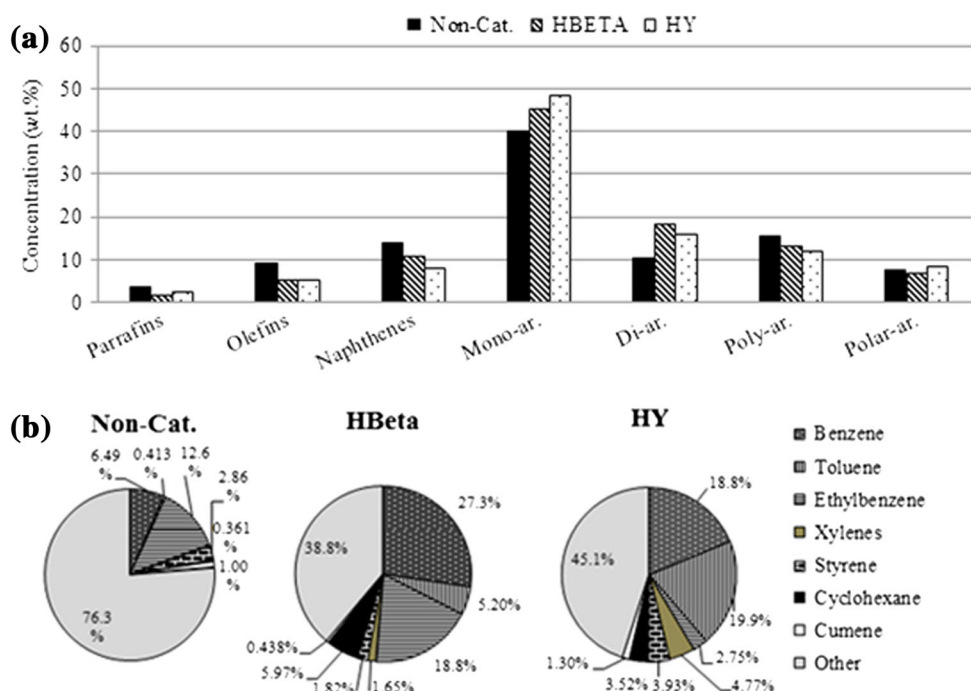
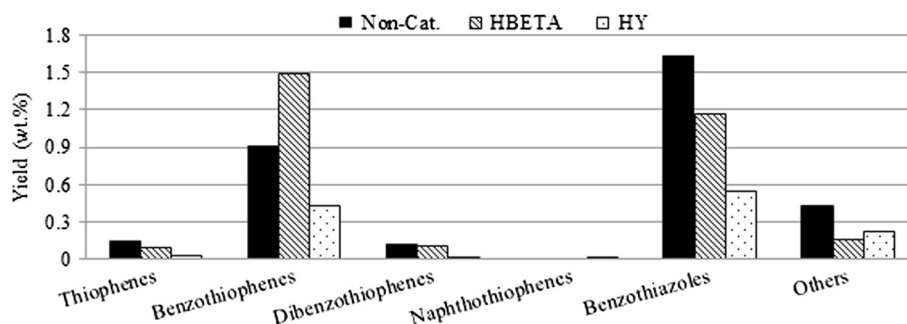


Fig. 7 Yields of sulfur-containing compounds in tyre-derived oils obtained from HBeta and HY



In the work of Boxiong et al. (2007a, b) and Williams and Brindle (2003a), tyre-derived oil was refined for the light fraction (<220 °C) prior to analysis using a GC–MS; therefore, the concentrations of valuable aromatics in the light fraction were reported. With the powerful GC × GC–TOF/MS machine employed in this work, the contents of each hydrocarbon species in tyre-derived oils were instead reported without having to refine the oils. The results can be summarized as follows:

- The acid catalyst (HMOR) was found to have a higher cracking activity than the basic one (KL) and found to produce greater petrochemicals production (a total of 2.32 % in oil) with more styrene, ethylbenzene, toluene, *m*-xylene, and cumene than KL (a total of 0.580 % in oil). However, KL seems to have better sulfur-removing ability (12.8 % removal) than HMOR (7.69 % removal).
- The pore channel structures affected the contact time of molecules to stay inside the pore. Owing to higher

contact time in the pore, 3D pore channel (HBeta) exhibited a better cracking ability and total petrochemicals production (10.8 % in tyre-derived oil) than 1D pore channel (HMOR) that gave only a total of 2.32 %.

- Moreover, pore size was found to control the size of obtained products. The large pore (HBeta) exhibited better cracking ability and total petrochemicals production (10.8 % in oil) than the medium pore (HZSM-5) that yielded 4.28 % in oil. Likewise, Williams and Brindle (2003a) compared the activity of ZSM-5 and Y zeolites in waste tyre pyrolysis, and they also made a similar conclusion that the ZSM-5 with a smaller pore size produced less single-ring aromatic hydrocarbons in the light fraction (<220 °C) of tyre-derived oil than the Y zeolite that have a larger pore size.
- Furthermore, with the same pore size and channel structure, HBeta with higher Si/Al ratio can produce lighter oil than HY with lower Si/Al ratio because the

higher acid strength of HBeta can provide the higher cracking ability. The valuable mono-aromatics (benzene, toluene, ethylbenzene, xylenes, styrene, cyclohexane, and cumene) produced from HY (7.33 % in oil) were lower than HBeta (10.8 % in oil), but HY had higher sulfur removal ability (19.4 % removal) than HBeta (5.98 % removal). Similarly, Boxiong et al. (2007a, b) compared the activity of ZSM-5 and Y zeolites that had the differences in both pore size and Si/Al ratio in waste tyre pyrolysis and concluded that the catalyst with a larger pore size and a lower Si/Al ratio (Y zeolite) was much more effective in the production of valuable aromatics (totally 41.25 % of benzene, toluene, ethylbenzene, and xylenes in the light fraction) than the ZSM-5 catalyst that yielded a total of 23.82 % in the light fraction (<220 °C) of oil.

It can be concluded that the use of zeolites increased the value of oil and also reduced sulfur content in oils for all cases. The sulfur-containing compounds in oils were classified into five groups: thiophenes, benzothiophenes, dibenzothiophenes, benzothiazoles, and a mixture of heteroatom (O and/or N)-containing sulfur compounds. All zeolites were found to decrease benzothiazoles and heteroatom (O and/or N)-containing sulfur compounds. In summary, a catalyst for high production of valuable C6–C8 petrochemicals with low sulfur content from waste tyre pyrolysis must be an acid catalyst, rather than a basic one, preferably with high strength, and have a complex channel structure with a large enough pore size (at least ~ 7 Å).

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Cu-doped catalysts and their impacts on tire-derived oil and sulfur removal



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ABSTRACT

Metal-loaded zeolites are potential catalysts for upgrading the quality and quantity of waste tire pyrolysis products. Acquired from metal and zeolite properties, the catalysts can exhibit multi-functions in catalysis, including hydrogenation, dehydrogenation, ring-opening, cracking, and aromatization. Cu is widely used in several applications such as selective hydrogenation of undesired unsaturated hydrocarbons in a mixed-C4 stream, and sulfur removal from liquid fuels. So, Cu was expected to be a promoter of zeolites for enhancing the quality of tire-derived oil in terms of sulfur removal and the increase in valuable petrochemicals in the oil. Therefore, the effect of Cu-support interaction on tire-derived oils, petrochemicals, and sulfur removal was studied using three types of zeolites (HBETA, HY and HMOR) as supports at a 5 wt% Cu loading. Catalytic pyrolysis of waste tire was operated in a bench reactor, and GC×GC-TOF/MS and SIMDIST-GC instruments were used to analyze the liquid products for chemical compositions and petroleum fractions, respectively. Sulfur in the pyrolysis products was determined by using an S-analyzer, whereas the gas composition was analyzed by using a GC-FID. As a result, all Cu-promoted catalysts can reduce more sulfur content in oils than their pure zeolites; therefore, Cu was found to enhance desulfurization of oils by converting sulfur compounds into thermodynamically stable forms on Cu. Furthermore, Cu-support interaction highly affected the sulfur removal from oils. Interestingly, it was revealed that valuable petrochemicals highly produced by Cu/HY were benzene, ethylbenzene and cyclohexane whereas Cu/HMOR highly produced benzene, toluene and ethylbenzene. Cu/HBETA highly yielded benzene and ethylbenzene in the oil. It can be observed that benzene and ethylbenzene are common petrochemicals highly produced by the Cu-loaded catalysts.

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1. Introduction

Two facts, known to the tire pyrolysis community, about tire-derived gas and oil are: (1) they contain a considerable amount of sulfur compounds, resulting in strong disturbing odors during uses, and (2) regardless of high aromatic contents, they may contain valuable petrochemicals such as light olefins, cooking gas, mixed-C4, limonenes, and C6–8 hydrocarbons. Indeed, sulfur in a whole tire (1.4 wt%) can distribute in each part of tire-derived products in different amounts of total sulfur in the system: 10.6 wt%, 48.8 wt%, and 40.6 wt% in gas, oil, and carbon black, respectively [1]. The gaseous

product contains 2.5–5.1 vol% H₂S while the oil and char contain 1.0–1.4 wt% S and 2.3–2.6 wt% S as reported in [2].

Generally, major sulfur species in gas products consist of H₂S, SO₂, COS and CS₂ [3,4]. Liquid products contain many types of sulfur containing compounds of which the main groups were thiophenes, benzothiazoles, benzothiophenes, dibenzothiophenes, and their alkylated derivatives while minor groups were also found such as naphthothiophenes, benzonaphthothiophenes, and their alkylated derivatives [1,5–7]. In the main groups of sulfur containing compounds, main species found in the reports as mentioned above were 2-methylthiophene, 3-methylthiophene, 2,3-dimethylthiophene, 2,5-dimethylthiophene, 2-ethylthiophene, dibenzothiophene, methylthiophenes, dimethylthiophenes and trimethylthiophenes. In the hydrodesulfurization process, sulfur-polycyclic aromatic hydrocarbons (PASH) can be removed, and petrochemicals can be produced such as toluene and styrene/ethylbenzene via

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hydrodesulfurization of 4,6-dimethylbenzothiophene [8] and benzothiophene [9], respectively. The reports indicated the potential of C6–C8 aromatics-containing tire-derived oils because PASH can be desulfurized, and then petrochemicals [8,9] such as toluene, ethylbenzene, and styrene can be formed.

Copper is an interesting metal because it is a non-noble metal, having a low cost for pyrolysis operation. Furthermore, Cu has potential usable properties beneficial to pyrolysis as well. Cu-loaded catalysts can be used in selective hydrogenation that can remove undesired compounds in the process. For example, Cu/SiO₂ catalyst was used to remove alkynes and butadiene in C4-stream by partial hydrogenation reaction converting into butenes [10]. Copper loading on hydrotalcite, malachite, SiO₂ and Al₂O₃ catalysts were used to convert propyne into propylene at high selectivity and undesired products at low selectivity [11]. Cu metal was widely used in hydrogenolysis reaction for alcohol production [12,13]. In other applications, Cu(I)-exchanged zeolites (HY, HY-Al₂O₃, or HBETA) can be used as an adsorbent for thiophene removal from liquid fuels as well [14–17]. Villarroel et al. [18] used the first row transition metals (Mn, Fe, Co, Ni, Cu and Zn) to promote Mo and W sulfides for sulfur removal of gas-oil containing 2700 ppm of sulfur compounds. They found that at an operating temperature of 325 °C the metal sulfides can generate spillover hydrogen on their surfaces, and then transfer hydrogen atoms to the surface of molybdenum or tungsten sulfides that can enhance hydrodesulfurization activity. Moreover, both quality and quantity of waste tire pyrolysis products can be enhanced by using catalysts. Due to their acid/basic properties and shape selectivity, zeolites were selected to be catalysts for enhancing the desired products.

For the catalytic pyrolysis of waste tire with the properties mentioned above, copper was expected to promote sulfur removal from oil and increase petrochemical products in oil as well. In this work, the effects of Cu doping on tire-derived oils and sulfur removal were studied. Cu was impregnated on several zeolites (HBETA, HY and HMOR), and the Cu-support interaction was examined using H₂-Temperature Programmed Reduction (TPR). The tire-derived oils were analyzed using a GC×GC-TOF/MS for their chemical composition.

2. Experimental

2.1. Catalyst preparation

Three types of zeolites, NH₄-BETA (Si/Al = 13.5), HY (Si/Al = 7.5), and HMOR (Si/Al = 9.5), purchased from TOSOH Company (Singapore) were calcined in static air at the conditions shown in Table 1. The calcination conditions were made different due to the different forms of purchased zeolites. The purchased BETA zeolite was in the NH₄-BETA form; therefore, it was calcined at 600 °C in order to completely change NH₄⁺ to H⁺ form. All calcined zeolites were impregnated with an appropriate amount of a copper solution (Cu(NO₃)₂·3H₂O) to obtain 5 wt% Cu, dried overnight in an oven at 120 °C, and calcined again at the same calcination conditions. Next, the calcined catalysts were reduced at 600 °C for 2 h in hydrogen atmosphere. Finally, the catalyst powders were pelletized, crushed and sieved to the pellet sizes in the range of 40–60 mesh.

Table 1
Calcination conditions of fresh zeolites before using as supports.

Zeolite	Calcination temperature (°C)	Heating rate (°C/min)	Holding time at calcination temperature (h)
BETA	600	2	5
Y	500	5	3
MOR	500	5	3

2.2. Catalyst characterization

XRD machine (Rikagu) was used to acquire the XRD patterns of the catalysts using CuKα radiation operated at 40 kV and 30 mA. The angles in the range of 5–65° were scanned at a scanning speed of 5°/min. Cu(1 1 1), with the highest intensity peak at the 2θ ~ 43.47°, was used to determine the thickness of Cu clusters on (1 1 1) plane, using the following equation:

$$L_{hkl} = \frac{k\lambda}{\beta \cos \theta}$$

where L is the thickness of a crystallite (Å), hkl is the diffracting plane ($hkl = 1\ 1\ 1$), λ is the wavelength of Cu Kα beam ($\lambda = 1.5418\ \text{\AA}$), β is the peak width (the full width at the half maximum intensity, FWHM), θ is the angle between the normal on the reflecting plane and the beam, k is a shape factor ($k = 0.9$).

Surface area and pore volume of catalysts were determined by N₂ physisorption using Thermo Finnigan Sorptomatic 1990 equipment. TPR profiles of catalysts were obtained for determining the metal-support interaction using Thermo Finnigan TPDRO 1100 operated from room temperature to 950 °C with a heating rate of 20 °C/min under 4.99% H₂/N₂ flow at 20 ml/min.

The amount of coke on spent catalysts was determined by using Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis), TG/DTA. The temperature was ramped up from room temperature to 900 °C with the heating rate of 10 °C/min. The amount of coke was calculated from the weight loss beyond 200 °C since the weight loss occurring below 200 °C was resulted from water or volatile organic compounds adsorbed on the catalyst surface. Sulfur content on catalyst surface was determined by using LECO® Elemental Analyzer (TruSpec®S), and calculated from the following equation:

$$S_{\text{Spent Cat}} = \frac{(W_{\text{Fresh Cat}} + W_{\text{Coke}}) \cdot (\%S_{\text{Spent Cat}})}{100}$$

where $S_{\text{Spent Cat}}$ = weight of sulfur on a spent catalyst surface (g), $\%S_{\text{Spent Cat}}$ = weight percentage of sulfur in spent catalyst, $W_{\text{Fresh Cat}}$ = weight of fresh catalyst (g), W_{Coke} = weight of coke in spent catalyst (g).

2.3. Pyrolysis of waste tire

Since waste tire in general is not a homogeneous material, only the thread of one waste tire (Bridgestone Turanza GR80) was therefore used as a raw material in every batch. Its particle size was controlled in the range of 20–40 mesh. Pyrolysis experiments were conducted using the same pyrolysis station as reported in D ng and coworkers [19]. The pyrolysis scheme was re-drawn and illustrated in Fig. 1. The catalytic pyrolysis of waste tire was operated at atmospheric pressure from room temperature to a temperature of 500 °C (the pyrolysis zone) and 350 °C (the catalytic zone) with a ramp rate of 10 °C/min and a holding time of 90 min after the final temperatures were reached in order to ensure that the tire was decomposed completely. Thirty grams of shredded tire (20–40 mesh) and 7.5 g of a catalyst (40–60 mesh) were packed in the pyrolysis zone and the catalytic zone, respectively. Nitrogen gas with a flow rate of 30 ml/min was used as a carrier gas. Liquid products were condensed in the condensers immersed in an ice-salt (NaCl) bath, while the gas products were collected by using a gas sampling bag. With the fixed controlled parameters, the impact of Cu-promoted catalysts on tire-derived oil and sulfur removal were investigated. The structure of zeolites and Cu-support interaction were the interested parameters examined in this work.

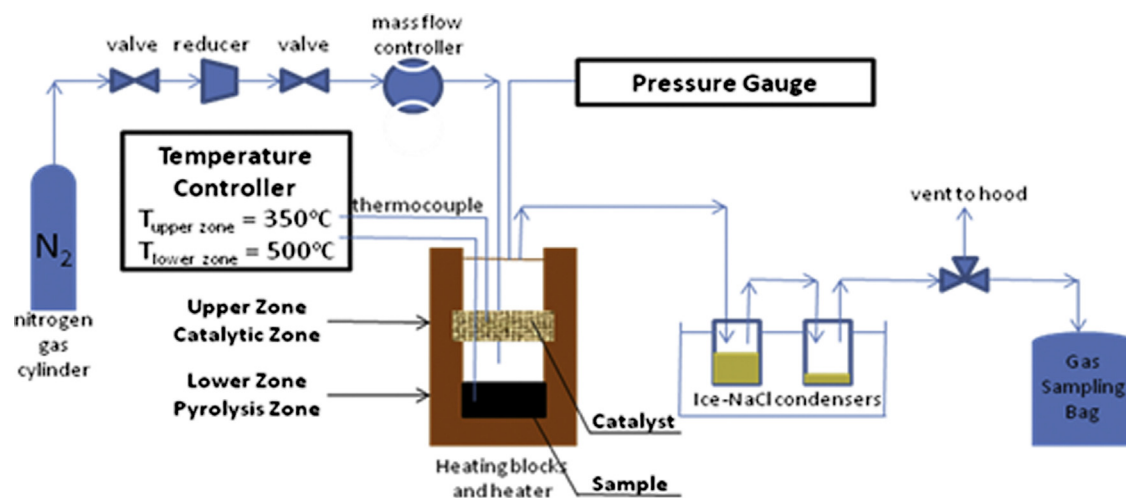


Fig. 1. Pyrolysis diagram.

2.4. Product analysis

Liquid and solid products were weighed for calculating the product yield. Before analysis, asphaltene was firstly precipitated from the liquid products via mixing with *n*-pentane in the oil/*n*-pentane mass ratio of 40:1. After that the precipitated asphaltene was filtered from the solution using a Teflon membrane (0.45 μm) in a

vacuum system, and then the maltene solutions were analyzed for the composition by using Gas Chromatography–Mass Spectrometry (GC $\times$ GC-TOF/MS). The Agilent gas chromatograph 7890 system consists of a cryogenic modulator and a LECO Pegasus 4D TOF/MS. The 1st column was a non-polar Rtx[®]-5Sil MS with 30 m $\times$ 0.25 mm ID $\times$ 0.25 μm film thickness installed in the main oven operated at 50 $^{\circ}\text{C}$, held for 2 min at the beginning of analysis, then ramped

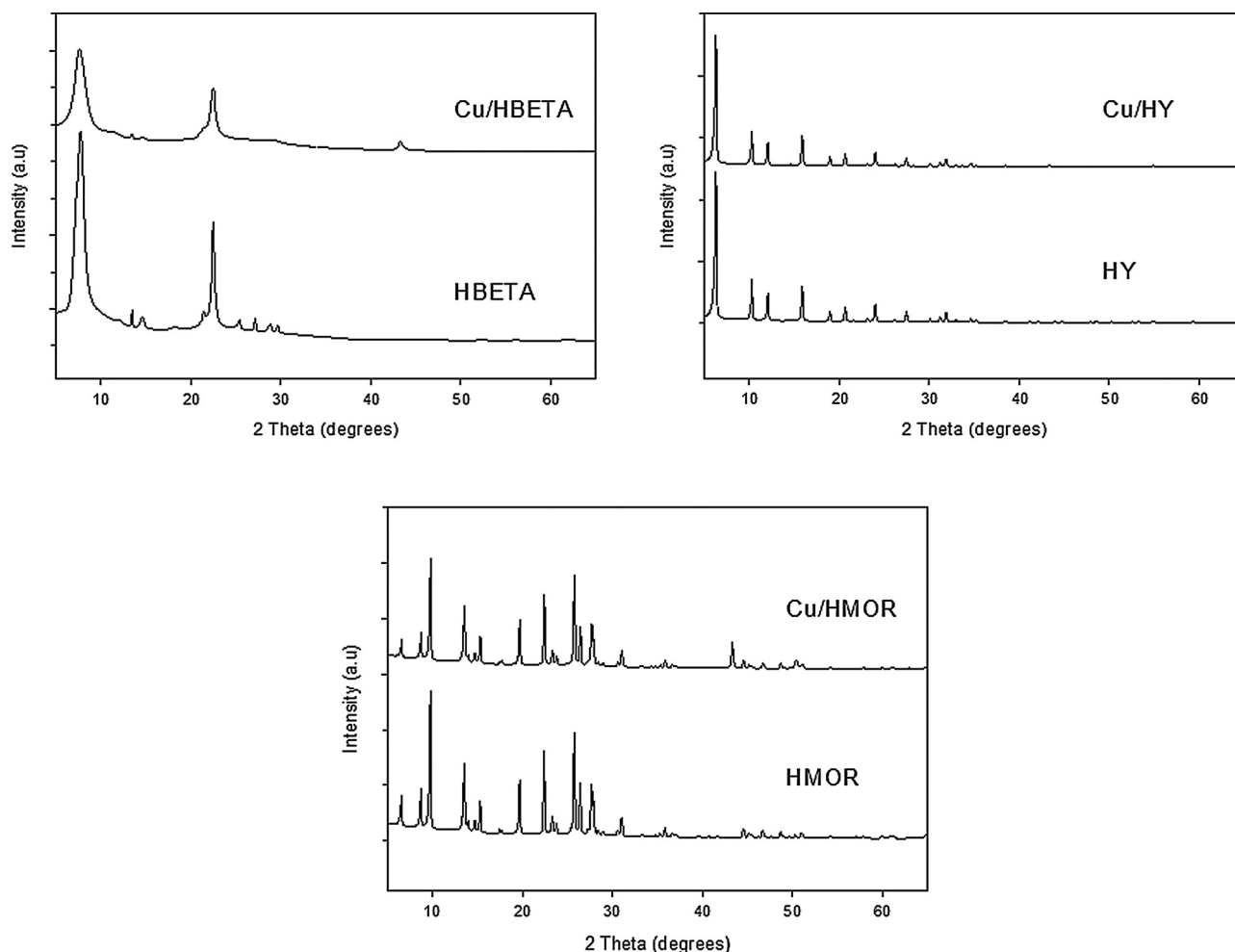


Fig. 2. XRD patterns of Cu-loaded catalysts.

to 310 °C with 5 °C/min, and held at the final temperature for 10 min. The 2nd column was an Rxi®-17 MS with 1.10 m × 0.10 mm ID × 0.10 μm film thickness installed in the second oven started at 60 °C, held for 2 min, then heated to 320 °C with 5 °C/min, and held for 10 min when the final temperature was reached. The modulator timing condition was set at the cycle time of 4 s and holding time of 0.5 s in the release position. Nitrogen (UHP) was used as a cryogen coolant set at least –80 °C of the modulation trap temperature. The electron impact ionization of –70 V was applied to provide mass spectral data collected in the range of 35–500 *m/z* with the data transfer of 100 spectra/s. The ion source and detector voltage were set at 250 °C and 1600 V, respectively. The transfer line was heated to 250 °C. The LECO ChromaTOF® software was used to record and analyze data, and spectral identification was provided by the NIST library. The accuracy and sensitivity of MS detector were calibrated and tested by using perfluorotributylamine (PFTBA) and hexachlorobenzene (HCB), respectively. Maltene solution samples were prepared from diluting 1 μl of maltene with CS₂ into 2 ml, and analyzed by injection into the instrument via a splitless injector operated at 250 °C. Helium at the flowrate of 1.0 ml/min was used as the carrier gas.

Furthermore, the true boiling point curves of maltene solutions were also analyzed by using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) conformed to the ASTM-D2887 method. The instrument equipped with FID and WCOT fused silica capillary column (15 m × 0.25 mm × 0.25 μm). The true boiling point curves were cut into petroleum fractions according to their boiling points; gasoline (<149 °C), kerosene (149–232 °C), gas oil (232–343 °C), light vacuum gas oil (343–371 °C) and heavy vacuum gas oil (>371 °C).

The gas products were analyzed for hydrocarbon species and concentrations by using a GC-FID, Agilent Technologies 6890 Network GC system (HP-PLOT Q column: 20 μm film thickness and 30 m × 0.32 mm ID). Furthermore, the liquid and solid products were also analyzed for their carbon, hydrogen, nitrogen, and sulfur contents by using a LECO® Elemental Analyzer (TruSpec® CHNS) whereas the sulfur content in gas products was calculated via mass balance.

3. Results and discussion

3.1. Catalyst characterization and Cu-support interaction

The XRD patterns of all zeolites and Cu-promoted catalysts are displayed in Fig. 2. The results show that the introduction of Cu onto HMOR and HY does not affect zeolite structures. However, the HBETA support loses some crystallinity after doped with Cu. The peaks of Cu appear at the 2θs of ~43.47° and 50.67°, and the thickness (*L*₁₁₁) of the Cu clusters on the 1 1 1 plane, Cu (1 1 1), shown in Table 2 is ranked as follows: Cu/HBETA < Cu/HMOR < Cu/HY. According to the Cu (1 1 1) crystallite thickness, the Cu dispersion

Table 2

Thickness of Cu clusters on various supports, *L*₁₁₁, (*k* = 0.9 and λ = 0.15418 nm).

Catalyst	2θ (deg)	β (deg)	<i>L</i> ₁₁₁ (Å)
Cu/HBETA	43.2055	0.6062	141
Cu/HY	43.2575	0.2660	523
Cu/HMOR	43.2792	0.1637	322

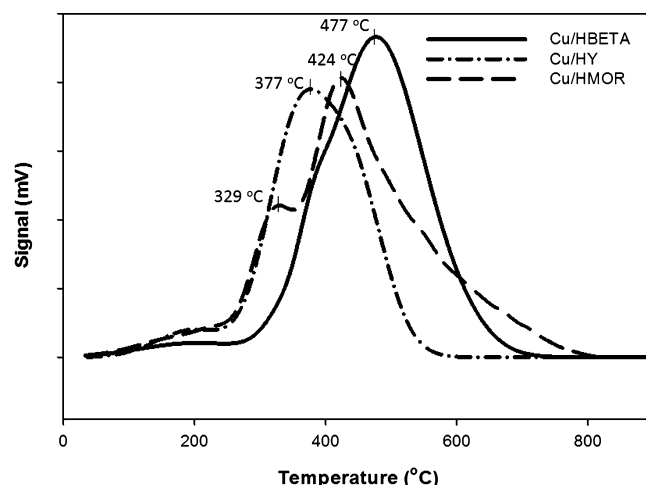


Fig. 3. TPR profiles of Cu-loaded catalysts.

on the supports can be ranked in the opposite way as Cu/HBETA > Cu/HMOR > Cu/HY. The highest Cu dispersion on HBETA indicates that the catalyst has the strongest Cu-support interaction. Similarly, The TPR profiles of catalysts are illustrated in Fig. 3. The profiles indicate the Cu-support interaction of all catalysts in comparison. Stronger metal-support interaction is considered from the peak evolving at a higher temperature [20]. The peaks appear in Fig. 3 at 477 °C and 377 °C for Cu/HBETA and Cu/HY, respectively, whereas Cu/HMOR gives two reduction peaks at 329 °C and 424 °C. So, it can be concluded that the interaction between Cu and the supports is ranked in the order: Cu/HBETA > Cu/HMOR > Cu/HY, which corresponds well with that determined from the cluster size, *L*₁₁₁ using the XRD patterns.

It is noted hereby that the two peaks in the TPR profiles of Cu/HMOR might be resulted from the change in the oxidation state of copper species from Cu²⁺ to Cu⁺ for the first peak, and then Cu⁺ was further reduced to Cu⁰ for the second peak. The changes, if they occur very fast on a support, can only give a peak on the TPR profiles. In our case, Cu/HMOR presents two peaks. Thus, it is possible that the changes from Cu²⁺ to Cu⁺ and from Cu⁺ to Cu⁰ occur more slowly on HMOR than those on the other supports. Moreover, it is also possibly resulted from two different sites of Cu loaded on the HMOR.

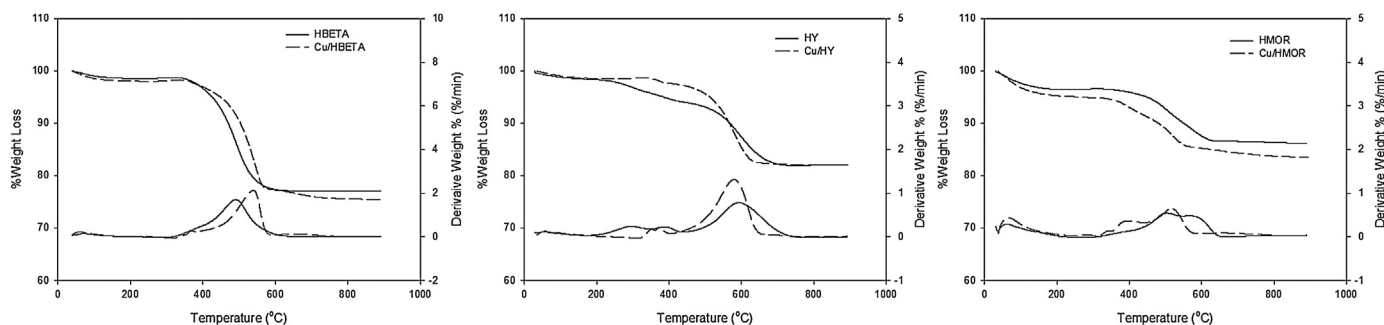


Fig. 4. TG/DTA profiles of spent catalysts.

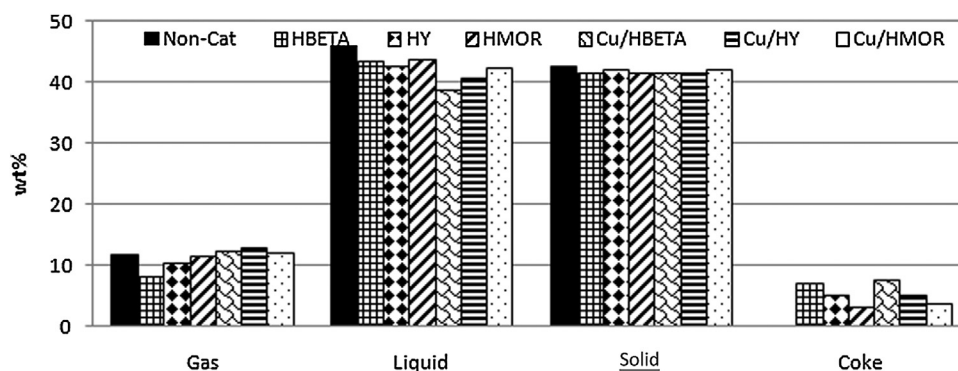


Fig. 5. Product distribution from using Cu-loaded catalysts.

Table 3
Elemental composition (wt.%) in coke on the spent catalysts.

Catalyst	C	H	N	S	H/C ratio
HBETA	20.0	1.87	2.01	0.411	9.39
HY	16.0	1.59	1.87	0.262	9.90
HMOR	10.3	1.27	2.10	0.143	12.3
Cu/HBETA	18.6	1.78	1.87	1.05	9.61
Cu/HY	15.7	1.10	1.84	1.10	7.05
Cu/HMOR	10.5	1.54	1.91	0.965	14.6

Coke deposited on catalyst surface can be acquired from the TG/DTA profiles (Fig. 4). Types of coke were generally defined into soft and hard cokes (with the weight loss at the temperature range of 200–400 °C [21] and above 400 °C [22], respectively). Soft coke is considered as coke precursors, i.e. aromatics and asphaltenes, whereas hard coke is a refractory one [22] or the polyaromatic coke located in the pore of zeolites. From Fig. 4, all Cu-promoted catalysts produce more hard coke than their corresponding parent zeolites, indicating higher cracking activity than the parent zeolites. The HBETA catalysts with and without Cu produce no soft coke whereas the HY ones slightly produce soft coke. The polyaromatic-type coke can be completely removed from HBETA, Cu/HBETA, HMOR, and Cu/HMOR at 600 °C, but it takes about 650–700 °C in order to remove the hard coke from HY and Cu/HY surfaces, possibly due the zigzag channel structure of HY zeolite that retains the coke from being removed easily.

Moreover, Cu loaded on HBETA and HMOR can produce higher H/C ratio of coke (See Table 3) than the parent zeolites because Cu potentially exhibit hydrogenation ability [21]. However, Cu/HY did not increase H/C ratio of coke as compared to HY, which might be caused by the poor dispersion of Cu on HY surface, resulting in

Table 4
BET specific surface area and pore volume of catalysts.

Catalyst	BET surface area (m ² /g)	Pore Volume (cm ³ /g) ^a
HBETA	539	0.257
HY	515	0.266
HMOR	395	0.199
Cu/HBETA	413	0.200
Cu/HY	488	0.256
Cu/HMOR	345	0.180

^a Horvath–Kawazoe (H–K) calculations.

lower hydrogenation activity as compared to the other Cu-loaded catalysts. The BET specific surface area and pore volume of catalysts are shown in Table 4. These results indicate that the introduction of Cu onto all zeolites reduces the specific surface area and pore volume because copper might partially block the pore of zeolites.

3.2. Tire-derived oil

Pyrolysis products can be divided into three types based on their phases; that are gas, liquid, and solid. Fig. 5 shows that the introduction of 5 wt% Cu onto HBETA (Si/Al = 13.5) and HY (Si/Al = 7.5) zeolites increases the gas production, decreases the liquid yields, and increases the amount of coke as well, indicating that the introduction of Cu can promote the activity in cracking of zeolites. The increment of coke formation can also indicate that the activities on the catalyst surface are increased when Cu was loaded. Particularly, the product from thermal pyrolysis of waste tire, which is fed to a catalyst bed, contains a considerable amount of aromatic compounds because the tire contains SBR rubber. The high cracking ability of an acid catalyst is likely to drive coke formation on the

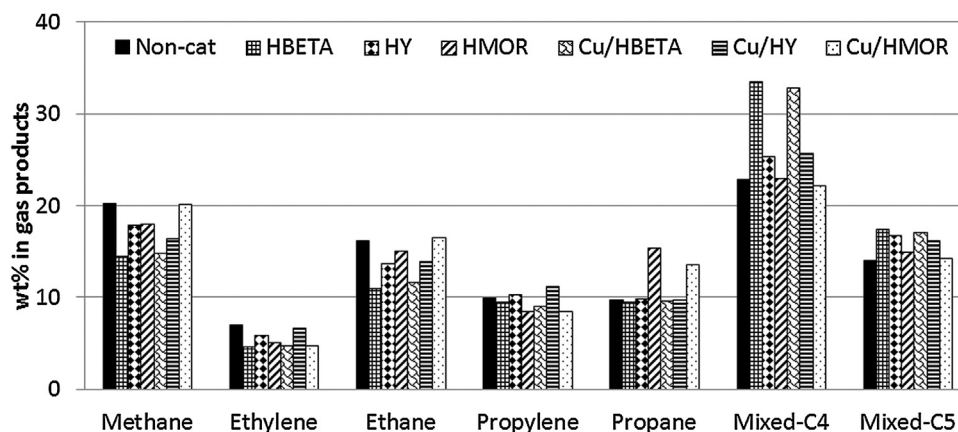


Fig. 6. Compositions in the gaseous products from using Cu-loaded catalysts.

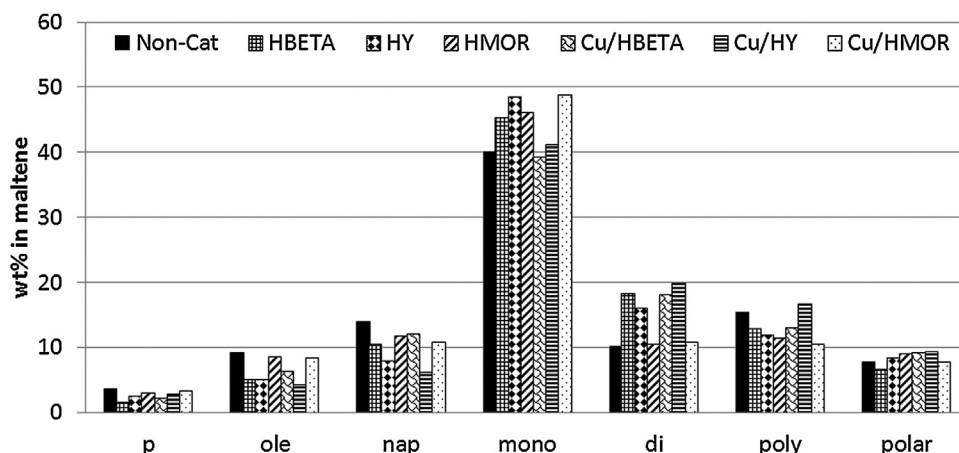


Fig. 7. Maltene compositions (p = paraffins, ole = olefins, nap = naphthenes, mono = monoaromatics, di = diaromatics, poly = polyaromatics, and polar = polar aromatics).

catalyst; therefore, coke formation is an indicator of high cracking ability.

