รายงานการวิจัย เรื่อง

กระบวนการใหม่สำหรับการพัฒนาคุณภาพน้ำมันเชื้อเพลิงโดยทดแทนด้วยผลิตภัณฑ์ที่ได้จากการหมักผลิตผลทางการเกษตร

A novel process for fuel oil quality improvement by replacing with fermentation products from agricultural products

ชื่อผู้วิจัย
ผู้ช่วยศาสตราจารย์ ดร. วรพล เกียรติกิตติพงษ์
ผู้ช่วยศาสตราจารย์ ดร. ชูวงศ์ ชัยสุข

ได้รับทุนอุดหนุนการวิจัยจาก
สถาบัน วิจัยและพัฒนา มหาวิทยาลัยศิลปากร

ปีที่ดำเนินการเสร็จ
พ.ศ. 2554

กิตติกรรมประกาศ

ขอขอบคุณสถาบันวิจัยและพัฒนา มหาวิทยาลัยศิลปากร สำนักงานกองทุนสนับสนุนการวิจัย (สกว.) และสำนักงานคณะกรรมการการอุดมศึกษา (สกอ.) ที่ให้การสนับสนุนงานวิจัยนี้ ขอขอบคุณศาสตราจารย์ ดร.สุทธิชัย อัสสะบำรุงรัตน์ ที่ปรึกษาโครงการที่กรุณาให้คำแนะนำที่มีค่าเป็นอย่างยิ่งเสมอมา ขอขอบคุณศาสตราจารย์ ดร.ปิยะสาร ประเสริฐธรรม หัวหน้าศูนย์เชี่ยวชาญเฉพาะทางด้านคาตาไลซิสและวิศวกรรมปฏิกิริยาที่ใช้ตัวเร่งปฏิกิริยา ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ที่ให้การสนับสนุนในการใช้เครื่องมือในการวิเคราะห์ต่างๆ และบริษัทไทยออยล์ จำกัด (มหาชน) ที่ได้อนุเคราะห์สารตัวอย่าง FCC แก๊สโซลีนเพื่อใช้ในงานวิจัย ตลอดจนต้นสังกัดของผู้วิจัย ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์และเทคโนโลยีอุตสาหกรรม มหาวิทยาลัยศิลปากร ที่เอื้อเฟื้อสถานที่และให้เวลาผู้วิจัยในการทำวิจัยเป็นอย่างดี

ชื่อโครงการ	กระบวนการใหม่สำหรับการพัฒนาคุณภาพน้ำมันเชื้อเพลิงโดยทดแทนด้วยผลิตภัณฑ์ที่ได้จากการหมักผลิตผลทางการเกษตร
ชื่อผู้วิจัย	ผู้ช่วยศาสตราจารย์ ดร. วรพล เกียรติกิตติพงษ์ (ผู้วิจัยหลัก) ผู้ช่วยศาสตราจารย์ ดร. ชูวงศ์ ชัยสุข
หน่วยงานที่สังกัด	ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์และเทคโนโลยีอุตสาหกรรม มหาวิทยาลัยศิลปากร
นักวิจัยที่ปรึกษา	ศาสตราจารย์ ดร.สุทธิชัย อัสสะบำรุงรัตน์ ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
แหล่งทุนอุดหนุนการวิจัย	สถาบันวิจัยและพัฒนา มหาวิทยาลัยศิลปากร
ปีที่เสร็จ	2554

บทคัดย่อ

งานวิจัยนี้ได้นำเสนอกระบวนการใหม่สำหรับการพัฒนาคุณภาพน้ำมันเชื้อเพลิงพร้อมกับการทดแทนด้วยวัตถุดิบหมุนเวียน (renewable feedstock) กระบวนการเกิดปฏิกิริยาอีเทอริฟิเคชันในตัวของน้ำมันที่ได้จากกระบวนการฟลูอิไดซ์คาตาไลติกแคร้กกิ้ง (FCC gasoline) ด้วยเอทานอลมีข้อดีที่เหนือกว่าการผสมเอทานอลลงในน้ำมันโดยตรง (ซึ่งเรียกว่า แก๊สโซฮอล์) อยู่หลายประการและเป็นการลดข้อจำกัดการทดแทนน้ำมันด้วยเอทานอลซึ่งจำกัดที่ 10-20 %โดยปริมาตรสำหรับเครื่องยนต์ทั่วไป (non-flex fuel engine) กระบวนการเกิดปฏิกิริยาอีเทอริฟิเคชันในตัวกับเอทานอลสามารถลดปริมาณสารประกอบประเภทโอเลฟินส์และเพิ่มค่าออกเทนของน้ำมันได้อย่างมีนัยสำคัญจากอีเทอร์ที่เกิดขึ้นจากการทำปฏิกิริยา ค่าความดันไอของสารผสม (bRvp) ที่ได้ต่ำกว่าแก๊สโซฮอล์มากซึ่งเหมาะกับประเทศเขตร้อนหรือการใช้งานในช่วงฤดูร้อน อีกทั้งไม่ก่อให้เกิดปัญหาการสตาร์ทเครื่องยนต์ที่อากาศเย็นเมื่อพิจารณาจากค่าอุณหภูมิสตาร์ทต่ำสุด (minimum cold start temperature) และค่าดัชนีการขับเคลื่อน (drivability index) น้ำมันผลิตภัณฑ์มีปริมาณเพิ่มขึ้นจากสารประกอบอีเทอร์ที่ผลิตได้จากเอทานอลซึ่งนับเป็นพลังงานหมุนเวียน โดยเมื่อเปรียบเทียบถึงความสามารถของตัวเร่งปฏิกิริยาพบว่าเบตาซีโอไลต์เหมาะกับปฏิกิริยาอีเทอริฟิเคชันในตัวกับเอทานอลมากกว่าแอมเบอลิสต์ 16 เนื่องจากให้ค่าออกเทนและค่าการเปลี่ยนของเอทานอลที่สูงกว่า และพบว่าตัวเร่งปฏิกิริยาเบตาซีโอไลต์ที่มีค่าอัตราส่วนซิลิกอนต่ออลูมิเนียมเท่ากับ 27 (Beta$_{27}$) ให้ค่าการเปลี่ยนของเอทานอลที่สูงกว่าเบตาซีโอไลต์ที่มีค่าอัตราส่วนซิลิกอนต่ออลูมิเนียมเท่ากับ 42 และ 77 อีกทั้งเมื่อทำการปรับปรุง Beta$_{27}$ ด้วยการเติมทองแดงพบว่าสามารถเพิ่มค่าเปลี่ยน (conversion) ของเอทานอลจาก 38.2% เป็น 55.1% และลดลงปริมาณโอเลฟินส์ลงได้ถึง 62.4% จาก 46.2% เมื่อป้อนเอทานอลในสัดส่วน 20% โดยปริมาตร และเมื่อเพิ่มปริมาณเอทานอลในสายป้อนเป็น 30% โดยปริมาตรพบว่าปริมาณเอทานอลจะถูก

เปลี่ยนเป็นสารประกอบอีเทอร์มากขึ้นโดยมีค่าการเปลี่ยน 49.6% และลดปริมาณโอเลฟินส์ลงได้ถึง 68.7% โดยปริมาณโอเลฟินส์จะเหลืออยู่ในน้ำมันเพียง 7% โดยปริมาตรซึ่งได้มาตรฐานยูโร 4 ที่กำหนดให้มีปริมาณโอเลฟินส์ไม่สูงกว่า 18% โดยปริมาตร เมื่อเปรียบเทียบกระบวนการเกิดปฏิกิริยาอีเทอริฟิเคชันในตัวกับกระบวนการลดปริมาณโอเลฟินส์อื่นๆ พบว่ามีความสามารถในการลดโอเลฟินส์สูงกว่ากระบวนการแบบ non-hydrogenation แต่ต่ำกว่า hydroisomerization อย่างไรก็ตามกระบวนการทั้งสองนี้มักประสบปัญหาการลดลงของค่าออกเทน หากการเพิ่มขึ้นของสารประกอบอะโรมาติกส์เพื่อมาชดเชยค่าออกเทนที่สูญเสียไปนั้นไม่เพียงพอ ในขณะที่กระบวนการเกิดปฏิกิริยาอีเทอริฟิเคชันในตัวสามารถเพิ่มค่าออกเทนได้อย่างเป็นอย่างดีโดยไม่ก่อให้เกิดสารประกอบอะโรมาติกส์

คำสำคัญ : น้ำมันที่ได้จากกระบวนการฟลูอิไดซ์คาตาไลติกแคร้กกิ้ง; การลดปริมาณโอเลฟินส์; การเพิ่มค่าออกเทน; การเกิดปฏิกิริยาอีเทอริฟิเคชันในตัว; เอทานอล; พลังงานหมุนเวียน

Research Title	A novel process for fuel oil quality improvement by replacing with fermentation products from agricultural products
Researcher	Assistant Professor Dr.Worapon Kiatkittipong (Principal investigator) Assistant Professor Dr.Choowong Chaisuk
Office	Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University
Research Advisor	Professor Dr.Suttichai Assabumrungrat, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University
Research Grants	Research and Development Institute, Silpakorn University
Year	2011

Abstract

This research proposes a novel process for fuel oil quality improvement with supplement by renewable feedstock. The process of self-etherifying the entire fluidized catalytic cracking (FCC) gasoline with ethanol is first illustrated here. The use of ethanol in the self-etherification process has several benefits and can overcome the constraint of using ethanol as fuel extender by direct blending method (as well known as “gasohol”) which is limited at ca. 10–20 vol.% for non-flex fuel engine. Self-etherification with ethanol decreased olefin content effectively opposing with increasing of research octane number (RON) due to broad range of ethers formation. The blending Reid vapor pressure (bRvp) of etherified FCC gasoline was found to be much lower than that of gasohol, indicating that the gasoline from this process is more suitable than gasohol especially for near tropical countries or in the summer period. As known that too low bRvp might cause a cold start problem, however, it might not be in this case as it was proven by satisfied minimum cold start temperature and drivability index. The gasoline volume is effectively increased by ethers produced from ethanol which is considered as renewable energy. Comparing the catalyst performance, Beta-zeolite is a more suitable catalyst than Amberlyst 16 for the etherification of FCC gasoline with ethanol because it offered products with higher RON and higher ethanol conversion. The influences of Si/Al ratio in Beta zeolite on the reaction performance were also investigated and found that Beta zeolite with Si/Al ratio of 27 (Beta_{27}) can enhance higher ethanol conversion than those of 42 and 77. In addition, with ethanol 20 vol.% feed, the modification of Beta_{27} by Cu (Cu-Beta_{27}) can further improve the ethanol conversion from 38.2% (Beta_{27})

to 55.1%, and the olefin content reduction from 46.2% ($Beta_{27}$) to 62.4%. With increasing ethanol substitution ratio up to 30 vol.%, higher amount of ethanol was converted with a conversion of 49.6% and olefin reduction of 68.7%. The amounts of remaining olefinic compounds (approx. 7 vol.%) are much lower than a limiting upper value of 18 vol.% as regulated by Euro IV gasoline standard. Comparison to other techniques for reducing olefin content in FCC gasoline, etherification with ethanol catalyzed by Cu-Beta catalyst provides intermediate values of olefin reduction between the hydroisomerization and non-hydrogenation process. However, hydroisomerization and non-hydrogenation process would suffer from the loss of RON if compensation by an increase of aromatics compound is not enough. Therefore, self-etherification proposed technique is prevail over by effectively improve RON without an increase of aromatic content.