In gas analysis as shown in Fig. 6, the gas compositions are slightly changed, indicating that the presence of Cu on the zeolites does not significantly promote any gas species. Fig. 7 shows the effect of Cu on the zeolites on maltene compositions. In this work, the components of maltenes are divided into 7 groups; that are, paraffins (p), olefins (ole), naphthenes (nap), and monoaromatics (mono), diaromatics (di), polyaromatics (poly) and polar aromatics (polar). Cu on HBETA and HY decreases the concentration of monoaromatics. Furthermore, the concentrations of paraffins, olefins and naphthenes are increased in the Cu/HBETA case while the concentrations of diaromatics and polyaromatics are increased in the Cu/HY case. It can be concluded that Cu/HBETA exhibits hydrogenation and ring-opening activities that convert monoaromatics into paraffins, olefins and naphthenes, while Cu/HY favors aromatization, producing multi-ring aromatics from monoaromatics, olefins and naphthenes because HY support has high acid density. The results indicate that small multi-ring aromatic molecules in Cu/HY are also cracked, which is governed by hydrogenation and ring-opening before breaking more C–C bonds [23] because gasoline is increased in the Cu/HY case as compared with the HY case (Fig. 8). So, Cu on both zeolites also promotes hydrogenation and ring-opening activities. The higher acid density and specific surface area of Cu/HY (higher cracking activity) also cause the lighter hydrocarbon portion (based on boiling points) in maltene than Cu/HBETA.

Copper on HMOR can increase the concentration of monoaromatics in maltene via hydrogenation and ring-opening of polyaromatics, and via aromatization of naphthenes. Furthermore, gasoline is also highly increased because copper promotes cracking activities. As compared between Cu on two zeolites with different pore channel structures (HY with 3 Dimensional pore channel structure and HMOR with 1 Dimensional pore structure), Cu/HMOR produces higher single ring-aromatics content in maltene than Cu/HY because 1D pore channel structure might be proper to monoaromatic production from cracking polyaromatics, while Cu/HY with 3D pore structure favors the productions of multi-ring aromatics because 3D pore channel structure catalyst has too much open space (pore size and architecture) for aromatization, resulting in lower concentration of olefins and higher bulky aromatics in oils [24].

Copper addition can increase gasoline fraction in oils, except Cu on HBETA since Cu/HBETA highly cracks hydrocarbons in the gasoline range to smaller molecules in the gas phase more than the other Cu-loaded catalysts. It can be explained that the strong Cu–HBETA interaction results in low sulfur deposition on the Cu surface that is the active sites for hydrogenation, cracking, and ring-opening. Moreover, the GC×GC-TOF/MS results indicate that the main compositions of oil are aromatics in all petroleum cuts (Table 5). So, tire-derived oils are not quite suitable for being used directly as fuels.

Petrochemicals in this paper are defined as primary petrochemicals (benzene, toluene and xylenes) and/or intermediates (styrene,

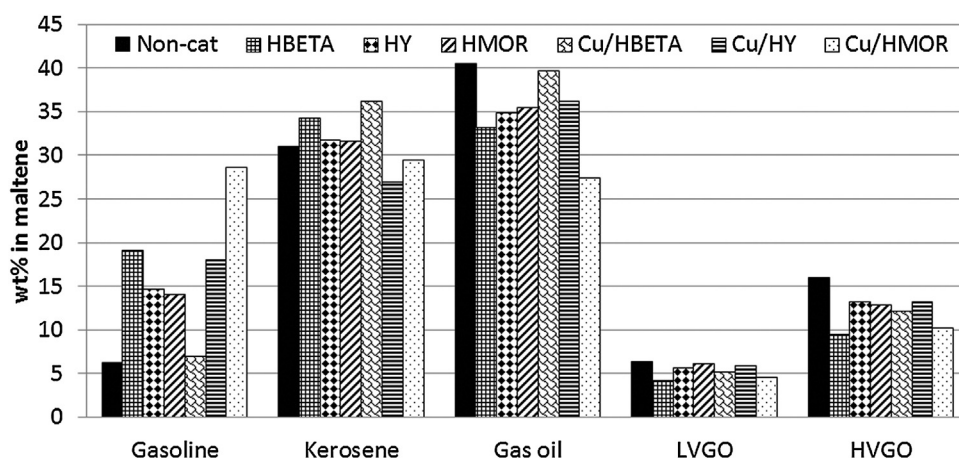


Fig. 8. Petroleum cuts of maltenes using Cu-loaded catalysts.

Table 5
Composition of each petroleum cuts.

	Gasoline	Kerosene	Gas oil	LVGO	HVGO
Paraffins	0.00–1.92	0.806–1.69	3.95–11.6	0.00–13.5	0.00–23.9
Olefins	2.69–11.3	4.55–9.04	4.46–9.51	0.00–22.3	–
Naphthenes	7.85–13.8	4.77–13.0	5.12–16.8	0.00–22.0	–
Aromatics	75.5–84.7 ^a	76.3–90.0	65.4–81.1	71.1–100	76.1–100

^a 37.5–71.9 wt% of monoaromatics in gasoline.

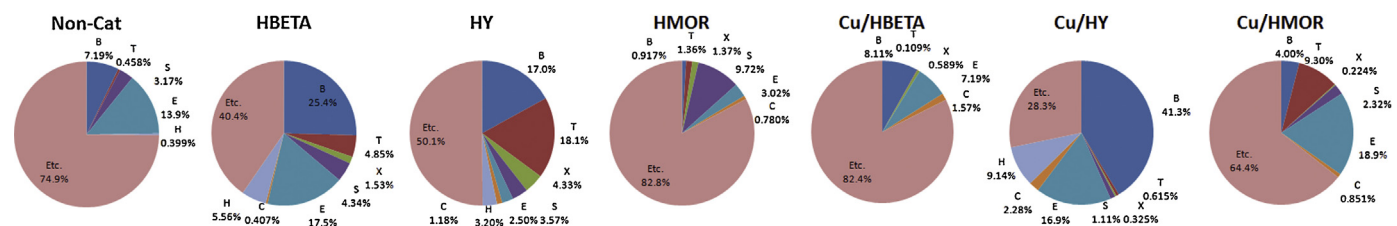


Fig. 9. Selectivity of petrochemicals in gasoline-range products (B = benzene, T = toluene, X = xylenes, S = styrene, E = ethylbenzene, C = cumene, and H = cyclohexane).

Table 6
Petrochemicals productivity from waste tire pyrolysis.

Catalyst	Petrochemical productivity (kg/ton of tire)
No Catalyst	7.15
HBETA	49.1
HY	31.2
HMOR	10.6
Cu/HBETA	4.74
Cu/HY	52.3
Cu/HMOR	43.0

ethylbenzene, cumene, and cyclohexane). In tire-derived oil, petrochemicals can be formed two ways: (1) conversion of hydrocarbons, and (2) conversion of sulfur-containing compounds. The petrochemicals productivity and selectivity in gasoline (Table 6 and Fig. 9) are increased when Cu was loaded on HY and HMOR zeolite. It is noted here that B = benzene, T = toluene, X = xylenes, S = styrene, E = ethylbenzene, C = cumene, and H = cyclohexane. With the same reason, Cu on HBETA highly promotes cracking reaction of small molecules (including these petrochemicals) in the gasoline range, forming gases; so, the selectivity of petrochemicals in the Cu/HBETA case is the lowest among those of all catalytic cases.

Cu on HY and HMOR reduces the amount of total BTz and ITC yields as compared with pure HY and HMOR cases, indicating that BTz and ITC can be converted into benzene. Furthermore, Cu/HY catalyst promotes benzene, ethylbenzene and cyclohexane production because Cu/HY might promote hydrogenation and dealkylation of HY. Cu/HMOR catalyst highly produces

ethylbenzene, toluene and benzene because Cu/HMOR might increase dealkylation activity.

Even though the amount of sulfur-containing compounds is markedly lower than that of petrochemicals and/or gasoline, the increase of petrochemical production is quite high because Cu-support interaction might strongly affect the petrochemical production. Cu-support interaction can relate to the adsorption of sulfur-containing compounds and desorption of sulfur atoms on the catalyst surface via reacting with hydrogen to form H₂S and/or hydrocarbons to form thiophenes. Desorption of sulfur atoms on the catalyst surface can form the molecular structures, similar to the sulfur-containing compounds that can also re-adsorb and form petrochemicals. Benzothiophenes can be formed from the reaction between H₂S and olefins [25] or from the reaction of two molecules of thiophenes [26].

3.3. Sulfur compounds in oil and sulfur removal

After pyrolysis, 50% of sulfur in waste tire is deposited in char, or carbon black originally existing in the tire, as illustrated in Fig. 10. It is suggested that tire, when pyrolyzed in the pyrolysis zone, releases sulfur in the forms that can be adsorbed on the char. The other 50% of sulfur is evolved in the effluents taken by nitrogen used as the carrier gas. Once the effluents come into contact with a catalyst in the catalytic zone, sulfur is distributed into oil and gaseous products, with a little amount that is deposited on the catalyst surface. From Fig. 10, it can be seen that, using a zeolite as a catalyst, sulfur is more distributed in the gaseous product than in the oil phase whereas only 2–6% is deposited on the zeolite surfaces. After



Fig. 10. Overall sulfur distribution.

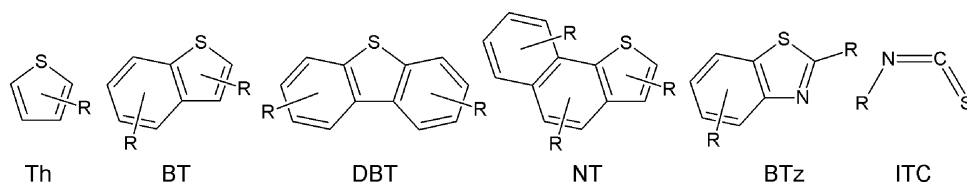


Fig. 11. Major sulfur-containing compounds found in tire-derived oils.

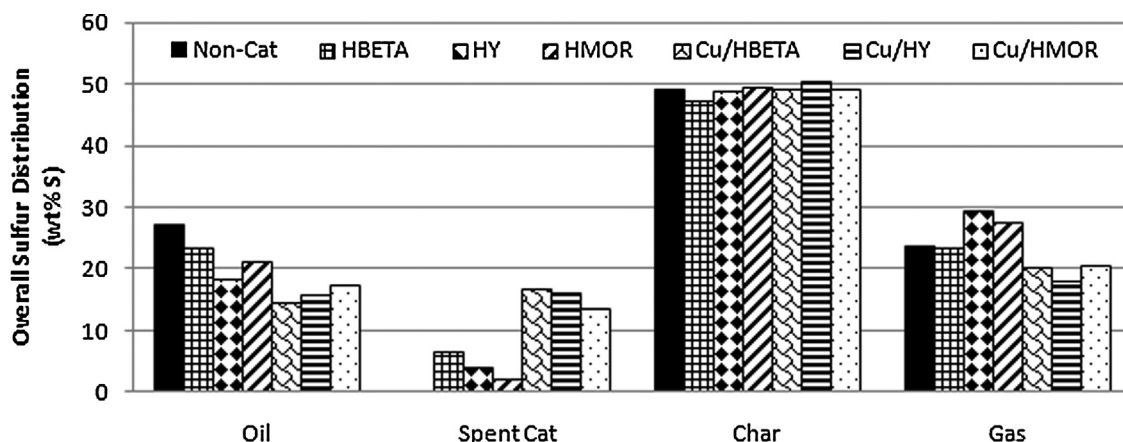


Fig. 12. Distribution of sulfur-containing species in maltenes.

Table 7
Sulfur content in oil (wt%).

Catalyst	Wt% sulfur in oil	S removal (%)	S removal by Cu (%)
No catalyst	1.22	–	–
HBETA	1.11	9.02	–
HY	0.889	27.1	–
HMOR	0.991	18.8	–
Cu/HBETA	0.764	37.4	28.4
Cu/HY	0.800	34.4	7.3
Cu/HMOR	0.842	31.0	12.2

doping with Cu, it is obvious that less sulfur is distributed in gas and oil, but more sulfur is distributed on the catalyst surfaces, indicating that sulfur is deposited on Cu.

Table 7 indicates that Cu can promote sulfur removal ability of the supports, especially when loaded on HBETA. The ability on S removal of the Cu-doped catalysts can be ranked in the order: Cu/HBETA > Cu/HY > Cu/HMOR. Therefore, Cu/HBETA seems to be the best catalyst in terms of the activity on sulfur removal from the tire-derived oils. However, considered from the differences on S removal ability of catalysts between with and without Cu, it can be seen that the ability of Cu dopant on S removal can be ranked as Cu on HBETA > Cu on HMOR > Cu on HY at a fixed Cu loading. This observation indicates that Cu-support interaction may affect the S removal ability of Cu.

Sulfur-containing compounds found in oils can be classified into six groups: thiophenes (Th), benzothiophenes (BT), dibenzothiophenes (DBT), naphthothiophenes (NT), benzothiazoles (BTz), and isothiocyanates (ITC) as shown in Fig. 11. Total Th, BT and DBT yields are decreased in all copper-loaded catalyst cases (Fig. 12) because copper can react with sulfur atoms in the compounds, and can form the thermodynamically stable form such as CuS or Cu₂S. This evidence indicates that the sulfur compounds that Cu dopant can remove are in the groups of thiophenes, benzothiophenes, and dibenzothiophenes.

Desulfurization can be divided into four steps; (a) the adsorption of an S-compound on a Cu-site, (b) the hydrogenation of the

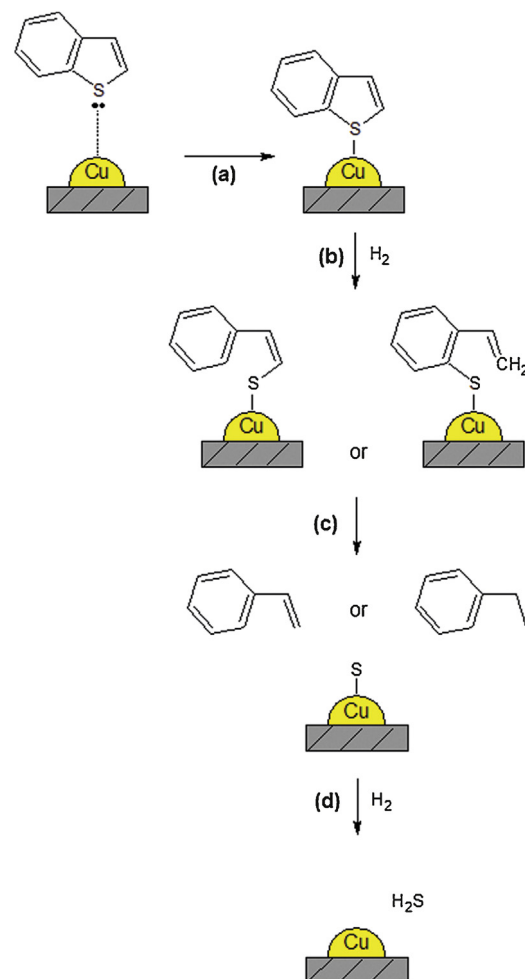


Fig. 13. Sulfur removal pathway of benzothiophene.

adsorbed S-compound and C–S bond breaking, (c) the desorption of a hydrocarbon and copper sulfide formation, and (d) the removal of S atoms on the surface (surface cleaning). The example of pathways to produce petrochemicals from sulfur-containing compounds is shown in Fig. 13. Sulfur removal ability of Cu doped on the zeolites can be possibly related to the Cu-support interaction. According to the TPR profiles (Fig. 3) and the cluster size (L_{111}) of Cu on each support, it has been concluded in Section 3.1 that the Cu-support interaction is ranked as follows: Cu/HBETA > Cu/HMOR > Cu/HY. This is in accordance with the rank in the ability of Cu dopant on S removal (Cu on HBETA > Cu on HMOR > Cu on HY) at a fixed Cu loading.

Likely, in this work, it can be postulated that high dispersion and strong interaction between Cu and HBETA causes high electron deficiency of the Cu site [27]. Consequently, the high electron-deficient site of Cu prefers to adsorb sulfur, in a sulfur-containing hydrocarbon, that is full of electrons, which creates strong Cu–S interaction and then makes a sulfur-containing adsorbate so unstable that the S–C bond in the molecule can be easily broken. Therefore, in this situation, the release of an S-free hydrocarbon molecule from the Cu/HBETA surface can occur easily, resulting in the lowest sulfur content in oils as compared with the other Cu-loaded catalysts. On the other hand, the interaction between Cu and HY or Cu and HMOR is weaker than that of Cu on HBETA, so they can adsorb a S-compound with lower strength, and a hydrocarbon cannot be easily released.

Since the interaction between Cu and HBETA on Cu/HBETA is the highest among that on the other Cu-doped catalysts, the highest Cu–S bond strength in copper sulfide is created after a hydrocarbon product leaves the surface. Thus, for surface cleaning, it is the most difficult to remove sulfur atoms on the spent Cu/HBETA surface among those of the other spent catalysts [27]. This is supported by the highest distribution of S on the spent Cu/HBETA catalyst as illustrated in Fig. 10.

4. Conclusions

Copper can be used to promote sulfur reduction from tire-derived oils of zeolites because it has sulfur adsorption properties. Sulfur content in oil of the copper-loaded catalysts was 0.764 wt%, 0.800 wt%, and 0.842 wt% in oil for Cu/HBETA, Cu/HY, and Cu/HMOR cases, respectively. The important effects of catalysts on sulfur removal are zeolite properties and Cu-support interaction. The catalysts with strong Cu-support interaction have high ability to adsorb sulfur on their surfaces. The removal of sulfur from sulfur-compounds can also result in the production of petrochemicals because the main species of sulfur-containing compounds have the molecular structures similar to several types of petrochemicals. Furthermore, the tire-derived oils are a potential alternative source for petrochemical production because the oils were

composed of the high amount of aromatics, especially monoaromatics. Interestingly, the introduction of copper highly promoted the production of valuable products in oils as well. The results indicated that copper on HY and HMOR zeolites had ability on enhancing the petrochemical productivity. Cu/HY highly produced benzene, ethylbenzene and cyclohexane, Cu/HMOR highly produced benzene, toluene and ethylbenzene, while Cu/HBETA did not promote petrochemical production as compared with HBETA.

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Effects of Fe supported on zeolites on structures of hydrocarbon compounds and petrochemicals in waste tire-derived pyrolysis oils

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ABSTRACT

Waste tire, a hydrocarbon-based material, exhibits potential to be used for petrochemical production. Valuable chemicals such as benzene, toluene, xylenes, and styrene for instances have been observed in pyrolytic oils. Furthermore, sulfur compounds causing the low quality of oil and the environmental pollutant are also absolutely found. Iron catalysts appear to be economically feasible in catalytic fields. Especially, iron can be used to substitute the noble metal promoters in the pyrolysis of waste tire due to its good activities on hydrogenation and ring opening reactions. This study therefore investigates the effects of iron supported on zeolites (HMOR, HBeta, HZSM-5, and KL) on structures of hydrocarbon compounds and petrochemicals in waste tire-derived oils. Fe-promoted zeolites were prepared by incipient wetness impregnation technique with the fixed amount of Fe at 5 wt.%. The products and catalysts were characterized by using GC, SIMDIST-GC, GC × GC-TOF/MS, elemental analyzer, XRD, and SAA. The results showed that the introduction of 5%Fe on zeolites can enhance the cracking ability of products. Namely, the gas yield increased, at the expense of liquid yield. In addition, light hydrocarbon gases increased in accordance with the reduction of heavier gases. Moreover, the light fractions in oil also increased with using iron-loaded zeolites. Moreover, olefins and naphthenes tended to decrease, but mono-aromatics increased with using all 5%Fe-loaded zeolites. Consequently, the reduction of di- and poly-aromatics was observed for all Fe-promoted catalysts, except 5%Fe/HBeta. Using 5%Fe-loaded zeolites, except 5%Fe/HBeta resulted in the increasing yields of petrochemicals such as benzene, toluene, ethylbenzene, xylenes, and styrene, for examples, in oil. Furthermore, 5%Fe-loaded catalysts resulted in the reduction of sulfur in oil. Dibenzothiophenes and benzothiazoles were the sulfur compounds in oil that decreased with the presence of 5%Fe, except 5%Fe/HZSM-5, whereas benzothiophenes tended to decrease.

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1. Introduction

Tire is difficult to degrade, and it has a long life; thus, resulting in a large amount of waste tire discarded. Over a half of waste tires go to land fill, resulting in losing a large amount of valuable landfill space. Moreover, the combustion of waste tire releases environmental pollutants. However, tires are hydrocarbon materials which exhibit potential to be used as a source for petrochemical production through waste tire pyrolysis that is an alternative technique to handle waste tire problems. Several researchers reported that products from waste tire pyrolysis can be used as fuels and feedstock for petrochemical production. Aromatics, especially benzene,

toluene, xylenes, and ethylbenzene, are important compounds in the production of petrochemicals and plastics. Moreover, styrene and cumene are also widely used in chemical industry. It has been reported that pyrolytic oils can be used as diesel fuel after upgrading such as removing sulfur or blending with commercial fuels [1–3]. In addition, the oil which has high sulfur is not permitted to use in vehicle due to the environmental regulations. The source of sulfur in pyrolytic oil is from vulcanization agents and accelerators such as benzothiazole, 2-mercaptobenzothiazole in vulcanization process during tire production [4,5]. In order to reduce sulfur in oil, sulfur removal technology has been developed. García-Cruz et al. [6] reported that small sulfur compounds are easier to be desulfurized than larger sulfur compounds. The activity of sulfur species towards hydrodesulfurization was ranked as thiophene > benzothiophenes > dibenzothiophenes > 4,6-dimethyldibenzothiophene.

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Several researchers used catalysts, especially zeolites, to improve the quality of pyrolytic oil evolved from using several raw materials such as solid wastes [7–9] and biomass [10–12]. Dũng et al. [7] used HMOR zeolite in waste tire pyrolysis. The results showed that introduction of HMOR led to the increasing amounts of gasoline and kerosene and the decreasing amounts of heavy vacuum gas oil due to the good cracking performance of catalyst. They mentioned that HMOR favored to produce gasoline, which was selective to pore size. The pyrolysis of waste tire with using HBeta and KL zeolites were studied by Saeng-arayakul and Jitkarnka [8]. The results showed that using HBeta produced higher gas yield than using KL. Moreover, HBeta zeolite reduced the concentration of heavy liquid fractions (long residues and heavy gas oil) more greatly than KL zeolite. The results demonstrated that long-chain hydrocarbons were more easily cracked by HBeta. Furthermore, both HBeta and KL can reduce the sulfur in oil. Olazar et al. [9] studied the effect of using HZSM-5 catalyst on waste tire pyrolysis. The gas product increased with using HZSM-5 due to cracking of heavy fractions. Additionally, light olefins which consisted of ethene and propene increased with the use of catalyst. Poly-aromatics in oil products increased with using the catalyst. It was suggested that cyclization, aromatization and condensation reactions occurred inside the pore to form aromatics. The formation of aromatic hydrocarbons and oxygen-containing aromatics (mostly phenolic compounds) was also observed using zeolites in pyrolysis of biomass such as eucalyptus wood [10,11]. Intensive investigation on the effects of zeolites properties on sulfur removal and production of aromatic-type petrochemicals from waste tire pyrolysis has been recently published [12].

Iron catalysts are environment-friendly ones with low toxicity, the usage of iron catalysts are mainly in Fischer-Tropsch (FT) synthesis [13] or selective catalytic reduction (SCR) [14], and appear to be economically feasible in catalytic fields [15]. Pour et al. [13] studied Fischer-Tropsch synthesis catalyzed by pure Fe and Fe supported on ZSM-5. They indicated that the Fe/ZSM-5 catalyst gave a longer chain of hydrocarbons than the pure Fe catalyst because ZSM-5 promoted oligomerization activity, cracking activity, and shape selectivity, followed by aromatization that led to the reduction of light products. Moreover, ZSM-5 improved the quality of gasoline by increasing C₅–C₁₁ hydrocarbons due to the enhancement on secondary chain growth. Fe catalysts supported on HBeta and HZSM-5 zeolites were investigated for selective catalytic reduction (SCR) in order to reduce nitrogen oxide (NO) from the diesel engine [15]. They found that iron loading at 2.5 wt.% gave the high conversion of NO about 97%. Additionally, Fe/HBeta gave higher activity of SCR than Fe/ZSM-5 due to higher surface area. Besides FT synthesis and SCR, Fe has been used in conversion of biomass-based raw materials, like bio-ethanol, to either olefins [16,17] or liquid hydrocarbons [18]. Fe promoted on HZSM-5 was found to be highly effective even in the presence of water in the feed, and the initial selectivity of C³⁺ olefins and distribution of products were not affected by iron precursors [16,18] and calcination temperature [16]. Moreover, as low as 1% Fe loading can result in a high selectivity of C³⁺ olefins [17]. The high activity of Fe/HZSM-5 catalysts could be possibly resulted from the stronger acidic site than an Al-type acidic site, which is created when Fe is introduced to zeolite framework [19].

Recently, an iron catalyst has been used in waste tire pyrolysis as a substitute for a noble metal catalyst (Ru) [20]. The result showed that the increasing amount of Fe loading on HBeta and HMOR zeolites tended to enhance the cracking ability of liquid to gas products. For liquid products, it was reported that presence of Fe catalyst led to sharp increase in saturated hydrocarbons in accordance with reduction of poly- and polar-aromatic hydrocarbons. It was attributed to Fe site that had an important role on promotion of hydrogenation and hydrosulfurization reactions of poly- and

polar aromatic hydrocarbons. Moreover, heavy fractions such as heavy gas oil and long residue increased with increasing Fe loading because the secondary reactions, which consist of oligomerization, aromatization and H-transfer, were enhanced on Fe. As observed above, the Fe catalyst had as high activity as the noble metals, Ru and Pd, which can be costly [20].

Currently, no study has been made on the effect of iron-loaded zeolites on the structure and distribution of hydrocarbons in waste tire pyrolysis. The aim of the present study was to investigate effects of iron promotion on zeolites on structures of hydrocarbon compounds and petrochemicals in tire-derived oils. A series of Fe supported zeolites was prepared by incipient wetness impregnation technique loading and the amount of Fe was fixed at 5 wt.% for all cases.

2. Experimental

2.1. Catalyst preparation

HMOR (Si/Al = 13.5), HBeta (Si/Al = 9.5), KL (Si/Al = 3), and HZSM-5 (Si/Al = 15) were purchased from Tosoh Company in Singapore and Zeolyst International. First, all zeolites were calcined to remove impurity. HMOR, HZSM-5, and KL were calcined at 500 °C for 3 h with the heating rate of 10 °C/min. HBeta was calcined at 600 °C for 5 h with 2 °C/min. Then, each zeolite was loaded with metal, iron(III) chloride hydrate hexahydrate (FeCl₃·6H₂O), using incipient wetness impregnation technique to obtain 5 wt.% metal-supported catalyst. After that, the catalysts were dried at 100 °C for 3 h, followed by calcination at the same conditions. Next, catalyst powders were pelletized, ground, and sieved to 400–425 μm of particle size. Finally, they were reduced at 800 °C for 2 h with H₂ to convert the iron oxides to metallic Fe.

2.2. Catalyst characterization

Temperature-programmed reduction (TPR) was used to identify the reducibility of the impregnated catalysts and the metal-support interaction. The temperature was ramped from 30 °C to 850 °C with a heating rate of 10 °C/min. X-ray Diffraction (XRD) was used to verify the structure and existence of metal of the catalysts. The detector scanned the peak position from the sample as a function of 2θ by starting at the 5° to 100° (2θ) range and a scan speed of 5° (2θ)/min. XRD patterns were matched to the standards to identify crystalline phases by smartlab guidance program. The amount of coke on spent catalysts was analyzed by using a Thermogravimetric/Differential Thermal Analysis (TG/DTA). The surface area and pore volume of catalysts were analyzed by using a surface area analyzer (Sorpomatic 1990). Moreover, an elemental analyzer was used to determine sulfur content on spent catalyst.

2.3. Pyrolysis of waste tire

The ultimate analysis of shredded waste tire samples (Bridgestone TURANZA GR-80) was performed using a LECO® elemental analyzer. A ceramic boat filled with nickel boat was added with com-aid and 0.1 g of each tire sample, and then the ceramic boat was put in the elemental analyzer. The temperature of furnace was next raised from room temperature to 600 °C and held for 15 min in the first step, and then raised again to 1350 °C in the analyzing step. For a pyrolysis experiment, a 30 g of waste tire was loaded into the lower zone of reactor, operated at 500 °C, and 7.5 g. of a catalyst was loaded to the catalytic zone, operated at 350 °C (the waste tire/catalyst ratio of 4). The experimental setup (see Fig. 1) and the pyrolysis conditions were the same as indicated in our published papers [21,22], which have been achieved from our successive studies [7,12,21]. Briefly, the heating rate was controlled at 10 °C/min

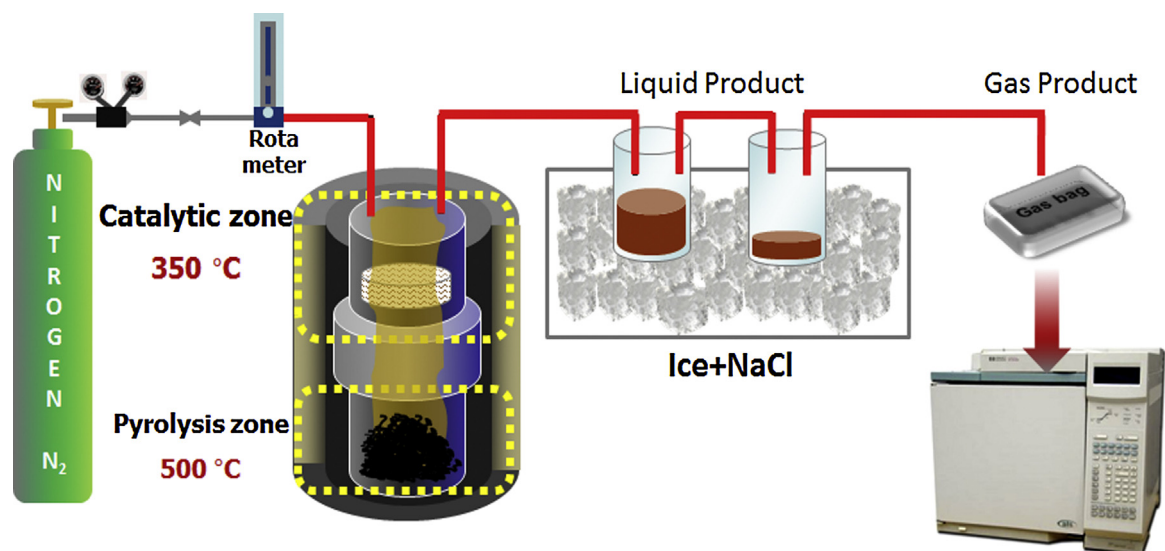


Fig. 1. Experimental setup for pyrolysis experiments.

and then kept for 2 h at the atmospheric pressure. The flow rate of N_2 was controlled at 30 ml/min, which was continuously flown to purge the oxygen out of the pyrolysis system. The obtained product was next passed through condensers in order to collect the liquid product, and subsequently the gas product was kept in a gas sampling bag. The solid and liquid products were weighed to determine the distribution of pyrolysis products.

2.4. Product analysis

Pyrolysis gas was analyzed by using a Gas Chromatography (GC), Agilent Technologies 6890, installed with HP-PLOTQ column: 20 μ m film thickness and 30 m $\times$ 0.32 mm ID and equipped with FID detector, using helium as the carrier gas. The oil products were dissolved in *n*-pentane to precipitate asphaltene, and then left for overnight. Subsequently, asphaltene was filtered from the mixture under vacuum using a polyamide membrane with the 0.45 μ m of pore size. The solution after asphaltene precipitation is called “maltene”. The true boiling point curves of maltenes were obtained by using a Varian GC-3800 Simulated Distillation Gas Chromatography (SIMDIST-GC) conformed to the ASTM-D2887 method, which were then cut into 5 petroleum fractions; that are, full range naphtha (<200 °C), kerosene (200–250 °C), light gas oil (250–300 °C), heavy gas oil (300–370 °C), and long residue (>370 °C). In addition, the compositions of maltenes were identified by using a LECO® 4D Pegasus two-dimensional Gas Chromatography with Time of Flight Mass Spectroscopy (GC $\times$ GC-TOF/MS). Maltene solution samples were prepared from diluting 1 μ l of maltene with CS_2 into 2 ml, and injected to the GC installed with two columns. The 1st column was a non-polar Rtx®-5Sil MS with 30 m $\times$ 0.25 mm ID $\times$ 0.25 μ m film thickness installed in the main oven operated at 50 °C, held for 2 min at the beginning of analysis, then ramped to 310 °C with 5 °C/min, and held at the final temperature for 10 min. The 2nd column was an Rxi®-17 MS with 1.10 m $\times$ 0.10 mm ID $\times$ 0.10 μ m film thickness installed in the second oven started at 60 °C, held for 2 min, then heated to 320 °C with 5 °C/min, and held for 10 min when the final temperature was reached. Other operating conditions such as modulator time, ionization voltage, ion source and detector voltages, and mass spectral data collection were set the same as in [22]. The LECO ChromaTOF® software recorded and analyzed data with spectral identification provided by the NIST library. The accuracy and sensitivity of the MS detector were cal-

ibrated and tested by using perfluorotributylamine (PFTBA) and hexachlorobenzene (HCB), respectively. Moreover, sulfur content in oils was determined by using a LECO® Elemental Analyzer (TruSpec® CHNS).

3. Results and discussion

3.1. Catalyst characterization

The TPR profiles of Fe-loaded catalysts are shown in Fig. 2. It is found that 5%Fe on HBeta, HZSM-5, HMOR and KL has the reduction peak at 500 °C, 503 °C, 552 °C, and 610 °C, respectively. Therefore, the interaction between Fe and the supports can be ranked in the following order: Fe/KL > Fe/HMOR > Fe/HZSM-5 > Fe/HBeta. Fig. 3 shows the XRD patterns of Fe-loaded catalysts. It exhibits that the introduction of 5% of Fe on zeolites results in the presence of the metallic Fe peaks at 2θ of 44.6° (1 1 0), 65° (2 0 0), and 82° (2 1 1) in the XRD patterns based on JCPDS 06-0696. The (1 1 0) peak was used to calculate the Fe cluster size, L_{110} , using Scherrer's equation;

$$L_{hkl} = \frac{k\lambda}{\beta \cos \theta_0}$$

where λ is the X-ray wavelength of $CuK\alpha$, which is 1.5406 Å, λ is the peak width (expressed in radian), θ_0 is the angle between the beam and the normal on the reflecting plane (expressed in radian), and k is a constant shape factor (often taken as 0.9). Moreover, the other physical properties of fresh catalysts are shown in Table 1. It can be seen that the physical properties of all catalysts are not markedly different, except the surface area.

3.2. Pyrolysis yield

Waste tire samples with the elemental compositions shown in Table 2 were pyrolyzed using the catalysts, and the distribution of pyrolysis products is illustrates in Fig. 4. The yield of char is constant for all cases, indicating that rubbers in the tire samples were totally converted to hydrocarbon products. All parent zeolites results in a slight reduction of the oil yield in accordance with the slight increase in gas or a high coke deposition on the catalyst as compared to the non-catalyst case. The introduction of 5 wt.% Fe on the zeolites in

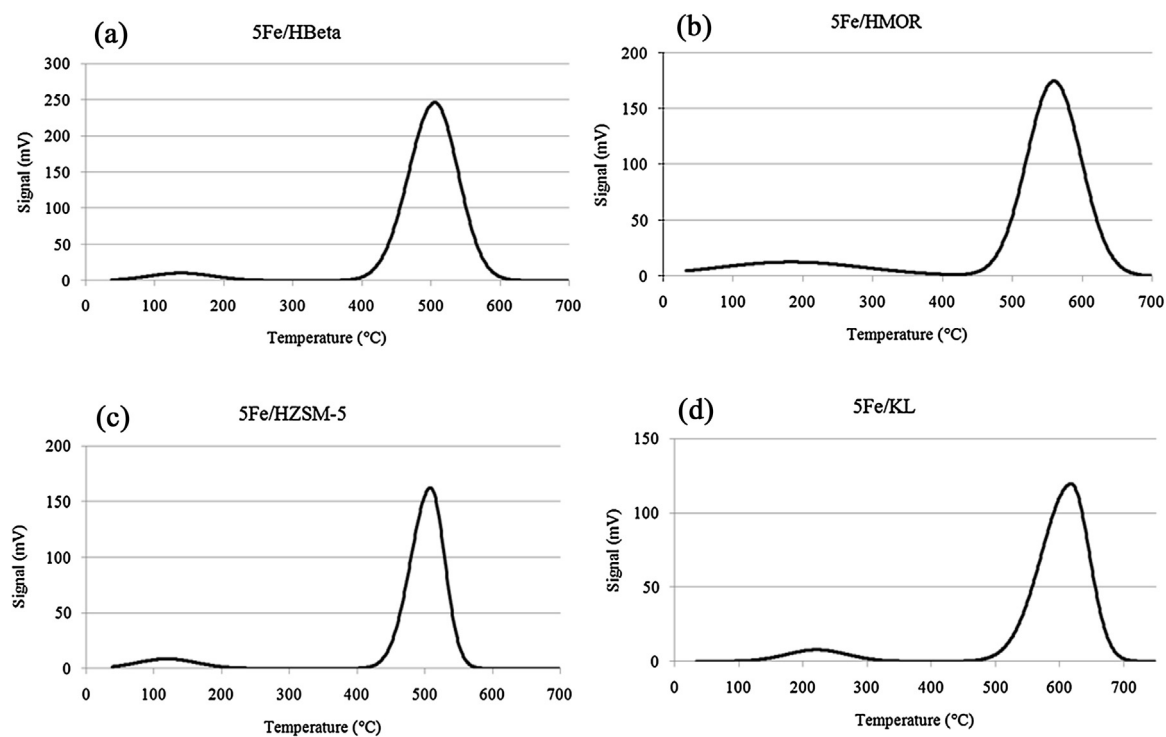


Fig. 2. H₂-TPR profiles: (a) 5%Fe/HBeta, (b) 5%Fe/HMOR, (c) 5%Fe/HZSM-5, and (d) 5%Fe/KL.

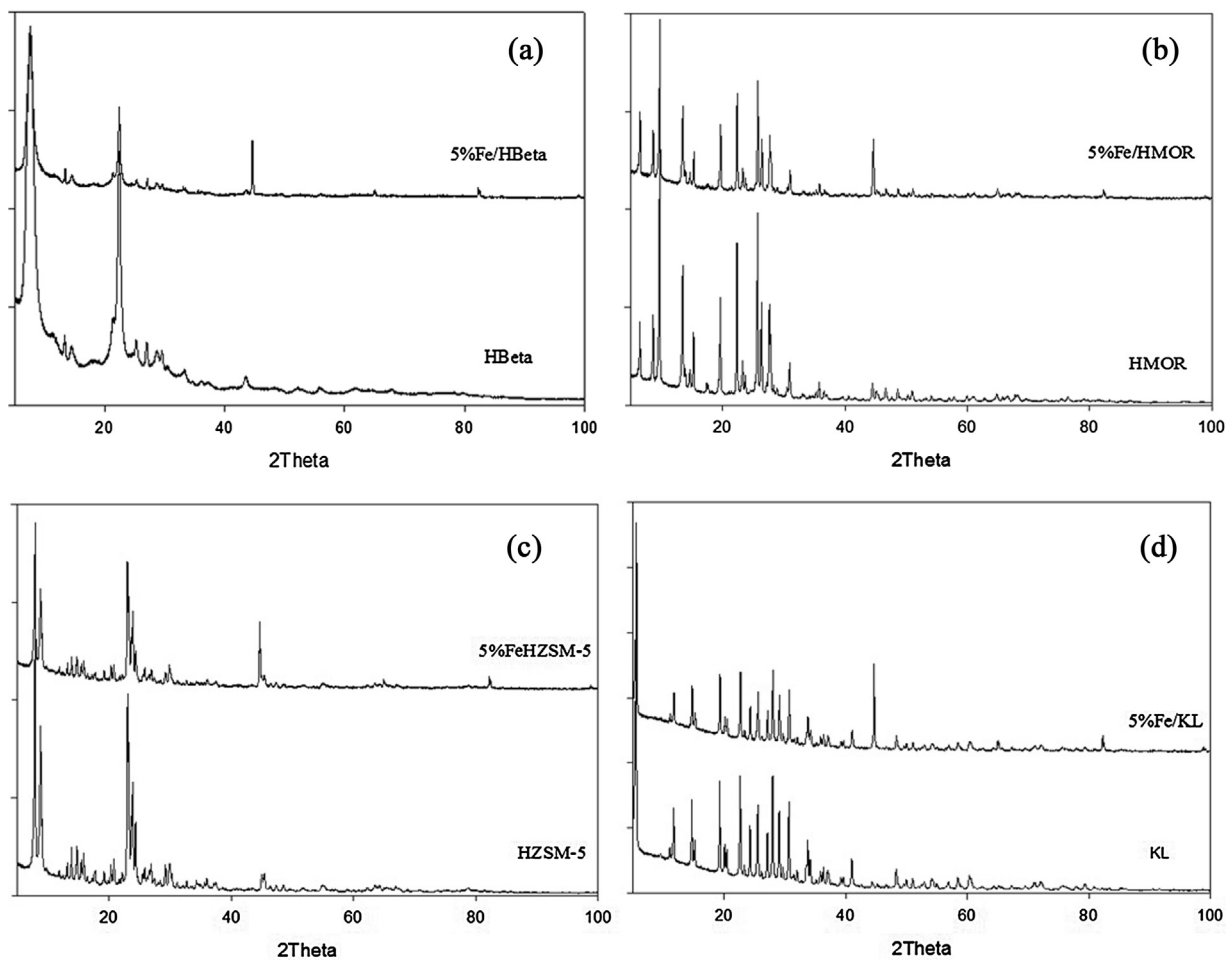
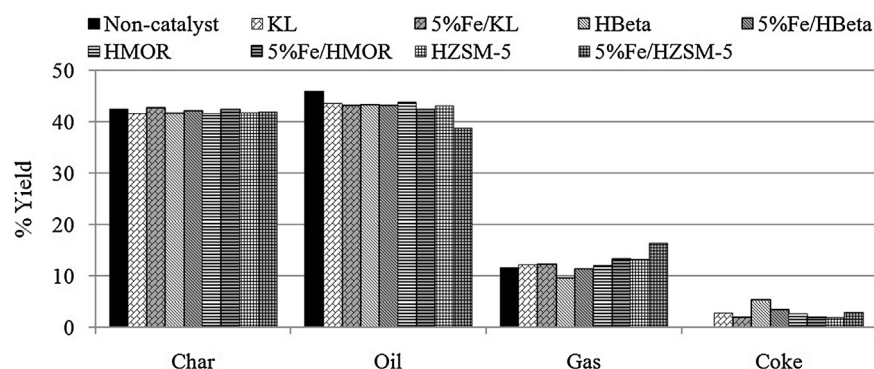
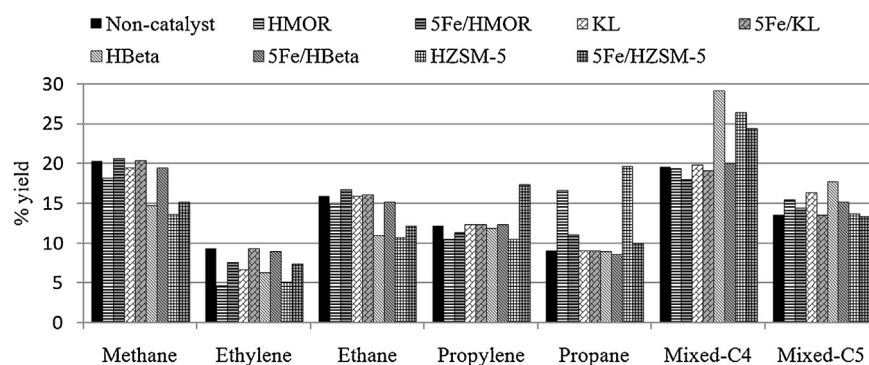


Fig. 3. XRD pattern of (a) 5%Fe/HBeta, (b) 5%Fe/HMOR, (c) 5%Fe/HZSM-5, and (d) 5%Fe/KL.

Table 1
Physical properties of fresh catalysts.

Catalyst	BET Surface area (m ² /g)	Pore volume ^a (cm ³ /g)	Maximum pore width ^a (Å)	Median pore width ^a (Å)	Fe cluster size ^b L_{110} (nm)
HBeta	539	0.257	8.15	8.35	–
HMOR	394	0.199	8.39	8.42	–
HZSM-5	366	0.178	7.77	7.44	–
KL	218	0.113	6.95	7.08	–
5%Fe/HBeta	406	0.234	6.59	8.11	68.4
5%Fe/HMOR	352	0.176	6.50	6.94	60.5
5%Fe/HZSM-5	265	0.131	6.82	6.96	77.6
5%Fe/KL	98.8	0.047	6.62	7.01	80.7

^a Calculated from Horvath–Kawazoe method.^b Calculated from Scherrer's equation.**Fig. 4.** Yield of pyrolysis products obtained from using the parent zeolites and 5%Fe-promoted catalysts.**Fig. 5.** Gas compositions obtained from using the parent zeolites and 5%Fe-promoted catalysts.**Table 2**
Elemental analysis of waste tire samples.

Element	% (By weight)
C	81.1 ± 2.85
H	6.81 ± 0.237
S	2.07 ± 0.0279
N	3.71 ± 0.415

general does not significantly affect the product distribution. Except Fe/HZSM-5, Fe loading further decreases the oil yield in accordance with increment of gas yield, indicating that Fe enhances the cracking ability, which can be confirmed by a higher deposition of coke that is also observed on Fe/HZSM-5 whereas the coke deposition decreases with 5%Fe loading on the other zeolites. However, the highest coke deposition is observed on the HBeta cases. In addition, the distribution of gaseous products obtained from all catalysts are illustrated Fig. 5. Briefly, Fe loading enhances the productions of ethylene and propylene, but suppresses those of mixed C4 and C5 hydrocarbons.

3.3. Petroleum fractions

The petroleum fractions, classified into full range naphtha, kerosene, light gas oil, heavy gas oil, and long residue, are revealed in Fig. 6. The results show that the amount of full range naphtha increases with using the parent zeolites. The effects of zeolites properties have been comprehensively discussed in Muenpol et al., [12]. Furthermore, Fe-loaded catalysts, except 5%Fe/HBeta, markedly enhance the production of full-range naphtha in conjunction with the significant decreases in light gas oil, heavy gas oil, and long residue. It can be concluded that Fe enhances the ability in cracking heavy fractions (especially, light gas oil, heavy gas oil, and long residue) to the lightest full-range naphtha. A tremendous increase in full-range naphtha is obviously observed when Fe is loaded on KL, HMOR, and HZSM-5, but not on HBeta. Since it was observed from the TPR experiments that the interaction between Fe and the three zeolite supports is strong, it can be implied that the strong Fe-support interaction is possibly responsible for the enhanced cracking activity of the catalysts. Similarly, based on Pan et al. the interaction between Fe and the supports (MOR, ZSM-5, and Beta), which decreases in the same

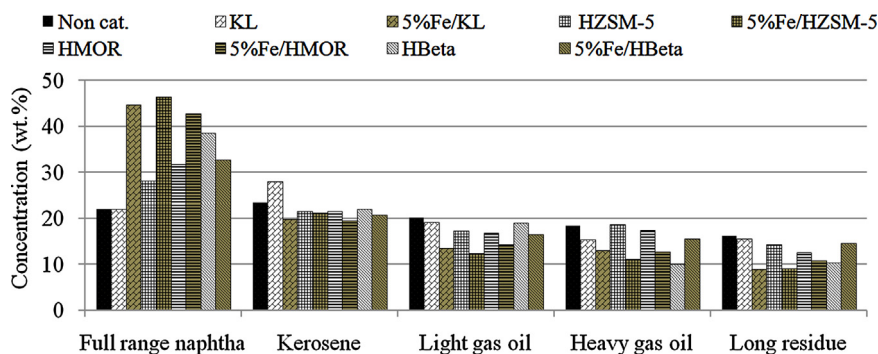


Fig. 6. Petroleum fractions in maltenes obtained from using the parent zeolites and 5%Fe-promoted catalysts.

order; Fe/MOR > Fe/ZSM-5 > Fe/Beta, was found responsible for a high adsorption and conversion of NO [23]. Moreover, Fe loading on these zeolites resulted in stronger acidic site and higher acidity, and Fe/MOR was found more acidic than Fe/ZSM-5 and Fe/Beta [24]. Therefore, the enhancement on cracking activity of the catalysts in waste tire pyrolysis could possibly be contributed from strong Fe-support interaction and the enhancement of acidity with Fe loading.

3.4. Petrochemicals in oils

Components in gasoline (C_5 – C_9), which are classified into paraffins, olefins, naphthenes, and aromatics, are exhibited in Fig. 7, and the content of petrochemicals in gasoline is shown in Fig. 8. In general, aromatics are the most abundant species in gasoline, co-existing with a considerable amount of olefins and naphthenes and a trace of paraffins. The parent KL, HMOR, and HBeta do not much alter the distribution of gasoline-range species whereas HZSM-5 significantly enhances the formation of olefins and naphthenes in expense of total aromatics. It can be possibly explained that HZSM-5 has the pore opening window that can selectively fit with the molecular size of gasoline components (C_5 – C_9) whereas the other zeolites have a larger pore opening window. Therefore, the components in this range can be selectively transformed from one to another in the suitable size of HZSM-5's pore. Furthermore, it can be seen that the introduction of Fe-loaded catalysts results in the change of species in gasoline. Especially, naphthenic group is enhanced using Fe/HMOR and Fe/HBeta in expense of olefins or aromatics, indicating that olefins and/or aromatics are transformed to naphthenes. Fe loaded on HZSM-5 and KL increases the aromatic content with the suppression of olefins, possibly via cyclization and then aromatization. It can be stated that Fe seems to drive cyclization of a non-cyclic to a cyclic molecule, either a naphthene or an aromatic, depending on the reactant.

It appears that the tire-derived oils are not suitable for direct use as a fuel in an internal combustion engine due to the high aromatics contents. However, the oils have a potential for use as a feedstock for petrochemicals production since they contain some valuable petrochemicals; that are, benzene, toluene, ethylbenzene, xylenes, styrene, cyclohexane, and cumene. Generally, using the zeolites in tire pyrolysis produces around 12–26 wt.% petrochemicals in gasoline, which is not significantly different from the quantity observed in thermal pyrolysis, except the case of using HBeta as a catalyst that gives ~60% (Fig. 8). Marked increases in petrochemicals production (~47–80 wt.% in gasoline) are observed with using Fe catalysts, regardless of the zeolite supports, especially 5%Fe/HMOR and 5%Fe/KL, even though Fe/HBeta does not alter the total petrochemicals content significantly. It indicates that Fe promoted on HMOR and KL, that have 1D pore channel, more sharply increases the petrochemicals content in gasoline than on HZSM-5 or HBeta

Table 3

Petrochemicals content (wt.%) in oils obtained from zeolites and Fe-loaded zeolites.

Petrochemical	Petrochemicals content (wt.% in oil)							
	HM	5Fe/HM	HB	5Fe/HB	HZ	5Fe/HZ	KL	5Fe/KL
Benzene	0.12	14.0	4.8	–	–	3.4	0.26	12.7
Toluene	0.18	0.053	0.92	0.095	0.20	0.65	0.005	1.2
Ethylbenzene	0.41	0.83	3.3	0.87	0.26	0.40	0.10	–
<i>m</i> -Xylene	0.18	–	–	–	0.098	0.84	–	0.39
<i>o</i> -Xylene	–	–	0.16	0.23	–	0.01	–	–
<i>p</i> -Xylene	–	0.28	0.13	0.25	0.030	0.044	–	0.21
Styrene	1.3	–	0.32	0.46	0.21	0.60	0.12	0.46
Cyclohexane	–	7.2	1.0	4.1	3.5	4.1	–	3.3
Cumene	0.1	0.88	0.08	0.5	0.03	1.1	0.083	0.68
Total	2.32	23.3	10.8	6.5	4.3	11.2	0.58	18.9

that has a 3D pore channel. In details, 5%Fe loading on HMOR sharply increases benzene and cyclohexane contents whereas the equal loading on KL results in the increase of benzene, cyclohexane and toluene. These observations also support our earlier findings that Fe was found to cyclize olefin to a cyclic or an aromatic compound. Moreover, it is observed that 5%Fe/HZSM-5 produces more amount of benzene than HZSM-5, and 5%Fe/HBeta increases the cyclohexane content in accordance with the reduction of benzene. It can be concluded that 5%Fe loading on KL, HMOR, and HZSM-5 resulted in more valuable products than the parent zeolites. Moreover, the introduction of 5%Fe on KL and HMOR (1D pore channel) enhances the production of valuable hydrocarbons more effectively than on HZSM-5 and HBeta (3D pore channel).

In order to get a clearer picture of how much petrochemicals are produced in the tire-derived oils, Table 3 exhibits the content of petrochemicals in oils (wt.%) obtained from waste tire pyrolysis using pure zeolites; that are, KL, HZSM-5 (HZ), HMOR (HM), and HBeta (HB) and Fe-promoted catalysts. From the results, it can be seen that 5%Fe/HMOR is the best catalyst to produce benzene (14.0 wt.% in oil) and cyclohexane (7.17 wt.% in oil), and HBeta can be used to produce ethylbenzene (3.31 wt.% in oil). On other hand, only a small amount of other petrochemicals; that are, styrene, toluene, cumene, and xylenes, are found in the oils.

3.5. Aromatics in maltenes

The chemical components in maltenes, especially the types of aromatic compounds, can also be illustrated more clearly as shown in Fig. 9. It also supports that the concentration of paraffins does not change significantly with using all catalysts, and the concentration of olefins and naphthenes tends to decrease with using Fe-loaded catalysts. It can be explained that olefins and naphthenes may convert to aromatics via Diels–Alder reaction [25,26]. Moreover, mono-aromatics increase significantly with using Fe-loaded catalysts, as compared to the parent zeolites whereas 5%Fe supported

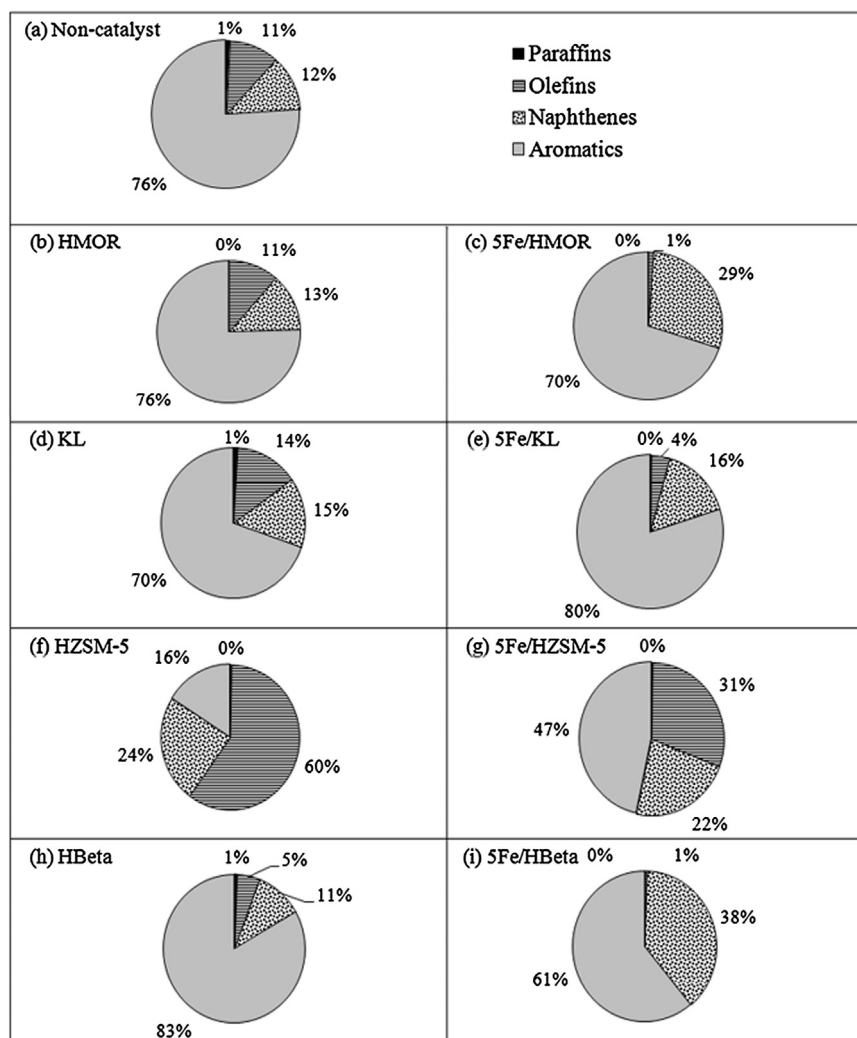


Fig. 7. Components in gasoline (wt.%): (a) the non-catalyst case, (b) HMOR, (c) 5Fe/HMOR, (d) KL, (e) 5Fe/KL, (f) HZSM-5, (g) 5Fe/HZSM-5, (h) HBeta, and (i) 5Fe/HBeta.

on KL, HMOR, and HZSM-5 gives a lower amount of di- and poly-aromatic hydrocarbons than the parent zeolites, but 5Fe/HBeta gives a higher amount of poly-aromatic hydrocarbons than the parent HBeta. It can be suggested that di- and poly-aromatics convert to mono-aromatics via hydrogenation and ring opening reaction, possibly enhanced by Fe [20,27]. However, the introduction of Fe also results in the reduction of some mono-aromatic species (see in Tables 4–7 in Supplementary materials) as evidently observed from the GC × GC-TOF/MS results. It can be suggested that these mono-aromatics might be converted to other hydrocarbon compounds or valuable petrochemicals, as observed earlier [12], by hydrogenation and ring opening, also enhanced by Fe. Additionally, polar-aromatic hydrocarbons, that are the combinations of S, O, and N-containing aromatics, slightly increase with loading Fe on KL, HZSM-5, and HMOR zeolites, but decrease with using Fe supported on HBeta.

3.6. Desulfurization activity

The sulfur content in pyrolytic oils as exhibited in Fig. 10 is determined by using an elemental analyzer. Originally, it is found that the sulfur content in oil is around 1.17 wt.%. All catalysts result in the reduction of sulfur in oils, as compared to the non-catalytic pyrolysis. In addition, the parent zeolites can reduce sulfur in oil significantly, and Fe-promoted catalysts further reduce sulfur in oils. The lowest sulfur in oils is obtained

from using 5Fe/HZSM-5 (0.73 wt.%), followed by 5Fe/HMOR (0.91 wt.%), 5Fe/KL (0.92 wt.%), and then 5Fe/HBeta (0.99 wt.%). Sulfur removed from the oils is deposited on the spent Fe catalysts as evidently seen from Fig. 11. Therefore, it can be concluded that Fe enhances sulfur removal activity.

Fig. 12 reveals that the yield of sulfur species in maltenes, which are classified into two groups: (1) sulfur-containing compounds, that consist of thiophenes (Ts), benzothiophenes (BTs), and dibenzothiophenes (DBTs), and (2) heteroatom-containing sulfur compounds, that consist of benzothiazoles (N-containing sulfur compound) and others (N or/and O-containing sulfur compounds). Nitrogen and oxygen are found in oils because nitrogen- and oxygen-containing compounds are used as vulcanization accelerators in rubber production, especially benzothiazoles, which are commonly used in vulcanization process [4,5,28]. The results show that Fe-loaded catalysts tend to decrease the amounts of benzothiophenes and dibenzothiophenes, except 5Fe/HZMS-5 that increases the amount of BTs, observed with the simultaneously-increasing formations of benzothiazoles and other N or/and O-containing sulfur compounds (see Fig. 11). However, the overall sulfur content in the oils is decreased with Fe loading. From the results, it can be suggested that Fe enhances the C–S bond breaking activity, resulting in the reduction of BTs and DBTs, whereas Fe loaded on HZSM-5 may partially plug the pore opening of HZSM-5, which is the smallest; thus, resulting in the lower activ-

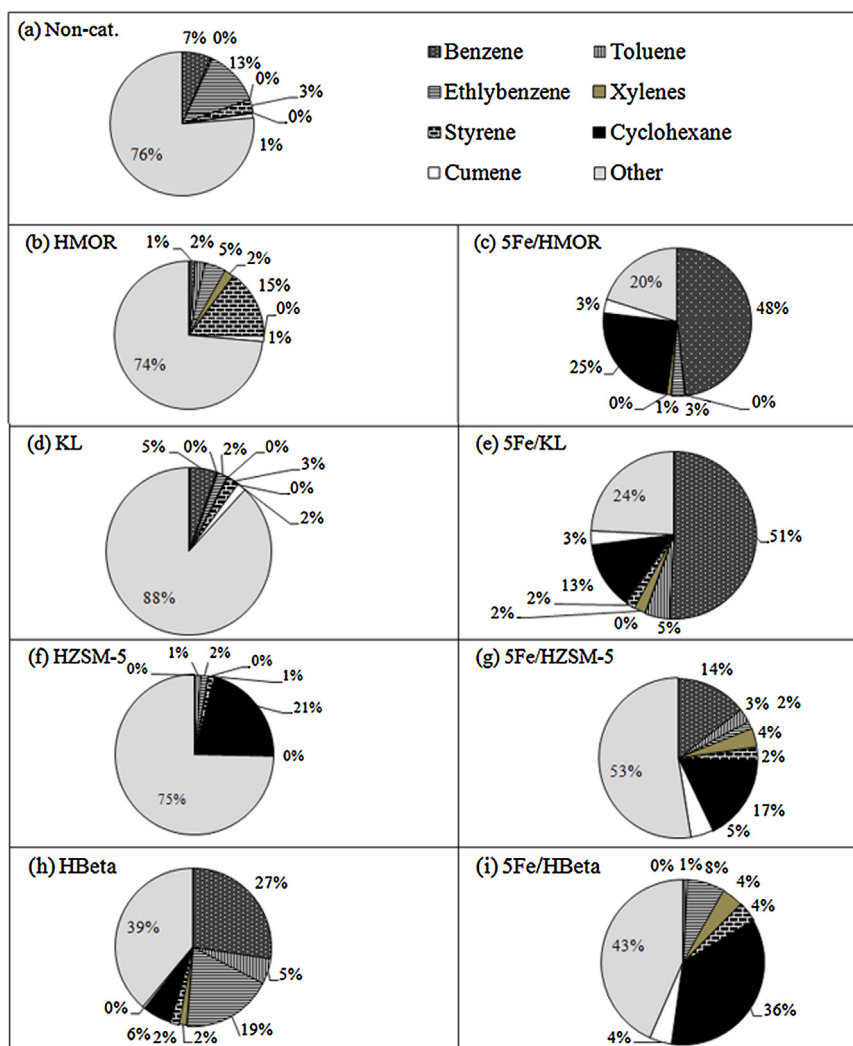


Fig. 8. Petrochemicals (wt.% in gasoline) obtained from (a) the non-catalyst case, (b) HMOR, (c) 5Fe/HMOR, (d) KL, (e) 5Fe/KL, (f) HZSM-5, (g) 5Fe/HZSM-5, (h) HBeta, and (i) 5Fe/HBeta.

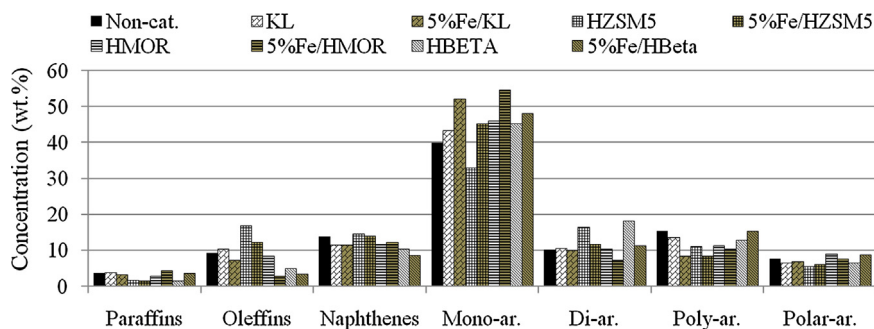


Fig. 9. Concentration of chemical components in maltenes obtained from using the parent zeolites and 5%Fe-promoted catalysts.

ity in reduction of BTs and DBTs. The discussion on the effects of zeolite supports has been previously reported in [12]. However, the increases in benzothiazole content in the oils using Fe-promoted catalysts were also simultaneously observed, which might be explained by two possible reasons: (a) while the C-S bond in the molecules of adsorbed benzothiophenes is broken by an Fe site, the benzothiophenes on the surface are partially attacked and reacted with N-containing compounds, forming benzothia-

zoles whereas the un-attached benzothiophenes desorb as S-free products from the surface, leaving sulfur on the Fe sites of spent catalysts as shown in Fig. 10, and/or (b) other S-containing compounds might adsorb on the Fe sites and then react with N-containing compounds, forming benzothiazoles and other multi-heteroatom containing compounds. Future mechanistic studies are needed to support the explanations.

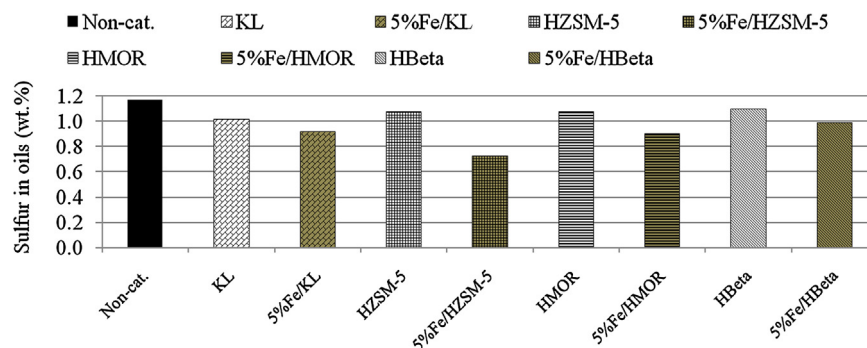


Fig. 10. Sulfur content in oils obtained from using the parent zeolites and 5%Fe-promoted catalysts.

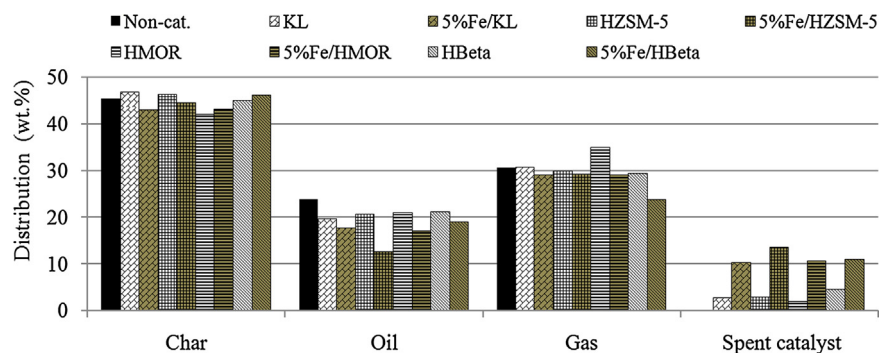


Fig. 11. Overall distribution of sulfur in pyrolysis products obtained from using the parent zeolites and 5%Fe-promoted catalysts.

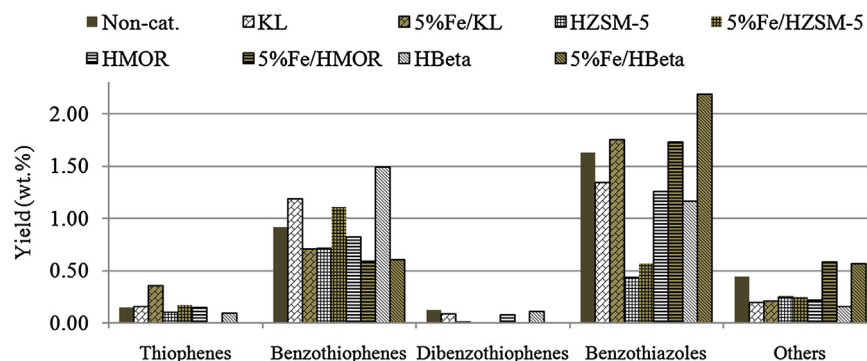


Fig. 12. Yield of sulfur species in maltenes obtained from using the parent zeolites and 5%Fe-promoted catalysts.

4. Conclusions

All Fe-promoted catalysts increased the light fraction (full range naphtha) at the expense of the heavier fractions in oil because Fe enhanced the cracking activity of zeolites. Especially, the total petrochemicals in oil were highly increased with using Fe-loaded catalysts, except 5%Fe/HBeta. It can be ranked as 5%Fe/HMOR > 5%Fe/KL > 5%Fe/HZSM-5 > 5%Fe/HBeta. 5%Fe/HMOR appeared to be the best catalyst to produce benzene and cyclohexane. 5%Fe/KL was the best catalyst for toluene production, whereas 5%Fe/HZSM-5 can be used to produce xylenes and cumene. Moreover, sulfur content in oils reduced with using Fe-loaded catalysts, and the lowest sulfur in oil was obtained from using 5%Fe/HZSM-5.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jaap.2015.12.003>.

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Impacts of nickel supported on different zeolites on waste tire-derived oil and formation of some petrochemicals



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ABSTRACT

Waste tire-derived oils commonly contain the considerable valuable aromatics such as benzene, toluene, ethylbenzene, toluene, xylenes and etc., but they also contain a significantly-high amount of sulfur compounds, which cause a low quality of pyrolytic oil. Ni is a cheap metal, which exhibits hydrogenation/dehydrogenation and ring-opening like a noble metal, and widely used as promoter in desulfurization of fuels. In this work, Ni was expected to be a catalyst promoter of zeolites for reduction of sulfur content in oil and enhancement of petrochemical formation in oil. Therefore, the effect of 5 wt.% nickel loading on different four type zeolites (HZSM-5, HMOR, HY, HBETA) on the sulfur removal and quality of waste-tire derived oil was studied. The results show that the incorporations of nickel on all zeolites significantly reduced sulfur contents in oil. However, the quality of waste tire-derived oil did not only depend on the nickel promoter, but also strongly depended on zeolite supports. The introduction of nickel on HZSM-5 zeolite, which possesses a smaller pore size than HBETA zeolites, provided a lighter oil with higher proportion of gasoline and kerosene than Ni/HBETA catalyst, and produced a higher amounts of valuable aromatic such as ethylbenzene, toluene, cumene, and mixed-xylenes than Ni/HBETA catalyst. Moreover, the addition of nickel on HMOR zeolite, which possesses a 1D zeolite channel structure, also provided a lighter oil with a high proportion of gasoline and kerosene than the Ni-loaded on HBETA (3D zeolite channel structure), and exhibited a better petrochemical production with a higher concentrations of ethylbenzene, toluene, cumene and styrene in maltene. On the other hand, Ni/HBETA provided the lower sulfur content in oil than Ni/HMOR catalyst, but the sulfur removal ability by nickel species on HMOR was higher than nickel species on HBETA zeolite. Furthermore, the introduction of nickel on HY zeolite provided the heavier oil with higher proportion of gas oil, LVGO and HVGO and lower proportion of petrochemical than Ni/HBETA zeolite whereas the sulfur removal of nickel species on the HBETA support with higher acid strength was better than on the HY support.

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1. Introduction

In recent decades, pyrolysis of waste tire is the useful process that can recovery valuable chemicals from waste tire and eliminate the environmental impacts from disposal of waste tire. Among the waste tire-derived products, waste tire-derived oils have received more attention since their properties are quite similar to those of commercial diesel and heating oil. Petrochemicals can be classified into olefins and aromatics, and utilized as a raw material in manufacturing of plastics, solvents, detergents, syn-

thetic rubber, cosmetic products and pharmaceuticals. From past to present, petrochemicals such as ethylene, propylene, butadiene and BTEX are mainly produced via cracking of naphtha and ethane derived from crude oil and natural gas [1]. However, the production of petrochemicals via petroleum and natural gas is not sustainable since the petroleum and natural gas resources continuously decrease. As a result, several alternative processes for production of petrochemical by utilization of methane, coal, biomass and waste tire have attracted a great attention. Among these alternative processes, waste tire pyrolysis is considered as an effective process since it can eliminate waste tire problems by breaking up the tire molecules into valuable chemicals or fuel. Moreover, several studies reported that tire-derived oils contain a considerable concentration of valuable aromatics such as benzene, toluene, ethylbenzene, styrene, xylenes and etc [2] and [3]. How-

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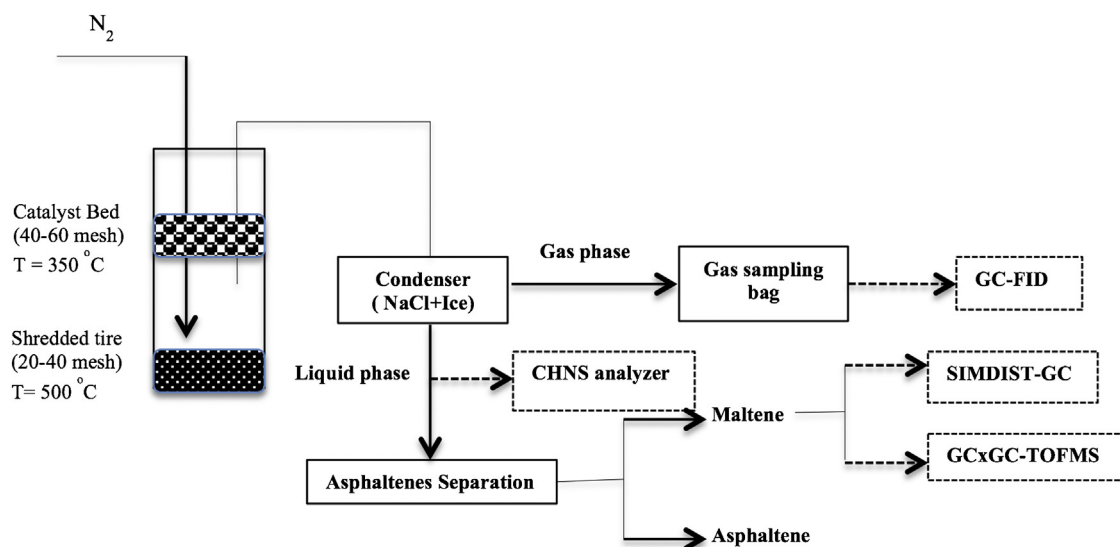


Fig. 1. Schematic of waste tire pyrolysis system for collection and analysis of products.