Keywords: Fluidized catalytic cracking gasoline; Olefin reduction; Octane enhancement; Self-etherification; Ethanol; Renewable energy

TABLE OF CONTENTS

CHAPTERS

LIST OF ABBREVIATIONS

2M1B	2-Methyl-1-butene
2M2B	2-Methyl-2-butene
2M1P	2-Methyl-1-pentene
2M2P	2-Methyl-2-pentene
bRvp	Blending Reid vapor pressure
CSTR	Continuous stirred tank reactor
DI	Drivability index
DTGA	Differential thermogravimetric analysis
DTBG	Di-tert-butyl ethers of glycerol
ETBE	Ethyl tert-butyl ether
EtOH	Ethanol
FBP	Final boiling point
FCC	Fluidized catalytic cracking
FID	Flame ionization detector
GC	Gas chromatograph
IA	Isoamylene
IB	Isobutene
IBP	Initial boiling point
ICP	Inductive couple plasma
MeOH	Methanol
MTBE	Methyl tert-butyl ether
MTBG	Mono-tert-butyl ethers of glycerol

RON	Research octane number
TAA	Tert-amyl alcohol
TAEE	Tert-amyl ethyl ether
TAME	Tert-amyl methyl ether
TBA	Tert-butyl alcohol
TGA	Thermogravimetric analysis
THEE	Tert-hexyl ethyl ethers
TTBG	Tri-tert-butyl ether of glycerol

CHAPTER 1

Introduction

Fluidized catalytic cracking (FCC) of gasoline is the main contribution of olefins when it is blended with gasoline pool. Such olefinic compounds usually present in an unstable form, which are easily oxidized by photochemical reaction, leading to an increase of ground ozone level. Hence the amounts of olefinic compounds are enforced to have limiting upper value of 18 vol.% as regulated by Euro 4 gasoline standard. Several studies on selective hydrogenation for olefins reduction have been proposed and some of them have already been performed the pilot-scale operations; however, this technique is still facing problems with low gasoline yield and loss in research octane number (RON) (Fan et al. 2005a; Ren and Li 2008). Converting olefins in FCC gasoline by hydroisomerization and aromatization was therefore developed and was succeeded in reducing the loss of octane number from olefin reduction due to compensation by the formation of iso-paraffins and aromatics (Fan et al. 2004; 2005a, b; Zhang et al. 2007). However, this process has to be operated at a high temperature between 270 and 370 °C with pure hydrogen at the pressure of 2.0-3.0 MPa. A catalyst modification for non-hydrogenation reduction of olefins, which is known as a process without hydrogen supply in feed, has been proposed as it is especially beneficial for the refineries where hydro-treating is limited or low-cost hydrogen could not be provided (Ding et al. 2007). The operating temperatures of non-hydrogenation reduction of olefins in this operation are normally in the range of 170-400 °C (Ding et al. 2007; Li et al. 2007; Lihua and Jinshen 2008). However, the RON of the products obtained from hydroisomerization and non-hydrogenation mostly depended on degree of aromatization. The gasoline obtained products would suffer from the loss of RON if compensation by an increase of aromatics compound is not enough. On the contrary, increasing aromatic compounds have a greater tendency to emit unburned hydrocarbons (Perry and Gee 1995) and hence Euro 4 standard has limited aromatics content must lower than 35 vol.%; therefore the loss of RON and increasing of aromatics content should be compromised. Moreover theses most conventional techniques are usually operated at relatively high temperatures.

Etherification reaction is proposed as an alternative way for upgrading FCC gasoline. By etherifying the entire FCC gasoline, the olefin content and bRvp of the gasoline could be reduced with an increase of gasoline yield, octane number and oxygen content. The etherification of the entire FCC gasoline has been successfully experimented with methanol (Pescarollo et al. 1993; Rihko and Krause 1996; Hu et al. 2006). However, the previous processes for upgrading FCC gasoline are still based on non-renewable energy. To enhance the renewability of gasoline, renewable feedstock could be substituted into gasoline with quality improvement aspects. An advantage of using such renewable reagents is that they are more environmentally friendly, which can partially reduce the global warming from gasoline utilization.

Our previous studies have been investigating the synthesis of oxygenated ethers which derived from renewable feedstock in different routes i.e. ethanol derived ethers such as ethyl tert-butyl ether (ETBE) (Assabumrungrat et al. 2002, 2003; Kiatkittipong et al. 2002) and tert-amyl ethyl ether (TAEE) (Boonthamtirawuti et al. 2009).

In this study, the etherification of the entire FCC gasoline, so called “self-etherification”, with renewable feedstock for improving gasoline quality and renewability simultaneously has been originally proposed. Ethanol, a main product of agricultural fermentation and glycerol, a by-product of biodiesel production were employed as fuel extender reactive agent. The wide range of ethers production by FCC self-etherification with ethanol or glycerol could effectively decrease olefinic compounds, enhance the RON and sustain the demand of oxygenated ethers.

CHAPTER 2

Literature review

The subject concerning energy crisis and environmental problem has been investigated for many decades. Recent environmental regulations have resulted in significant changes in the formulation of transportation fuels both in view of emission control and supplement of renewable fuel. For example, the amounts of benzene, olefinics and aromatics are enforced to have a limiting upper value of 1, 18 and 35 vol.% as regulated by Euro 4 gasoline standard. Moreover, the Energy Independence and Security Act (EISA) increased the volume of renewable fuel required to be blended into transportation fuel from 9 billion gallons in 2008 to 36 billion gallons by 2022. (http://www.epa.gov/otaq/fuels/renewablefuels/index.htm).

However, since benzene, olefinics and aromatics has high octane number therefore the treated gasoline products might suffer from octane loss due to the cut-off of these compounds. Oxygenate compounds i.e. alcohols and ethers were blended into gasoline to reduce air pollution and enhance octane number. Furthermore, good burning characteristics and low atmospheric reactivity of oxygenates have been interested to use for the fuel quality improvement. Typically, ethers are lower blending Reid vapor pressure (bRvp) than alcohols and also much less photochemically reactive than alcohol. Therefore, ethers are more suitable as oxygenate for gasoline than alcohol. Ethers can be derived from the etherification of alcohol with olefins. The researches of their production also review for a useful knowledge such as operating condition and catalyst selection.

2.1 Etherification of olefins with alcohol

Methyl tert-butyl ether (MTBE) synthesized commercially by the exothermic liquid phase reactor of methanol and isobutene over an acid ion exchange resin catalyst was introduced as gasoline additives in 1979 and are currently the most frequently used gasoline additive. However, the use of MTBE has already been forbidden in 25 states of USA and many countries because it may contaminate underground water (Szklo et al. 2007). Therefore, the higher molecular of ethers which having lower water solubility such as tert-amyl methyl ether (TAME) were explored to substitute the use of MTBE. However, methanol derivatives such as MTBE and TAME are not favorable in an environmental view point because they are mostly derived from natural gas whose production may contribute to global warming. Ethanol, one of biofuels, is a renewable energy source for alleviate the oil crisis and global climate change. Carbon dioxide produced from ethanol combustion is not considered as a global warming contributor since it is carbon neutral. Ethanol can be blended directly into gasoline (called "gasohol"); however, many recent researches reported disadvantages of the gasohol. One of good reviews on the effect of ethanol in gasoline is reported by Niven (2005). The overall air pollutant emissions from the use of gasohol are usually higher than those from the use of conventional gasoline because its high bRvp leads to higher evaporative emissions. Ethanol-derived ethers can overcome the drawbacks of gasoline with direct ethanol blend. Ethers/gasoline fuel shows less volatility than gasohol. Therefore, ethers derived from ethanol still have drawn a number of research activities. Commercially, ETBE and TAEE can be produced by etherification of ethanol with isobutene (IB) and isoamylene (IA), olefinic compounds, respectively. Physical properties of oxygenated compounds are summarized in Table 2.1. The RON of ETBE and TAEE are 118 and 105, respectively, which are lower than that of ethanol, however their bRvp and water solubility are lower than that of ethanol and MTBE.

Table 2.1 Physical properties of oxygenated compounds[a]

Properties	**MeOH**	**EtOH**	**MTBE**	**ETBE**	**TAME**	**TAEE**
CAS No.	67-56-1	64-17-5	1634-04-4	637-92-3	994-05-08	919-94-8
RON[b]	133	129	117	118	112	105
MON[c]	105	102	101	101	98	95
Mol. Wt.	32.04	46.07	88.15	102.18	102.18	116.20
BP(°C)	64.6	78.3	55.2	67.0	86.0	106.0
Density (g/mL)	0.791	0.795	0.741	0.752	0.764	0.761
Water Solubility (mg/l)	Miscible	Miscible	43,000 - 54,300	26,000	20,000	4,000
Blending Rvp (psi)	40	18	8	4.7	1.5[d]	1.2[d]
Neat Rvp (psi) 100 °F	NA	2.3	7.8	4	2.5	1.2
Oxygen (wt.%)	49.9	34.8	18.2	15.7	15.7	13.8

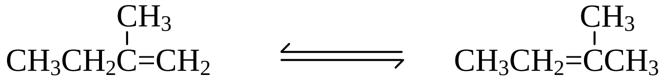
a: Multiple sources; The Handbook of MTBE and Other Gasoline Oxygenates, Mealey's MTBE Conference.
b: RON = Research octane number simulates fuel performance under low severity engine operation with engine speed 600 rpm.
c: MON = Motor octane number simulates more severe operation that might be incurred at high speed or high load with engine speed 900 rpm.
d: Reid vapor pressure, Rvp and NA = Not Available

Several reports for the production of ETBE and TAEE have been focused on the liquid phase etherification of isobutene (IB) or isoamylene (IA) (C_4 and C_5 reactive olefins, respectively) with ethanol as shown in Equations (2.1-2.2).

$$\text{IB} + \text{EtOH} \rightleftharpoons \text{ETBE} \qquad (2.1)$$

$$\text{IA} + \text{EtOH} \rightleftharpoons \text{TAEE} \qquad (2.2)$$

IA composes of two reactive iso-olefins i.e. 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B) which are in isomerization equilibrium as shown in Equation (2.3).



$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \rightleftharpoons CH_3CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}CH_3 \qquad (2.3)$$

(2M1B) (2M2B)

Rihko and Krause (1993) reported that 2M1B was more reactive than 2M2B for etherification with ethanol which also confirmed by other researches (Oktar et al. 1999; Boz et al. 2004). Datta and coworkers investigated the thermodynamic equilibrium of liquid phase ETBE (Jensen and Datta 1995) and TAEE (Kitchaiya and Datta 1995) production catalyzed by Amberlyst 15 ion exchange catalyst. For the TAEE synthesis, thermodynamic analysis of the liquid phase etherification of ethanol with two reactive C_5 iso-olefins, 2M1B and 2M2B were analyzed accompanied by their isomerization simultaneously. The experimental data obtained at equilibrium were used to calculate the thermodynamic equilibrium constants. The UNIFAC method for prediction of activity coefficients was employed in their study. Gomez et al. (1997) studied a simultaneous liquid-phase synthesis of MTBE and ETBE in batch reactor by using macroporous sulfonic resin, Bayer K2631 as the catalysts. The equilibria constants were determined experimentally in the temperature range 313-353 K at 1.6 MPa. MeOH reacts with IB faster than EtOH and, as a consequence, the formation of MTBE reached the equilibrium faster than that of ETBE. The kinetics and equilibrium of TAEE liquid-phase synthesize heterogeneously catalyzed by Amberlyst 16 were studied by Linnekoski et al. (1997). The experiments were carried out in a CSTR at 0.8 MPa and the operating temperature in range of 323-363 K. Three kinetic models; homogeneous, Eley-Rideal type, and Langmuir-Hinshelwood type were fitted to the measured reaction rates. The Langmuir-Hinshelwood is the best fitted model to describe the experimental results.