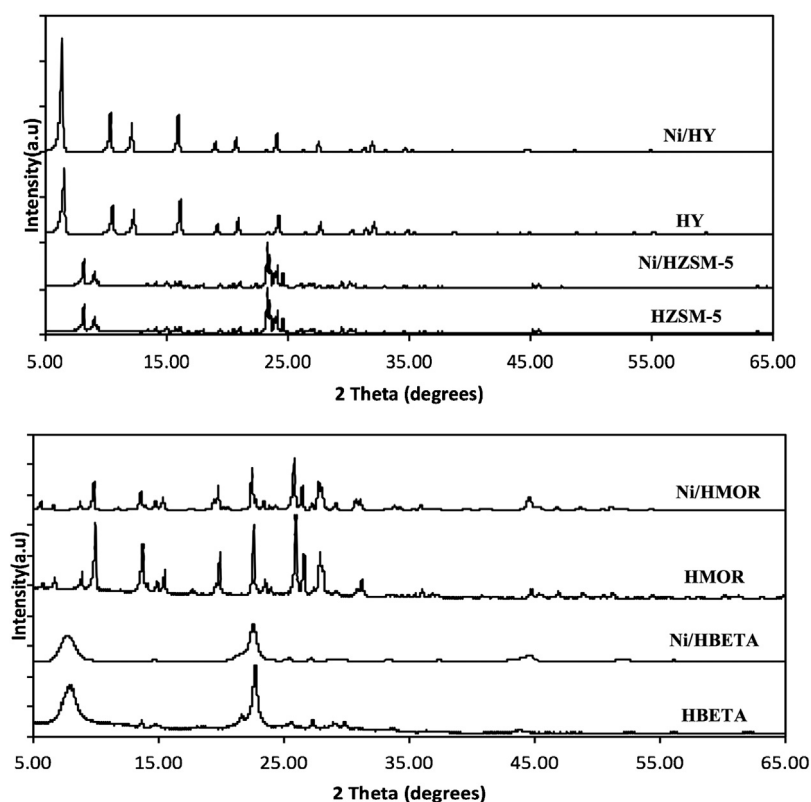


Fig. 2. XRD patterns of zeolites and impregnated catalysts.

ever, the major drawback is the relatively high concentrations of sulfur and nitrogen, which vary in the range of 0.5–3 wt.%, depending on the pyrolysis system and catalysts [4]. They contain a great amount of sulfur since the sulfur is an additive in vulcanization process. Acidic zeolites such as HBETA, HMOR, HY, HZSM-5 have been proven to be able to reduce sulfur content in oil and enhance the quality of tire-derived oil. Duñg et al. [5] stated that HMOR increased the concentration of mono-aromatics in oil, whereas the polycyclic aromatics, especially polar-aromatics significantly decreased. In addition, HMOR also increased the naphtha fraction in oil, whereas the heavy fraction drastically decreased. HBETA and

HY zeolites increase naphtha and kerosene fractions, whereas the heavier fraction slightly decreased [6]. Thus, these studies indicate that different zeolites provide different product distribution because each zeolite has unique properties. In particular, HZSM-5 zeolite is commonly used as a catalyst in the petrochemical industry due to its pore size, strong acidity and strong resistance to deactivation. Boxiong et al. [7] found that the HZSM-5 enhanced the production of benzene, toluene and xylenes. The high acid strength of zeolite is favorable for production of valuable aromatics, but the high acid density is favorable for sulfur removal from oil. The pore size of zeolite plays an important role in governing the molecular

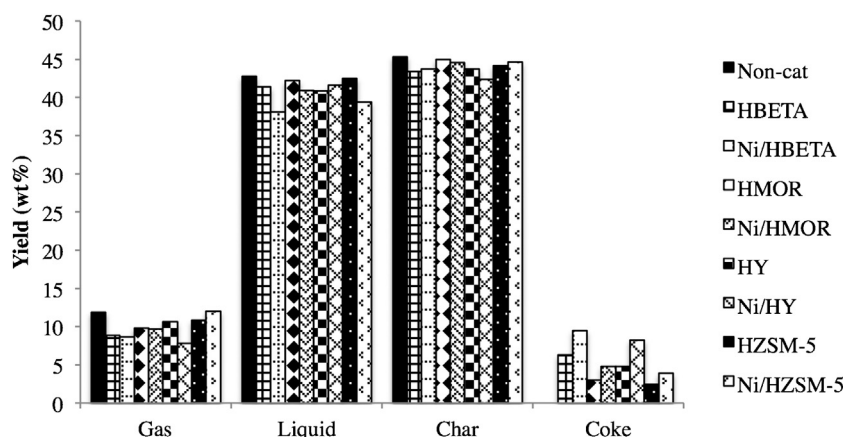


Fig. 3. Effect of nickel based catalysts on pyrolysis yields.

size of products. The large pore size of HBETA provided better cracking activity and petrochemical formation in oil than the HZSM-5 zeolite with medium pore size. The 3D pore channel structure of HBETA zeolite provided a higher cracking activity and petrochemical productivity than 1D pore channel structure of HMOR due to the longer contact time of molecules in the pore. A zeolite support with a sufficiently pore size (~ 7 Å) with 3D complex channel structure was suggested for producing a high quality of oil with a high formation of petrochemicals [8].

Bi-functional catalysts have also been tested in waste tire pyrolysis, and provided the interesting results. Recently, Cu doped on HBETA, HY and HMOR zeolites significantly reduced the sulfur content in oil by 31.0–37.4%, respectively and also enhanced the petrochemical formation in oil [9]. Nickel is favorable to hydrogenation/dehydrogenation reactions, or promotes aromatization and cracking reactions [10]. For example, Ni over hierarchical ZSM-5 and Beta zeolites enhanced the production of gas and gasoline from hydroreforming of polyethylene-derived thermal cracking oil. In addition Ni/HZSM-5 catalyst can promote the transformation of olefins into aromatics and iso-paraffins [11]. Another common application of nickel-based catalyst is desulfurization. The sulphur removal efficiency increased with the increase of nickel loading on SBA-15 in adsorptive desulfurization of diesel [12]. In addition, Rodríguez-Castellón et al. [13] revealed that nickel supported on zirconium-doped mesoporous silica promoted the hydrogenation and ring-opening of tetralin.

In our earlier work, Ni promoted on HBeta zeolite at various percentages of loading (0–20 wt.%) was investigated for its effect on waste tire pyrolysis products, and it was found that a higher % loading of Ni enhanced olefins yield in gaseous product, but the yield of olefins dropped slightly at the highest % Ni loading (20%). The high amount of Ni loaded catalyst produces the higher concentration of light and heavy gas oil, but suppressed the kerosene content [14]. Later, the catalytic pyrolysis of waste tire was performed over Ni catalyst supported on HZSM-5 zeolite [15]. It was found that Ni doping significantly enhanced the yields of ethylbenzene, toluene, mixed-xylenes, and cumene in oil, and enhanced the overall petrochemical productivity. Since the properties of zeolite supports also contributed to the catalyst abilities as previously reported in our study [8], the introduction of Ni on different zeolite supports could also result in different impacts. In this work, nickel was therefore loaded at a fixed 5 wt.% on different zeolites; that are, HBETA, HMOR, HY and HZSM-5, aiming to investigate the activity of Ni on reduction of the sulfur in tire-derived oil and on the enhancement of formation of valuable petrochemicals in oils when promoted on zeolites with different properties. The effect of nickel loading on each pair of zeolites [8] was discussed mainly

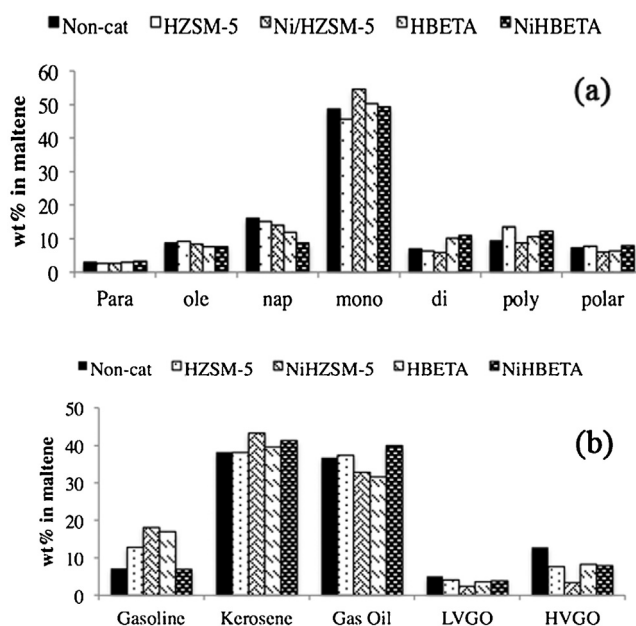


Fig. 4. (a) Concentration of each chemical group, and (b) Petroleum fractions in maltene using Ni-loaded on HBETA and HZSM-5 zeolites.

on chemical species in waste tire-derived oil and sulfur removing ability.

2. Experimental

2.1. Catalyst preparation

The commercial zeolites selected in this research were purchased from TOSOH Corporation (Singapore); HBETA (931HOA, Si/Al = 14, H-form), HMOR (640HOA, Si/Al = 9, H-form), HY (360HUA, Si/Al = 7.5, H-form) and HZSM-5 (840NHA, Si/Al = 20, NH₄-form). Prior to activity testing and metal impregnation, HMOR, HY, and HZSM-5 were calcined in standing air at 500 °C for 3 h (Ramping rate of 10 °C/min). HBETA was calcined in standing air at 650 °C for 2 h (Ramping rate of 2 °C/min). The calcination conditions were made different due to the different forms of the purchased zeolites. For instance, the purchased BETA zeolite was in the NH₄-BETA form; therefore, it was calcined at 600 °C in order to completely convert NH₄⁺ to H⁺ form [5,9]. Ni-loaded zeolites were prepared using incipient wetness impregnation of (NiNO₃)₂·6H₂O until 5 wt.% metal loading based on the mass of catalysts. The cat-

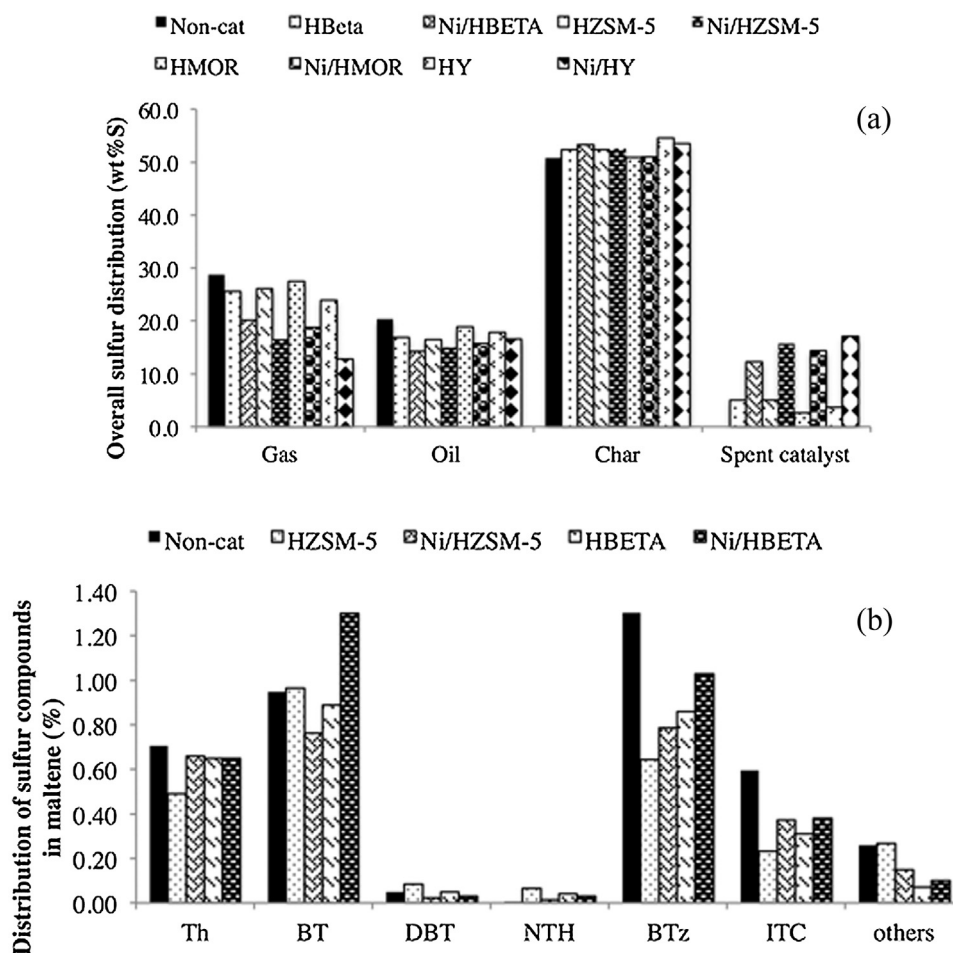


Fig. 5. (a) Overall sulfur distribution on waste tire pyrolysis products and spent catalysts, and (b) Distribution of sulfur compounds obtained from Ni/HBETA and Ni/HZSM-5.

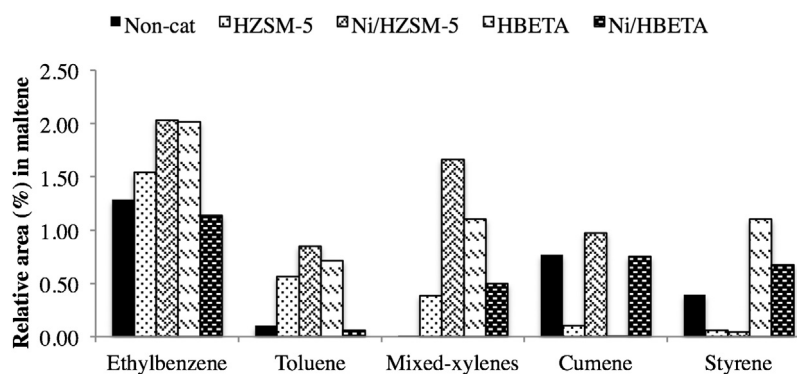


Fig. 6. Petrochemicals in maltenes obtained from Ni/HBETA and Ni/HZSM-5.

alysts were then dried overnight at 105 °C, and calcined at same conditions. The catalyst powders were pelletized, crushed and sieved to 40–60 mesh of particle sizes. The catalysts were activated by reduction under hydrogen flow (30 ml/min) at 600 °C for 2 h (heating rate 10 °C/min).

2.2. Catalyst characterization

The catalyst samples were characterized by different physicochemical characterization methods. X-ray diffraction (CuK α radiation), carried out in a Rigaku SmartLab X-ray Diffractometer, was used to identify the crystallinity of catalysts. XRD patterns were

recorded in the 5–65° (2 θ) range using a scan speed of 10° (2 θ)/min. The surface area and pore volume of catalysts were measured using N₂ adsorption–desorption isotherms with Thermo Finnigan Sorptomatic 1990 instrument. The amount of coke deposition on the spent catalysts was measured by thermogravimetric/differential thermal analysis (TG/DTA), carried out under flowing of nitrogen (10 ml/min) and oxygen (20 ml/min) on a PerkinElmer/Pyris Diamond (thermogravimetric/differential thermal analysis, TG/DTA). The sample were heated up from room temperature to 900 °C with ramping rate of 10 °C/min. CHNS analyzer was used to determine the sulfur and nitrogen content on spent catalyst using LECO® Elemental Analyzer.

2.3. Waste tire pyrolysis

Only the thread of one waste tire (Bridgestone Turanza GR80) was used as a raw material in every batch in order to prevent the impacts from variation of the components in the feed. The analysis of the same model of tire tread was reported in our previous papers [5,16]. Nevertheless, the ultimate analysis of shredded waste tire samples was performed using a LECO® Elemental Analyzer. A 0.1 g of the tire sample was put in the elemental analyzer, and next the temperature of furnace was raised from room temperature to 600 °C and held for 15 min in the first step, and then raised again to 1350 °C in the analyzing step. The schematic pyrolysis system is displayed in Fig. 1. Firstly, 30 g of shredded tire (20–40 mesh) was pyrolyzed in the lower zone of the reactor at 500 °C under atmospheric pressure. The pyrolysis products were carried by 30 ml/min of nitrogen flow to the catalytic bed filled with 7.5 g of catalyst and heated to 350 °C. After the temperatures of lower and upper zones reached to the desired one, the temperature of two zones was kept at desired temperature for 2 h. The resulting products were separated into gas and liquid fraction by condensers (ice-salt condensing system). Gas product was collected in Tedlar PVF bag.

2.4. Product analysis

Liquid and solid products were weighed to determine the product yield. The gas yield was determined by mass balance. The gaseous products were analyzed by GC, Agilent Technologies 6890 equipped with HP-PLOT Q column (300 mm × 0.32 mmID and 20 μm film thickness) and FID detector. The liquid products were dissolved in n-pentane (mass ratio of n-pentane/oil = 40:1) to precipitate asphaltene. Asphaltene was filtered by using a polyamide membrane (0.45 μm). The maltene solutions were then analyzed by Comprehensive Two-Dimension Gas Chromatography (Agilent Technologies 7890) with Time-of-Flight Mass Spectrometer (LECO, Pegasus® 4D TOF/MS) equipped with the 1st GC column was a non-polar Rtx®-5Sil MS (30 m × 0.25 mmID × 0.25 μm) and the 2nd GC column was an Rxi®-17MS (1.790 m × 0.1 mmID × 0.1 μm). The primary column was held up at 50 °C for 2 min, and then heated up to 310 °C with a ramping rate of 5 °C/min. After the final temperature was reached, it was held at 310 °C until the analysis was finished. The temperature of secondary column was held at 60 °C for 2 min, and then ramped up to 320 °C with the ramping rate of 5 °C/min. After reached, the final temperature of column was held

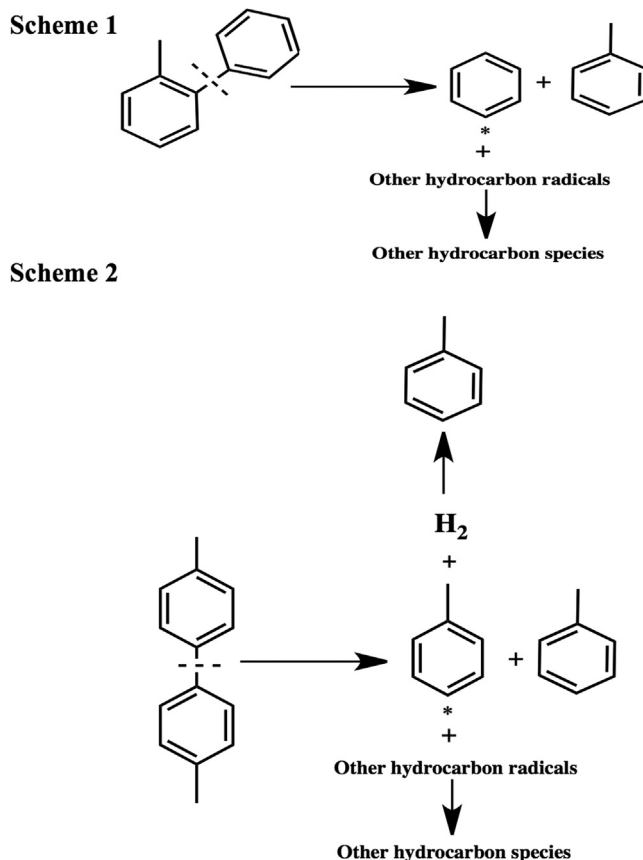


Fig. 7. Possible reaction pathways for transformation of 2-methylbiphenyl and 4,4'-dimethylbiphenyl to valuable aromatics by Ni/HZSM-5.

at 320 °C until the analysis was finished. The simulated true boiling point curves were determined by using a Varian GC-3800 simulated distillation gas chromatography equipped with FID detector and a 15 m × 0.25 mm × 0.25 μm WCOT fused silica capillary column. The petroleum fractions were cut based on their boiling point ranges according to the ASTM D2887: gasoline (<149 °C), kerosene (149–232 °C), gas oil (232–343 °C), light vacuum gas oil (343–371 °C) and heavy vacuum gas oil (>371 °C). Moreover, sulfur

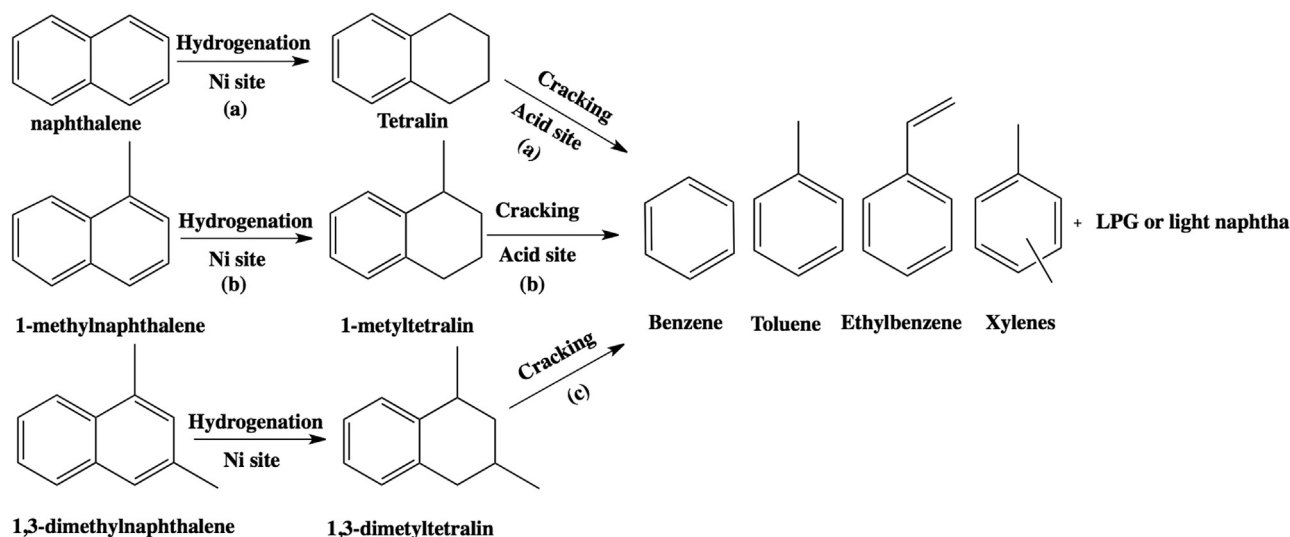


Fig. 8. Possible reaction pathways of naphthalene, 1-methylnaphthalene and 1,3-dimethylnaphthalene by Ni/HZSM-5 adapted from Kim et al. [18] (a), Park et al. [19] (b), and Bredael and Vinh [20] (c).

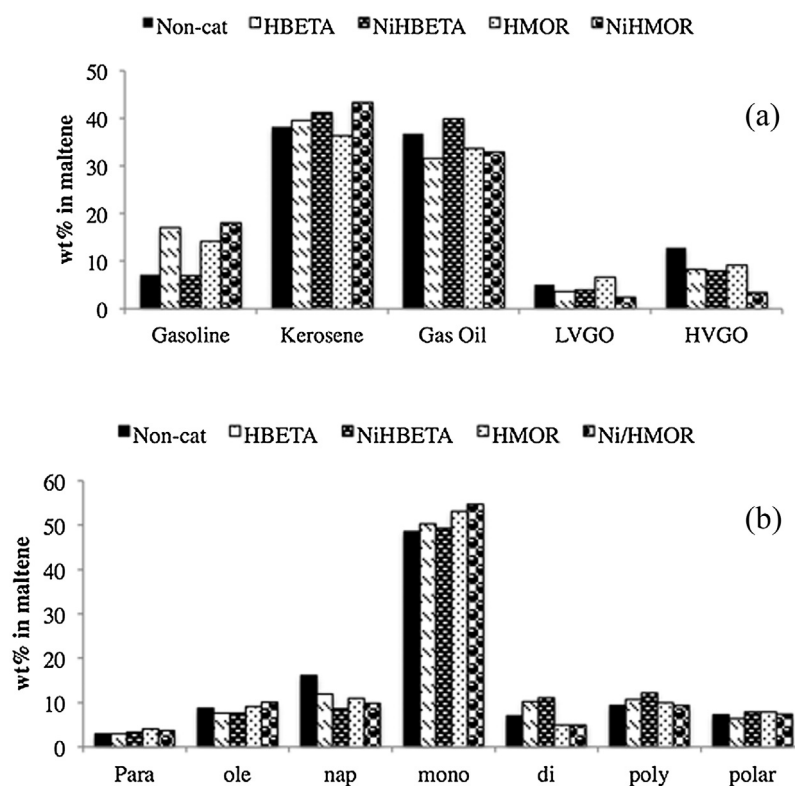


Fig. 9. (a) Petroleum fractions, and (b) Concentration of each chemical group in maltenes using Ni/HBETA and Ni/HMOR catalysts.

Table 1
BET specific area and pore volume of catalysts.

Catalyst	Surface area (m ² /g)	Micropore volume (cm ³ /g)
HBETA	559	0.280
HMOR	395	0.199
HY	546	0.277
HZSM-5	365	0.178
Ni/HBETA	466	0.215
Ni/HMOR	308	0.158
Ni/HY	537	0.264
Ni/HZSM-5	290	0.142

and nitrogen content in tire-derived oil and char were determined by LECO® Elemental Analyzer (TruSpec® CHNS). Furthermore, sulfur content in the gas products was determined from mass balance.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the HBETA, HMOR, HY, HZSM-5 zeolites and the supported Ni catalysts are displayed in Fig. 2. Both impregnated catalysts and parent zeolites clearly display the characteristic XRD patterns of BEA, FAU, MOR and MFI structure. Therefore, the introduction of nickel on zeolites seems not to destroy the zeolite structure, but slightly affects the zeolite crystallinity. The characteristic peaks of metallic nickel are present at $\sim 44.5^\circ$ and $\sim 51.8^\circ$.

From Table 1, the decreases in BET surface area and micropore volume clearly indicate that Ni cluster might be located inside the zeolite pore, and partially block the zeolite channel [17]. In addition, some metallic nicks may undergo sintering during the reduction of nickel oxide and then move to external surface of catalyst [10].

3.2. Pyrolysis yields

Elemental analysis of waste tire samples revealed that the tire tread samples contained 81.1 ± 2.85 wt.% C, 6.81 ± 0.237 wt.% H, 2.07 ± 0.0279 wt.% S, and 3.71 ± 0.415 wt.% N. These tire samples were then used in pyrolysis experiments. As a result, the pyrolysis product distribution from using parent zeolites and impregnated catalysts are displayed in Fig. 3. It can be seen that when catalysts are used, the liquid and gas yields are suppressed while the coke formation over spent catalysts significantly increases. The reduction of liquid yield when catalysts are used in waste tire pyrolysis indicates that catalysts promote cracking activity of pyrolysis liquid. Nickel-modified catalysts are more effective than the parent zeolites since they give higher gas yields and lower liquid yields. Coke formations over spent the nickel modified catalysts is higher than that on parent zeolites since the incorporation of metallic nickel on zeolites increase surface activity and hydrogen transfer, which favors for coke formation.

3.3. Effect of Ni loading on zeolites with different pore sizes

Similarly classified as 3D channel structured possessing zeolites, HBETA has the pore size of 6.4×7.6 Å and HZSM-5 a smaller pore size of 5.3×5.6 Å. The effect of Ni loading was investigated on two supports with different pore sizes, HZSM-5 and HBETA zeolites. Fig. 4a and b illustrate the concentration of petroleum fractions in maltenes and maltene compositions, respectively. The results indicate that the incorporation of nickel on HZSM-5 zeolite strongly enhances the gasoline and kerosene, whereas the gas oil, LVGO and HVGO reduce, indicating that the nickel species on HZSM-5 strongly promote cracking activity of HZSM-5 catalyst. Moreover, Ni/HZSM-5 strongly enhances the formation of mono-aromatic, whereas the formation of olefins, naphthenes, di-, poly-, and polar-aromatics reduced. These results indicate that

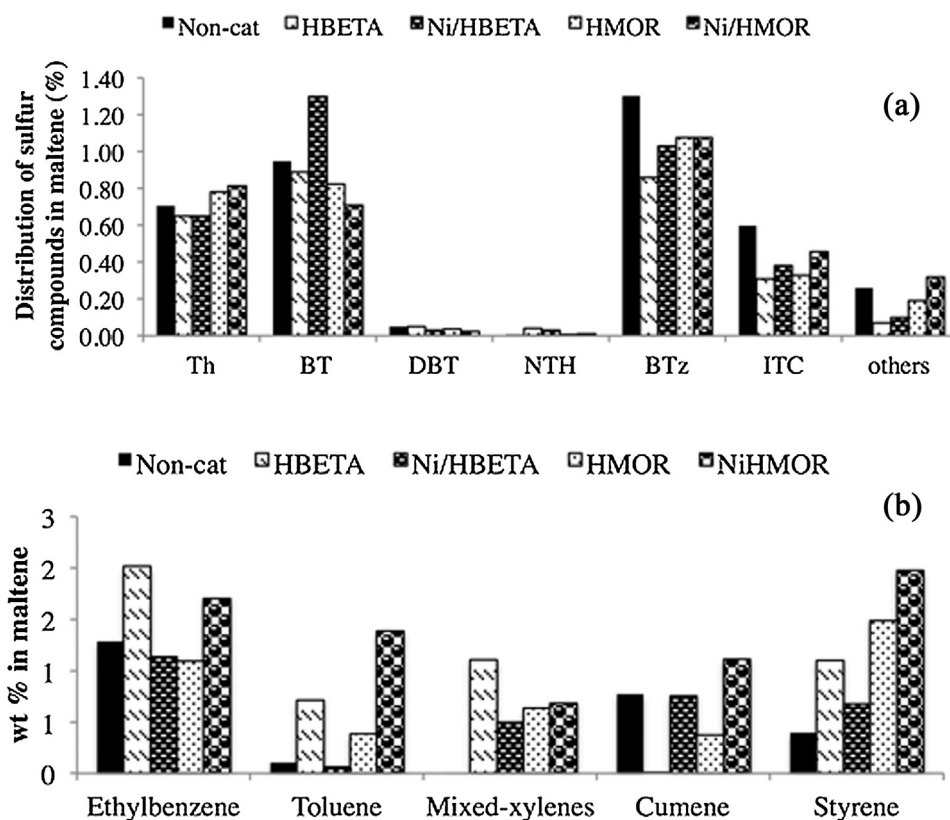


Fig. 10. (a) Distribution of sulfur compounds, and (b) Petrochemicals in maltene using Ni/HBETA and Ni/HMOR catalysts.

Table 2
Sulfur content in oils obtained from Ni/HBETA and Ni/HZSM-5.

Catalyst	Non-catalytic	HBETA	HZSM-5 ^a	Ni/HBETA	Ni/HZSM-5 ^a
Sulfur content in oil (wt.%)	0.96	0.83	0.78	0.75	0.68
Sulfur reduction (%)	Base	14.1	18.8	21.6	29.2

^a As reported in [15].

the addition of nickel on HZSM-5 promote the transformation of multi-ring aromatics to mono-aromatics and aromatization of naphthenes and olefins to mono-aromatics. Significant differences are observed on the petroleum fractions and maltene composition with Ni doped on HBETA zeolite. The results show that the gasoline fraction drastically reduces, whereas the kerosene, gas oil, LVGO fractions clearly increase. This result indicates that the incorporation of nickel on HBETA strongly promotes the formation of heavier fraction in maltene. A similar effect of the addition of nickel on the maltene composition is also observed on HBETA. The formations of naphthenes and mono-aromatics significantly decrease, whereas the formations of di-, poly-, and polar-aromatics are drastically increased. It is reasonable to conclude that Ni species on HBETA strongly promote the formation of heavier fractions, especially polycyclic aromatics via the secondary reactions (oligomerization, cyclization, aromatization, etc.) of naphthenes and mono-aromatics.

The different catalytic behaviors of Ni species on HZSM-5 and HBETA zeolites associate with different characteristics of the supports. HBETA and HZSM-5 zeolites have 3D pore channel with close Si/Al ratios. Therefore, the major difference of two acidic supports is pore size, the pore size of HZSM-5 is $5.3 \text{ \AA} \times 5.6 \text{ \AA}$ and pore size of HBETA is $6.4 \text{ \AA} \times 7.6 \text{ \AA}$. Thus, HBETA zeolite has larger pore size than HZSM-5 zeolite, so its pore size provides a higher probability of formation of larger hydrocarbons than the smaller pore size

of HZSM-5. Generally, cracking is the main reaction in the catalytic pyrolysis of waste tire. However, the secondary reactions also occur simultaneously, depending on the catalyst properties. Hence, the addition of nickel on supports with a large pore size provides a higher probability of undergoing of hydrocarbons via secondary reactions resulting in the high production of multi-ring aromatics. Therefore, the formation of heavy fractions is favorable with the presence of Ni/HBETA catalyst. Table 2 provides the information about the sulfur contents in oil. In all cases, the sulfur contents in oil significantly decrease by the addition of nickel species to the zeolites. The sulfur in tire samples of around $2.07 \pm 0.0279 \text{ wt.}\%$ is distributed into products and catalysts as shown in Fig. 5a. It can be observed that Ni-doped catalysts result in a higher sulfur distribution on the spent catalysts than that obtained from the parent zeolites.

These results indicate that sulfur compounds favorably adsorb on the nickel site. Generally, Ni has strong molecular orbital, which can attract sulfur atom from sulfur compounds. The sulfur compounds can donate the electron density to Ni, and further form a bond with Ni. Once favorably forming a bond with Ni, further desulfurization depends on the interaction of nickel with the support and available hydrogen in pyrolysis system. Desulfurization activity of Ni can be also prohibited by coke formation on the Ni sites of catalyst, which also affects to sulfur removal since the Ni site is less available for adsorption of sulfur compounds, causing the

Table 3

Dominant di- and polyaromatics in maltene obtained from Ni/HBETA and Ni/HZSM-5.

Hydrocarbons	wt.% in maltene			
	HBETA	Ni/HBETA	HZSM-5	Ni/HZSM-5
2-Methyl biphenyl	0.00	0.63	0.46	0.00
4,4'-Dimethyl biphenyl	0.45	0.89	0.45	0.05
4-Isopropyl biphenyl	0.35	0.55	0.40	0.31
Naphthalene	0.36	0.06	0.38	0.28
1-Methyl naphthalene	0.99	0.68	0.42	0.03
1,3-Dimethyl naphthalene	1.24	0.92	0.71	0.15
1-Ethyl naphthalene	1.14	1.93	0.93	0.96
7-Isopropyl-1-methylnaphthalene	0.51	0.86	0.10	0.15

highly-competitive adsorption between hydrocarbons and sulfur compounds. The sites of nickel might be reduced when adsorbed hydrocarbons have undergone hydrogen transfer reaction, leading to coke formation. From Fig. 3, it can be clearly seen that the coke formation on Ni/HBETA catalyst is roughly twice as much as that formed on the Ni/HZSM-5. Therefore, sulfur content in oil produced from Ni/HBETA is higher than that produced by Ni/HZSM-5 catalysts since the nickel sites are more highly covered by coke, resulting in the reduction of desulfurization activity.

Moreover, sulfur contents in oil might be affected by different pore size of zeolites as well. Previously, it was found that Ni/HZSM-5 reduced sulphur contents in tyre-derived oil by 29.2% [15]. It can be clearly seen that the addition of nickel on HBETA slightly results in the higher sulfur content than that obtained from Ni/HZSM-5 catalyst [15] (see also Table 2). The large pore size of HBETA zeolite allows a higher amount of sulfur-containing compounds to go inside the pore, and then some of sulfur-containing compounds can be desulfurized. Some molecules of sulfur-containing compounds such as thiophene can also be transformed to benzothiophene via undergoing hydrogen transfer reaction with available olefins, followed by cyclization and dehydrogenation [9]. Moreover, some free sulfur molecules, which are formed from cracking of tire, are very active, so they can react with olefins and mono-aromatics to form thiophenic compounds [5]. From Fig. 5b, it can be clearly seen that sulfur atoms are more distributed in the forms of benzothiophenes when using Ni/HBETA as a catalyst. This evidence confirms that the higher amount of benzothiophene is preferably formed in large pore size of zeolite, leading to the increment of sulfur content in the oil.

Regarding the petrochemical contents in oil, the incorporation of nickel on HBETA zeolite significantly suppresses the formation of ethylbenzene, toluene, cumene, styrene and mixed-xylene (see Fig. 6), whereas di- and polyaromatics such as 7-isopropyl-1-methylnaphthalene, 1-ethylnaphthalene and 2-methylbiphenyl significantly increase (see Table 3). This can be explained that these di- and polyaromatics can be formed by combination of valuable small aromatics. It is well known that the pore size of a zeolite governs the molecular size of products, so the molecular size of products cannot be larger than the pore size of a zeolite, unless they are formed at the external surface of a zeolite. Therefore, the addition of nickel on a large pore of HBETA provides a higher possibility of forming of multi-ring aromatics than Ni doped HZSM-5, resulting in the higher amount of di- and poly- and polar- aromatics in maltene.

A different behavior is observed with the Ni/HZSM-5 catalyst. In this case, the formation of ethylbenzene, toluene, cumene and mixed-xylene increase, whereas the concentrations of di-, and polyaromatics such as 2-methylbiphenyl, 4,4'-dimethylbiphenyl, naphthalene, 1,3-dimethylnaphthalene, and 1-methylnaphthalene decrease. Therefore, the introduction of Ni on HZSM-5 might promote the transformation of these di- and polyaromatics to valuable aromatics such as ethylbenzene, toluene, mixed-xylene and etc. If

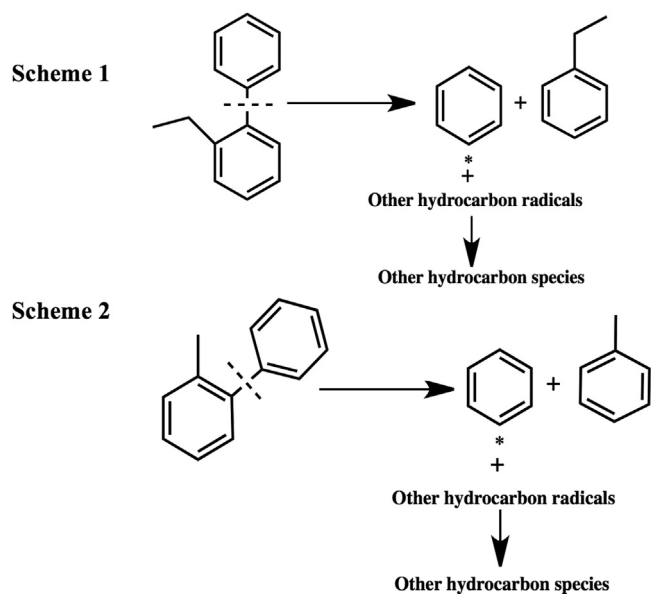


Fig. 11. Possible reaction pathways for transformation of 2-ethylbiphenyl, 4-methylbiphenyl to valuable aromatics promoted by Ni/HMOR.

the carbon–carbon scission takes place at the position between two benzene rings of 2-methylbiphenyl, the obtained products are benzene and toluene as displayed in Scheme 1 in Fig. 7. However, the concentration of benzene has been not found to increase, so it might possibly convert to other hydrocarbon because the radical benzene ring is very active to react with other hydrocarbons.

In addition, two molecules of toluene can be formed via these steps as shown in Scheme 2 in Fig. 7. First, the carbon–carbon scission take places at the position between the two benzene rings of 4,4'-dimethylbiphenyl, resulting in toluene and a radical of benzene derivative of toluene. If the toluene radical reacts with hydrogen, toluene can be formed. However, this radical of toluene is very active, it can react with other hydrocarbons to form other hydrocarbon species as well. Furthermore, di-aromatics such as naphthalene, 1,3-dimethylnaphthalene, and 1-methylnaphthalene can be also transformed to valuable aromatics via two steps. One rings of naphthalene, 1,3-dimethylnaphthalene and 1-methylnaphthalene are firstly hydrogenated at a nickel site to form tetralinic species [18] and [19]. Second, the naphthenic ring of tetralinic species are cracked to formed valuable petrochemicals as displayed in Fig. 8 [18–20].

3.4. Effect of nickel loading on zeolites with different channel structures

With an almost equal pore size, HBETA with 3D pore channel structure and HMOR with 1D pore channel structure were used as the supports for investigating the effect of Ni loading on different pore channel structures. The oil produced by Ni/HMOR is lighter than that produced by Ni/HBETA since the composition of oil contains a higher amount of gasoline and kerosene and a lower amount of gas oil, LVGO and HVGO (see Fig. 9a). In addition, the introduction of nickel on HMOR strongly enhances the formation of mono-aromatics and olefins, whereas the formation of di-, poly-, polar-aromatics and naphthenes reduces (see Fig. 9b). These results clearly indicate that nickel species on HMOR zeolite promote the formation of mono-aromatics and olefins together with suppression of di-, poly-, and polar-aromatics and aromatization of naphthenes. In the opposite, the Ni/HBETA catalyst enhances the formation of heavy components, with a significant increment of di-, poly- and polar-aromatics. Ni doping on HMOR and HBETA zeolites

Table 4
Sulfur content in oil obtained from Ni/HBETA and Ni/HMOR catalysts.

Catalyst	Non-catalytic	HBETA	HMOR	Ni/HBETA	Ni/HMOR
Sulfur content in oil (wt.%)	0.96	0.83	0.9	0.75	0.78
Sulfur reduction (%)	Base	14.1	5.8	21.6	19.1
Sulfur reduction by Ni (%)	–	Base	Base	9.64	13.3

promotes aromatization activity of catalysts; Ni doped on HMOR favors the aromatization of naphthenes, forming mono-aromatics, whereas Ni doped on HBETA favor the aromatization of naphthenes and olefins, forming multi-ring aromatics. This is probably a result of the different pore channel structures of zeolites. HMOR zeolite possesses a 1D channel structure, which allows a hydrocarbon molecule can further react with other hydrocarbons at a shorter time than the 3D channel structure of HBETA zeolite. In a 3D channel structure, intermediate hydrocarbons formed from previously-cracked molecules diffuse along the zeolite channel, and then might be combined with other hydrocarbons at nickel sites at a longer contact time, leading to the high formation of multi-ring aromatics. Therefore, the long residence time in a zeolite channel provides a higher possibility of multi-ring aromatics formation.

Table 4 illustrates the sulfur content in oils obtained from Ni/HBETA, Ni/HMOR catalysts and parent zeolites. HBETA zeolite with a 3D channel structure provides a lower amount of sulfur content in oil than that produced by HMOR zeolite since the complex channel structure of HBETA allows the sulfur compounds to stay inside the zeolite channel for a longer residence time, resulting in the higher possibility of desulfurization of sulfur compounds. In addition, the introduction of Ni on both zeolites clearly reduced the sulfur content in oil. The sulfur content in oil obtained from Ni/HBETA is slightly lower than that obtained from Ni/HMOR cat-

alysts. This clearly indicates that the nickel located on 3D zeolite channel provides better desulfurization activity since the sulfur compounds can stay longer in zeolite channel, and then are desulfurized at nickel site more effectively than 1D zeolite channel. Regarding the sulfur reduction by Ni species, the addition of Ni on HMOR zeolite give a better sulfur reduction than that obtained from the Ni/HBETA catalyst. This can be explained that the coke formation on the spent Ni/HBETA is higher than on Ni/HMOR, resulting in the reduction of available Ni sites, which directly affects the desulfurization activity of catalysts since the desulfurization of sulfur compounds mainly take places on the Ni site. Fig. 10a displays that benzothiophene (BT) significantly reduces when Ni is doped on HMOR, but sharply increases for Ni/HBETA zeolite. This clearly indicates that the incorporation of Ni on 3D zeolite channel does not only promote sulfur removal from sulfur-containing compounds, but also the interaction of sulfur compounds with other hydrocarbons. The longer residence time of hydrocarbons or sulfur-containing compounds in the channel can provide a higher interaction of hydrocarbons and free sulfur atom, which are directly evolved from cracking of tire molecules.

Regarding the petrochemical species in maltene, nickel doping on HBETA zeolite significantly decreases the formation of ethylbenzene, toluene, styrene and mixed-xylenes (see Fig. 10b). On the other hand, it was found that the concentrations of 2-methyl biphenyl and fluorene in oil clearly increase with using Ni/HBETA catalyst (see Table 5). Therefore, the Ni loading in 3D zeolite channel might promote the interaction of any valuable aromatics as mentioned above to multi-ring aromatics such as 2-methylbiphenyl, fluorene and etc.

On the other hand, using Ni/HMOR, the formation of ethylbenzene, toluene, cumene and styrene significantly increases, whereas

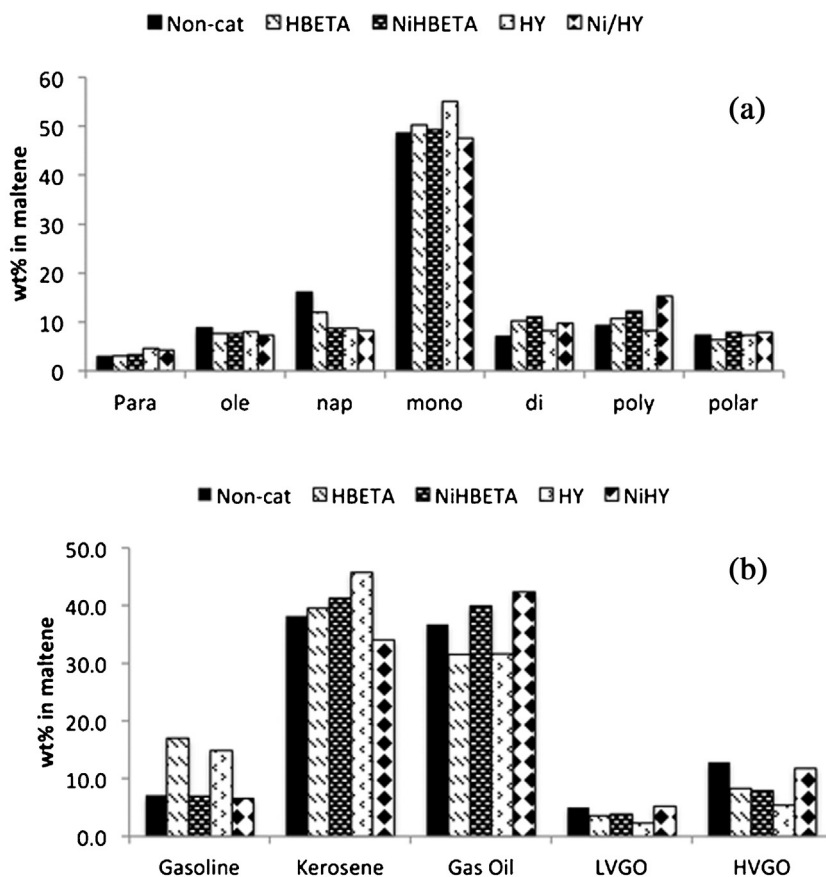


Fig. 12. (a) Concentration of each chemical group, and (b) Petroleum fractions in maltene using Ni/HBETA and Ni/HY catalysts.

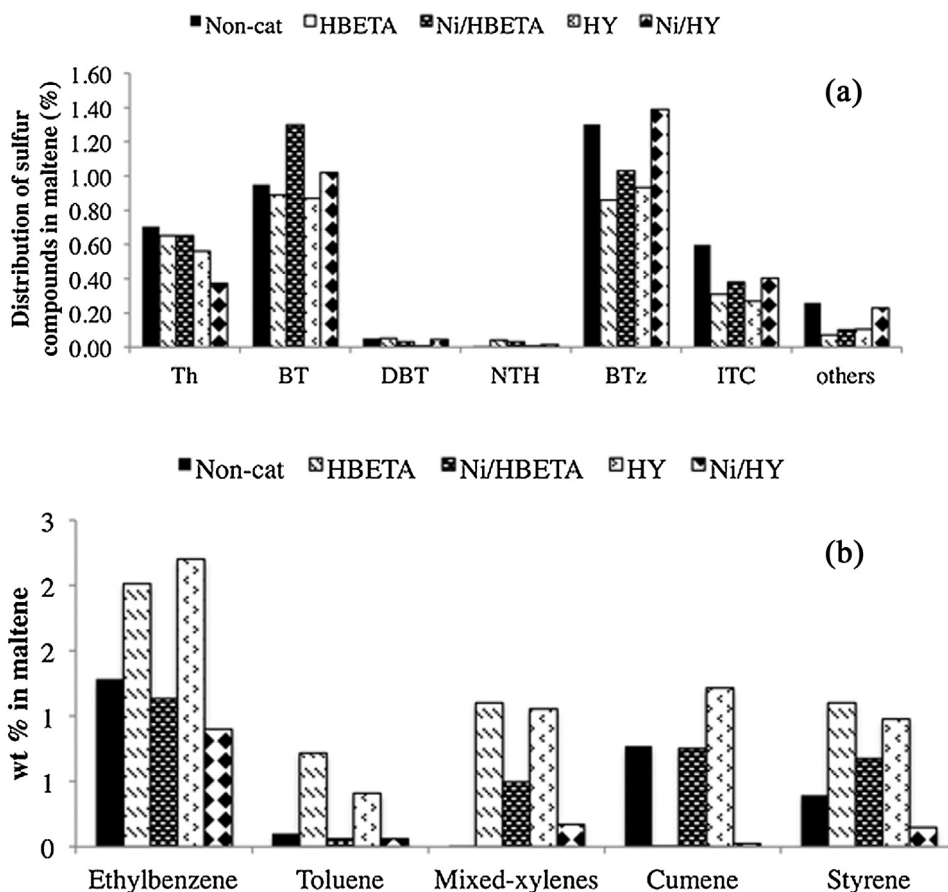


Fig. 13. (a) Distribution of sulfur-containing compounds, and (b) Petrochemicals in maltenes obtained from Ni/HBETA and Ni/HY catalysts.

Table 5

Dominant polyaromatics species in maltenes obtained from Ni/HBETA and Ni/HMOR catalysts.

Hydrocarbons	wt.% in maltene			
	HBETA	Ni/HBETA	HMOR	Ni/HMOR
2-Methylbiphenyl	1.18	1.49	1.38	1.24
2-Ethylbiphenyl	1.32	1.12	1.15	0.65
Fluorene	0.14	0.26	0.12	0.10

the concentration of polyaromatics in maltene decreases. Simultaneously, it is also found that the concentration of 2-ethylbiphenyl and 4-methylbiphenyl slightly decreases (see Table 5), and these two polyaromatics can be transformed to ethylbenzene and toluene as illustrated in Fig. 11. Therefore, the introduction of nickel on HMOR zeolite might promote cleavage of biphenyl compounds. Ethylbenzene and benzene can be directly formed via carbon-carbon scission at the position between two benzene rings of 2-ethylbiphenyl. However, it was found that the concentration of benzene in maltene is extremely lower than that of ethylbenzene, so the benzene radical might react with other hydrocarbon radicals to form other hydrocarbon species as displayed in Scheme 1. Toluene and benzene can be directly formed via carbon-carbon scission at the position between two benzene rings of 4-methylbiphenyl as displayed in Scheme 2, but benzene might also be converted to other hydrocarbons because benzene with radical is very active to react with other hydrocarbons molecules (see Fig. 10b).

In summary, the effect of zeolite channel structure is one of important factors, which should be considered in selecting a catalyst for enhancement of oil quality and petrochemical production

from pyrolysis of waste tire. The introduction of nickel on a zeolite with 1D channel structure is better than on a zeolite with a 3D channel structure in terms of petrochemical formation and quality of oil. Therefore, it can be suggested that for the enhancement of oil quality and petrochemical production by using Ni is not recommended as a promoter, a zeolite that has a complex channel structure since the combination of complex 3D zeolite channel and Ni species do not only promote cracking activity of catalyst, but also promote the secondary reactions (oligomerization, cyclization, aromatization and etc.), leading to the high formation of heavy hydrocarbons. Moreover, Ni catalysts normally promote the high formation of coke on the nickel sites, so the combination of nickel with 3D channel structure promoted the higher coke formation than the nickel supported on a zeolite with 1D channel structure since the hydrocarbons, which can stay inside in the 3D channel with a long residence time, easily undergo aromatization and combination reactions, forming coke on the catalyst. The high formation of coke on catalyst strongly decreases the catalytic activity, leading the rapid deactivation of catalyst.

3.5. Effect of nickel loading on zeolites with different acid densities

The effect of Ni loading was investigated on two zeolites with different acid densities. With a similar pore size, HBETA ($6.4 \times 7.6 \text{ \AA}$) with the Si/Al ratio of 14 was used in comparison with HY ($7.4 \text{ \AA}$) with the Si/Al ratio of 7.5. Similarly, the introduction of nickel on HBETA and HY zeolites favorably produces the heavier oils with a high proportion of di-, poly-, and polar-aromatics as compared to the parent zeolites. However, the oil produced from Ni/HY catalyst

Table 6
Sulfur content in oils obtained from Ni/HBETA and Ni/HY catalysts.

Catalyst	Non-catalytic	HBETA	HY	Ni/HBETA	Ni/HY
Sulfur content in oil (wt.%)	0.96	0.83	0.88	0.75	0.8
Sulfur reduction (%)	Base	14.1	8.4	21.6	16.5

slightly is heavier than the one produced from Ni/HBETA catalyst. Moreover, it is clearly seen that the amounts of di-, poly- and polar-aromatics in the oil obtained from Ni/HY catalyst are higher than those produced by Ni/HBETA catalyst. This can be suggested that nickel species on these two acidic zeolites might promote the combination of lighter hydrocarbons (naphthene, olefins, mono-aromatics) to form multi-ring aromatics. The increment of heavy hydrocarbons might associate with the acidity of catalyst and coke formation on the catalyst. Generally, nickel promotes the hydrogen transfer reactions, leading to the formation of hydrocarbons with various C/H ratios, which can act as a coke precursor. Moreover, the introduction of nickel on a zeolite with a higher acid density (lower Si/Al ratio), for this case, can drive a higher formation of heavy hydrocarbon, especially multi-ring aromatics than the parent zeolite since the high acid density of zeolite promotes cyclization and aromatization activity of catalyst, resulting in reduction of olefins and naphthenes in the maltene (see Fig. 12a). Furthermore, the high coke formation on the spent catalysts is a clear indicator that the introduction of nickel with HBETA and HY zeolites provides a higher cracking activity than the parent zeolites. However, the higher cracking activity obtained with nickel promoter does not result in the formation of lighter hydrocarbons, but the higher amount of heavier hydrocarbons was formed. Therefore, the high catalytic activity usually associates with coke formation on the catalyst. The high coke formation over nickel-based catalysts might reduce the active sites, which is favorable for cracking of hydrocarbons. Therefore, it can be concluded that the introduction of nickel on HY zeolite with a higher acid density promotes the higher formation of di-, poly-, and polar-aromatics than those obtained from the Ni/HBETA catalyst, resulting in the higher proportions of gas oil, LVGO and HVGO (see Fig. 12b).

Furthermore, the introduction of nickel on HBETA and HY zeolites causes a higher reduction of sulfur content in oil than those obtained from the parent zeolites (see Table 6). Apparently, the Ni/HBETA catalyst produces the oil with a lower sulfur contents than the Ni/HY catalyst.

These results indicate that the introduction of nickel on a zeolite with higher acid strength (higher Si/Al ratio) slightly results in a lower sulfur content in oil since the competition adsorption between other hydrocarbons and sulfur compounds occurs on nickel sites. Moreover, the high content of total aromatics are produced from Ni/HY than from Ni/HBETA. Therefore, the higher amount of aromatics might be adsorbed on the nickel sites of HY zeolite, resulting in the reduction of desulfurization activity of nickel species on HY zeolite. Moreover, the aromatic adsorptions have less influence on the desulfurization activity of catalysts with higher acidity [21]. Fig. 13a displays that thiophenes decrease with using Ni/HY as a catalyst, but not Ni/HBETA. These results indicate that high acid density of HY zeolite favorably breaks the C–S bond of thiophene. Moreover, the other sulfur species slightly increase with the presence of nickel on HBETA and HY zeolite. It can be explained that the introduction of nickel on these two zeolites might reduce the active sites of HBETA and HY zeolites, which favorably breaks C–S and C–N bonds of sulfur-containing compounds. Generally, the first step of the sulfur removal from of sulfur-containing compounds is adsorption of sulfur atom on nickel sites. The Ni/HBETA and Ni/HY catalysts generate a high amount of coke on the catalyst, especially on the nickel sites, so the available nickel sites, which is favorable for removal of sulfur-containing compounds, are reduced

Table 7
Dominant di- and polyaromatics in maltenes obtained from Ni/HBETA and Ni/HY catalysts.

Hydrocarbons	wt.% in maltene			
	HBETA	Ni/HBETA	HY	Ni/HY
2-Methyl biphenyl	1.18	1.49	1.13	1.92
4-Isopropyl biphenyl	0.35	0.55	0.20	0.49
2-Ethylbiphenyl	1.32	1.12	1.05	1.56
7-Isopropyl-1-methylnaphthalene	0.51	0.86	0.34	0.35

when the coke formation and competitive adsorption of aromatics hydrocarbons take place on the nickel sites.

Regarding the petrochemical species in maltenes, nickel species on HBETA and HY zeolites significantly decrease the formation of ethylbenzene, toluene, styrene and mixed-xylenes (see Fig. 13(b)). On the other hand, it is also found that the concentrations of 2-methylbiphenyl, 2-ethylbiphenyl and 4-isopropylbiphenyl significantly increase with the addition of nickel on the HY zeolite, and the concentrations of 7-isopropyl-1-methylnaphthalene, 2-methylbiphenyl and 2-ethylbiphenyl also increase with using the Ni/HBETA catalyst (see Table 7).

This can be explained that some of petrochemicals and other mono-aromatics, naphthenes and olefins might be converted to these polyaromatics. The amounts of these polyaromatics depend on the acid density and acid strength of the two zeolites since the two supports have quite similar pore size and 3D pore channel structure. Therefore, it can be concluded that the introduction of nickel on a zeolite with high acid density such as HY, promotes the higher formation of polyaromatics such as methylbiphenyl, ethylbiphenyl, isopropylbiphenyl and etc. The introduction of nickel on HBETA zeolite, which exhibits a higher acid strength promote the formation of the polyaromatics as well, but the high acid density is more effective for enhancement of multi-ring aromatic formation.

4. Conclusions

The effect of nickel promoter loaded on different zeolites; that are HBETA, HZSM-5, HMOR, and HY, were studied. The result showed that all Ni doped catalysts enhanced the aromatic formation and sulfur removal from oil. However, the catalytic behaviors of nickel promotion strongly depended on zeolite properties. The pore size of zeolite supports was found to govern the size of hydrocarbons products and sulfur removing ability of Ni catalysts. The incorporation of Ni on a HZSM-5 with a smaller pore size produced the lighter oil with higher proportion of gasoline, kerosene and valuable petrochemicals than the Ni/HBETA. Moreover, Ni/HZSM-5 provide the oil with a lower sulfur content than the Ni/HBETA due to lower coke formation and a lower possibility of forming of large hydrocarbons and sulfur-containing compounds. The channel structure of zeolite supports was found to govern the hydrocarbon products and sulfur removing ability of Ni catalyst due to the effect of residence time of hydrocarbons in the pore. The introduction of Ni on HMOR zeolite with 1D channel structure produced the slightly higher sulfur oil with a higher proportion of gasoline, kerosene and valuable petrochemicals than Ni loaded on HBETA zeolite (3D channel structure) due to lower coke formation and a shorter contact time of hydrocarbons. The acid density of zeolite supports was found to promote the formation of heavy aromatics and control the sulfur removing ability of Ni catalysts. The incorporation of nickel on HY zeolite with a higher acid density (lower Si/Al ratio) produced the higher sulfur oil the with a higher proportion of gas oil, LVGO and HVGO, but a lower amount of valuable petrochemicals due to higher competition adsorption of hydrocarbons and sulfur-containing compounds on Ni sites. In conclusion, for the enhancement of oil quality and petrochemical production,

Ni is not recommended as a promoter on a zeolite that has a complex channel structure and a large pore size since the introduction of Ni on this kind of supports promoted the formation of heavy hydrocarbons and reduced the sulfur removing ability of Ni catalyst. Therefore, for the production of the waste tire-derived oil with high petrochemicals and low sulfur contents by using Ni promoter, the zeolite supports must have a suitable pore size of around 5.5–7 Å and 1D channel structure that allows hydrocarbons and sulfur compounds can stay inside at enough contact time to form valuable petrochemical and to remove sulfur compounds.

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An Attempt on Using a Regenerated Commercial NiMoS/Al₂O₃ as a Catalyst for Waste Tyre Pyrolysis

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A used commercial sulfided NiMoS/Al₂O₃ catalyst from the hydrodesulfurization unit of a refinery in Thailand was employed as a catalyst for waste tire pyrolysis since it contains both acid and metal sulphide functions that could potentially benefit cracking and sulphur removal simultaneously. It was regenerated prior to use in a catalytic zone operated at 350 °C of the pyrolysis reactor. As a result, as compared to the non-catalytic case, the catalyst gave less long residue with a higher amount of full range naphtha in the tire-derived oil that contained a higher amount of mono-aromatics. Moreover, the oil contained a fewer amount of polar-aromatics as well as less sulphur content. Furthermore, the oils were analyzed for sulphur species by using GC-TOF. The results showed that the oil obtained from sulphided NiMoS/Al₂O₃ had a higher amount of sulphur-containing molecules in the range of gasoline than the non-catalytic oil. Most of the sulphur-containing molecules found in gasoline, kerosene and gas oil ranges were benzothiophene derivatives such as 3-methylbenzothiophene (C₉H₈S), benzo[b]thiophene, 2,5-dimethyl- (C₁₀H₁₀S), and dibenzothiophene derivatives such as naphtho[2,3-b]thiophene, 4,9-dimethyl- (C₁₄H₁₂S).

1. Introduction

Tire pyrolysis has been generally known as a feasible and economical method because it allows the valuable substances to be recovered. The products are regained in three main phases comprised of char, oil and gas, which have different applications. Char can be used as a blending, carbon black, or converted to activated carbon. The derived oil can be the source of chemicals in chemical industry since it contains a high concentration of benzene, toluene, xylene and other aromatic derivatives. It is also added to petroleum refinery feedstock due to the gross calorific value of about 40.0 MJ/kg similarly to light fuel oils (Cunliffe and Williams, 1998). The gas products are mainly composed of light hydrocarbons such as olefins and C₁-C₄ paraffins that are also useful as a fuel. Due to the vulcanization of tire, large network between sulphidic crosslinks and rubber chains are formed, which can be monosulphidic (-S-), disulphidic (-S-S-) and polysulphidic (-S-S_x-S-) (Bilgili et al., 2001). The release of sulphur from the tire structure during pyrolysis affects to the quality of oil products. In consequence, it is expected to be removed to obtain the light oil with less sulphur. Therefore, the cracking and desulphurization abilities of a pyrolysis catalyst are needed simultaneously. A hydrodesulphurization (HDS) catalyst is a commercial catalyst used for removing sulphur compounds from oils to produce the clean fuel. After the regular operation, the activity of the catalyst continuously decreases; however, the spent catalyst can be regenerated for reuse. In exclusive of the economic benefit, a spent commercial NiMoS/Al₂O₃ catalyst has the potential to be used as a tire pyrolysis catalyst because it has both acid and metal sulphide functions that can simultaneously promote the ability of cracking and desulphurization. H₂ required in desulphurization reaction can be supplied from cracking of waste tire. However, the activity on removal of sulphur-containing compounds during pyrolysis is highly acquired from the commercial HDS catalyst. It has been reported that the hydrogenation ability of NiMo sulphide catalyst resulted in high activity in HDS of 4,6-di-methyl-dibenzothiophene (Kim et al., 2003). From the work of Rodríguez-Castellón et al. (2008), a presulphided Ni5-Mo11 catalyst (using 90/10 % of N₂/H₂S at atmospheric pressure) gave the highest dibenzothiophene (DBT) conversion at 3.0 MPa and 300-340 °C as compared to the conventional sulphided Co(Ni)Mo(W)

catalyst. They also concluded that Ni-promoted catalysts had greater performance than Co-promoted catalysts at high temperatures because of high hydrogenation ability, similar to the result of Li-hua et al. (2011). They found that the sulphided catalyst containing 18% of Mo and 4% of Ni showed high HDS activity, hydrogenation selectivity, and favoured the hydrogenation of phenyl ring in the DBT molecule due to the high stacking number of MoS₂ which is the active site facilitating the adsorption of sulphur-containing reactants and desorption of hydrogen sulphide products (Villarroel et al., 2008). Since a regenerated NiMoS/Al₂O₃ catalyst is comprised of acid (Al₂O₃) and metal sulphide (NiMoS), the objective of this work was to investigate the ability of the catalyst in waste tire pyrolysis and desulphurization, aiming to improve the quality and quantity of pyrolysis oil that have a lower sulphur level. Sulphur species and sulphur distribution in products are also reported in this work.

2. Experiment

2.1 Material and Preparation

A regenerated commercial NiMoS/Al₂O₃ obtained from a refinery in Thailand was first screened for the clean pellets, then crushed, and sieved into the size range of 400-425 µm by using 40-60 mesh sizes of sieves. To prepare a waste tire sample, the side wall of a used tire sample, Bridgestone TURANZA GR-80, was scraped and then sieved into a particle size range of 8-18 mesh.

2.2 Pyrolysis Process

The tire sample was pyrolyzed in the lower zone (thermal pyrolysis zone) of reactor from room temperature to the final temperature of 500 °C with the heating rate of 10 °C/min, and then the pyrolytic effluent with ~30 vol% H₂ (Aylón et al., 2007) carried by nitrogen flow to the upper zone packed with a catalyst. The catalytic zone was controlled at 350 °C. The system was held for 90 mins to ensure the complete conversion of tire. The tire pyrolysis experiments were performed according to the procedure written in Dũng et al. (2009). The product effluent carried by nitrogen was condensed to liquid products by using ice-salt condensers. The incondensable product was passed to the condensers and collected by a gas sampling bag.

2.3 Catalyst characterization

The element composition of a catalyst sample was characterized by X-ray fluorescence spectrometry (XRF). Thermo Finnigan/Sorptomatic 1990 was used to determine the specific surface area and total pore volume of the catalyst using Brunauer-Emmet-Teller (BET) method. The sample was out-gassed at 150 °C, overnight, to primarily clean up the impurity, and then was in a helium environment at 300 °C for 4 hours prior to the adsorption of nitrogen gas. The acidity of catalyst was analyzed by Temperature Programmed Desorption of isopropylamine (IPA-TPD) via manual injection. 0.05 g of sample was firstly purged by He flow to eliminate the moisture until no peak of water was observed. The IPA-TPD was conducted from room temperature to 800 °C with a heating rate of 20 °C/min under the He flow. The desorption of isopropylamine (m/e = 44), ammonia (m/e = 17) and propylene (m/e = 41) were detected by a mass spectrometer (Kresnawahjuesa et al., 2000) and previously Farneth and Gorte (1995). Besides the polar-aromatic content in oil as reported previously (Manchantrarat and Jitkarnka, 2012), the used catalyst was also characterized by LECO® Elemental Analyzer, TruSpec®S at the furnace temperature of 1,350 °C to determine the amount of sulphur in the catalyst. The amount of coke on the spent catalyst was analyzed by Thermogravimetric/Differential Thermal Analysis (TG/DTA), heated from room temperature to 700 °C (10 °C/min) with oxygen gas (50 mL/min).

2.4 Product analysis

The liquid and solid products were weighed to determine the product distribution. The amount of gas was then determined by mass balance. An incondensable product in the gas sampling bag was analyzed by using a Gas Chromatograph (GC), Agilent Technologies 6890 Network system, using HP-PLOT Q column with FID detector with He as a carrier gas. Asphaltene was first separated from the liquid products by dissolving in n-pentane with the ratio of 1:40 (oil: n-pentane). Saturated hydrocarbons, mono-, di-, poly- and polar-aromatics were fractionated from the obtained maltenes by specific solvents (Šebor et al., 1999) using liquid adsorption chromatography, then further analyzed for the true boiling point curves (TPBs) by using a Varian CP-3800 stimulated distillation gas chromatography (SIMDIST GC), equipped with an FID according to the ASTM D2887 method. The TBPs of liquid hydrocarbons were cut to petroleum fractions, which are full range naphtha (<200 °C), kerosene (200 – 250 °C), light gas oil (250 – 300 °C), heavy gas oil (300 – 370 °C), and long residue (>370 °C). The oils were also analysed for the sulphur content by using elemental analysis (LECO, US). Finally, a Gas Chromatograph-Mass Spectrometer (Time of Flight),

GC-MS (TOF), with 2D dimension mode was used to identify sulphur-containing compounds in the oil by using helium and nitrogen as a carrier and cooling gas, respectively.

3. Results and Discussion

3.1 Effect of spent NiMoS/Al₂O₃ to catalytic pyrolysis of waste tire

The results of pyrolysis with and without the catalyst including the product yield, liquid composition, petroleum cuts and light gas yield are given Figure 1. The results from product yield in Figure 1a indicate that the spent NiMoS/Al₂O₃ decreases the yield of liquid products from ~42 wt% to ~32 wt% in accordance with the increasing amount of gas products and coke formation while the solid yield remains constant. It means that using a catalyst promotes the decomposition of tire-derived product evolved from the thermal pyrolysis zone, resulting in a higher amount of lighter product (gases) that indicates high reaction activity of the catalyst. It is not surprised that coke is formed on the spent catalyst. The amount of coke per gram of the catalyst is also shown in Table 1. Figure 1b presents the chemical composition in the maltene fractions. It is observed that the spent NiMoS/Al₂O₃ catalyst can reduce polar-aromatics, but it shows low performance in poly-aromatics reduction, resulted in the shortage of saturated hydrocarbons. The remarkable result is found on the increase in mono-aromatics in the catalytic case. The TBP of maltene oil was cut into petroleum fractions that are shown in Figure 1c. The amount of the lightest fraction, full range naphtha, is increased from the expense of heavy fractions in the experiment using spent NiMoS/Al₂O₃ catalyst. Nevertheless, the minor decrease of gas oils and long residue is possibly due to the mild acidity of Al₂O₃ support. It is interesting that using the spent NiMoS/Al₂O₃ shows high selectivity in alkane gas products (Figure 1d), possibly because of the hydrogenation ability (Li-hua et al., 2011). It is known that an alkane is a saturated hydrocarbon, so alkane was easily formed by hydrogenation. Hence, the spent NiMoS/Al₂O₃ is a good catalyst for producing light alkane gas products from waste tire pyrolysis if compared with the non-catalytic experiment.

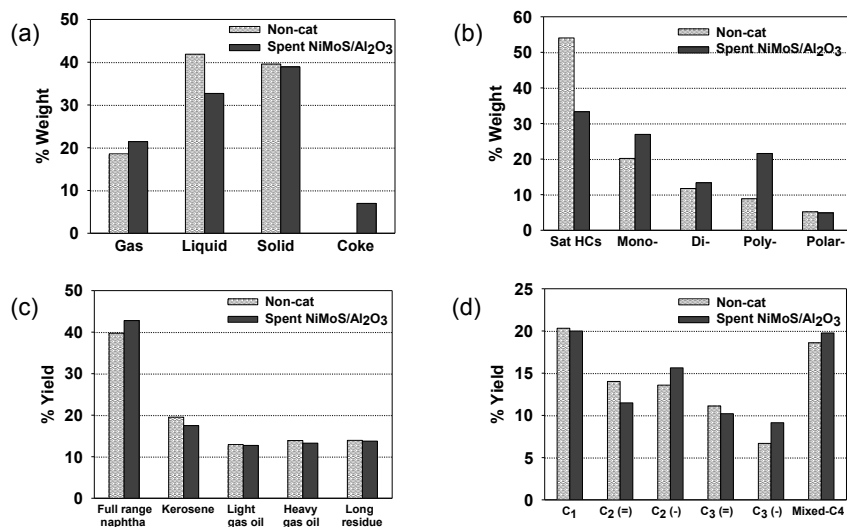


Figure 1: Effects of spent NiMoS/Al₂O₃ on the pyrolysis products: (A) product distribution, (B) liquid composition, (C) petroleum cuts, and (D) light gas yield.

The shift of pyrolysis products from using the spent NiMoS/Al₂O₃ catalyst can be explained by IPA-TPD results. The TPD profiles in Figure 2 present the MS signal of isopropylamine ($m/e = 44$), ammonia ($m/e = 17$) and propylene ($m/e = 41$) from mass spectrometer. The maximum desorption of unreacted isopropylamine was observed at 120 °C, associated to weak acid sites on the surface of the spent NiMoS/Al₂O₃ catalyst while the maximum desorptions of propylene and ammonia around 300 - 400 °C represent brønsted acid sites due to the fact that isopropylamine is decomposed on brønsted acid sites (not Lewis acid sites), producing propylene and ammonia. The catalyst has both weak and brønsted acid sites; however, weak acid sites are dominant, meaning that the catalyst has mild acidity or fewer amounts

of strong brønsted acid sites. It can be explained that the slight changes on heavy to light products are caused by the mild cracking ability of the spent NiMoS/Al₂O₃ acid catalyst.

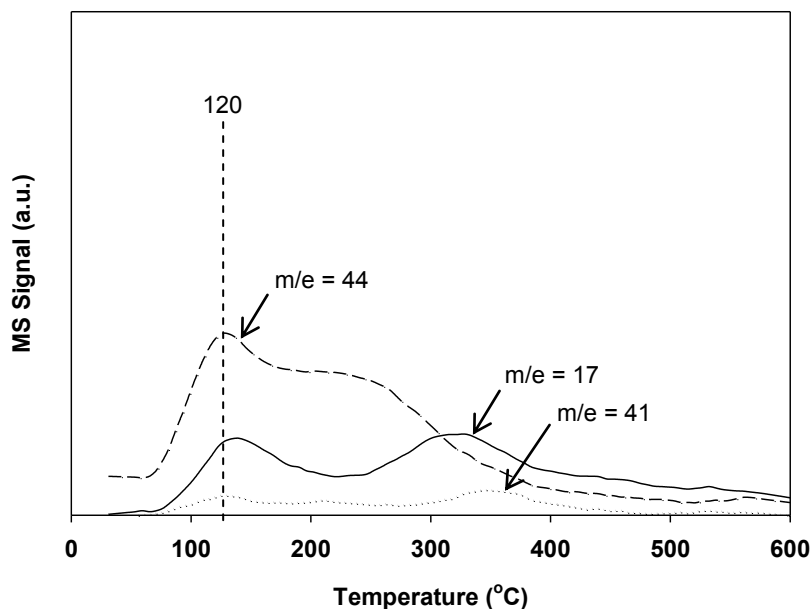


Figure 2: IPA-TPD profiles of isopropylamine ($m/e = 44$) desorption, ammonia ($m/e = 17$) and propylene ($m/e = 41$) formations on the spent NiMoS/Al₂O₃ catalyst.

It is possible that the reactions occur mostly in the pore of catalyst, so it can be suggested that coke is formed in the pore of acid catalyst. The physical properties of catalyst and the amount of coke in the used catalyst are shown in Table 1.

Table 1: Physical properties of spent NiMoS/Al₂O₃ and the amount of coke in the used catalyst

Catalyst	Specific surface area (m ² /g)	Pore specific volume (cm ³ /g)	Median pore width (Å)	Coke (g/g cat)
NiMoS/Al ₂ O ₃	198.75	0.42	8.86	0.36

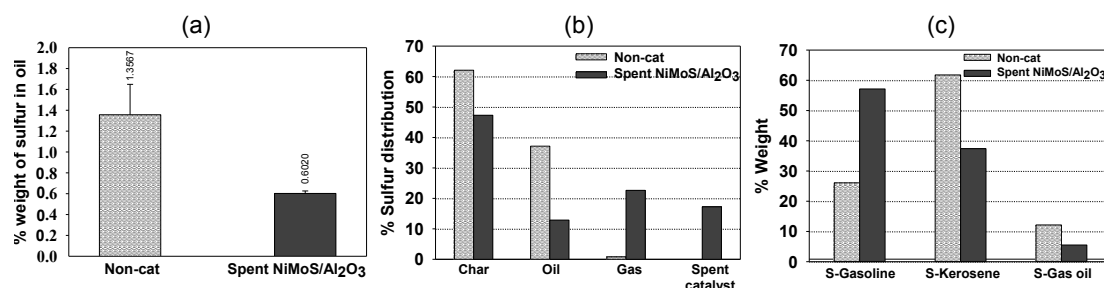


Figure 3: Effect of spent NiMoS/Al₂O₃ on the sulphur contents: (a) sulphur in oil, (b) sulphur distribution in products, and (c) petroleum cuts.