The ion exchange resins are formed as assemble of gel like micro spheres having macro pores between these micro spheres diffusion resistances. Both the macro pores and within the gel like micro gains may have significant influence on the observed rate (Dogu et al., 2003). Relative diffusion resistances among macro pores and micro pore are strongly dependent on the state (vapor or liquid) of the reactant. In the liquid phase major diffusion resistance was reported to be in the macro pore. However, in vapor phase macro pore and micro pore diffusion resistances are equally significant (Dogu et al., 2003). The activity of ion exchange resin, Amberlyst 15, which having different hydrogen exchange capacities ranging between 1.3 to 5.1 meq H^+/kg for TAEE synthesis from IA and EtOH was investigated in a fixed bed reactor (Boz et al. 2004). The TAEE production increases almost linearly with an increase in hydrogen ion-exchange capacity of the catalysts in the case of 2M2B. However, for 2M1B, which was much more reactive than 2M2B, hydrogen ion-exchange capacity of the catalyst becomes insignificant over the capacity of 2.8 meq H^+/g. This might be mainly due to a significance of diffusion resistance on the reaction rate of 2M1B with ethanol over Amberlyst-15 catalyst.

Unconventional routes for ethers synthesis were also investigated. Tert-butyl alcohol (TBA), a major by-product of propylene oxide production, and tert-amyl alcohol (TAA), a major component of fusel oil which is a by-product obtained from biomass fermentation were employed as a reactant with ethanol for ETBE (Assabumrungrat et al. 2002, 2003; Kiatkittipong et al. 2002) and TAEE synthesis, respectively (Boonthamtirawuti et al. 2009).

Heavier reactive olefins have been considered as additional reactants for ether production. Tert-hexyl ethyl ethers (THEE) can also be produced by the liquid-phase etherification of C_6 olefins with ethanol. The equilibrium constant and the equilibrium conversion to THEE decreased with increasing temperature. The equilibrium conversion from the experiments (Zhang et al. 1997) agrees well with their theoretical calculation (Zhang and Datta 1995a), where ETBE formation is substantially higher than that of 2-ethoxy-2-methylpentane and TAEE, respectively. 3-Methoxy-3-methylheptane was firstly investigated by etherified 2-ethyl-1-hexene with methanol (Karinen and Krause 2000). Consequently, etherification of C_5- and C_8- alkenes i.e. 2-methyl-1-butene and 2,4,4-trimethyl-1-pentene, respectively, with different C_1- to C_4-alcohols was studied (Karinen et al. 2001).

FCC gasoline containing several C_4–C_8 reactive olefins which are promising sources for etherification. The following sections are the literature reviews on the etherification of FCC gasoline.

2.2 Etherification of FCC gasoline

Fluidized catalytic cracking (FCC) gasoline is a potential valuable feedstock of reactive olefins for production of oxygenated ethers. On the contrary, these olefinic compounds are among the most photochemical reaction components of hydrocarbon emissions from automotive engines which strongly affect on ground ozone level. Therefore they should be diminished also in order to meet the new mandatory of gasoline composition which allows the olefin content not to exceed 20 or 18 vol.% as regulated by the International charter on clean fuels and Euro 4 standard, respectively. Pescarollo et al. (1993) studied the etherification of the entire light FCC gasoline with methanol. IA conversion was 68.8% close to thermodynamic equilibrium while conversions of C_6 and C_7 reactive olefins were 42.9% and 23.2%, respectively. Simultaneous improvements in octane number and gasoline volume with reductions in olefinicity, atmospheric reactivity and bRvp of gasoline were obtained. The reactive olefins presence in FCC gasoline and their corresponding ethers formed by methanol addition proposed by (Pescarollo et al. 1993) are summarized in Table 2.2.

Table 2.2 the reactive olefins present in FCC gasoline and their corresponding ethers formed by methanol addition (Pescarollo et al. 1993)

Reactive olefins	B.P. (°C)	Methylic ethers
C_4		
Isobutene	-6.3	2-methyl-2-methoxy propane (MTBE)
C_5		
2-methyl-2-butene	31.1	2-methyl-2-methoxy butane (TAME)
2-methyl-l-butene	38.6	2-methyl-2-methoxy butane (TAME)
C_6		
2-methyl-l-pentene	62.0	2-methyl-2-methoxy pentane
2-methyl-2-pentene	67.3	2-methyl-2-methoxy pentane
cis-3-methyl-2-pentene	67.7	3-methyl-3-methoxy pentane
truns-3-methyl-2-pentene	70.4	3-methyl-3-methoxy pentane
2-ethyl-l-butene	64.7	3-methyl-3-methoxy pentane
2,3-dimethyl-l-butene	53.6	2,3-dimethyl-2-metoxy butane
2,3-dimethyl-2-butene	73.2	2,3-dimethyl-2-metoxy butane
l-methylcyclopentene	75.5	l-methyl-l-methoxy cyclopentane
C_7		
2-methyl-l-hexene	92.0	2-methyl-2-methoxy hexane
2-methyl-2-hexene	95.2	2-methyl-2-methoxy hexane
cis-3-methyl-2-hexene	97.3	3-methyl-3-methoxy hexane
truns-3-methyl-2-hexene	95.2	3-methyl-3-methoxy hexane
cis-3-methyl-3-hexene	95.4	3-methyl-3-methoxy hexane
trans-3-methyl-3-hexene	93.5	3-methyl-3-methoxy hexane
2-ethyl-l-pentene	94.0	2-ethyl-2-methoxy pentane
2,3-dimethyl-l-pentene	84.2	2,3-dimethyl-2-methoxy pentane
2,3-dimethyl-2-pentene	97.4	2,3-dimethyl-2-methoxy pentane
cis-3,4-dimethyl-2-pentene	89.2	2,3-dimethyl-3-methoxy pentane
truns-3,4-dimethyl-2-pentene	91.5	2,3-dimethyl-3-methoxy pentane
2-ethyl-3-methyl-l-butene	86.3	2,3-dimethyl-3-methoxy pentane
2,4-dimethyl-l-pentene	81.6	2,4-dimethyl-2-methoxy pentane
2,4-dimethyl-2-pentene	83.3	2,4-dimethyl-2-methoxy pentane
3-ethyl-2-pentene	96.0	3-ethyl-3-methoxy pentane

2,3,3-trimethyl-l-butene	77.6	2,3,3-trimethyl-2-methoxy butane
l-ethylcyclopentene	106.3	l-ethyl-l-methoxy cyclopentane
1,2-dimethylcyclopentene	106.8	1,2-dimethyl-l-methoxy cyclopentane
1,5-dimethylcyclopentene	102.0	1,2-dimethyl-l-methoxy cyclopentane
1,3-dimethylcyclopentene	92.0	1,3-dimethyl-l-methoxy cyclopentane
1,4-dimethylcyclopentene	93.2	1,3-dimethyl-l-methoxy cyclopentane
l-methylcyclohexene	110.0	l-methyl-l-methoxy cyclohexane

Similar reaction was also studied by using Amberlyst 16, a cation-exchange resin, as a catalyst in a temperature range of 50-80 ^{o}C (Rihko and Krause 1996). They reported the initial etherification rates and thermodynamic limitations for the reaction of methanol with the C_5 and C_6 olefinic compounds. The equilibrium constants of C_6 olefins etherified with ethanol were lower than those of IA, C_5 olefins and TAME was observed to be the main ether products. It should be noted the lower conversion of 2-methyl-1-pentene (2M1P) and 2-methyl-2-pentene (2M2P) with methanol in this study (51.8%) (Rihko and Krause 1996), compared to that with ethanol (59.6%) (Zhang and Datta 1995b) is unexpected. Hu et al. (2006) investigated various catalysts i.e. Beta-, MOR-, ZSM5-zeolite and D005 cationic exchange resin for FCC etherification with methanol. They reported that Beta-zeolite provides the highest conversion and catalytic stability.

CHAPTER 3

Self-etherification process for cleaner fuel production

3.1 Introduction

At the moment, transport fuel is mainly derived from fossil and the attention has been focused on biomass derived fuel production. Ethanol is one of the most widely-used renewable liquid fuel and may be among the most suitable choices for use with the existing infrastructure i.e. road, gas station and automobile engine. CO_2 produced from ethanol combustion is not considered as a global warming contributor because it is a part of the carbon cycle and therefore is carbon neutral. Since the CO_2 is recycled to the tissue during plant growth, with modern agriculture, soil organic matter can be built up and therefore net CO_2 can be removed from the atmosphere (Agarwal 2007). However, some researchers have severely questioned the claim of its renewabilility. Pimentel (1991) claimed that ethanol might not be a renewable energy source. Its overall production system is uneconomic and causes environmental burden. In addition, the important concept of life cycle assessment was illustrated for ethanol production (Wang et al. 2007; Wu et al. 2006). CO_2 emissions over the life cycle of ethanol production are such that the net greenhouse benefit of low ethanol blends is marginal (Wang et al. 1997). Although the advantages of using ethanol for fossil fuel substitution are controversy, ethanol consumption still extends over the world.

Ethanol can be blended directly into gasoline which is called as gasohol. Flexible-fuel cars can be run on up to 85 vol.% (E85) or pure ethanol. However, most of present cars can be run on gasoline blended with lower concentration of ethanol i.e. 10-20 vol.%. Therefore the chance of using ethanol as a fuel extender is limited. Furthermore, many recent researches reported disadvantages of the gasohol (Niven 2005). With a present standard of engine and the use of catalytic converter, the emissions at the end pipe are relatively small while evaporative emissions have become significant. Evaporative emissions are considered as a loss of fuel which can be occurred from diurnal, running loss, hot soak and refueling (French and Malone 2005). Therefore, some researchers found that the overall air pollutant emissions (exhaust and evaporative emissions) by the use of gasoline-ethanol blend appear to be higher than those posed by conventional gasoline because of its high blending Reid vapor pressure (bRvp) (Niven 2005). An ethanol-gasoline mixture also undergoes a phase separation on contact with water which increases the corrosion of steel underground storage tanks, increasing the risk of leakage to surrounding soil. Even though ethanol/gasoline (gasohol) can tolerate significantly higher water content than conventional gasoline before phase separation, the problem on the engine is more serious. Ethanol partitions preferentially into an aqueous phase and therefore causes an off-spec gasoline. Combustion of this partition causes the lean burn effects (French and Malone 2005). Refiners and auto-makers prefer to use ethers to meet the octane number and oxygenate requirement for technical reasons because ethers can overcome the drawbacks of gasoline with direct ethanol blend.

Most of ethers are derived from methanol (Karinen and Krause 2001; Caetano et al. 1994; Kiviranta-Paakkonen et al. 1998; Ferreira et al. 2007) and ethanol (Assabumrungrat et al. 2002, 2003; Kiatkittipong et al. 2002; Boz et al. 2004) and some from butanol (Sow et al. 2005) and glycerol (Karinen and Krause 2006; Klepacova et al. 2005; Richter et al. 2008). Although methanol can also be produced from biomass, the production is cost-intensive and therefore it is currently made from natural gas which is more cost-competitive (Demirbas 2007). As a result, ethers derived from ethanol could be the most suitable additives for gasoline extender and octane modifier. The most well-known ethanol-derived ethers are ethyl tertiary butyl ether (ETBE) and tertiary amyl ethyl ether (TAEE). Commercially, ETBE and TAEE can be produced by etherification of ethanol with isobutene (IB) and isoamylene (IA), olefinic compounds, respectively. Several researchers investigated the liquid phase reaction of ETBE synthesis. The kinetic expressions (Zhang et al. 1997; Francoisse and Thyrion 1991; Fite et al. 1994) and thermodynamic equilibrium were reported (Jensen and Datta 1995). For TAEE synthesis, the major isomer of IA is 2-methyl-2-butene (2M2B) which is usually assumed to be in isomerization equilibrium with 2-methyl-1-butene (2M1B). Rihko and Krause (1993) found that 2M1B was more reactive than 2M2B which is in good agreement with other researches (Oktar et al. 1999; Boz et al. 2004). There are a number of studies focusing on etherification of 2M1B and 2M2B with ethanol in both kinetics (Linnekoski et al. 1997; Linnekoski et al. 1998) and the reaction equilibrium (Kitchaiya and Datta 1995; Rihko et al. 1994). It still has drawn the attention from some researchers (Umar et al. 2008; Umar et al. 2009; Vlasenko et al. 2006).

However, unfortunately, the production of these olefinic compounds, i.e. IA and IB are unlikely to meet demands for etherification feeds. Heavier reactive olefins should be considered as additional reactants for ether production. As mentioned in Chapter 2, FCC gasoline was one of the potential feedstock. Producing tertiary ethers from entire FCC gasoline was an economic alternative to reduce olefins and consequently Rvp together with an increase of the octane number of gasoline. It is worthy to note that olefinic compounds in FCC gasoline are typically diminished by hydroisomerization and aromatization which have been recently investigated by many researchers (Fan et al. 2005a; Ren and Li 2008; Fan et al. 2004; Niu et al. 2005). The loss of octane number from olefin reduction was compensated by the formation of iso-paraffins and aromatics. This process is beneficial in the viewpoint of olefin reduction; though aromatic compounds which have a greater tendency to emit unburned hydrocarbons (Perry and Gee 1995) might be produced.

However, the previous processes for upgrading FCC gasoline are still based on non-renewable energy. To enhance the renewability of gasoline, ethanol could be more partly substituted into gasoline with quality improvement aspects. In this study, the entire FCC gasoline was fed with ethanol in a molar ratio of 80:20 and 70:30. The gasoline composition, olefin and ethanol conversion, and the amount of ethers production were clarified. The gasoline properties i.e. RON, bRvp, distillation temperature (IBP, T_{10}, T_{50}, T_{90} and FBP), estimated minimum cold start temperature and drivability index were compared between original FCC gasoline, commercial E10 gasohol, FCC with direct blend of ethanol and etherified FCC gasoline. Aspect of catalyst characterization on catalytic activity was also discussed.

3.2 Materials and method

3.2.1 Chemicals

FCC gasoline is cut off from a catalytic cracking unit of an oil refinery. Ethanol (99 vol.%) and other chemicals needed in the experiment were analytic grade. All chemicals were used without further purification.

3.2.2 Catalysts

The ion exchange resin catalyst, Amberlyst 16 and the strong acid solid catalyst, Beta-zeolite with Si/Al=40 (H^+ form) were selected for this study. Amberlyst 16 and Beta-zeolite were purchased from Fluka and Tosoh (Japan), respectively. The catalysts were dried overnight in an oven at 110 ^{o}C before use. The properties of the catalysts are shown in Table 3.1.

Table 3.1 Properties of catalysts.

Catalysts	Surface Area (m^2/g)	Pore Diameter (nm)	Acidity (mmol H^+/g)
Amberlyst 16	45	20	5.0
Beta-Zeolite	625	0.58	1.03

The acidity of the catalysts and pore size were reported by the producer. BET surface area of the catalysts was measured by Micromeritics ASAP 2020. A sample of 0.3 g was degassed at 300 ^{o}C for 3 h and the amount of N_2 adsorption was recorded. The thermogravimetric analysis (TGA) curves were obtained in flowing air on SDT Q600 (TA instruments) with a temperature increasing rate of 5 °C/min in the range of 30-1000 °C.

3.2.3 Apparatus

The reaction was carried out in a cylindrical shape autoclave reactor as shown in Fig. 3.1. The 100 cm^3 reactor was maintained at a constant temperature by circulating hot water in jackets. The turbine was used to stir the mixture at the maximum speed of 1163 rpm by a speed controller in all experiments to minimize the external mass transfer resistance. A valve for liquid sampling and a port for the thermocouple were installed at the top.

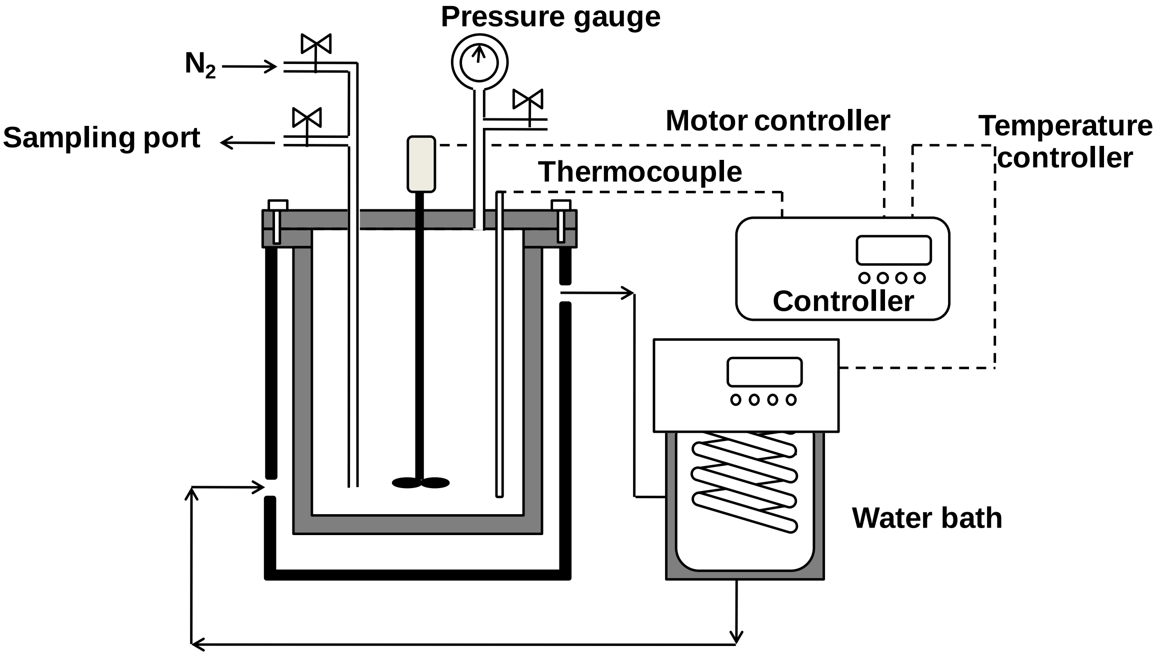


Figure 3.1 Schematic diagram of the reactor apparatus.

3.2.4 Analysis

In gasoline investigations, the compounds called “PIANO” consisting of paraffins, isoparaffins, aromatics, naphthenes and olefins were determined with the amount of the oxygenates. They were analyzed by an FID gas chromatograph with a Supelco capillary column. The analysis was done by injecting 1 μl of sample in the column. It should be noted that a sample must be centrifuged before the injection in order to separate residue catalyst which can damage the GC column. The injector and detector temperature were 250 ^{o}C. The column was heated with three ramps. Firstly, the column was heated from 5 ^{o}C to 65 ^{o}C with a ramp rate of 6 ^{o}C min^{-1} and holding at 65 ^{o}C for 45 min. Afterwards, heated to 180 ^{o}C, with a ramp rate of 3 ^{o}C min^{-1} and holding for 5 min. Finally, the temperature was increased at a ramp rate of 10 ^{o}C min^{-1} to 200 ^{o}C where it was held for 0.5 min. The amount of ethanol was further analyzed by Shimadzu GC 14B with hydrogen flame ionization detector. The separation column was a DB-1 capillary column and He was used as a carrier gas. The standard test methods of ASTM D-2699, ASTM D-5191 and ASTM D-86 were employed to determine research octane number (RON), blending Reid vapor pressure (bRvp) and distillation temperature, respectively. It is worthy to note that due to a large amount of gasoline was needed for gasoline properties determination, e.g. 1 liter for RON, therefore many replicate of experiments were done to obtain this requiring amount.

3.2.5 Operation procedure

The experiments were carried out at 70 ^{o}C for 10 h in the batch reactor. The system was pressurized by N_2 at 0.8 MPa to ensure that all reaction components were in the liquid phase. The reaction system consisted of FCC gasoline and ethanol with a volume ratio of 80:20 and 70:30 with 10 g of catalyst. The samples of feed and product were collected at the initial and final of the experiment. It should be noted that for collecting the final product after run for 10 h, the reactor was cooled down to room temperature before opening the reactor and collecting the sample in order to minimize the evaporation loss.

3.3 Results and Discussion

3.3.1 Gasoline composition and reaction activities

The distributions of the hydrocarbon groups present in the FCC gasoline feed are shown in Table 3.2. Most olefins were in a range of C_5 through C_7 hydrocarbons. The fraction of total olefins was about 25 vol.%.

Table 3.2 Compositions of FCC gasoline (vol.%)

Carbon number	n-paraffins	i-paraffins	olefins	naphthenes	aromatics	Total
C_4	0.435	0.268	1.976	0	0	2.679
C_5	1.054	8.109	8.739	0.112	0	18.014
C_6	0.816	7.759	6.856	1.821	0.333	17.584
C_7	0.766	0.18	6.097	3.023	2.373	18.439
C_8	0.932	4.805	1.129	3.737	4.979	15.582
C_9	0.28	3.991	0.655	2.522	4.944	12.391
C_{10}	0.249	3.214	0.218	0.564	2.782	7.026
C_{11}	0.133	1.33	0	0.21	1.26	2.933
C_{12}	0.046	0.135	0	0.049	0.31	0.54
C_{13}	0.014	0	0	0	0	0.014
Total	4.726	35.79	25.67	12.038	16.98	95.204

Table 3.3 provides the gasoline composition, olefins conversion and ethanol conversion of FCC gasolines directly blended and etherified with ethanol with a volume ratio of 80:20. Since pure ethanol was supplemented into the FCC gasoline with 20 vol.% (approx. 22.4 wt.%) for both cases, the amount of final gasoline product was increased. In the case of ethanol direct blend, the amount of each component is constant because the reaction cannot occur without the catalyst. In the cases of etherified gasoline, Amberlyst 16 and Beta-zeolite were used as catalysts. Olefins and ethanol were mainly converted to ethers. Comparing between two catalysts, it was found that Beta-zeolite gives higher ethanol and olefins conversions, resulting in higher ether products. It is worthy to note that olefins conversions are lower with larger atomic number of olefins in both catalysts because large molecular of olefins hardly enters to pores of catalyst (Hu et al. 2006). The tendency of these results was similar to that of the etherified FCC gasoline with methanol experimented by Pescarollo et al.