3.2 Sulphur removal ability

The sulphur contents in pyrolysis oil obtained from the elemental analyzer are given in Figure 3a. A high amount of sulphur content was found in the non-catalytic case; however, it can be reduced from 1.36 to 0.60 wt% by using the catalyst. The disappearance of the sulphur in oil occurs in conjunction with a higher

distribution of sulphur in the gas product and the used catalyst as indicated by the sulphur balance (Figure 3b). The high amount of sulphur in the gas fraction is possibly in the form of H₂S (Lin et al., 1997). It has been reported that H₂S can be adsorbed on the active site catalyst (Sidhpuria et al., 2008), resulting in a high deposition of sulphur on the spent catalyst. By using the GC-MS (TOF), the distribution of sulphur in light petroleum cuts illustrated in Figure 3C indicates that the spent NiMoS/Al₂O₃ catalyst can change the high distribution of sulphur, which is formerly in kerosene (C₁₀-C₁₃) and gas oil (C₁₄-C₂₀), to in gasoline (C₅-C₉). It can be concluded that the catalyst had the ability in both cracking and desulphurization simultaneously.

Table 2: Prominent C, H, S-containing molecules found in gasoline (C₅-C₉), kerosene (C₁₀-C₁₃) and gas oil (C₁₄-C₂₀) ranges of the oil

Petroleum cuts	Compounds	Formula	Area (%) [*]	
			Non-cat.	Cat.
Gasoline	Thiophene, 2-ethyl-5-methyl-	C ₇ H ₁₀ S	-	0.0523
	Thiophene, 3-(1,1-dimethylethyl)-	C ₈ H ₁₂ S	-	0.0470
	Benzo[b]thiophene	C ₈ H ₆ S	0.0283	0.0613
	3-Methylbenzothiophene ^I	C ₉ H ₈ S	0.0499	0.1657
Kerosene	Benzo[b]thiophene, 2,7-dimethyl- ^{II}	C ₁₀ H ₁₀ S	0.1138	0.0279
	5-Ethylbenzo[b]thiophene	C ₁₀ H ₁₀ S	0.0137	0.0529
	Benzo[b]thiophene, 2,5-dimethyl-	C ₁₀ H ₁₀ S	0.0409	0.0897
	Benzo[b]thiophene, 7-ethyl-2-methyl-	C ₁₁ H ₁₂ S	0.0077	0.0547
Gas oil	2,8-Dimethyldibenzo(b,d)thiophene	C ₁₄ H ₁₂ S	0.0062	0.0059
	3,7-Dimethyldibenzothiophene	C ₁₄ H ₁₂ S	0.0091	0.0067
	Naphtho[2,3-b]thiophene, 4,9-dimethyl-	C ₁₄ H ₁₂ S	-	0.0140

^{*}% Area of C,H,S-containing molecules in maltene fraction determined by GC-MS (TOF)

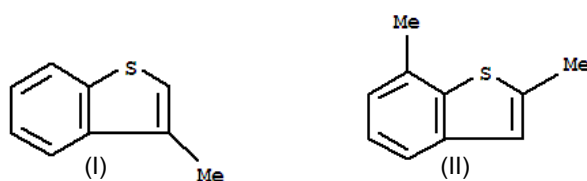


Figure 4: Examples of sulphur-containing compounds found in pyrolysis oils.

Table 2 shows the prominent C, H, S-containing molecules in each petroleum cuts. It is observed that sulphur species obtained in the highest amount from the non-catalytic case are benzo[b]thiophene, 2,7-dimethyl- in kerosene (C₁₀-C₁₃) fraction whereas those observed from the spent NiMoS/Al₂O₃ case is 3-methylbenzothiophene in gasoline fraction (C₅-C₉), which contains less number of alkyl groups than the non-catalytic case as shown in Figure 4. Most of the sulphur-containing molecules found in gasoline, kerosene and gas oil ranges are benzothiophene derivatives such as 3-methylbenzothiophene (C₉H₈S), benzo[b]thiophene, 2,5-dimethyl- (C₁₀H₁₀S), and dibenzothiophene derivatives such as naphtho[2,3-b]thiophene, 4,9-dimethyl- (C₁₄H₁₂S). However, the sulphur species found the most in this study are benzothiophene derivatives, which is different from Williams and Bottrill (1995) who found dibenzothiophene derivatives in majority.

4. Conclusions

The roles of a commercial hydrodesulphurization catalyst in the catalytic pyrolysis of waste tire and sulphur removal was proven in this study. The spent commercial NiMoS/Al₂O₃ catalyst can reduce the amount of sulphur in oil from 1.36 to 0.60 wt%, and can help cracking waste tyre to lighter products. Nevertheless, the cracking activity was not considerably high due to its mild acidity. Therefore, it can be concluded that the spent HDS catalyst can be used as a catalyst for the waste tyre pyrolysis since it can produce the better quality of pyrolysis oil containing a lower sulphur level because of its acid and sulphide functions.

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NiMo/HBETA as Catalysts with Dual Functions Beneficial to Waste Tyre Pyrolysis

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The world is running out of petroleum with the increasing demand in the fuel consumption. Oil from waste tyres is one of interesting fuels to be developed, and pyrolysis is one of the suitable processes to utilize these waste tyres. In the pyrolytic oil from waste tyres, sulphur compounds are largely present in the form of polar-aromatics such as thiophene, benzothiophene, and dibenzothiophene, which can cause poisoning of the active sites on the catalyst. Moreover, if sulphur-containing oils are used as fuels, SO₂ that is a pollutant can be produced during combustion. In our previous work, Ni/HBETA was proven to be a potential waste tyre pyrolysis catalyst; thus, since NiMo is one of good desulphurization catalyst, it was also expected to have both pyrolysis and sulphur removal activities beneficial to waste tyre pyrolysis. The purposes of this work were to study the cracking ability as well as the desulphurization ability of NiMo loaded on HBETA catalyst for tyre pyrolysis, and to study the change of sulphur compounds when the compositions of the bimetallic catalysts are varied. The results showed that 5%Ni with 20%Mo catalyst had both good cracking and desulphurization abilities. The pyrolytic oil obtained from the catalyst had lower polar-aromatic and sulphur contents than those from the other catalysts. It was mainly composed of full-range naphtha which had large amounts of saturated hydrocarbons and mono-aromatics. Moreover, the sulphur compounds in the pyrolytic oils were analyzed by GC-MS (TOF). It was found that sulphur compounds were mainly in the kerosene range (C₁₀–C₁₃) such as benzo[b]thiophene, 2,7-dimethyl, benzo[b]thiophene, 2-ethyl-7-methyl- and dibenzothiophene.

1. Introduction

The increases in petroleum demand and price have driven the world to seek for alternative fuels. Waste tyres discarded in a gigantic quantity are an adequate supply for producing oil substitute through pyrolysis process. Waste tyre pyrolysis is the thermal degradation of waste tyre in the absence of the oxygen. Three products; pyrolytic gas, oil, and char (Chang, 1996) can be obtained. Pyrolytic oil can be used directly as a chemical feedstock or fuel oil substitute. In the pyrolytic oil from waste tyres, sulphur compounds are largely present in the form of polar-aromatics such as thiophene, benzothiophene, and dibenzothiophene (Pakdel et al., 2001), which can cause poisoning of the active sites of a catalyst. Moreover, if fuels contain sulphur, SO₂ that is a pollutant is produced during combustion. With this reason, many countries limit the amount of sulphur content in transportation fuels. Therefore, not only are the cracking of heavy hydrocarbons to light hydrocarbons as well as hydrogenation and ring-opening needed, but hydrodesulphurization is also important in the pyrolysis process. There were many researchers that used catalysts to improve the quality and quantity of the pyrolytic products. Bifunctional catalysts (metals supported on zeolites) become interesting to order to improve the efficiency of catalytic pyrolysis. Noble metals supported on acidic zeolite were used to optimize the high value products because noble metals can promote hydrogenation and ring opening (Du et al., 2005). For examples, Pt/HBETA showed good ability for polar-aromatic reduction, leading to a decreasing amount of sulphur in the pyrolytic oil (Düng et al., 2009). With the high prices of the noble metals, some of non-noble metals were used instead of noble metals. Ni based catalysts have been effective for many reaction such as pyrolysis and partial oxidation

(Tagawa et al., 2013). Saeae et al. (2012) found that Ni loaded on HBETA zeolite increased the cracking ability of HBETA in tyre pyrolysis because it increased the gas yield with a consequent decrease in the oil yield. They also found that the sulphur content in oil was further reduced by using Ni/HBETA catalyst. Ni/HBETA also increased the quality of the pyrolytic oil by decreasing long residue and then increasing the full range naphtha. They found that some of non-noble metals can be used to substitute noble metals when used in a higher amount. Moreover, bimetallic catalysts, such as NiMo, NiW, CoMo, and CoW (Mo and W as second metals doped to Ni and Co) supported on Al_2O_3 are normally used in hydrodesulphurization process (Torres-Mancera et al., 2005). Therefore, in this work, Mo was chosen as a second metal promoter on Ni/HBETA since the pyrolysis of waste tyre requires both cracking and desulphurization functions of the catalyst. The purposes of this work were, therefore, to study the cracking ability as well as the desulphurization ability of modified Ni/HBETA catalysts (bimetallic NiMo) in tyre pyrolysis, and to study the change of sulphur compounds when the compositions of the bimetallic catalysts were varied. Ni was fixed at 5 wt%, whereas the loading of Mo was varied to 10 and 20 wt%. Types and amounts of sulphur compounds in the oil were also studied.

2. Experimental

2.1 Catalyst Preparation

The zeolite, which is HBETA ($\text{Si}/\text{Al} = 13.5$) obtained from Tosoh Company in Singapore, was calcined at 600 °C for 5 h with a heating rate of 2 °C/min. To prepare the bimetallic catalysts, NiMo/HBETA, appropriate amounts of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot \text{H}_2\text{O}$) were loaded on the HBETA zeolite by incipient wetness impregnation technique. The composition of bimetallic catalysts was varied as 10 and 20 wt% of Mo with the fixed amount of Ni at 5 wt%. After that, the samples were dried at 110 °C for 3 h in an oven, and calcined at 500 °C for 3 h with the heating rate of 5 °C/min and further reduced at 800 °C for 1 h to obtain the catalysts in the bimetallic form.

2.2 Catalyst Characterization

X-ray Diffraction (XRD) was used to verify the metallic form of catalysts. X-ray diffraction (XRD) patterns were taken by using a Bruker X-ray diffractometer system (D8 Advance) equipped with a 2.2 kW Cu anode long fine focus ceramic X-ray tube for generating a $\text{CuK}\alpha$ radiation (1.5405 Å). The detector scans the peak position from the sample as a function of 2θ by starting at the 10° to 60° (2θ) range and a scan speed of 0.02° (2θ)/0.6 s. The XRD patterns were matched to the standards to identify crystalline phases. Temperature-programmed reduction (TPR) was used to identify the reducibility of the impregnated catalysts and the metal-metal interaction. The TPR experiments were conducted from 30 °C to 850 °C.

2.3 Pyrolysis Experiment

There are 2 zones of pyrolysis reactor; that are, catalytic zone (the upper zone) and pyrolytic zone (the lower zone). The pyrolysis experiments were conducted according to the procedure in Dũng et al. (2009). First, 30 g of the waste tyre with sizes in the range of 8-18 mesh was loaded into the lower zone with a heating rate of 10 °C/min from the room temperature to final temperature. The final temperature of this zone was controlled at 500 °C and then kept for 90 minutes at the atmospheric pressure. In the catalytic zone of the reactor, 7.5 g of pellet catalyst was loaded and controlled at 350 °C. N_2 flow rate was controlled at 30 ml/min for purging the oxygen out of the system prior to pyrolysis and subsequently for carrying the pyrolysis product through two condensers and then to a gas sampling bag. These condensers were placed into the ice bath in order to collect the condensable products (pyrolytic oils). The gas sampling bag collected the non-condensable products (pyrolytic gases). Non-decomposable components of the tyres were collected as pyrolytic chars.

2.4 Product Analysis

Pyrolytic gases were analyzed by using a Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm ID and 20 μm film thicknesses. A detector was FID type using He as the carrier gas. Pyrolytic oil was separated into asphaltene (n-pentane insoluble) and maltene (n-pentane soluble), and then the maltene solution was fractionated using specific solvents (Šebor et al., 1999) into 5 fractions, which are saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics and polar-aromatics in a liquid chromatography column. The liquid fraction was analyzed using a Varian CP-3800 stimulated distillation gas chromatograph (SIMDIST GC) equipped with an FID, according to the ASTM D2887 method. Each fraction was classified according to its boiling point range, which are full range naphtha (< 200 °C), kerosene (200 - 250 °C), light gas oil (250 - 300 °C), heavy gas

oil (300 – 370 °C) and long residue (> 370°C). The sulphur compounds in the pyrolytic oil were determined using a Gas Chromatography equipped with a mass spectrometry of Time of Flight type (GC-TOF).

3. Results and Discussion

3.1 Characterization

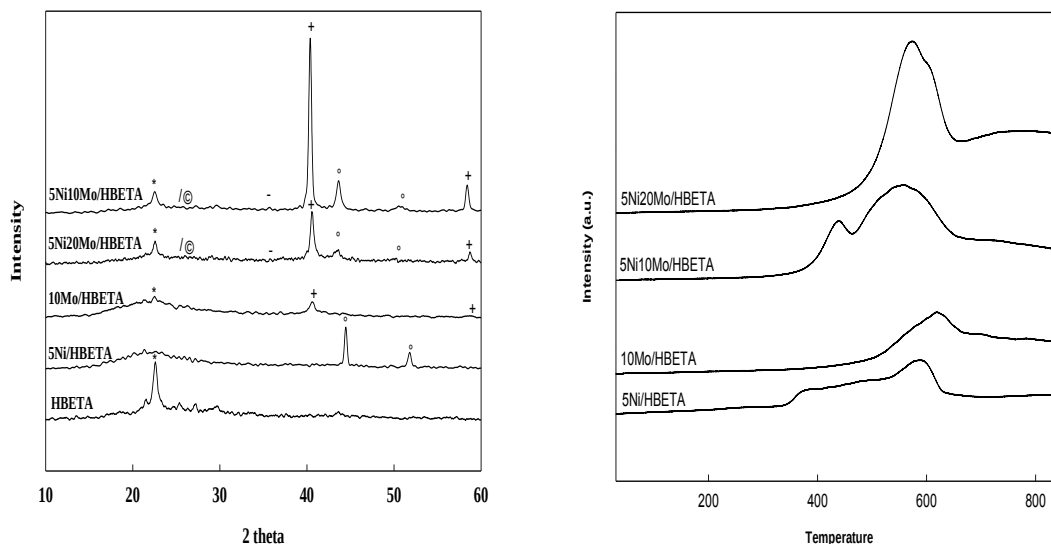


Figure 1: XRD (left) and TPR (right) obtained from modified Ni/HBETA catalysts in comparison with 10Mo/HBETA

Figure 1 illustrates XRD and TPR obtained from the modified Ni/HBETA catalysts. The XRD confirms that the bimetallic NiMo clusters (+ and o) are formed on the zeolite. The TPR profile of 5Ni20Mo/HBETA catalysts show a strong Ni-Mo interaction peak whereas that of the 10 % Mo doping shows two strong interaction peaks. The strong interaction is believed to be responsible for the cracking and desulphurization abilities of 5Ni20Mo/HBETA catalyst.

3.2 Cracking ability

The results exhibit the qualities and quantities of the pyrolytic products from the Mo-doped Ni/HBETA catalysts. The product distribution can be shown by the ratio of gas to liquid in Figure 2. The solid product remains constant at about 40 wt%.

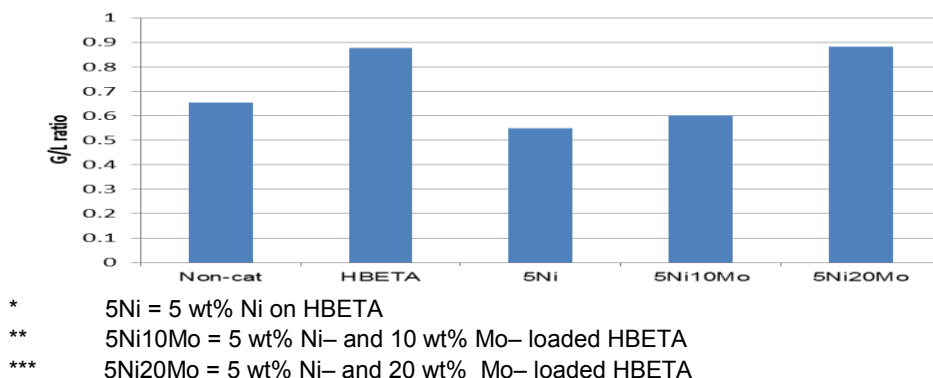


Figure 2: G/L ratio obtained from modified Ni/HBETA catalysts

Figure 2 shows the ratio between gas and liquid obtained from the modified Ni/HBETA catalysts as compared to that of pure HBETA zeolite and the non-catalytic case or non-cat (thermal pyrolysis). The higher G/L ratio gave the higher the cracking ability because the heavy molecules can be cracked into

lighter molecules over the acid sites of the catalysts. For the 5Ni/HBETA catalyst, the reduction of the G/L ratio can be resulted from the interaction between the metal and the support. However, with using the bimetallic catalysts (NiMo), the G/L ratio increases with the increase of the amount of the Mo loading, which indicates that, the modified Ni/HBETA catalysts (5Ni10Mo/HBETA and 5Ni20Mo/HBETA) can increase the cracking ability from the monometallic 5Ni/HBETA catalyst. 5Ni20Mo/HBETA has the highest cracking ability among the others because it had the highest G/L ratio (0.88). Nevertheless, although Mo can enhance the cracking ability of the Ni/HBETA catalyst, the bimetallic catalysts still have the same cracking ability as the parent HBETA zeolite. Therefore, the doping of Mo to Ni/HBETA catalyst helps maintain the cracking activity of the parent zeolite.

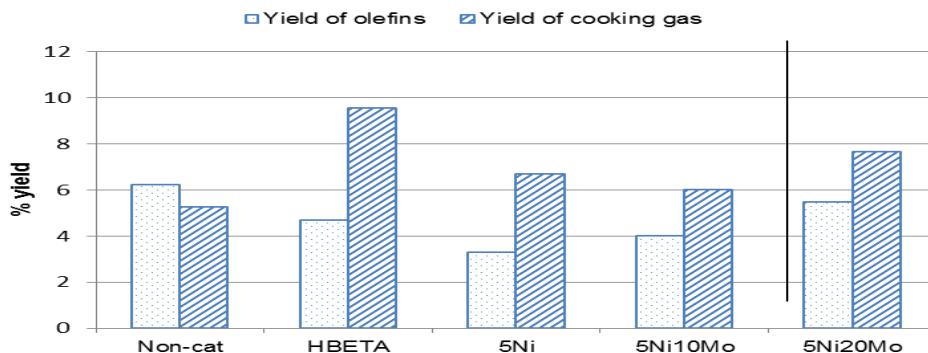


Figure 3: Yield of olefins and cooking gas obtained from pyrolysis with modified Ni/HBETA catalysts

Non-condensable gases are composed of gases in the range of C₁-C₅. Some of these gases are valuable petrochemical products such as olefins (ethylene and propylene), and cooking gas (propane mixed with mixed C₄). Figure 3 show the yield of these petrochemical gases obtained from modified Ni/HBETA catalysts. The results indicate that the non-catalytic case gives 6.25 and 5.27 wt% yield of olefins and cooking gas, respectively. With using the catalysts, the yields of olefins decrease in accordance with the increase in the yield of cooking gases. 5Ni/BETA gives the lowest yield of olefins; however, when the modified Ni/HBETA catalysts are used, the yields of olefins increase significantly. The yield of olefins increases with the increasing contents of Mo. The pure HBETA gives the highest yield of cooking gas (9.6 %) among the other catalysts; including the non-catalytic case. 5Ni/HBETA gives about 6.7 wt% yield of cooking gas. 5Ni10Mo/HBETA does not increase the yield of cooking gas whereas using 5Ni20Mo/HBETA increases the yield of cooking gas significantly. This can be concluded that although the bimetallic catalysts, especially 5Ni20Mo/HBETA, do not enhance the cracking ability, they can increase the yield of the valuable gases.

3.3 Quality of the pyrolytic oil

After asphaltene was separated from the liquid products of waste tyre pyrolysis, the maltene solutions were separated into 5 fractions; saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics and polar-aromatics, as shown in Figure 4, by using liquid column chromatography (Šebor et al., 1999). These 5 fractions were analyzed by using a SIMDIST-GC for the true boiling point curves that later were cut to the petroleum fractions; naphtha (< 200 °C), kerosene (200 - 250 °C), light gas oil (250 - 300 °C), heavy gas oil (300-370 °C), and long residue (> 370 °C)..

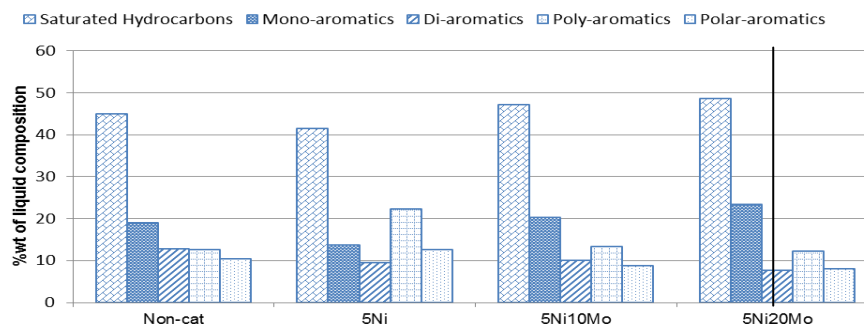


Figure 4: Chemical compositions in maltenes from using modified Ni/HBETA catalysts

Figure 4 indicates the chemical compositions in maltenes from various catalysts. With using 5Ni/HBETA, the light components (saturated hydrocarbons and mono-aromatics) decrease in conjunction with the increase in the heavy components (poly- and polar-aromatics). However, when the bimetallic catalysts (NiMo on HBETA) are used, saturated hydrocarbons and mono-aromatics increase dramatically in the same trend; resulting in the consequently decreases in poly- and polar-aromatics, which indicates the good abilities in cracking and ring-opening of the large aromatic molecules. The NiMo/HBETA catalyst, especially 5Ni20Mo/HBETA, gives the highest concentration of saturated hydrocarbons and mono-aromatics, which are about 48.6 % and 23.5 % by weight. It can be concluded that the modification of Ni/HBETA catalyst with Mo can increase the qualities of the pyrolytic oils because it can help to convert the heavy components such as poly- and polar aromatics to the lighter components (saturated hydrocarbons and mono-aromatics with a lower average carbon number) as compared with the non-catalytic case (Nor et al., 2013). Figure 5 shows the petroleum fractions in maltenes obtained from using modified Ni/HBETA catalysts. It can be seen that using the 5Ni/HBETA catalyst can increase the amount of full range naphtha. The results show that the bimetallic NiMo catalysts are likely to produce the light oils since 5Ni20Mo/HBETA gives the highest amount of the full range naphtha while 5Ni10Mo/HBETA gives the highest amount of kerosene. It can be seen that the higher the loading of the second metal (Mo), the higher full range naphtha is obtained. In addition, pure HBETA produces the heavier oils than all other catalysts. Therefore, it can be concluded that the promotion of Mo in the Ni/HBETA catalyst can improve the quality of oil.

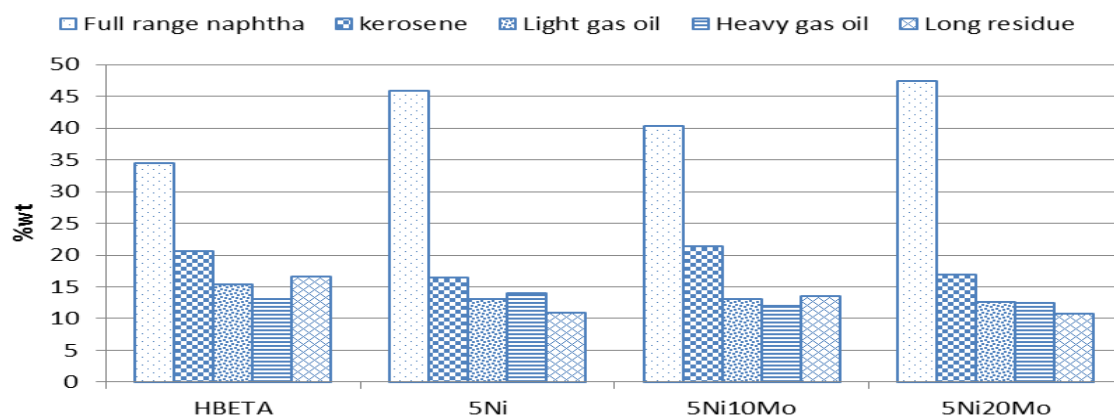


Figure 5: Petroleum fractions in maltenes obtained from using modified Ni/HBETA catalysts

3.4 Desulphurization ability

The sulphur contents in pyrolytic oil and sulphur deposition on spent catalysts were determined by a CHNS analyser, and the sulphur compounds in the pyrolytic oils were analyzed by GC-MS (TOF).

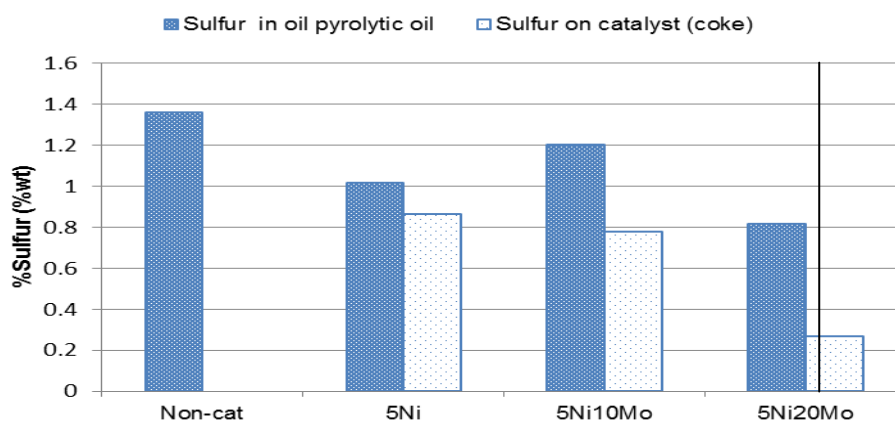


Figure 6: Sulphur contents (%wt) on spent catalysts and in the pyrolytic oils obtained from modified Ni/HBETA catalysts

Figure 6 shows the presence of sulphur contents obtained from the modified Ni/HBETA catalysts. The sulphur content in pyrolytic oil is about 1.36 %wt when none of the catalyst used. 5Ni/HBETA and all of modified Ni/HBETA catalysts show good hydrodesulphurization ability because they can reduce the sulphur content in the pyrolytic oil. When 5Ni/HBETA is used, it can reduce the sulphur content in the pyrolytic oil to 1.02 wt%, and sulphur content on the spent catalyst (coke) is reduced to 0.87 wt%. Using 5Ni10Mo/HBETA, the sulphur content in the pyrolytic oils increases in conjunction with the decrease in sulphur content on the spent catalyst, whereas 5Ni20Mo/HBETA gives the lowest sulphur contents in the pyrolytic oil (0.82 wt%) and the lowest sulphur contents on the spent catalysts (0.27 wt%) among all others. 5Ni20Mo/HBETA is a good catalyst for the sulphur reduction as indicated by the lowest sulphur contents in oil. This can be suggested that 5Ni20Mo/HBETA can breakdown the C-S bonds due to the hydrodesulphurization activity (Songdong et al., 2012). Moreover, it can be concluded that 5Ni20Mo/HBETA catalyst can produce high quality of oil that contains low sulphur content.

The sulphur compounds in the pyrolytic oils were analyzed by GC-MS (TOF). The sulphur compounds in the oil obtained from 5Ni20Mo/HBETA are mainly in the range of C₅-C₉, such as thiophene, 2-(1-methylethyl)-, benzo[b]thiophene, 4-methyl and benzo[b]thiophene whereas the sulphur compounds from the non-catalytic case are mainly in the range of C₁₀-C₁₃, such as benzo[b]thiophene, 2,7-dimethyl, benzo[b]thiophene, 2-ethyl-7-methyl- and dibenzothiophene.

4. Conclusions

The effects of modified Ni/HBETA catalysts on the quantity and quality of pyrolysis products were investigated. The results showed that the modification of Ni/HBETA catalyst with both 10 % and 20 %wt of Mo can increase the quality of pyrolytic oil, which contained a high amount saturated hydrocarbons and light petroleum fractions. Moreover, 5Ni20Mo/HBETA also had a good desulphurization ability because it gave the lowest sulphur contents in oil (0.82 wt%).

Acknowledgement

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Comparison of Components in Oil Derived from Tyre Pyrolysis with and without KL Catalyst Using GC × GC / TOF-MS

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Typically, the products from waste tyre pyrolysis consist of (i) gas fraction (18 – 23 %wt), (ii) liquid fraction (41 – 49 %wt), and (iii) char fraction (38 – 40 %wt). The liquid amount is considered the highest among those obtained from waste tyre pyrolysis. The improvements of tyre-derived oils (liquid fraction) could be accomplished by increasing mono-aromatics as a result of the reductions in di-aromatics and poly-aromatics through hydrogenation and the conversion of terpenes through aromatization. A basic catalyst that has potassium as a cation such as potassium tert-butoxide ($K^+(CH_3)_3CO^-$) can provide hydrogenation and aromatization. KL zeolite is a representative of a solid basic catalyst. It has a pore diameter 0.71 Å and 1-dimensional pore structure. Moreover, the 1-dimensional pore structure can align the incoming molecules parallel on the surface of KL, resulting in high yields of hydrogenated products. Two-Dimensional Gas Chromatography coupled with Time-of-Flight Mass Spectrometry (GC × GC / TOF-MS) that can separate and identify the chemicals that have same retention time and boiling points due to overlapped mass spectra was employed for better identification of components in tyre-derived oils. The objective of this research was thus to observe the changes the hydrocarbon species upon the use of a KL catalyst. The GC × GC / TOF-MS was used to investigate hydrocarbon species in the maltenes (liquid fraction without asphaltene) from the non-catalyst and KL batches. The liquid products were categorized into saturated hydrocarbons (SATs), olefins (OLEs), terpenes (TERs), mono-aromatics (MAHs), di-aromatics (DAHs), poly-aromatics (PAHs), and polar-aromatics (PPAHs), including sulphur compounds. The pyrolysis experiments were performed in a bench-scaled autoclave reactor from room temperature to 500 °C (for the pyrolysis zone) and 350 °C (for the catalytic zone) with the heating rate of 10°C/min. As a result, KL was found to increase the MAHs from 20.1 to 26.8 %wt (mostly, 2-ethyltetralin) and decrease DAHs from 13.31 to 6.37 %wt (mostly, 2-ethylnaphthalene), and TERs from 4.06 to 2.56 %wt (mostly, d-limonene and 3-carene). The sulphur compounds in tyre-derived oils were found to be thiophenes, phenylthiophenes, benzothiophenes, methylbenzothiophenes, dibenzothiophenes, and naphthols.

1. Introduction

Questions concerning about the quality of tyre-derived oil have been arisen since tyre-derived oil was composed of a considerable amount of aromatics that can be pollutants and carcinogenic agents. Dai et al. (2001) studied the pyrolysis of waste tyres in a circulating fluidized-bed reactor, and reported that 12.10 %wt in aromatic fraction was di-aromatics, for examples, naphthalene and methylnaphthalenes. Laresgoiti et al. (2004) characterized the liquid products from tyre pyrolysis, and reported that poly-aromatics generally consisted of three main groups: fluorenes, phenanthrenes, and pyrenes.

To be converted, di-aromatics and poly-aromatics need to be first hydrogenated. Bianchini et al. (2004) studied the role of a single-site catalyst on the hydrogenation of thiophenes, and reported that it produced non-aromatic hydrocarbons and H₂S. Piyawongpinoy and Jitkarnka (2013) reported that doping 10 and 20 %wt Mo on Ni/HBETA increased a high amount of saturated hydrocarbons and light petroleum fractions.

Moreover, Saeng-araku and Jitkarnka (2013) revealed the spent commercial NiMoS/Al₂O₃ catalyst was effective enough to reduce the sulphur in oil from 1.36 to 0.60 %wt and produced lighter products.

A basic catalyst that has a K⁺ as a cation such as potassium tert-butoxide (K⁺(CH₃)₃CO⁻) and K/Al₂O₃ can provide both hydrogenation and aromatization. Stapp and Kleinschmidt (1965) studied the isomerization of cyclooctadienes to cis-Biscyclo[3.3.0]oct-2-ene, and reported that potassium tert-butoxide can hydrogenate linear dienes, like 1,5-hexadiene, to hexane. Moreover, Slaugh (1967) studied metal hydrides as hydrogenation and isomerization catalysts, and found that potassium hydride (KH) appeared to be several hundred times more active than sodium hydride. In addition, Slaugh (1968) studied the hydrogenation of benzene to phenylcyclohexane using supported alkali metal catalysts, and found that the catalytic properties of alkali metals could be changed drastically by depositing them on certain supports. Furthermore, Friedman et al. (1971) found that alkali metals and alkali metal alloys can be used as catalysts for the hydrogenation of poly-aromatic hydrocarbons to products containing an isolate aromatic ring. In addition, a basic catalyst can also provide aromatization of hydrocarbon compounds. Moreover, Brown (1973) revealed potassium hydride with amine can provide aromatization of *d*-limonene to *p*-cymene at room temperature.

The KL zeolite is a solid basic catalyst that contains K⁺ as a cation. It has basic property and one dimensional channel of 12-membered rings with a pore size of 0.71 nm (Sato et al., 1999). KL has been employed as a support of Ru for the hydrogenation of unsaturated aldehyde (Álvarez-Rodríguez et al., 2005). Azzam et al. (2010) studied the aromatization of hexane over Pt/KL catalyst, and they found that L-zeolite channels inhibited the coke formation and catalyst deactivation. Previously, KL has been tested in our group as tyre pyrolysis catalyst, and its effects on pyrolysis products were reported in terms of petroleum cuts in tyre-derived oil. No details on chemicals in oils were reported.

Comprehensive two-dimensional gas chromatography (GC × GC) consists of two columns connected in series. The first column (a primary non-polarity column) can separate the components based on carbon number, and it consequently provides the second column (a secondary polar column) with a series of sub-samples containing the same carbon number that can be further separated based on the polarity. Time-of-flight (TOF/MS) instrument is able to scan at the high scan rates of ≥ 50 spectra/s. The data can be collected at high rates, which are shown obviously at separated retention time with accurate quantification (Dalluge et al., 2002a). The analysis of an unresolved complex mixture such as oil spill (Nelson et al., 2006), rich biodegraded crude oil (Melbye et al., 2009), cigarette smoke (Dalluge et al., 2002b), and standard polycyclic aromatics have been well accomplished by using this technique (Manzano et al., 2012). Therefore, in this work, the effect of KL zeolite on the chemical components of tyre-derived oil was determined using GC × GC / TOF-MS as an analysis instrument. The components in the oils derived from tyre pyrolysis with and without KL catalyst are hereby compared and discussed.

2. Experimental setup

2.1 Catalyst preparation

The zeolite, Linde Type L (LTL, K-form, Si:Al = 3) supplied by the TOSOH Company (Singapore) was first calcined in air at 500 °C with the heating rate of 5 °C min⁻¹ for 3 h. After that, the zeolite was pelletized, ground, and then sieved to a specific particle size range of 400-425 µm before use.

2.2 Pyrolysis of waste tyre

A used passenger tyre tread, Bridgestone TURANZA GR-80, was shredded and sieved to a size range of 8-18 mesh. The tyre pyrolysis experiments were conducted using the same pyrolysis system as in (Dũng et al., 2009). The tyre sample was pyrolyzed in the reactor where the temperature was ramped from room temperature to the final temperature of 500 °C with the ramping rate of 10 °C min⁻¹, and kept at the final temperature for one hour to ensure the total conversion of tyre. 7 g of the KL catalyst was packed and heat at 350 °C in the catalytic zone. A 25 mL min⁻¹ nitrogen was used to purge the reactor before the experiment and to carry the product out of the reactor. The obtained product was passed through the ice-salt condensing system containing two consecutive containers in order to separate the liquid product from incondensable compounds. After the experiment, the solid and liquid were weighed to determine the product distribution. The amount of gas was calculated from mass balance. Only the oil was brought to analysis in this study. It was first dissolved in *n*-pentane with the ratio of 40:1 (*n*-pentane:oil) to separate asphaltene. The clear solution after filtration is called maltene.

2.3 Analysis using GC × GC – TOF/MS

The GC × GC–TOF/MS system was composed of an Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA), a thermal modulator, and a Pegasus® 4D TOF-MS (LECO, St. Joseph, MI, USA). The GC was installed with two columns: the first column was a non-polar Rtx 5 silms®

(30 m x 0.25 mm i.d. x 0.25 μm film thickness), and the second column a Rxi®-17 ms (1.10 m x 0.10 mm i.d. x 0.10 μm film thickness). Both columns were made by Thames Restek (Sounderton, UK). The main GC oven was operated from at 50 $^{\circ}\text{C}$ with 2 min holding at the beginning and then ramped to 310 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C min}^{-1}$ with 10 min holding at 310 $^{\circ}\text{C}$, and the secondary oven was operated at 60 $^{\circ}\text{C}$ held for 2 min at the beginning and ramped to 320 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C min}^{-1}$ with 10 min holding at the final temperature. One μL of the 10 mg/mL maltenes in carbondisulfide (CS_2) was injected via a spiltless injector at 250 $^{\circ}\text{C}$ using He as the carrier and a constant column flow rate of 1.0 mL/min. The modulator was operated under modulation timing of 4-s cycle time and 0.5-s holding time in the release position. The nitrogen cryogen coolant maintained the temperature of the modulation trap to at least 30 $^{\circ}\text{C}$. A Pegasus 4D® TOF/MS instrument was used to acquire mass spectral data, using -70 V electron impact ionization. The ion source temperature was set at 250 $^{\circ}\text{C}$. The detector voltage was set at 1,600 V. The transfer line temperature was 250 $^{\circ}\text{C}$. The mass range collected was from 35 to 500 m/z , with 100 spectra/s transferred to the data station. The data processing was set S/N value of 10, match required to combine 500, and dt that was used to calculate the percentage area. Data were recorded and analyzed using the LECO ChromaTOF® software. The NIST library provided with the instrument was used for spectral searching. The analysis was repeated for 3 times.

3. Results and discussions

3.1 Total ion chromatograms and grouping of components in tyre-derived oils

Figure 1 shows the contour plots of total ion chromatogram (2D TIC) of maltenes from (a) non-catalyst and (b) KL batches. They indicate that the conditions used to analyze the tyre-derived oil are satisfied to separate the complex components, which were found in a total of more than 1,500 compounds. As the structural complexity of the components increases, partial overlapped for component classes can occur even though they are shown by GC x GC/TOF in the total ion chromatogram. For examples, the compounds in the circle are identified by the NIST database as monoaromatic hydrocarbons (MAHs). After using the KL catalyst, the contour plot in the circle appears darker than that from the non-catalyst batch. It means that the concentration of MAHs is increased with using the KL catalyst. However, the GC x GC/TOF can reveal the separation of components in overlapped chromatograms as seen on the surface plots of total ion chromatogram (3D plots) in Figure 2 since the secondary column (the polar column) can separate the components with different polarities, which emerge at the same retention. These components are separated layer by layer as seen in the profile on the contour plot, continuing as the carbon number increases.

For the analysis of TICs, the components are thus categorized into groups, according to their chemical structures; namely, saturated hydrocarbons (SATs), mono-aromatics (MAHs), di-aromatics (DAHs), poly-aromatics (PAHs), polar-aromatics (PPAHs), terpenes (TERs), and olefins (OLEs). MAHs are the most valuable chemicals in the petrochemical industry. Some of them play an important role as upstream petrochemicals in either polymer or advanced material industries. It can be seen that the MAHs increases when the KL catalyst is used. Two main groups of MAHs are mono-aromatics with saturated substituents (MAHs-SS) and mono-aromatics with unsaturated substituents (MAHs-US). Mono-aromatics with saturated substituents are classified into four sub-groups; that are, benzene, alkylbenzenes, indanes, and 1,2,3,4-tetrahydronaphthalenes (tetralins), and those with unsaturated substituents are classified into two sub-groups; that are, indenenes and alkenylbenzenes. SATs consist of aliphatic hydrocarbons starting at C14 to C17. OLEs consist of unsaturated hydrocarbons also starting at C14 to C17. TERs consist of 3-carene and d-limonene. DAHs consist of naphthalene and alkylnaphthalenes. PAHs consist of 1-1'biphenyl, anthracene, pyrene, and benzopyrene whereas PPAHs consist of thiophenes, benzo thiophenes, and dibenzo thiophenes.

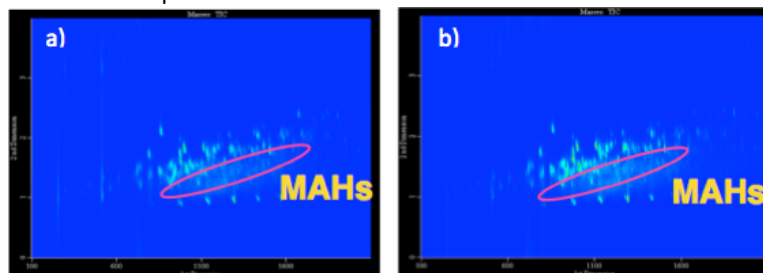


Figure 1: 2D-Total ion chromatogram (contour plot) of the maltenes from (a) non-catalyst and (b) KL batches

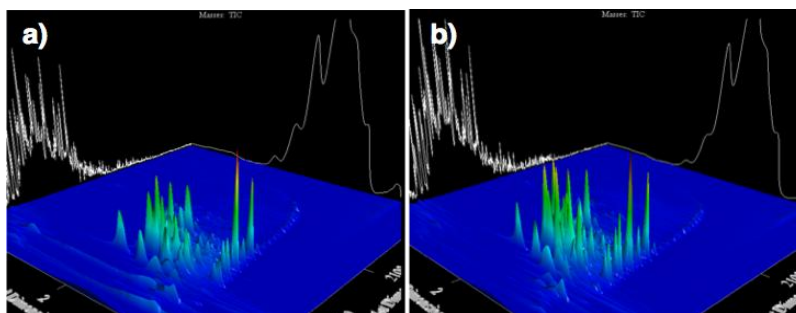


Figure 2: 3D-Total ion chromatogram (surface plot) of the maltenes from: a) non-catalyst b) KL

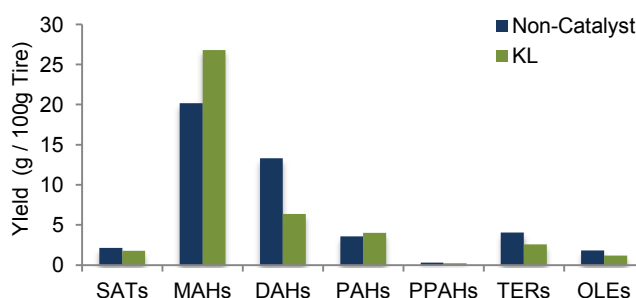


Figure 3: Yield of hydrocarbon species in tyre-derived oils from non-catalyst and KL batches

3.2 changes of oil components with using KL

Figure 3 indicates the changes of components upon the use of KL as follows. The yield of MAHs increases from 20.1 to 26.8 g/100 g tyre (mostly, 2-ethyl-1,2,3,4-tetrahydronaphthalene (2-ethyltetralin), ($m/z = 160$)). The yield of DAHs decreases from 11.3 to 6.3 g/100 g tyre (mostly, 2-ethylnaphthalene ($m/z = 156$)), whereas that of TERs from 4.0 to 2.9 g/100 g tyre (mostly, d-limonene ($m/z = 136$) and 3-carene ($m/z = 136$)). SATs, PAHs, PPAHs, and OLEs are not found significantly changed upon using the KL catalyst.

3.2.1 Changes of hydrocarbon species in MAHs

According to Figure 3, the significant decrements of DAHs and TERs are observed in conjunction with the increase in MAHs. Since a significant increase of MAHs is found with using the KL catalyst, the changes of compounds in MAHs are then examined in details. Figure 4 shows the changes of hydrocarbon species in the MAHs groups. It can be seen that benzene, alkylbenzenes, indanes, and 1,2,3,4-tetrahydronaphthalenes (tetralins) significantly increase; whereas indenenes and alkenylbenzenes dramatically decrease when the KL catalyst is used.

3.2.2 Changes of hydrocarbon species in TERs

According to Figure 5(a), dominant components in the TERs (C₁₀) group are d-limonene ($m/z = 136.125$), 3-carene ($m/z = 136.125$) and 3-methyl-4-methylenebicyclo[3.2.1]oct-2-ene (3-m-4-mb-2-e) ($m/z = 136.125$). The others in the figure are described to the combination of all minorities in TERs. When the KL catalyst is used, the yields of d-limonene and 3-carene decrease.

3.2.3 Change of hydrocarbon species in PAHs

From Figure 5(b), the yield of 1,2-dihydroacenaphthylene (ace) decreases with the increase in phenanthrene (phen). The yield of 4-methyl-1,1'-biphenyl (4-m-1,1'-bph) ($m/z = 166.078$) decreases with the increase in 2-methyl-9H-fluorene (2-m-9-flu) ($m/z = 180.094$). Finally, the yields of 9H-fluorene (9-flu), 2,2'-dimethyl-1,1'-biphenyl (2,2'-dbph), and 1,1'-biphenyl (1,1'-bph) decrease when the KL catalyst is used.

3.2.4 Change of hydrocarbon species in SATs

It was found the SATs hydrocarbon species are tridecane (C₁₃), tetradecane (C₁₄), and hexadecane (C₁₆). From Figure 6(a), the yield of tetradecane drastically decreases whereas the yield of tridecane increases when the KL catalyst is used.

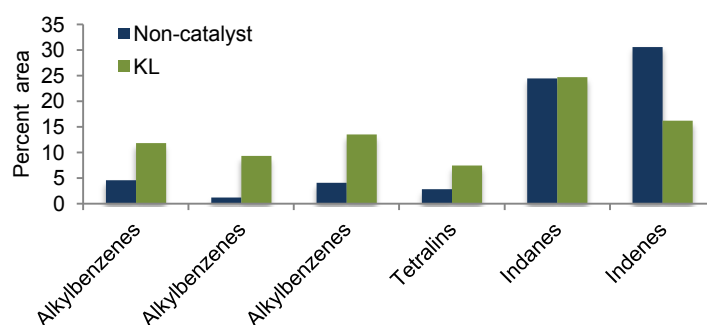


Figure 4: Changes of hydrocarbon species in the MAHs groups with using KL catalyst

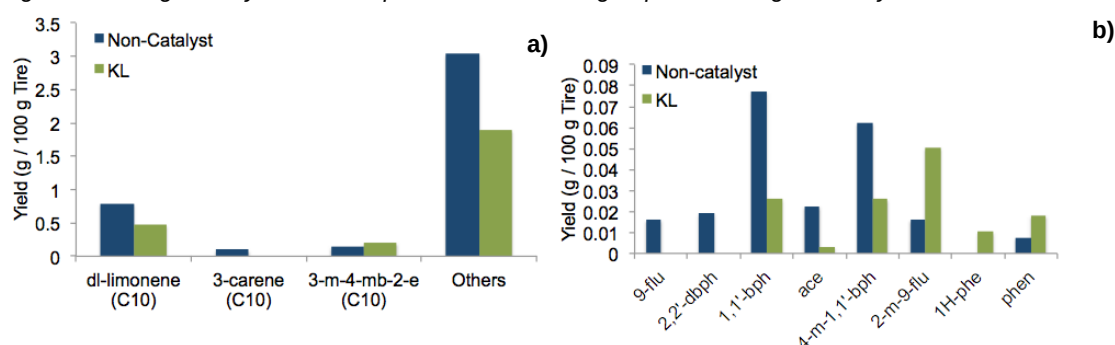


Figure 5: Changes of hydrocarbon species in (a) TERs (C10) and (b) PAHs with using KL catalyst

3.2.5 Change of hydrocarbon species in PPAHs

The sulphur compounds in PPAHs were found to be 2-(1-methylethyl)thiophene, ($m/z = 126.050$), methylbenzothiophene ($m/z = 148.035$), 3-phenylthiophene, ($m/z = 160.035$), dimethylbenzothiophene ($m/z = 162.050$), dibenzothiophene ($m/z = 184.035$), dimethyldibenzothiophene ($m/z = 212.066$), and naphtho[2,3-b]thiophene, 4,9-dimethyl- ($m/z = 212.066$). Figure 6(b) shows that thiophenes (thos) and benzothiophenes (b-thos) are increased with the decreases in phenylthiophenes (p-thos), benzothiophenes (b-thos), and dibenzothiophenes (db-thos) when the KL catalyst is used.

4. Conclusions

The KL catalyst was found to increase the yield of MAHs (mostly, 2-ethyltetralin) from 20.1 to 26.8 %wt but decrease that of DAHs (mostly, 2-ethylnaphthalene) from 13.31 to 6.37 %wt. Moreover, the yield of TERs (mostly, d-limonene and 3-carene) decreased from 4.06 to 2.56 %wt. It was due to the fact that the KL catalyst can hydrogenate DAHs and aromatize TERs. Moreover, the bulky pyrolysis products decreased when the KL catalyst was used. The PPAHs, PAHs, SATs, and OLEs did not significantly change with using the KL catalyst. Finally, the sulphur compounds in tyre-derived oils were found to be thiophenes, phenylthiophenes, benzothiophenes, methylbenzothiophenes, dibenzothiophenes, and naphthols.

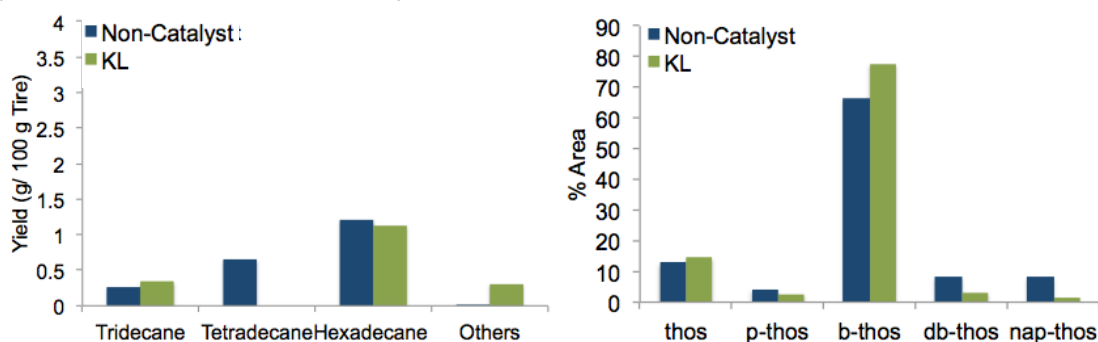


Figure 6: Changes of hydrocarbon species in (a) SATs and (b) PPAHs with using KL catalyst

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Impact of Zeolite Channel Structure on Structure of Hydrocarbon Compounds and Petrochemicals in Waste Tyre-Derived Oils

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Waste tyre, a hydrocarbon-based material, exhibits potential to be used for a derivation of petrochemicals. Valuable chemicals such as benzene, toluene, and xylenes were observed in pyrolytic oils. Furthermore, sulphur compounds causing the low quality of oil products and environmental problem were also found. HBeta and HMOR acidic zeolites whose pore sizes are very close, which are 6.4x7.6 Å and 6.5x7.0 Å have different channel structures. The channel structure of HBETA is zigzag whereas that of HMOR is straight. Since the channel structure of zeolites may affect the residence time of molecules to stay in the pores; therefore, the objective of this work was to investigate the channel structure of zeolites that affect the structure and the size of pyrolysis products. The products were analyzed by using a SIMDIST-GC, GC and elemental analyser, whereas a GCxGC-TOF/MS was used to investigate species in oils. The catalysts were characterized by using XRD, TGA, and SAA. The results showed that the compositions of pyrolytic oils classified in terms of paraffins (P), olefins (O), naphthenes (N), and aromatics (A) were different with using different zeolites. Catalytic pyrolysis caused the decreases in olefins and naphthenes with the increases of aromatics. Furthermore, HBeta gave the higher amount of aromatics than HMOR, and gave the lower amounts of olefins and naphthenes than HMOR. It can be explained that the complex pore of HBeta converted more olefins and naphthenes to aromatics inside the pore than the straight pore of HMOR. In addition, HBeta gave a higher amount of light fractions in oils than HMOR that gave a higher amount of heavy fractions such as gas oil and long residue. However, these two zeolites can reduce sulphur in oils, and the species of sulphur were different. Moreover, both HBeta and HMOR catalysts caused the increment in the group of benzothiophenes and the reduction in the group of benzothiazoles.

1. Introduction

Conventionally, all petrochemicals are produced from petroleum. Olefins and aromatic hydrocarbons are important petrochemicals. Light olefins include ethylene, propylene and butylenes, which are produced from fluid catalytic cracking unit in oil refineries and steam cracking of natural gas. Ethylene and propylene are important olefins used as raw materials in plastic and chemical industries. Butadiene is dominated in rubber and elastomer industries. Useful aromatic hydrocarbons such as benzene, toluene, and xylenes are derived from the catalytic reforming of naphtha. They are used in a wide range of raw materials. Tyres are hydrocarbon-based materials, which exhibit potential to be used as a source for petrochemical production. In addition, tyres have long-life and complication to recycle, resulting in a large amount of waste tyres discarded. Pyrolysis of waste tyres is an interesting process to treat and recover valuable products (Piyawongpinyo, 2013). Islam et al. (2008) studied waste tyre pyrolysis products, especially liquid products. They found that pyrolytic oils were complex mixtures, which consisted of aliphatic and aromatic compounds. Limonene was the most abundant species in pyrolytic oils as well as benzene, toluene, and xylenes. Moreover, the results showed that pyrolytic oils can be directly used as fuels for furnace, power

plant, and boilers. It can be used as diesel fuel after improving the quality such as desulphurization or blending with commercial fuels. Banar et al. (2012) studied pyrolytic oil from waste tyre pyrolysis. They found that the fuel properties (H/C, HHVs, and density) of pyrolytic oil was similar to those of the diesel and gasoline. Additionally, they suggested that the pyrolytic oil can be used as chemical feedstocks for aromatic production. D  ng et al. (2009) used HMOR catalyst in waste tyre pyrolysis. The result showed that the presence of HMOR increased the light products, which caused the increment of gas yield and the reduction of oil yield. In addition, the introduction of HMOR led to the increasing amounts of gasoline and kerosene and the decreasing amounts of fuel oil and heavy vacuum gas oil due to the good cracking performance of catalyst. They mentioned that HMOR favoured to produce gasoline, which was selective to pore size. Olazar et al. (2008) studied the effect of using HY and HZSM-5 catalysts on waste tyre pyrolysis. The gas product increased with using HZSM-5 due to cracking of heavy fractions, and it slightly decreased with using HY because HY favoured the activation of olefin alkylation and condensation to form heavy products. Additionally, olefins which consisted of ethylene and propylene increased with the use of both catalysts. Poly-aromatics in oil products increased with using catalysts, especially HY. Thus, it was suggested that larger pore size and more hydrogen transfer capacity of HY caused more cyclization, aromatization, and condensation reactions to occur inside the pore to form aromatics. Recently, the pyrolysis of waste tyre using HBeta and KL zeolites was studied by Saeng-arayakul (2013) in order to compare the effect of acid and basic supports (HBeta and KL, respectively). The results showed that using HBeta produced higher gas yield than using KL, and HBeta zeolite reduced the concentration of heavy liquid fractions (long residues and heavy gas oil) more greatly than KL zeolite. The results demonstrated that long-chain hydrocarbons were more easily cracked by HBeta.

Currently, no study has been conducted on the impact of zeolite on the structure and distribution of hydrocarbon in oil. Thus, the effect of zeolites channel structure on the structure and species of hydrocarbon compounds and petrochemicals in waste tyre-derived oil was studied in this work. HMOR and HBeta zeolites that have different channel structures, which are 2D and 3D channel structure, respectively, were selected in this study. They are acidic zeolites and have no difference in pore size, which is 6.5×7.0    for HMOR and 6.4×6.7    for HBeta. Both zeolites need to have the same Si/Al ratio; however, since it is difficult to synthesize or find exactly the same Si/Al ratio of both zeolites in the market, HMOR with the Si/Al ratio of 9.5 and HBeta with the ratio of 13.5 were selected.

2. Experiment Section

2.1 Catalyst Preparation

HMOR and HBeta zeolites were obtained from Tosoh Company in Singapore. In order to remove impurity from zeolites, HMOR zeolite was calcined at 500   C for 3 h with the heating rate of 10   C/min, and HBeta was calcined at 600   C for 5 h with 2   C/min. After that, HMOR and HBeta powders were pelletized, crushed, and sieved into the particle size range of 20-40 mesh.

2.2 Catalyst Characterization

X-ray diffraction patterns were taken using a Bruker X-ray diffractometer system equipped with a 2.2 kW Cu anode in a long fine focus ceramic X-ray tube for generating a CuK   radiation (1.5405   ). The detector scanned for the diffractive peaks from the sample as a function of 2θ by starting at the 5   to 100  (2θ) range and a scan speed of 5  (2θ)/min. The specific surface area and pore volume were characterized by using a ThermoFinnigan/Sorptomatic1990 equipment. In addition, Thermogravimetric/Differential Thermal Analysis (TG/DTA) was used to determine coke deposited on spent catalysts. The temperature was ramped to 900   C with heating rate of 10   C/min.

2.3 Pyrolysis of Waste Tyre

There were 2 zones of the pyrolysis reactor, which are catalytic zone (the upper zone) and pyrolytic zone (the lower zone). Firstly, 30 g of the waste tyre with sizes in the range of 20-40 mesh was loaded into the lower zone, and 7.5 g of pellet catalyst was loaded to the catalytic zone. Then, the pyrolysis zone was heated with the rate of 10   C/min from the room temperature to 500   C, and then kept for 120 min at the atmospheric pressure. The temperature of pyrolytic zone was controlled at 350   C. The flow rate of N₂ was controlled at 30 ml/min, continuously flown to purge the oxygen out of the system prior to pyrolysis and subsequently for carrying the pyrolysis products to condensers and a gas sampling bag. These condensers were placed into an ice bath in order to collect the liquid product. A gas sampling bag collected the incondensable products.

2.4 Product Analysis

The liquid products were dissolved in *n*-pentane to precipitate asphaltene, and then asphaltene was filtered using polyamide membrane (pore size: 0.45  m). Then, the maltenes were analysed for true boiling

point curve and petroleum fractions using a Simulated Distillation Gas Chromatography (SIMDIST-GC) conformed with ASTM D-2887. Finally, the chemical composition of maltenes was analysed using a two-dimensional Gas

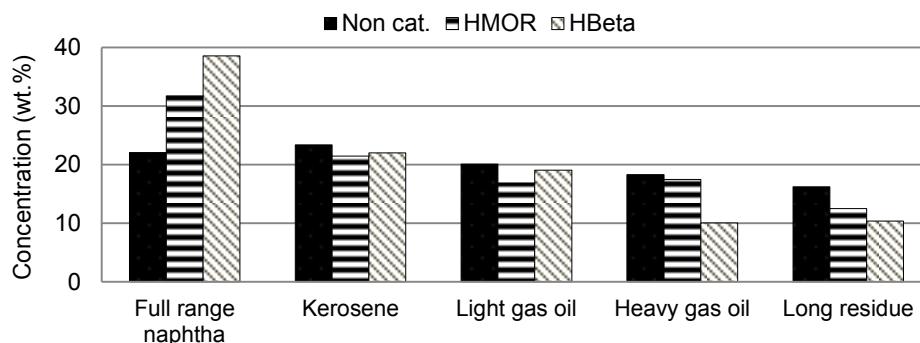


Figure 1: Petroleum fractions in maltenes obtained from HMOR and HBeta catalysts

Chromatography with Time of Flight Mass Spectrometer (GC×GC-TOF/MS). The gas products were analysed for their compositions using a Gas Chromatography (GC-FID). In addition, an elemental analyser was used to analyse the sulphur content in solid products and spent catalysts.

3. Result and Discussion

3.1 Petroleum Fractions

Figure 1 illustrates the petroleum fractions in maltenes obtained from HMOR and HBeta catalysts. It shows that full range naphtha in maltenes obtained from HMOR and HBeta increases with the use of both zeolites, whereas the heavier fractions including kerosene, light gas oil, heavy gas oil, and long residue accordingly reduce. In addition, using HBeta gives a higher amount of the light fraction and then a less amount of heavier fractions than using HMOR. Thus, it can be concluded that using HBeta (3D-channel structure) results in the lighter liquid product than using HMOR (2D-channel structure). It may be possible that the 3D-channel structure allows molecules to stay inside the zeolite channel with a longer residence time, and then heavy fractions can be cracked into light fractions more effectively than in the 2D-channel structure. However, using both zeolites give a higher quality of liquid products as compared to the non-catalytic pyrolysis.

3.2 Liquid Compositions

The concentrations of chemical components in maltenes are illustrated in Figure 2. They exhibit that HMOR and HBeta increase the amount of total aromatics with the decreases in paraffins, olefins, and naphthenes as compared to the non-catalytic pyrolysis. Moreover, using HBeta, 3D-channel structure, gives the higher amount of overall aromatics than HMOR, 2D-channel structure, and consequently gives the lower amount of paraffins, olefins, and naphthenes than those from HMOR. It can be explained that aromatic compounds can be formed via Diels-Alder reaction of light olefins (ethylene, propylene, and butene), which occur from thermal degradation of tyre, to cyclic hydrocarbons, and subsequently aromatics are formed via condensation reaction (Cypres, 1987). Moreover, Meng et al. (2013) reported that large intermediate olefins, such as octenes and multi-branched octenes, were favoured to drive cyclization reaction to occur, forming naphthenes. After that, aromatization of naphthenes produces aromatics, followed by condensation of aromatics, forming polycyclic aromatics. These are confirmed by the decreases of light olefins in the gas products, which are illustrated in Figure 3, as well as the decreases of olefins and naphthenes in accordance with the increase of aromatics in maltenes. In addition, it can be seen that the most abundant species of aromatic compounds are mono-aromatics. HBeta gives a higher yield of mono-aromatics, di-aromatics, and poly-aromatics than HMOR, and it gives a lower yield of paraffins, olefins, and naphthenes than HMOR. In addition, the results obtained from the surface area analyser reveal that HBeta has higher surface area and bigger pore volume than HMOR. A bigger pore volume allows molecules to go and stay inside HBeta (3D-channel structure) longer than HMOR (2D-channel structure); thus, molecules can be more easily transformed to mono-, di-, and poly-aromatics via cyclization and condensation reactions inside the zeolite channel.

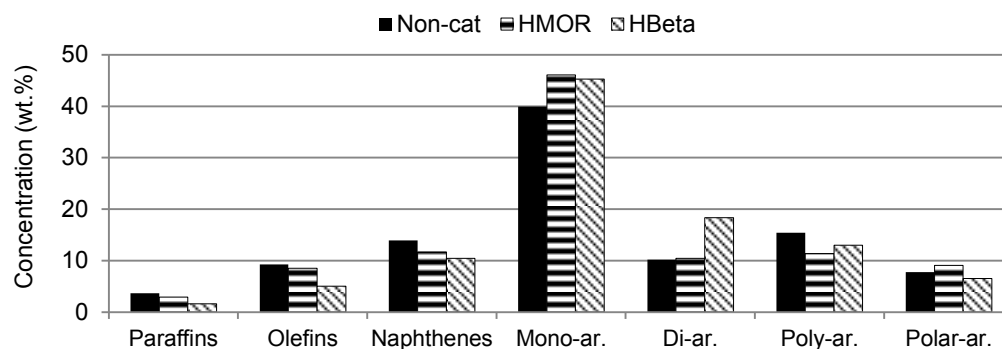


Figure 2: Concentration of components in maltenes obtained from HMOR and HBeta catalysts

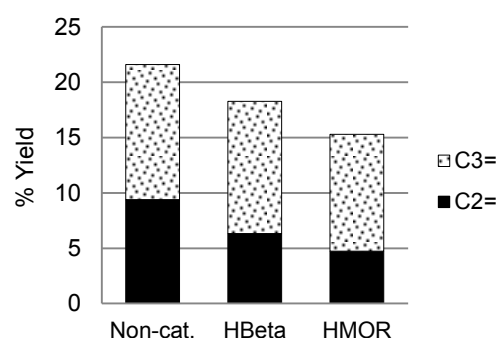


Figure 3: Yield of light olefins in gas products obtained from HMOR and HBeta catalysts

3.3 Hydrocarbons in maltenes

Valuable hydrocarbon compounds in maltenes are shown in Table 1. HBeta can produce a higher amount of benzene, ethylbenzene, toluene, and cyclohexane than HMOR and the non-catalytic pyrolysis. The non-catalytic pyrolysis does not produce xylenes, whereas o-xylene and p-xylene are produced by HBeta, and only m-xylene is produced by HMOR. In addition, styrene is increased from 0.189 wt.% (the non-catalytic pyrolysis) to 1.31 wt.% (HMOR), and the amount of cumene is not significantly changed for all cases. Additionally, the amount of all valuable hydrocarbons in maltenes can be ranked as HBeta (10.8 wt.%) > HMOR (2.32 wt.%) > the non-catalyst case (1.57 wt.%). It can be indicated that HBeta gives the highest value of liquid products, followed by HMOR and the non-catalyst case.

Table 1: Valuable compounds in maltene (wt.%)

Valuable compounds	Catalyst		
	1. Non-cat.	2. HMOR	HBeta
Benzene	3. 0.430	4. 0.124	5. 4.81
6. Toluene	7. 0.0274	8. 0.184	9. 0.917
10. Ethylbenzene	11. 0.833	12. 0.408	13. 3.31
14. m-xylene	15. -	16. 0.185	17. -
18. o-xylene	19. -	20. -	21. 0.161
22. p-xylene	23. -	24. -	25. 0.129
26. Styrene	27. 0.189	28. 1.31	29. 0.320
30. Cyclohexane	31. 0.0239	32. -	33. 1.05
34. Cumene	35. 0.0660	36. 0.105	37. 0.0771
38. Total	39. 1.57	40. 2.32	41. 10.8

Table 2: Sulphur content (wt.%) on spent catalysts and in oils obtained from HMOR and HBeta

	Sulphur content (wt.%)		
	42. Non-cat.	43. HMOR	HBeta
Spent catalyst	44. -	45. 0.41	46. 0.18
47. Oil	48. 1.17	49. 1.10	50. 1.08

3.4 Desulphurization activity

The results show the higher sulphur distribution in the gas and on the spent HMOR and HBeta catalysts in the expense of sulphur distribution in oils. In addition, the sulphur content in oils is reduced when the catalysts are applied as shown in Table 2. HMOR gives a slightly-lower sulphur content in oils than HBeta. It can be concluded that both zeolites exhibit the activity on sulphur reduction in oils.

Moreover, sulphur species are determined. Figure 4 exhibits the distribution of sulphur compounds in maltenes. It can be seen that the 3D-channel structure of HBeta produces less amount of thiophenes than the 2D-channel structure of HMOR. Benzothiophenes dramatically increase with using both catalysts, and benzothiazoles tend to decrease with using these catalysts. It can be suggested that S-compounds in the oil, obtained from HBeta, are easier to be desulphurized than those in oil obtained from HMOR (García-Cruz et. al., 2008). Benzothiophenes are easier to be desulphurized than benzothiazoles because C-N bond has a higher bond dissociation energy than C-S bond (Cottrell, 1958). In addition, dibenzothiophenes are slightly decreased with the use of these two catalysts. The mixture of all other heteroatom (S, O and N)-containing aromatic and aliphatic hydrocarbons (so-called "the others") is reduced with using both catalysts.

4. Conclusions

HBeta (3D-channel structure) gives the lighter liquid products than using HMOR (2D-channel structure). Since the 3D-channel structure allows molecules to stay inside the zeolite channel with a longer residence time, and then heavy fractions can be cracked into light fractions more effectively than in the 2D-channel structure. For components in maltene, the use of HBeta exhibited a higher yield of mono-aromatics, di-aromatics and poly-aromatics than the use of HMOR, and consequently gave a lower yield of paraffins, olefins, and naphthenes than HMOR. Since a bigger pore volume and higher surface area allows molecules to pass through and stay inside HBeta longer than HMOR; thus, molecules can be more easily transformed to mono-, di-, and poly-aromatics via cyclization and condensation reactions inside the zeolite channel. Additionally, the amount of all valuable hydrocarbons in maltenes obtained from HBeta (10.8 wt.%) was significantly higher than that from HMOR (2.32 wt.%). Both zeolites have a good activity in sulphur reduction in oils. However, HBeta exhibited slightly-better desulphurization activity than HMOR.

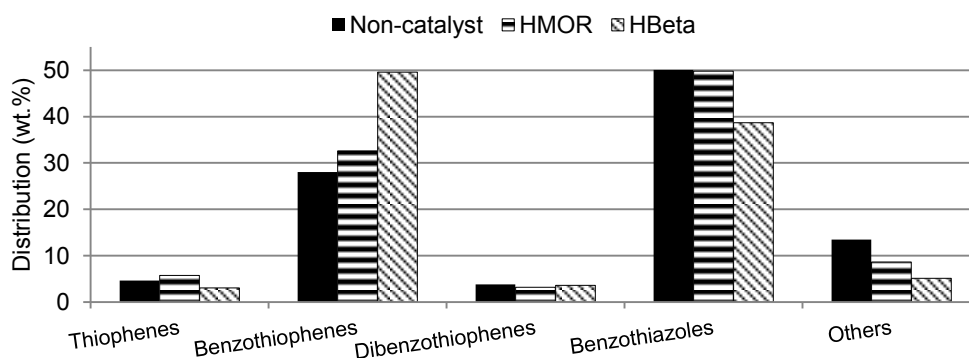


Figure 4: Distribution of sulphur species in maltenes obtained from HMOR and HBeta catalysts

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Quality Improvement of Waste Tyre Pyrolysis Oil by Using Cu/HMOR as a Catalyst

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Metal-loaded zeolites are interesting catalysts for the improvement of the quality and quantity of waste tyre pyrolysis products. Since the catalysts exhibit multi-functions in catalysis, including hydrogenation, dehydrogenation, ring-opening, cracking, etc. that can be acquired from metal and zeolite properties. This work studied the effect of 5 wt%Cu/HMOR catalyst on waste tyre pyrolysis products. Since copper is widely used in several applications such as selective hydrogenation of undesired unsaturated hydrocarbons in a mixed-C₄ stream, and sulphur removal from liquid fuels, etc. Catalytic pyrolysis of waste tyre was operated in a bench reactor. GCxGC-TOF/MS and SIMDIST-GC instruments were used to analyze the liquid products. Sulphur distribution in the pyrolysis products was determined by using an S-analyzer. As compared with the HMOR catalyst, the Cu/HMOR decreased the amount of olefins, naphthenes, poly-aromatics, and polar aromatic compounds in oils while the amounts of paraffins, di- and mono-aromatics in oils were increased because the presence of copper can promote hydrogenation, ring-opening, and cracking activities of HMOR zeolite. Furthermore, Cu/HMOR catalyst not only reduced heavy compounds in the oil but also sulphur content in the oil (reduced from 1.08 wt% to 0.907 wt% in the HMOR case), indicating that the quality of the oil as a combustion fuel was improved by using copper as a promoter of HMOR zeolite. An interesting result was that the valuable products produced in the Cu/HMOR case were benzene (1.14 wt% in oil), toluene (2.65 wt% in oil), and ethylbenzene (5.39 wt% in oil), which have never been found in the non-catalytic case or in the case when the parent HMOR was used.

1. Introduction

From the past to present, waste tyre elimination has been an important problem because tyres are highly stable in chemicals and environments. Pyrolysis is a thermal degradation method of waste tyres, which is more effective process than other waste tyre elimination methods because it can not only eliminate waste tyres but also recover usable products (Williams, 2013); so, waste tyre pyrolysis is widely adopted nowadays in many countries where land and resource are limited. The waste tyre pyrolysis can produce three parts of products consisting of gases, oils and char. The interested product is pyrolysis oil that can be fractionated according to boiling points into gasoline, kerosene, gas oil, heavy gas oil, light vacuum gas oil, and heavy vacuum gas oil (Dũng et al., 2009a). Furthermore, some components in oil can be used as chemicals (Boxiong et al., 2007) such as benzene, toluene, xylenes, etc.

Zeolites are widely used as a commercial catalyst in the production of petrochemicals because they have several interesting properties such as catalytic cracking and hydrocracking (USY), catalytic dewaxing (ZSM-5, ZSM-22, and SAPO-11), cracking and alkane isomerization (BETA) (Martínez and Corma, 2011), and transalkylation and paraffin skeletal isomerization using HMOR (Busca, 2007), etc. For catalytic pyrolysis of waste tyre, zeolites can be effective catalysts for increasing desired products as proven by many researchers. For examples, Williams and Brindle (2003) found that ZSM-5 and Y zeolites can increase the amount of value added products in pyrolysis oils; for examples, benzene, toluene, xylene, styrene, etc. HBETA zeolite can produce the high amount of saturated hydrocarbons and the naphtha fraction of tyre-derived oil (Saeae and Jitkarnka, 2012). Dũng et al. (2009a) studied the effect of HMOR

zeolite on catalytic pyrolysis oils. HMOR zeolite can increase the amount of mono-aromatics in the oil, and gasoline and kerosene yields, while heavier fractions and total-aromatics were also decreased, indicating that the oil quality can be upgraded. Furthermore, an introduction of metal onto a zeolite might improve some quality of pyrolysis products as well. Copper is widely used as a selective hydrogenation catalyst and adsorbent in sulphur removal from liquid fuels. Copper-loaded catalysts can be used in selective hydrogenation that can remove undesired compounds in the process. For examples, Cu/SiO₂ catalyst was used to remove alkynes and butadiene in C₄-stream by partial hydrogenation by converting them into butenes (Setiawan and Cavell, 1995). Copper loading on hydrotalcite, malachite, SiO₂ and Al₂O₃ supports was used to convert propyne into propylene at high selectivity and undesired products at low selectivity (Bridier et al., 2010). In the other applications, Cu(I)-exchanged zeolites can be used as an adsorbent for thiophene removal from liquid fuels as well (Tang and Shi, 2011). For catalytic pyrolysis of waste tyre, copper was expected to promote hydrogenation that might cause cracking and ring-opening reactions to occur easily. Furthermore, copper was expected to enhance sulphur reduction of the pyrolysis oil as well. In this work, the effect of copper on waste tyre pyrolysis products was therefore studied, using HMOR zeolite as the support.

2. Experiment

2.1 Catalyst and sample preparation

HMOR zeolite (Si/Al = 9.5) supplied by TOSOH Company (Singapore) was calcined in static air with the heating rate of 5 °C/min from room temperature to 500 °C with holding for 3 h after the final temperature was reached. The calcined zeolite was subsequently impregnated with the copper solution (Cu(NO₃)₂·3H₂O) at the copper loading of 5 wt%, dried overnight in an oven at 120 °C, and calcined again at the same calcination condition. Next, the calcined catalyst was reduced at 600 °C for 2 h in hydrogen atmosphere. Finally, the catalyst powder was pelletized, crushed, and sieved to the size range of 40-60 mesh. A waste tyre sample, Bridgestone TURANZA GR-80, was shredded and then sieved into a particle size of 20-40 mesh.