(1993). They reported that the conversions of C_4, C_5, C_6 and C_7 olefins were 0.84, 0.64, 0.43 and 0.23 respectively. Even though the FCC feed composition and the ratio of alcohol to FCC were different, a simple comparison between the performance of methanol (Pescarollo et al. 1993) and ethanol (as shown in Tables 3.3 and 3.4) for etherification could be noticed. Higher conversion of isobutene (C_4) and isoamylene (C_5) in FCC with methanol than with ethanol were observed. These results are similar to the individual study of C_4 and C_5 olefins with alcohol in the literature (Rihko and Krause 1993; Rihko et al. 1994; Colombo et al. 1983; Izquierdo et al. 1992; Vila et al. 1993). The activity of ethanol was less than that of methanol as a result of the decrease of dielectric constant or polarity. The value of dielectric constants decreased with increasing of molecular weights of alcohols which were 32.6 and 24.3 for methanol and ethanol, respectively. The more polar component could be preferably adsorbed over the actives sites than the less polar component (Karinen et al. 2001).

However, the comparable or some higher conversions of C_6 and C_7 olefins with ethanol compared to those with methanol were unexpected. The higher conversion of C_6 olefins with ethanol over that with methanol also has been previously observed by Rihko and Krause (1996). These contrasting results might be explained by the study of Cruz et al. (2005). They declared that ethanol can react with alkenes easier than methanol due to the higher acidity of ethanol. The complexity of the system might be related to the complicated mechanism of adsorption over active site. Many components; i.e. alcohol, ether and hydrocarbon having significantly different polarity should play a role; therefore, this issue should be further investigated.

Table 3.3 Gasoline composition, olefins conversion and ethanol conversion of FCC gasoline with different treatments (FCC: ethanol volumetric ratio = 80:20).

Component	FCC Gasoline (g)	Ethanol (g)	20 vol% Ethanol		
			Direct Blend (g)	Etherified Gasoline	
				Amberlyst 16 (g)	Beta-Zeolite (g)
Olefins					
- C4	1.76	-	1.76	0.92	0.86
- C5	8.85	-	8.85	6.15	5.1
- C6	5.69	-	5.69	4.42	3.54
- C7	4.54	-	4.54	3.56	2.73
- C8	1.09	-	1.09	0.29	0.28
- C9	0.44	-	0.44	0.29	0.29
- C10	0.35	-	0.35	0	0.15
Other hydrocarbon	54.84	-	54.84	55.79	55.08
Oxygenates					
- Ethanol	0	22.44	22.44	15.87	14.29
- Ether	0	-	-	12.71	17.68
Total	77.56	22.44	100	100	100
C4 Olefins conversion (-)	-	-	0	0.48	0.51
C5 Olefins conversion (-)	-	-	0	0.31	0.42
C6 Olefins conversion (-)	-	-	0	0.22	0.38
C7 Olefins conversion (-)	-	-	0	0.22	0.40
Ethanol conversion (-)	-	-	0	0.29	0.36

Table 3.4 Gasoline composition, olefins conversion and ethanol conversion of FCC gasoline with different treatments (FCC: ethanol volumetric ratio = 70:30).

Component	FCC Gasoline (g)	Ethanol (g)	30 vol% Ethanol		
			Direct Blend (g)	Etherified Gasoline	
				Amberlyst 16 (g)	Beta-Zeolite (g)
Olefins					
- C4	1.72	-	1.72	0.78	0.67
- C5	7.72	-	7.72	3.39	3.19
- C6	5.12	-	5.12	3.79	2.28
- C7	3.86	-	3.86	2.07	1.88
- C8	0.94	-	0.94	0.51	0.58
- C9	0.39	-	0.39	0.12	0.17
- C10	0.29	-	0.29	0.22	0.06
Other Hydrocarbon	46.81	-	46.81	48.32	47.82
Oxygenates					
- Ethanol	-	33.15	33.15	18.69	16.06
- Ether	-	-	-	22.11	27.29
Total	66.85	33.15	100	100	100
C4 Olefins conversion (-)	-	-	0	0.55	0.61
C5 Olefins conversion (-)	-	-	0	0.56	0.59
C6 Olefins conversion (-)	-	-	0	0.26	0.55
C7 Olefins conversion (-)	-	-	0	0.46	0.51
Ethanol conversion (-)	-	-	0	0.44	0.52

The ratio of FCC gasoline and ethanol was changed to 70:30 and the reaction was carried out at the same operating condition described earlier. The results are summarized in Table 3.4. Beta-zeolite still shows a better catalyst performance than Amberlyst 16. Compared with Table 3.3, the ethanol conversion and all C_4 to C_7 olefins conversions increased with increasing ethanol fraction in feed. The remaining unreacted ethanol from the case with the feed ratio of 70:30 did not exceed the ethanol content of 15 vol.% in the case of Beta-zeolite. Therefore it is not over the gasoline specification of i.e. E15 and E20 which are limited by ethanol content of 15 and 20 vol.%, respectively. The effect of gasoline composition in both Tables 3.3 and 3.4 are further discussed with the gasoline properties shown in Table 3.5.

3.3.2 Gasoline properties and their quality improvement

Table 3.5 summarizes the gasoline properties comparison. FCCs with direct ethanol blend at 20 and 30 vol.% increased RON from original of 88 up to 94.8 and 97.9, respectively. However, unfortunately their bRvp also increased dramatically. As shown experimentally, FCCs etherified with ethanol by using both Amberlyst 16 and Beta-zeolite catalysts can effectively decrease the values of bRvp because the reactive olefins in FCC gasoline and ethanol are converted to ethers which have lower bRvp. FCCs etherified with 30 vol.% ethanol both catalyzed by Beta-zeolite and Amberlyst 16 give lower bRvp than FCC with direct ethanol blend at 20 vol.%. These results also confirm the increase of ethanol substitution ability into gasoline. Comparing with original FCC gasoline, the bRvp value of etherified gasoline catalyzed by Beta-zeolite is lower or similar in the cases of using 20 and 30 vol.%, respectively.

Table 3.5 Comparison of gasoline properties.

Properties	ASTM Standard	FCC Gasoline	Gasohol E10	20 vol.% Ethanol			30 vol.% Ethanol		
					Etherified Gasoline			Etherified Gasoline	
				Direct Blend	Amberlyst 16	Beta-Zeolite	Direct Blend	Amberlyst 16	Beta-Zeolite
RON	D-2699	88.0	95.0	94.8	93.0	94.1	97.9	96.9	98.2
bRvP (psi)	D-5191	6.5	< 9.0	7.441	7.05	5.657	8.0	7.24	6.58
Density (g/cm^3)		0.683	0.749	0.735	0.739	0.745	0.735	0.739	0.745
Viscosity x 10^6 (g_f.s/cm^2)		6.213		6.325	5.374	6.310	6.152	6.035	5.160
Distillation Temperature ^{o}C (^{o}F)	D-86								
IBP		35.5(95.9)		41.9(107.4)	43.3(109.9)	47.7(117.9)	N.D.	N.D.	N.D.
T 10		57.1(134.8)	< 70(158)	55.2(131.4)	56.9(134.4)	59.7(139.5)			
T 50		99.0(210.2)	70-110 (158-338)	70.2(158.4)	75.0(167)	73.8(164.9)			
T 90		168.7(335.7)	< 170(338)	165.9(330.6)	167.1(332.8)	170.2(338.4)			
FBP		196.0(384.8)	< 200(392)	194.7(382.5)	193.1(379.6)	198.2(388.8)			
Driveability Index, DI ^{o}C (^{o}F)		631(1168)	<677(1250)	617(1143)	635(1175)	638(1182)			
Estimated minimum cold start temperature ^{o}C (^{o}F)		-6.7 (19.9)	-	-8.1 (17.42)	-6.9 (19.58)	-5.1 (22.82)			

These results may strongly depend on the decrease of olefins content and the amount of unreacted ethanol remaining in the solution. Therefore, it is worthy to note that the difference of bRvp between original FCC gasoline and etherified gasoline may not be as significant as that of bRvp between FCC with direct ethanol blend and etherified gasoline. The decrease in bRvp reduces the evaporative loss of fuel hence preventing vapor lock in summer. As known that too low bRvp might cause a cold start problem, however it might not be in this case as it was proven by minimum cold start temperature and drivability index (DI) which will be discussed later.

Comparing the RON between ethanol directly blended and etherified gasolines, the gasoline etherified by Amberlyst 16 shows slightly lower octane number than ethanol directly blended gasoline because ethanol has higher value of octane number (RON = 118) than ethers, e.g., ETBE, TAEE and tert-hexyl-ethyl-ether (THEE) whose RON are 118, 105 and 110, respectively. However, the gasoline etherified using Beta-zeolite as catalyst shows similar RON to that of ethanol direct blended gasoline and slightly higher than that of etherified gasoline catalyzed by Amberlyst 16. (Fan et al. 2004) found that Beta-zeolite was an effective catalyst for upgrading FCC gasoline via isomerization and some aromatizations. However, fortunately the amounts of aromatic are not increased in the case of FCC gasoline etherified with Beta-zeolite (not shown here). As the amounts of aromatic are not increased, there is no greater tendency in damage to elastomers and increased of toxic aromatic emissions as unburned hydrocarbons. Therefore, the enhancement of octane number in the case of FCC etherified by Beta-zeolite is not from etherification reaction only but also from isomerization. In addition, Corma et al. (1999) studied various zeolites as catalysts for the cracking of *n*-heptane, a model molecule of gasoline range. When using Beta-zeolite as a catalyst, the ratio of isobutene to *n*-butene and isopentene to *n*-pentene products were 1.27 and 2.0, respectively. Therefore, ether products may not be possibly limited by the amount of reactive olefins originally present in gasoline, the reactive olefins could be further obtained via cracking by Beta-zeolite.

In the case of Amberlyst 16, Slomkiewicz et al. (1997) reported that Amberlyst showed high catalytic activity for double bond isomerization or the cis-/trans-transformation. However, the isomerization from linear olefin to branched olefin is much more difficult because the reaction normally required significantly higher temperature at which Amberlyst could not resist (Harmer and Sun 2001).

Apart from bRvp which represents the volatility property of gasoline, T_{10}, T_{50} and T_{90} (D-86 temperature at 10, 50 and 90 vol.%, respectively) and drivability index are key motor gasoline specifications in the US. The distillation temperature (IBP, T_{10}, T_{50}, T_{90} and FBP) and drivability index are also provided in Table 3.5. Initial boiling point (IBP) increased with the presence of ethanol both in gasoline with direct ethanol blend and etherified gasoline with some unreacted ethanol. Comparing with unmodified FCC gasoline, T_{10}, T_{50}, T_{90} and FBP decrease in the case of gasoline with direct ethanol blend and etherified with Amberlyst 16. While in the case of etherified with Beta-zeolite, the distillation temperature decreases only for T_{10} and T_{50}. IBP and T_{10} affect cold starting ability and inversely vapor lock problem. Increase these front end distillation temperature may increase minimum cold start temperature while decrease the possibility of vapor lock. The minimum cold start temperature could be estimated by the empirical relation as (Aronov and Noreiko 1967)

$$\text{Minimum cold start temperature (°C)} = 5.62\ \sqrt{T_{10} - 40} - 30$$

As shown in Table 3.5, the estimated minimum cold start temperature of etherified gasoline did not pose a cold start problem comparing to original FCC gasoline. However, the appropriate values strongly depend on the regional and seasonal of their used.