2.2 Waste tyre pyrolysis process

The pyrolysis system employed in the experiment was the same as in D ng et al. (2009b). The catalytic pyrolysis of waste tyre was operated at atmospheric pressure from room temperature to a temperature of 500 °C (the pyrolysis zone) and 350 °C (the catalytic zone) with a ramping rate of 10 °C/min and a holding time of 2 hours after the final temperatures were reached. 30 g of shredded tyre (20 - 40 mesh) and 7.5 g of HMOR or 5 wt%Cu/HMOR catalyst (40 - 60 mesh) were packed in the pyrolysis zone and the catalytic zone, respectively, (at catalyst/tyre ratio = 0.25). Nitrogen gas was used as carrier gas. Liquid products were condensed in the condensers immersed in an ice-salt (NaCl) bath, while the gas products were collected by using a gas sampling bag.

2.3 Catalyst characterization

XRD machine (Rikagu) was used to acquire the XRD patterns of the catalysts using CuK  radiation operated at 40 kV and 30 mA. The angles in the range of 5-65  were scanned at a scanning speed of 5  /min. Surface area and pore volume of catalysts were determined by N₂ physisorption using Thermo Finnigan Sorptomatic 1990 equipment. The amount of coke on spent catalysts was determined by using Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA). The temperature was ramped up from room temperature to 900 °C with the heating rate of 10 °C/min. Sulphur content on catalyst surface was determined by using LECO Elemental Analyzer (TruSpec S).

2.4 Product analysis

Liquid and solid products were weighed for calculating the product yield. Before analysis, asphaltene was firstly precipitated from the liquid products via mixing with *n*-pentane in the oil/*n*-pentane mass ratio of 40:1. After that the precipitated asphaltene was filtered from the solutions using a Teflon membrane (0.45  m) in a vacuum system, and then the maltene solutions were analyzed for the composition by using Gas Chromatography-Mass Spectrometry (GCxGC-TOF/MS). The Agilent gas chromatograph 6890 system consists of a cryogenic modulator and a Pegasus 4D TOF/MS. The 1st column was a non-polar Rtx -5 Sil MS with 30 m x 0.25 mm ID x 0.25  m film thickness. The 2nd column was an Rxi -17 MS with 1.10 m x 0.10 mm ID x 0.10  m film thickness. Furthermore, the true boiling point curves of maltene solutions were also analyzed by using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) conformed to the ASTM-D2887 method. The instrument equipped with FID and WCOT fused silica capillary column (15 m x 0.25 mm x 0.25  m) The true boiling point curves were cut into petroleum fractions according to their boiling points; full range naphtha (< 200 °C), kerosene (200-250 °C), light gas oil (250-300 °C), heavy gas oil (300-370 °C) and long residue (> 370 °C). The gas products were analyzed

for hydrocarbon species and concentrations by using a GC-FID, Agilent Technologies 6890 Network GC system (HP-PLOT Q column: 20 μm film thickness and 30 m x 0.32 mm ID). Furthermore, the liquid and solid products were also analyzed for their sulphur content by using a LECO®Elemental Analyzer (TruSpec®S); whereas the sulphur content in gas products was calculated via mass balance.

3. Results and discussion

3.1 Catalyst characterization

XRD patterns of HMOR and Cu/HMOR catalysts are displayed in Figure 1. The results show that the introduction of copper onto the zeolite does not affect the zeolite structure. The peaks of copper appear at the 2θ of 43.47° and 50.67° . The BET specific surface area and pore volume of catalysts are shown in Table 1. These results indicate that the introduction of copper onto HMOR zeolite reduces the specific surface area and pore volume because copper might partially block the pore of zeolites (Garrido Pedrosa et al., 2006).

3.2 Effect of Cu/HMOR on waste tyre pyrolysis products

Figure 2 shows that HMOR does not increase the gas yield even though the liquid yield decreased because the catalyst generates a considerable amount of coke on the surface. The presence of copper on HMOR zeolite promotes gas production, and reduces the liquid yield while the solid yield is constant. Furthermore, the amount of coke is increased with using the copper-loaded catalyst as well. It can be concluded that copper promotes the cracking activity of the zeolite.

Table 1: BET specific surface area and pore volume of catalysts

Catalyst	Specific surface area (m^2/g)	Specific pore volume (cm^3/g)
HMOR	395	0.199
Cu/HMOR	345	0.180

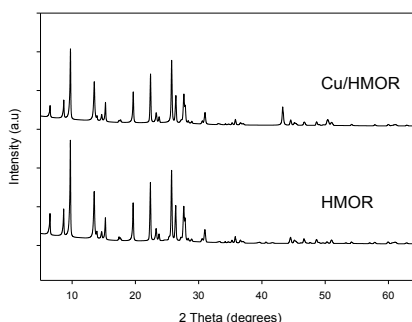


Figure 1: XRD patterns of HMOR and Cu/HMOR catalysts

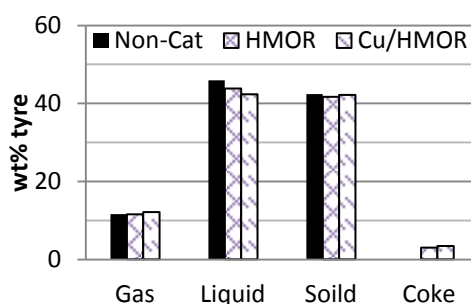


Figure 2: Product distribution in HMOR and Cu/HMOR cases

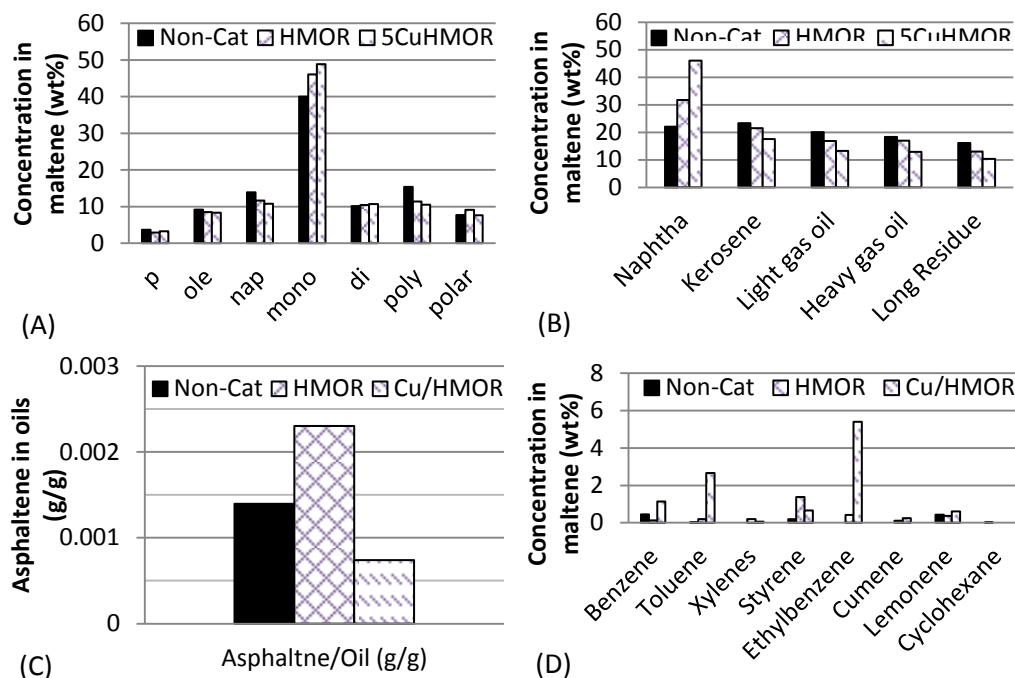


Figure 3: Oil analysis in HMOR and Cu/HMOR cases; (A) Concentrations of each group in maltene, (B) Petroleum cuts, (C) Asphaltene content in oils, and (D) Petrochemical valuable products

Table 2: Average carbon number of each group in maltenes in HMOR and Cu/HMOR cases

Catalyst	P	O	Nap	Mono	Di	Poly	Polar	Total
No catalyst	15.7	12.2	12.3	11.8	12.1	14.7	11.4	12.5
HMOR	16.1	11.9	12.1	11.6	11.9	14.7	11.6	12.2
Cu/HMOR	14.1	11.3	11.0	10.9	11.8	14.4	11.7	11.6

For oil analysis (Figure 3A), the oil components were categorized into seven groups: paraffins (P), olefins (O), naphthenes (Nap), mono-aromatics (Mono), di-aromatics (Di), poly-aromatics (Poly), and polar-aromatics (Polar). HMOR reduces the concentrations of olefins and naphthenes while the concentration of mono-aromatics is highly increased as compared with the non-catalyst case, indicating that HMOR catalyst exhibits aromatization ability. Furthermore, the concentration of poly-aromatics is decreased because the catalyst might also exhibit hydrogenation and ring-opening abilities (Du et al., 2005) that it can convert poly-aromatics into mono-aromatics. The oil obtained from HMOR has the lower overall average carbon number (Table 2) than that from the non-catalyst case, resulting in a significant increase in full-range naphtha and subsequent decrease in heavier petroleum cuts as shown in Figure 3B. As compared with HMOR zeolite, copper promotes the production of mono-aromatics in the oil (Figure 3A) possibly via hydrogenation and ring-opening of poly-aromatics, and via aromatization of olefins and naphthenes. Full-range naphtha (Figure 3B) is also increased because copper promotes cracking activity, resulting in the decrement of the overall average carbon numbers of the maltene (Table 2). Furthermore, Cu/HMOR also reduces polar-aromatic concentration and asphaltene content. As observed from the species in mono-aromatics shown in Figure 3D, the valuable petrochemicals highly produced are styrene (1.37 wt% in oil) in the HMOR case, and benzene (1.14 wt% in oil), toluene (2.65 wt% in oil) and ethylbenzene (5.39 wt% in oil) in the Cu/HMOR case. It can indicate that the catalytic pyrolysis of waste tyre has high potential for chemical production as well.

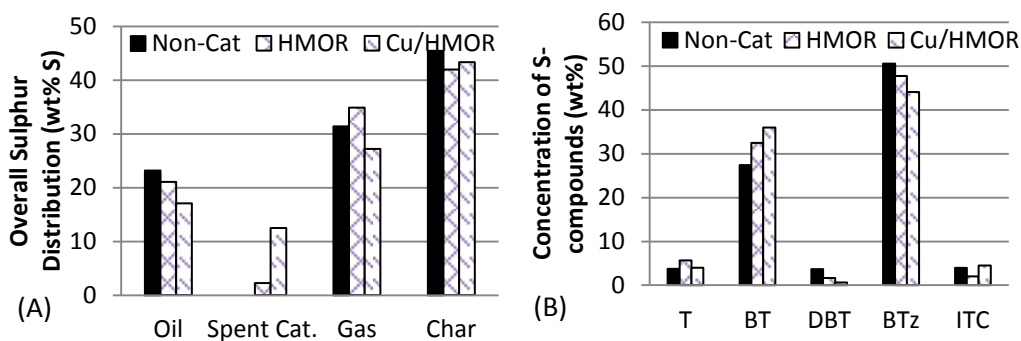


Figure 4: Sulphur analysis in HMOR and Cu/HMOR cases; (A) Overall sulphur distribution, and (B) Distribution of major groups of sulphur-containing compounds in maltenes

3.3 Quality improvement of pyrolysis oil

The quality of pyrolysis oil can be improved using Cu/HMOR not only due to light oil production and the reduction of concentration of poly- and polar-aromatics, and asphaltene content in the oil, but also due to the reduction of sulphur content in the oil. HMOR can reduce sulphur content in the oil (Figure 4A) by converting sulphur-containing compounds in the oil, and releasing sulphur into gas and coke. The increment of sulphur in gas indicates that the catalyst also exhibits cracking and desulphurization abilities. Furthermore, HMOR catalyst can reduce the average carbon number of all groups of sulphur-containing compounds in maltene (Table 2), indicating that the sulphur-containing compounds in the oils can be removed easily via desulphurization. Sulphur-containing compounds found in the oils were classified into five groups: thiophenes (T), benzothiophenes (BT), dibenzothiophenes (DBT), benzothiazoles (BTz), and isothiocyanates (ICT). For sulphur species in the maltenes, the proportions of benzothiazoles and isothiocyanates are decreased with using HMOR, indicating that HMOR can promote breaking C-S and C-N bonds, and/or can adsorb these species more on the catalyst surface. Cu/HMOR gives lower sulphur content (0.907 wt%) in the oil than HMOR zeolite (1.08 wt%) because copper can adsorb sulphur-containing compounds in both oil and gas onto the catalyst surface, subsequently forming coke, which is similar to the work of Twigg and Spencer (2001) reporting that copper is rapidly deactivated by sulphur-containing compounds. For the species of sulphur-containing compound (Figure 4B), Cu/HMOR reduces benzothiazoles, and thiophenes more than HMOR zeolite. Moreover, the reduction of average carbon numbers in all groups of sulphur-containing compounds also indicates that copper can help remove sulphur atoms more easily.

4. Conclusions

Cu/HMOR catalyst was studied in this work to determine its effect on the quality of waste tyre pyrolysis oil. It was found that the introduction of copper on HMOR zeolite can promote gas and full-range naphtha productions, indicating that copper promoted cracking activity. Cu/HMOR also enhanced the selectivity of mono-aromatics due to the increasing activities in hydrogenation and ring-opening of poly-aromatics, as well as the aromatization of olefins and naphthenes. Interestingly, the introduction of copper highly promoted the production of valuable products in oils. HMOR was found to be more selective for styrene production (1.37 wt% in oil) than thermal pyrolysis. Cu loading to HMOR resulted in better production of benzene (1.14 wt% in oil), toluene (2.65 wt% in oil) and ethylbenzene (5.39 wt% in oil). So, the catalytic pyrolysis of waste tyre using HMOR or Cu/HMOR as catalysts had high potential for chemical production as well. However, the presence of copper on HMOR zeolite increased coke formation possibly occurred from the deposition of polar-aromatics and asphaltene on the catalyst surface. Nevertheless, the quality of pyrolysis oil using Cu/HMOR can be improved since the poly-, polar-aromatics, and asphaltene contents in the oil was reduced in conjunction with the production of lighter and sweeter oil. Cu/HMOR catalyst can reduce sulphur content in the oil from 1.08 wt% to 0.907 wt%.

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Upgrading of Waste Tyre-Derived Oil from Waste Tyre Pyrolysis over Ni Catalyst Supported on HZSM-5 Zeolite

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The catalytic pyrolysis of waste tyre was investigated using Ni-doped HZSM-5 zeolite as a catalyst in a bench-scale reactor ramped from room temperature to 500 °C (pyrolysis zone) and 350 °C (catalyst bed), aiming to improve the quality of tyre-derived oil in terms of sulphur reduction and enhancement of valuable petrochemical production. 5 wt% of nickel was introduced on HZSM-5 zeolite using incipient wetness impregnation, and characterised using XRD, surface area analyser, and XPS. Gaseous products were analysed by GC-FID. The GCxGC-TOF/MS and SIMDIST-GC were used for analysis of pyrolysis oil. The sulphur content in tyre-derived oil was determined by S-analyser. The introduction of metallic nickel on HZSM-5 zeolite significantly changed textural properties, also modified the catalytic behaviour. When compared to parent HZSM-5 zeolite, Ni/HZSM-5 catalyst significantly improved gasoline and kerosene production in waste tyre-derived oil, whereas the heavy fractions, such as gas oil and light vacuum gas oil, drastically decreased. In addition, Ni doping drastically reduced sulphur contents in tyre-derived oil by 29.2 %. Benzothiophenes, dibenzothiophenes, and naphthothiophene were the sulphur species that significantly decreased. Furthermore, with Ni loading, the production of cumene, ethylbenzene, toluene, and mixed xylenes in oil was also enhanced. These results indicated Ni/HZSM-5 was a promising catalyst for enhancement of tyre-derived oil quality.

1. Introduction

Due to the petroleum resources that continuously decrease with a rapid rate in association with the growth of waste tyre that constantly increases, the pyrolysis of waste tyre is one of alternative ways for producing of chemicals and fuels. Recent study has reported that waste tyre-derived oil contains a relatively-high concentration of aromatics such as mono-, di-, poly- and polar aromatics, which cannot be directly used as vehicle fuels (Yuwapornpanit et al., 2015). However, the aromatic compounds in oil are valuable chemicals such as benzene, toluene, xylenes, styrene and ethylbenzene, which can be utilized as a petrochemical feedstocks in refinery. As a result, several catalysts have been used in catalytic pyrolysis of waste tyre in order to improve of valuable chemical production in waste tyre-derived oil, and reduce of polycyclic aromatics and sulphur-containing compounds. Many acidic zeolites, such as Mordenite, Y, and Beta have been tested in catalytic pyrolysis of waste tyre, and provided interesting results. Dũng et al. (2009) stated that HMOR increased the concentration of mono-aromatics in oil, whereas the polycyclic aromatics, especially polar-aromatics significantly decreased. In addition, HMOR also increased the naphtha fraction in oil, whereas the heavy fraction drastically decreased. HBETA and HY zeolites increase naphtha and kerosene fractions, whereas the heavier fraction slightly decreased (Manchantrarat and Jitkarnka, 2012). Thus, these studies indicate that different zeolites provide different product distribution because each zeolite has unique properties. In particular, HZSM-5 zeolite is commonly used as a catalyst in the petrochemical industry due to its pore size, strong acidity and strong resistance to deactivation. Boxiong et al. (2007) found that the HZSM-5 enhanced the production of benzene, toluene and xylenes. In general, the addition of a transition metal on a catalyst can modify the catalyst activity. Nickel is favourable to hydrogenation/dehydrogenation reactions, or promotes aromatization and cracking reactions (Botas et al.,

2014). For example, Ni over hierarchical ZSM-5 and Beta zeolites enhanced the production of gas and gasoline from hydrotreating of polyethylene-derived thermal cracking oil. In addition Ni/HZSM-5 catalyst can promote the transformation of olefins into aromatics and iso-paraffins (Yin et al., 2005). Another common application of nickel-based catalyst is desulphurization. The sulphur removal efficiency increased with the increase of nickel loading on SBA-15 in adsorptive desulphurization of diesel (Ko et al., 2007). The aim of this work was therefore to investigate the effect of nickel on waste tyre pyrolysis products in terms of oil quality improvement and enhancement of valuable petrochemical production. HZSM-5 zeolite was selected as the support since the pore size and channel structure are suitable for producing valuable aromatic hydrocarbons. Furthermore, the introduction of nickel on HZSM-5 was expected to promote the formation of valuable chemicals and reduction of polycyclic compounds in oil, especially sulphur containing-compounds. Moreover, the sulphur content in pyrolytic oil might be reduced with nickel doping.

2. Experiment

2.1 Catalyst preparation

ZSM-5 zeolite (840NHA, Si/Al=20, NH₄-form) was purchased from TOSOH Corporation (Singapore). Prior to activity testing and metal impregnation, HZSM-5 was calcined in standing air at 500 °C for 3 h (Ramping rate of 10 °C/min). Ni-promoted HZSM-5 was prepared by incipient wetness impregnation of nickel compound (Ni(NO₃)₂•6H₂O) with 5 wt% metal loading based on the mass of catalyst. The catalysts were then dried overnight at 105 °C and calcined at same condition as mentioned above. The catalyst powders were pelletized, crushed and sieved to 40-60 mesh of particle size. The Ni/HZSM-5 catalyst was activated by reduction under hydrogen flow (30 mL/min) at 600 °C for 2 h (heating rate 10 °C/min).

2.2 Waste tyre pyrolysis

The schematic pyrolysis system was the same as Yuwaporpanit et al. (2015). Firstly, 30 g of shredded tyre (20 - 40 mesh) was pyrolysed in the lower zone of the reactor at 500 °C under atmospheric pressure. The pyrolytic products were carried by 30 mL/min of nitrogen flow to the catalytic bed, filled with 7.5 g of catalyst and heated to 350 °C. After the temperatures of lower and upper zone reached to the desired ones, they were kept 2 h. The resulting products were separated into gas and liquid fractions by using an ice-salt condensing system. The gas product was collected in a Tedlar PVF bag.

2.3 Catalyst characterization

The catalyst samples were characterized by different physicochemical characterization methods. X-Ray diffraction (XRD) (CuK α radiation), carried out in a Rigaku SmartLab X-Ray Diffractometer, was used to identify the crystallinity of catalysts. XRD patterns were recorded in the 5 - 65° (2 θ) range using a scan speed of 10° (2 θ)/min. The species of nickel was determined by using X-Ray Photoelectron Spectroscopy (XPS) with an AXIS ULTRADLD (Kratos) equipped with a monochromatic Al X-ray source and a hemispherical analyser. The spectrometer was carried out at the pass energy of 160 eV and 80 eV to acquire wide scan and core level spectra. All peaks were calibrated from C1s spectra (Binding energy = 285.0 eV). The surface area and pore volume of catalyst were measured using N₂ adsorption-desorption isotherms with Thermo Finnigan Sorptomatic 1990 instrument. The amount of coke deposition on the spent catalysts was measured by thermogravimetric analysis (TGA), carried out under flowing of nitrogen (10 mL/min) and oxygen (20 mL/min) on a Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA) The samples were heated up from room temperature to 900 °C with 10 °C /min ramping rate. CHNS analyser was used to determine the sulphur and nitrogen content on spent catalysts using LECO®Elemental Analyzer.

2.4 Product analysis

Liquid and solid products were weighed to determine the product yield. The liquid product was dissolved in n-pentane (mass ratio of n-pentane/oil = 40:1) to precipitate asphaltene. Asphaltene was filtered by using a polyamide membrane (0.45 μ m). The maltene solution was then analysed by Comprehensive Two-Dimension Gas Chromatography (Agilent Technologies 7890) with Time-of-Flight Mass Spectrometer (LECO, Pegasus® 4D TOF/MS) (GCxGC-TOF/MS) equipped with the 1st GC column was a non-polar Rtx®-5Sil MS (30 m $\times$ 0.25 mm ID $\times$ 0.25 μ m) and the 2nd GC column was an Rxi®-17 MS (1.790 m $\times$ 0.1 mm ID $\times$ 0.1 μ m). The simulated true boiling point curves were determined by using a Varian GC-3800 simulated distillation gas chromatography (SIMDIST-GC) equipped with FID detector and a 15 m $\times$ 0.25 mm $\times$ 0.25 μ m WCOT fused silica capillary column. The petroleum fractions were separated based on their boiling point ranges according to the ASTM D2887; gasoline (<149 °C), kerosene (149 - 232 °C), gas oil (232 - 343 °C), light vacuum gas oil (343-371 °C) and heavy vacuum gas oil (>371 °C). Moreover, sulphur content in tyre-derived oils and char were determined by LECO®Elemental Analyser (TruSpec®CHNS). Moreover, sulphur content in a gaseous product was determined by mass balance.

3. Results and discussion

3.1 . Catalyst characterization

The XRD patterns of the parent HZSM-5 zeolite and the supported Ni catalyst in Figure 1 (left) clearly display the characteristic XRD patterns of MFI structure. Therefore, the introduction of nickel on zeolites seems not to destroy the structure, but slightly affects the zeolite crystallinity. From Table 1, the decreases in BET surface area and micro-pore volume clearly indicate that Ni cluster might be located inside the zeolite channels, and partially block the zeolite channels (Maia et al., 2010).

Table 1: BET specific surface area and pore volume of catalysts

Catalyst	Surface area (m ² /g)	Micro-pore volume (cm ³ /g)
HZSM-5	365	0.178
Ni/HZSM-5	290	0.142

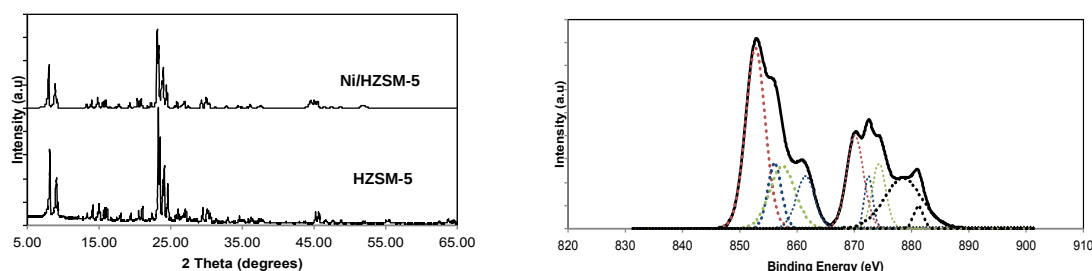


Figure 1: XRD patterns of HZSM-5 zeolite and Ni-promoted catalyst (left) and XPS spectrum of Ni-promoted catalyst (right)

Table 2: XPS result of Ni-promoted catalyst

Ni species	Ni 2p _{3/2} (eV)	Ni 2p _{3/2} (sat) (eV)	Ni 2p _{1/2} (eV)	Relative amount of Nickel species (%)
Ni ⁰	852.7	-	870.1	57.45
Ni ²⁺	856.1	861.5	872.4	14.82
NiAl ₂ O ₄	857.4	-	874.3	27.73

The XPS spectrum of supported Ni catalyst in Figure 1 (right) has three peaks assigned to Ni 2p_{3/2} with binding energies of 852.7, 856.1 and 857.4 eV, indicating the presence of metallic nickel, Ni²⁺ and NiAl₂O₄, (Karthikeyan et al., 2008) as shown in Table 2. The reduction of nickel on HZSM-5 zeolite is rather difficult since the multiple species of nickel are formed on the surface of HZSM-5 zeolite. Moreover, it is very difficult to reduce Ni²⁺ specie due to the strong interaction between Ni²⁺ and support (Xiao and Meng, 1994)

3.2 Pyrolysis yields

When metallic nickel was introduced on HZSM-5 zeolite, the liquid yield is suppressed from 42.5 to 39.4 %, whereas the gas yield slightly increases from 10.8 to 12.0 %. These results indicate that the incorporation of nickel over HZSM-5 zeolite promotes the cracking activity of HZSM-5 zeolite. Furthermore, coke formation on Ni/HZSM-5 catalyst drastically increases roughly twice as much as that on the parent HZSM-5 zeolite. These results show that the introduction of metallic nickel on HZSM-5 zeolite greatly increases surface activity and hydrogen transfer, which favors for coke formation.

3.3 Waste tyre-derived oil

Figure 2(a) provides the information about the petroleum fractions in maltenes. The HZSM-5 zeolite gives a higher concentration of gasoline, whereas the kerosene, gas oil and HVGO are lower than the non-catalytic case. These results indicate that the medium pore size and acidity of HZSM-5 can promote the cracking of heavy fractions. Significant differences are observed in the proportion of petroleum fractions with using HZSM-5 zeolite loaded with nickel. The impregnation of ZSM-5 with nickel drastically increases the production of gasoline and kerosene whereas gas oil, LVGO and HVGO fractions significantly decrease. This clearly indicates that metallic nickel on the HZSM-5 zeolite strongly promotes cracking of heavy fractions, leading to formation of lighter fractions. Figure 2(b) displays the maltene composition.

The maltene compositions are classified into 7 groups; that are, paraffins (para), olefins (ole), naphthenes (nap), mono-aromatics (mono), di-aromatics (di), poly-aromatics (poly) and polar-aromatics (polar). For the parent HZSM-5, the concentrations of mono-aromatic and naphthenes significantly decrease, whereas the concentration of poly-aromatics drastically increases. The HZSM-5 catalyst enhances the production of bi-phenyl species such as 4,4'-dimethylbiphenyl and 2-methyl-biphenyl. This result indicates that HZSM-5 catalyst might promote the combination of naphthenes and/or mono-aromatics via oligomerization/aromatization reactions, resulting in high formation of poly-aromatics. However, kinetic diameters molecules of 4,4'-dimethylbiphenyl and 2-methylbiphenyl calculated from Joback method are 6.81 and 6.52 Å, which are larger than the pore size of HZSM-5 zeolite. There are two possible reasons that can explain the formation of poly-aromatics over HZSM-catalyst. First, it is well known that the pore-size of HZSM-5 zeolite is 5-6 Å. However, it can be expanded at a high temperature. The effective pore size of ZSM-5 zeolite can expand between 6.62 Å and 7.27 Å at 300 °C, and can increase to 7.64 Å at 370 °C (Borm et al., 2010). This fact can explain the high formation of poly-aromatics in ZSM-5 pore. In addition, the formation of poly-aromatics possibly occurs at acid sites located at the external surface of HZSM-5 zeolite. On the other hand, the impregnation of HZSM-5 catalyst with nickel strongly increases the production of mono-aromatics, whereas the yields of olefins, naphthenes and poly-aromatics decrease. These results indicate that the Ni/HZSM-5 exhibits hydrogenation and ring opening of poly-aromatics, which transforms poly-aromatics to mono-aromatics. Furthermore, the introduction of nickel on HZSM-5 zeolite might promote cyclization and dehydrogenation of olefins and aromatization of naphthenes, leading to the high formation of mono-aromatics.

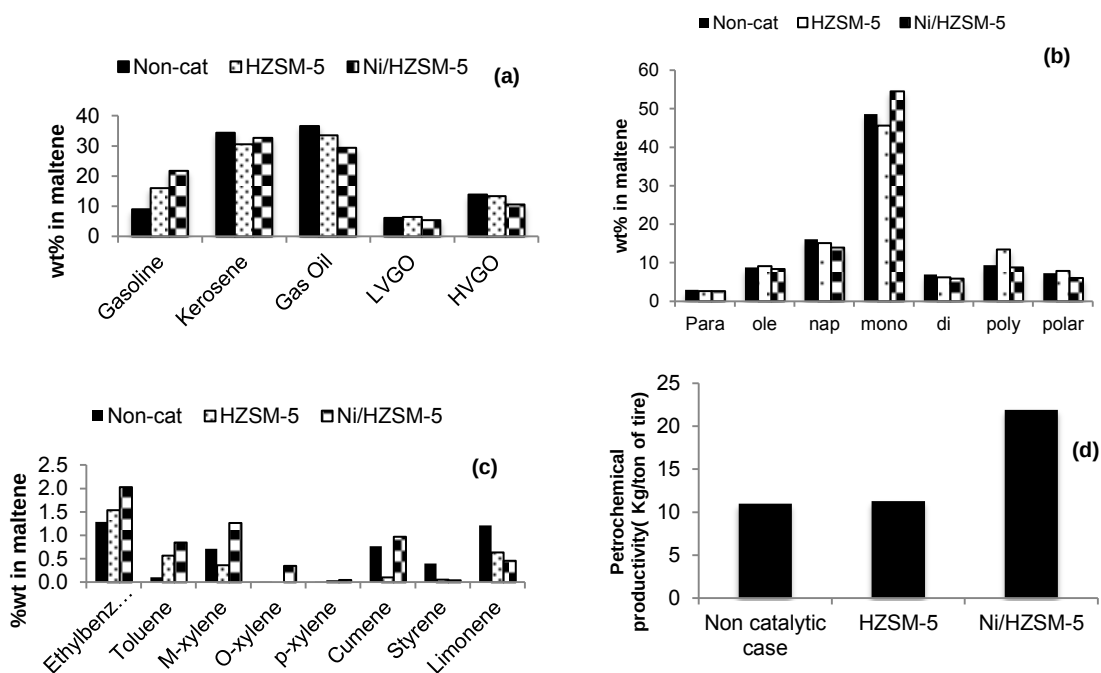


Figure 2: Oil analysis: (a) Concentrations of each group in maltenes, (b) Petroleum fractions, (c) Petrochemicals in maltenes, and (d) Petrochemical productivity

Although waste tyre-derived oil is not suitable for using as vehicle fuel due to the high content of aromatics as displayed in the Figure 2(b), but there are some valuable chemicals in waste tyre-derived oil, which can be easily separated in refinery. As a result in Figure 2(c), HZSM-5 catalyst clearly enhances the yields of ethylbenzene and toluene, whereas yields of styrene, cumene and limonene significantly decrease. On the other hand, Ni doping significantly enhances the yields of ethylbenzene, toluene, mixed-xylenes, and cumene, whereas the yields of styrene and limonene decrease. Furthermore, Ni/HZSM-5 enhances the overall petrochemical productivity roughly twice as much as HZSM-5 catalyst. The introduction of nickel on HZSM-5 might transform limonene to petrochemical species such as ethylbenzene and m-xylene (Pines and Ryer, 1995). In addition, it can be clearly seen that the formation of ethylbenzene is favoured over HZSM-5 and Ni-impregnated HZSM-5 since these two catalysts might promote the dehydrogenation of styrene. Moreover, naphthalene, 1,3-dimethyl naphthalene, and 1-methyl naphthalene also decrease with doping of nickel on HZSM-5. This indicates that some of these di-aromatics might be transformed to

valuable mono-aromatics via these two steps. First, one ring of naphthalene might be hydrogenated into tetralin at a nickel site, and then the naphthenic ring of tetralin was cracked to form valuable products such as benzene, toluene, ethylbenzene, xylenes and etc.

Table 3: Sulphur content in oils

Catalyst	Sulphur content in oil (wt%)	Sulphur reduction (%)
Non-catalytic	0.96	Base
HZSM-5	0.78	18.8
Ni/HZSM-5	0.68	29.2

Table 3 shows the sulphur content in oil and sulphur reduction of the HZSM-5 and Ni/HZSM-5. It can be seen that when catalysts are used, the sulphur content in oil is lower than in non-catalytic case. HZSM-5 mainly removes the sulphur compounds from oil with the formation of coke on the spent catalyst, similar to the results reported by Al-Bogami and De Lasa (2013). Furthermore, the modification of HZSM-5 zeolite by nickel species significantly decreases the sulphur content in oil by 29.2 %. It can be clearly seen that the increase of sulphur deposition on the spent Ni/HZSM-5 catalyst causes the reduction of sulphur content in oil (see in Figure 3(a)). Therefore, it is reasonable to conclude that Ni species selectively remove sulphur compounds via adsorption of sulphur species on the metallic site. It can be suggest that sulphur-containing compounds are more preferably adsorbed on Ni/HZSM-5 catalyst than HZSM-5 zeolite since the incorporation of nickel with HZSM-5 zeolite might increases the Lewis acidity of zeolites, which promote the adsorption of sulphur containing compounds (Pang et al., 2007). The main sulphur-containing compound found in waste tyre-derived oil is benzothiazoles species (BTz), which is commonly used as an accelerator in vulcanization process. Thiophenes (Th), benzothiazoles (BTz) and isothiocyanate strongly decrease, whereas benzothiophenes (BT), dibenzothiophene (DBT) and naphthothiophene (NTH) slightly increase with using HZSM-5 catalyst. This result indicates that HZSM-5 catalyst is active for breaking C-S and C-N bonds of benzothiazole and isothiocyanate and breaking C-S bonds of thiophenes. On the hand, the formations of BT and DBT slightly increase since the acidity of HZSM-5 catalyst might promote formation of poly-thiophenic compounds via thiophenic speices (Düng et al., 2009). The different result is observed in the case of Ni/HZSM-5 catalyst. In this case, the sulphur-containing compounds, except BT, DBT and NTH, significantly increase since the Ni might reduce the active sites of HZSM-5 zeolite that favors for C-S and C-N breaking of thiophenic compounds. In addition, the reduction of benzothiophenes might cause the formation of ethylbenzene and styrene (Yao et al., 2005). The ethylbenzene can be formed via the hydrogenation of BT, followed by hydrogenolysis of dihydrobenzothiophene. Styrene can be directly formed via hydrogenolysis of BT.

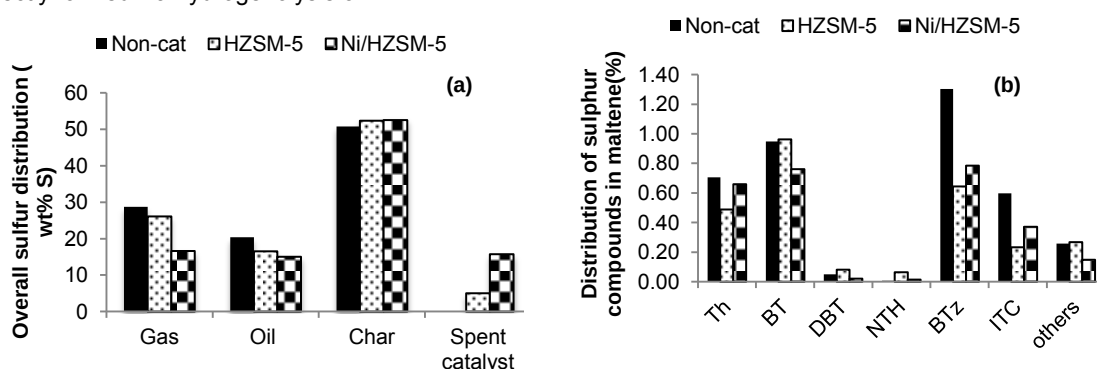


Figure 3: Sulphur analysis: (a) Overall sulphur distribution, and (b) Distribution of sulphur-containing compounds in maltenes.

4. Conclusions

Ni-loaded HZSM-5 zeolite can be considered an interesting catalyst for the improvement of quality of waste tyre-derived oil via conversion of polycyclic aromatics to lighter hydrocarbons and reduction of sulphur from waste tyre-derived oil. The results indicated that the incorporation of nickel over HZSM-5 zeolite strongly promoted the production of gasoline, indicating that with nickel loading the cracking activity of catalyst highly increases. Moreover, Ni/HZSM-5 favoured the conversion of polycyclic aromatics, naphthenic and olefins to mono-aromatics, whereas parent HZSM-5 catalyst favoured the formation of

poly-aromatics. In addition, the production of petrochemicals in oil was enhanced with using Ni/HZSM-5. HZSM-5 provided a slightly better production of ethylbenzene and toluene than the non-catalytic case. On the other hand, Ni doping strongly enhanced the production of ethylbenzene, toluene, cumene and mixed-xylenes. It is reasonable to conclude that nickel on HZSM-5 has the ability on improving the petrochemical production from waste tyre-derived oil. Furthermore, the introduction of nickel on HZSM-5 also reduced sulphur content in waste tyre-derived oil from 0.78 to 0.68 wt%

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