From the above results, these may imply that distillation temperatures of ethanol containing fuels are dependent on the evaporation of ethanol and its amount. These results can also be confirmed with the decrease of the bRvp as shown in the Table 3.5, i.e. with higher ethanol converted, the distillation temperatures in the case of Beta-zeolite seem to be higher than those of Amberlyst 16 and ethanol directly blended, respectively. It is worthy to note that T_{50} of FCC-ethanol blend is marginal with the specification value of gasohol E10, it is possibly that blending with higher amount of ethanol i.e. 30 vol.% may make the T_{50} off specs. Therefore, the distillation temperature test of ethanol 30 vol.% was not performed but the available results are enough for discussion.

A drivability index (DI) has been developed to predict cold-start and warm-up drivability. The drivability index, DI is defined as follows (French and Malone 2005; Magyar et al. 2005).

$$DI = (1.5 \times T_{10}) + (3 \times T_{50}) + T_{90}$$

When oxygenate are present in the gasoline, the DI could be corrected as follows (Lippa 2006).

$$DI = (1.5 \times T_{10}) + (3 \times T_{50}) + T_{90} + 20 \times \text{wt.\% oxygen}$$

Drivability index provides the relationship between drivability and distillation properties. T_{10} represents the gasoline ability to vaporize rapidly and enable cold starting. T_{50} and T_{90} represent the heavier gasoline components' ability to vaporize as the engine warms up and be burnt during combustion. Therefore, lower values of DI generally result in better cold-start and warm-up performance; however low DI can indicate poor drivability in that the combustion is too rich of stoichiometry (Lippa 2006). Therefore once good drivability is achieved, there is no benefit to further lowering the DI (http://www.chevron.com/products/ourfuels/prodserv/fuels/documents/Motor_Fuels_Tch_Rvw_complete.pdf).

As shown in Table 3.5, DI values of FCC gasoline and those of etherified FCC gasoline do not show considerable difference, however, the values of DI of the gasoline products are in the satisfied range of the gasoline specification.

3.3.3 Aspect of catalyst characterization on catalytic activity

Linnekoski et al. (1998) investigated the etherification and hydration of isoamylene catalyzed by ion exchange resin. Addition of only small amount of water resulted in significantly dropped in ethanol and olefins conversion (Linnekoski et al. 1998). Karinen et al. (2001) reported that water reacted to tertiary alcohol at an early stage relative to the other reactions. This is because the higher acidity of water compared to that of ethanol resulted in the increasing of basic solvated proton which lowers activity as previously mentioned in the literature (Ancillotti et al. 1977; Gicquel and Torck 1983). In our experiments, although both catalysts were dried at 110 °C overnight, the remaining water adsorbed in the pore of catalyst might be examined by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA).

TGA and DTGA of Amberlyst 16 were investigated as shown in Figs. 3.2 and 3.3, respectively. The weight loss of Amberlyst 16 at the temperature lower than 200 °C are almost 10 wt.% which should be corresponding to the amount of water desorption (Balcerowiak 1997; Zholobenko 1997). The consecutive mass loss step of Amberlyst 16 might be the thermal desulfonation (Balcerowiak 1997). The final peak at 470 ^{o}C of DTGA (Fig. 3.3) might be the thermooxidative decompositions of a polymers matrix (Balcerowiak 1997) which corresponds well with high intensity exothermic as shown in Fig. 3.2.

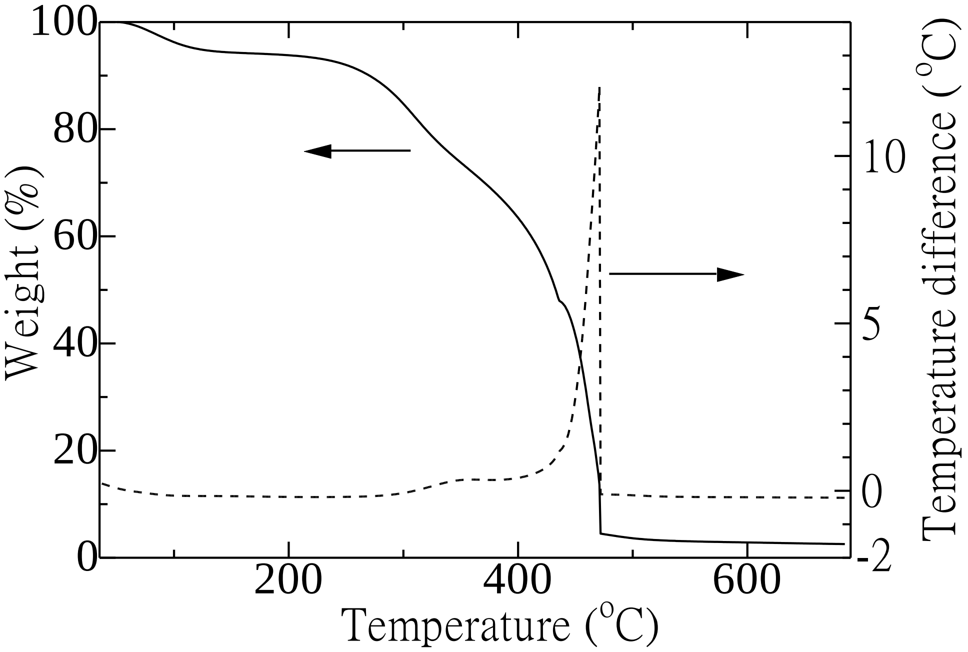


Figure 3.2 Thermogravimetric analysis (TGA) of Amberlyst 16.

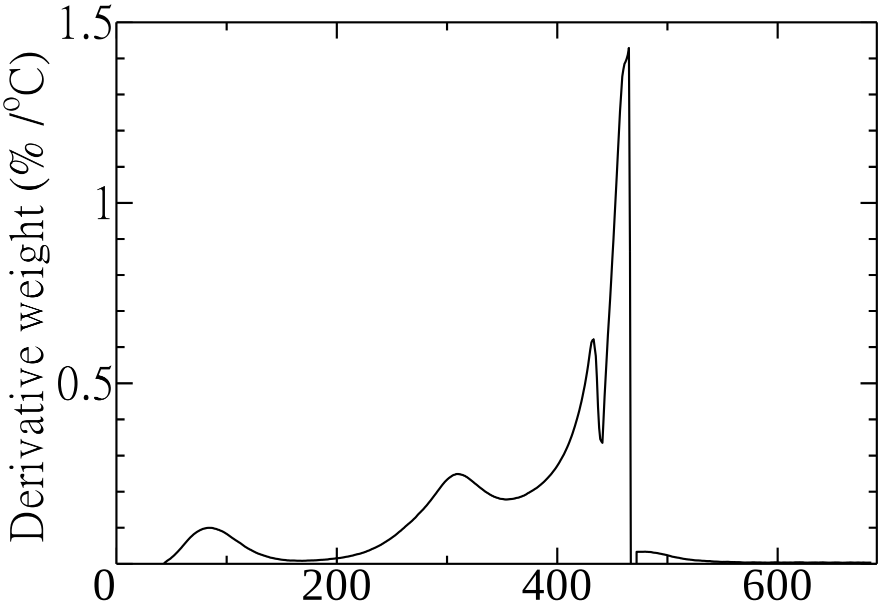


Figure 3.3 Differential thermogravimetric analysis (DTGA) of Amberlyst 16.

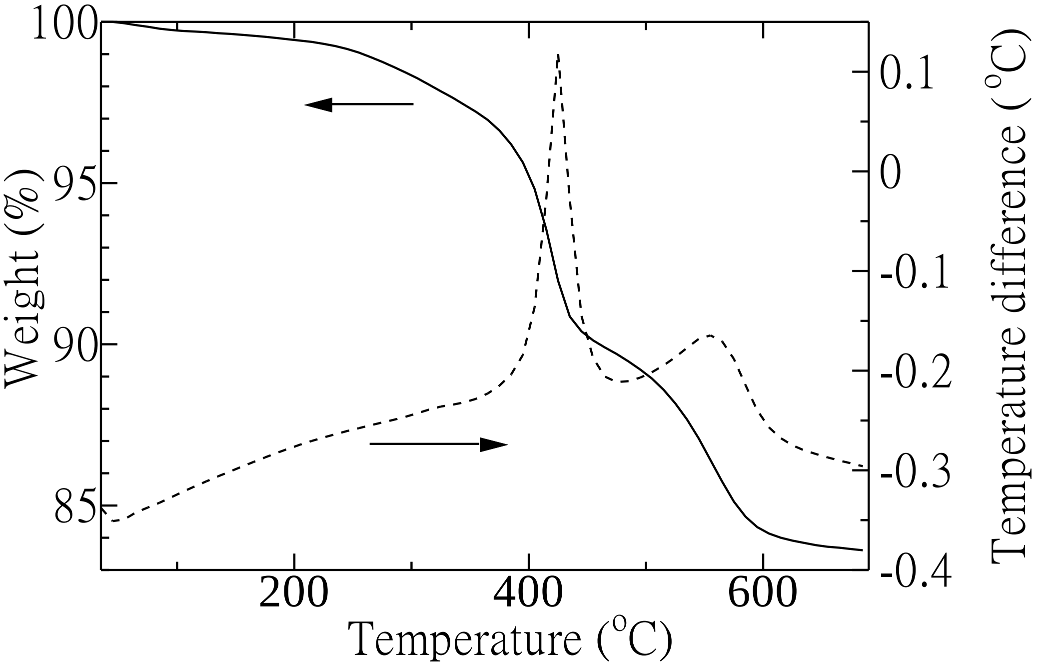


Figure 3.4 Thermogravimetric analysis (TGA) of Beta-zeolite.

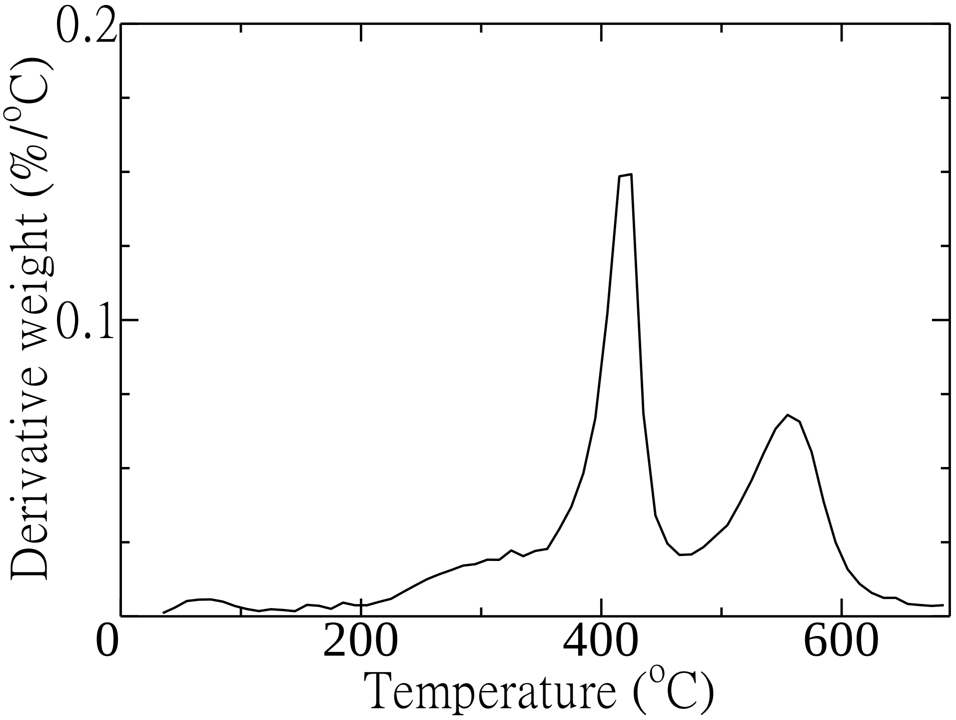


Figure 3.5 Differential thermogravimetric analysis (DTGA) of Beta-zeolite.

On the contrary, insignificant weight loss at the temperature lower than 200 °C can be observed in the case of Beta-zeolite as shown in Fig. 3.4, indicating traces of water desorption. Thermal analysis also revealed desorption of precursor component such as organic template (Zholobenko et al. 1997) i.e. at the temperature of 420 and 560 ^{o}C. The DTGA in Fig. 3.5 showed corresponding well of intense exothermic heat. However, it should be noted that weight loss and exothermic heat were much more pronounced in the case of Amberlyst 16. This TGA results also confirm the higher thermal stability of Beta-zeolite than that of Amberlyst 16.

Therefore, it can be concluded here that Beta-zeolite is a more suitable catalyst for upgrading FCC gasoline with ethanol compared to Amberlyst 16. For other gasoline properties, the density and the viscosity of the etherified gasoline are close to those of the commercial gasohol.

In summary, etherification of FCC gasoline enhances the possibility of ethanol substitution and therefore its renewability without increasing gasoline volatility. Olefinic compound was consumed in the reaction process which lessens cost for the refining industry to limit total gasoline olefins following the regulations without octane loss.

3.4 Summary

Although ethanol direct blend increased RON of FCC gasoline, the value of bRvp became also significantly higher. Etherification of FCC gasoline with ethanol decreased the bRvp significantly and could be possibly lower than that of original FCC gasoline. Beta-zeolite was a more suitable catalyst than Amberlyst 16 for upgrading FCC gasoline. This was due to the higher of catalytic activity for etherification, ethanol could be converted more and therefore increased the renewability of the gasoline while olefinic compounds could be decreased to meet the Euro 4 standard. Normally, the FCC etherified gasoline might give slightly lower of RON compared to ethanol direct blend because RON of ethers were usually lower than that of ethanol. However, Beta-zeolite also showed a catalytic activity of isomerization reaction, RON of the gasoline product was enhanced. The etherified gasoline also showed satisfactions in term of minimum cold start temperature and driveability index. Therefore the process allows the use of ethanol to substitute in gasoline at higher content than conventional method with direct blending and more suitable gasoline properties can be obtained.

CHAPTER 4

Gasoline upgrading by self-etherification with ethanol on modified Beta-zeolite

4.1 Introduction

In the previous Chapter, we found that Beta-zeolite is a more suitable catalyst than Amberlyst 16 for upgrading FCC gasoline by etherification with ethanol and the amounts of remaining olefinic compounds in the products are in compliance with the limiting values regulated by Euro 4 standard. However, converting the rest olefinic compounds would be beneficial both in terms of olefins reduction and enhanced ethanol substitution in gasoline. It is known from previous studies that only tertiary olefins (double bond attached to a tertiary carbon) are reactive for etherification (Rihko and Krause 1993; Kitchaiya and Datta 1995; Zhang and Datta 1995a). Moreover, the etherification reactions are strongly limited by the thermodynamics. Many studies on the thermodynamics of various ethanol etherification reactions with e.g. C_4-isobutene (Zhang et al. 1997; Vila et al. 1993), C_5-isoamylene (Rihko and Krause 1993) and various C6 reactive olefins (Zhang and Datta 1995a, 1996) have been published. The equilibrium conversion from the experiments (Zhang et al. 1997) agrees well with their theoretical calculation (Zhang and Datta 1995a), where ETBE formation is substantially higher than that of 2-ethoxy-2-methylpentane and TAEE, respectively. Therefore, higher demand of ethanol to substitute in gasoline by converting to ethers cannot be implemented by only etherification. The idea of this study is to combine the catalytic isomerization of non-reactive olefins to produce a surplus reactive olefins and etherification with ethanol as a synergy for ethanol supplementary in gasoline with olefin reduction. Many researchers have studied on skeletal isomerization especially n-butenes to isobutene, in which various metals e.g. magnesium (Baeck and Lee 1998) and copper (Nieminen et al. 2003) were loaded on silica-alumina or zeolite supported for skeletal isomerization enhancement. In this study, we focus on the modification of Beta-zeolite to achieve higher ethanol and olefin conversions with preferable gasoline properties for enhancing renewability and environmental friendliness of gasoline.

4.2 Materials and method

4.2.1 Chemicals

FCC gasoline was obtained from the catalytic cracking unit of an oil refinery; its compositions are given in Table 4.1. Chemical precursors employed in the study for modifying Beta-zeolite are copper nitrate ($Cu(NO_3)_2 \cdot 2.5H_2O$) and magnesium chloride ($MgCl_2 \cdot 6H_2O$) supplied from Ajax Finechem Ltd. Commercial Beta-zeolite with Si/Al = 27 in the form of Na^+ (mean particle size of 3-6 μm) was purchased from Tosoh company, Japan.

Table 4.1 Compositions of FCC gasoline (vol.%).

Carbon number	n-paraffins	i-paraffins	olefins	naphthenes	aromatics	Total
C_4	0.215	0.111	1.208	0	0	1.534
C_5	0.996	7.691	6.693	0	0	15.380
C_6	1.102	11.764	7.053	1.631	0.323	21.874
C_7	0.794	7.146	7.246	2.564	2.230	19.980
C_8	1.059	5.953	0.688	2.230	4.608	14.538
C_9	0.391	3.030	1.937	2.827	5.079	14.264
C_{10}	0.257	2.620	0	0.137	5.563	8.577
C_{11}	0.281	0.829	0	0.087	0.766	1.864
C_{12}	0.077	0.446	0	0.205	0.909	1.637
Total	5.072	39.591	24.825	9.681	20.478	99.647

4.2.2 Catalyst modification

Removal of Na^+ from Beta-zeolite

Beta-zeolite was exchanged into H^+ form by dissolving 10 g of Beta-zeolite in 150 ml of 1M NH_4Cl aqueous solution at 80°C for 5 h. The exchanged process was performed for 3 times. After that Beta-zeolite was washed with deionized water for 3 times. The Beta-zeolite was separated by centrifugation and dried at 110°C for 3 h. At this stage, the obtained crystals were in the NH_4^+ form. Then, the sample was calcined at temperature of 550°C under air stream for 6 h to dissociate the ammonium into H^+ form, as NH_3 escapes to the atmosphere and H^+ stays on the catalyst to balance the ionic charge (Assabumrungrat et al. 2002).

Dealumination of Beta-zeolite

Beta-zeolite was dealuminated by following the procedure reported by (Collignon et al. 1997), from which 10 g of Beta-zeolite was dissolved in 200 ml of 0.5 M HNO_3 solution and stirred at 80°C for a desired period. The zeolite was then washed with deionized water for several times and dried at 110°C for 3 h.

Modification by ion exchanging with metal cation

After exchanged Beta-zeolite to H^+ form, HBeta-zeolite was then back exchanged with cations Cu and Mg. The procedure of the back exchange is similar to that reported by Nieminen et al. (2003) and Canizares et al. (2000), in which 10 g of HBeta-zeolite was mixed with 150 ml aqueous solution of 0.1 M copper nitrate or 0.5 M aqueous magnesium chloride at 80 °C. Metal-HBeta-zeolite was then washed with deionized water, dried at 110 °C for 12 h and calcined under air flow at 500 °C for 3 h.

4.2.3 Experimental technique

Etherification of FCC gasoline with ethanol was carried out in a cylindrical shape autoclave reactor with similar procedure as detailed in previous chapter (see section 3.2.3).

4.2.4 Catalyst characterizations

Structural characteristics of the catalysts were investigated by powder X-ray diffraction (XRD) analysis using a Siemens D5000 diffractometer equipped with CuKα radiation and Ni filter. Its surface area and mean pore diameter were determined by N_2 adsorption (BET method) using a BEL-SORP automated system. Chemical analysis was determined by inductive couple plasma (ICP), Varian: liberty 220. Acidity of catalyst was investigated by Micromeritics 2000 TPD/TPR ammonia-temperature programmed desorption (NH_3-TPD).

4.2.5 Product analysis

The standard analysis of research octane number (RON), blending Reid vapor pressure (bRvp) and distillation temperature were carried out following the standard methods of ASTM D-2699, ASTM D-5191 and ASTM D-86, respectively.

4.3 Results and discussion

4.3.1 Catalyst characterization

The surface area and mean pore diameter of the catalysts with Cu and Mg loading and dealumination are illustrated in Table 4.2.

Table 4.2 Properties of catalysts.

Catalysts	**Si/Al [-]**[a]	**Metal content (Cu, Mg) [wt.%]**[a]	**Surface area [m^2g^{-1}]**[b]	**Mean pore diameter [nm]**[b]
$Beta_{27}$	27	-	667	0.59
$Beta_{42}$	42	-	625	0.58
$Beta_{77}$	77	-	563	0.59
$Cu\text{-}Beta_{27}$	27	0.92	550	0.57
$Mg\text{-}Beta_{27}$	27	1.04	535	0.53

[a] Determined by ICP, [b] Determined by BET

It can be seen that the catalyst surface area and mean pore diameter decrease with metal loading. The chemical composition of the catalysts is shown in Table 4.2 in terms of Si/Al molar ratio and metal content (Cu, Mg). Beta-zeolite starting material with Si/Al = 27 was dealuminated to two levels (i.e., Si/Al of 42 and 77) and Cu and Mg were exchanged with H^+ in similar level at approximately 1 wt.%.

Fig. 4.1 shows the XRD patterns of Beta-zeolite with different Si/Al ratios and metal loadings. The spectrum of Beta-zeolite has characteristic peaks similar to those previously reported in the literature (Assabumrungrat et al., 2002). It is noted that these peaks are also observed in all catalyst samples indicating that the incorporation of metal does not change crystalline structure of the modified Beta-zeolite. In addition, no significant peaks of Cu and Mg are observed from the XRD due to low amount of metal loading.

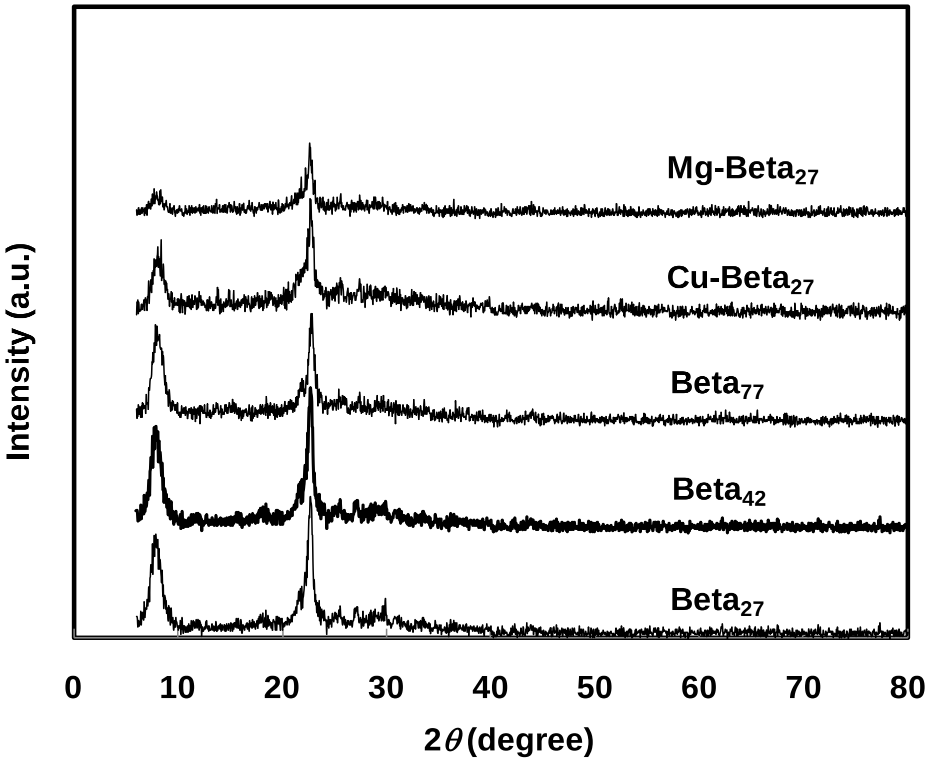


Figure 4.1 XRD patterns of Beta-zeolite catalysts.

4.3.2 Catalyst performance

The catalyst performance for etherification of FCC gasoline with ethanol is presented in terms of ethanol conversion as shown in Fig. 4.2.

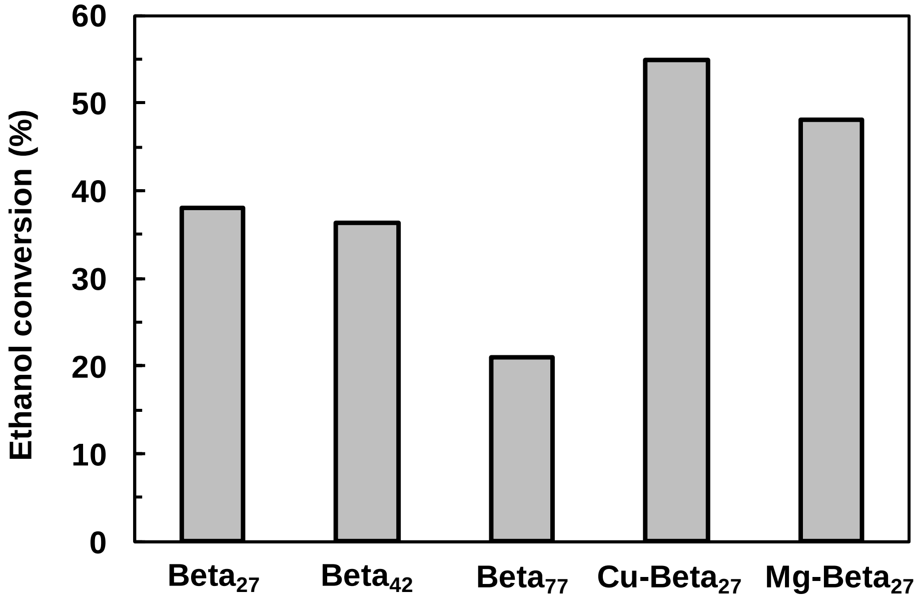


Figure 4.2 Ethanol conversion from etherification with FCC gasoline catalyzed by various Beta-zeolite based catalysts (FCC gasoline:ethanol = 80:20 by volume).

It can be seen that Beta-zeolite with Si/Al of 27 shows a greater activity toward the FCC etherification with ethanol compared to Beta-zeolite with Si/Al of 42 and 77. It is noted that ethanol conversion slightly decreases (from 38.0% to 36.3%) with increasing Si/Al ratio from 27 to 42; however, it drastically decreases (from 38% to 21% when Si/Al ratio is increased to 77. The role of copper and magnesium on the reaction performance was investigated as shown in Fig. 4.2. It was found that the addition of both copper and magnesium into Beta-zeolite with Si/Al ratio of 27 (denoted as Cu-Beta$_{27}$ and Mg-Beta$_{27}$) can significantly enhance the etherification of FCC gasoline with ethanol. The highest ethanol conversion of 55.1% could be obtained with Cu-Beta$_{27}$ catalyst at 20 vol.% ethanol. With increasing ethanol substitution ratio up to 30 vol.%, higher amount of ethanol was converted with a conversion of 49.6% as shown in Table 4.3. The characterization of obtained gasoline products is provided in the next section.

Table 4.3 Comparison of gasoline properties.

Properties	FCC Gasoline	Gasohol E10	20 vol% Ethanol			30 vol% Ethanol		
				Etherified Gasoline			Etherified Gasoline	
			Direct Blend	Beta$_{27}$	Cu-Beta$_{27}$	Direct Blend	Beta$_{27}$	Cu-Beta$_{27}$
RON	88	95	94.8	94.2	94.8	97.9	98.2	98.5
bRvP (psi)	6.5	< 9.0	7.42	5.64	5.22	8.0	6.47	6.08
Density (g cm^{-3})	0.683	0.749	0.735	0.745	0.748	0.735	0.745	0.749
Viscosity (Pa s)	6.09 x 10^{-4}	5.05 x 10^{-4}	6.20 x 10^{-4}	6.19 x 10^{-4}	6.17 x 10^{-4}	6.03 x 10^{-4}	5.09 x 10^{-4}	5.14 x 10^{-4}
Ethanol conversion (%)			0	38.2	55.1	0	40.3	49.6
Olefins reduction (%)			0	46.2	62.4	0	60.1	68.7
Free ethanol left (wt%)		Approx.11%	22.4	13.9	10.1	33.1	19.8	16.7
Ethers conc. (wt%)			0	16.2	22.4	0	22.8	26.2

4.3.3 Characterization of gasoline products

The composition of FCC gasoline (as shown in Table 4.1) illustrates that the main components of olefins are C_5 –C_7 hydrocarbons and about 25 vol.% of olefins are found in gasoline. Table 4.3 presents the gasoline properties, olefins conversion, and ethanol conversion of FCC gasoline for FCC:ethanol initial feed ratios of 80:20 and 70:30, respectively. It can be seen that the original FCC gasoline has RON of 88 and bRvp of 6.5. The RON increases to 94.8 and 97.9 with ethanol direct blending at 20 and 30 vol.%, respectively; however, bRvp increases up to 7.42 and 8.0. An increase of bRvp induces higher evaporative loss and leads to vapor lock which is not favorable especially in summer or in tropical countries. It is worthy to note that recently more restriction on gasoline volatility is enforced i.e. California Reformulated Gasoline Phase 3 (CaRFG3) regulation with the cap limit of bRvp at 6.4-7.2 seasonally (http://www.arb.ca.gov/fuels/gasoline /carfg3/carfg3.htm). As presented in Table 4.3, FCC etherified with ethanol by using either $Beta_{27}$ or Cu-$Beta_{27}$ could effectively decrease the values of bRvp because the olefins in FCC gasoline and ethanol are converted to ethers which have lower bRvp. The main ether product obtained in this study is TAEE, which is similar to the case of etherification of FCC gasoline with methanol as reported by (Rihko and Krause 1996), where TAME is obtained as a main ether product. The concentration of ethers and some free ethanol remaining in the final products are provided in Table 4.3. The less free ethanol left in gasoline indicates higher possibility of using the gasoline in a non-flex fuel engine. The oxygen contents determined from ethanol and ethers left in final product are approximately 6.7-7.0 and 9.6-10.0 wt.% in cases of etherification with 20 and 30vol.% ethanol, respectively. By incorporating copper in $Beta_{27}$ (Cu-$Beta_{27}$), the etherification reaction is enhanced as indicated by an increase of ethanol conversion and olefins reduction. It is worthy to note that from the analysis of the olefin distribution, both the amounts of tertiary olefins and non-reactive branched olefins decreased. This will be discussed in more details in the next paragraph. For other gasoline properties, density and viscosity of the etherified gasoline are found to be close to those of the commercial gasohol. When ethanol is increased to 30 vol.%, similar trend to those of 20 vol.% ethanol is observed for all properties studied.

The results of distillation temperatures carried out following the ASTM D-86 standard method are shown in Fig. 4.3.

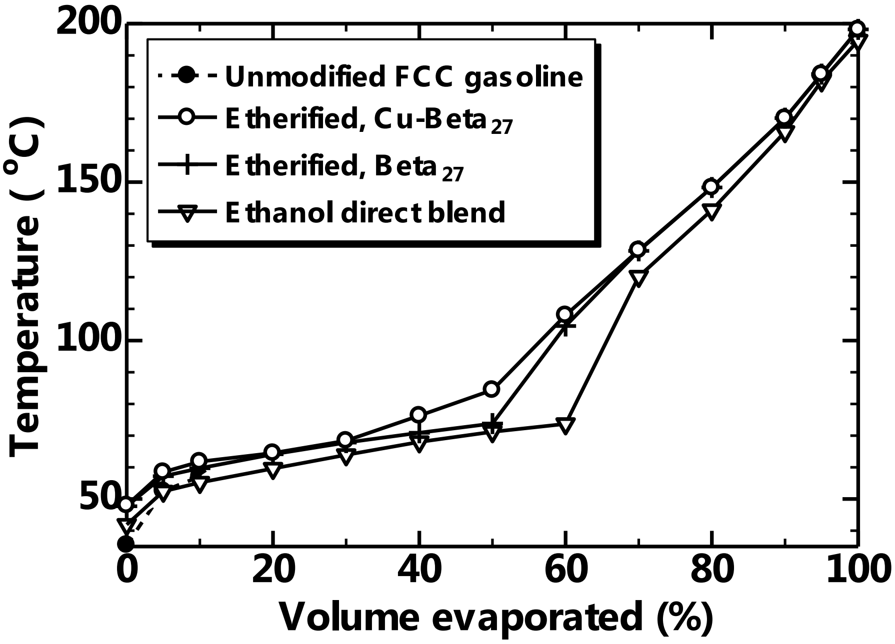


Figure 4.3 Distillation temperatures (following the ASTM D-86 standard method).

The direct blending of ethanol significantly changes the distillation curve compared to that of the original FCC gasoline as the distillation temperature is drastically affected at the temperature of 50-60 evaporated volume (T_{50} and T_{60}). Apart from the initial boiling point (IBP), the distillation temperature of direct blending ethanol decreases throughout the percent volume of evaporated gasoline.

In case of FCC gasoline etherified with ethanol using catalyst either Cu-Beta$_{27}$ or Beta$_{27}$, the gasoline products showed higher values of IBP, T_5, and T_{10} than those of the original FCC gasoline. The higher values of these front end distillation temperatures support the results of lower value of the bRvp, which are in the order of Cu-Beta$_{27}$ < Beta$_{27}$ < original FCC gasoline < ethanol direct blending. The least remaining of ethanol from unconverted in etherified gasoline with Cu-Beta$_{27}$ makes the most similar distillation curve compared to the original FCC gasoline as shown by the closer distillation temperature in the range of $T_{30} – T_{60}$. From the results, we could presume that higher olefin consumption, which are mostly in C_5-C_7 range, might mainly contribute to higher front end distillation temperature while higher ethanol conversion mainly contribute to higher middle range distillation temperature.

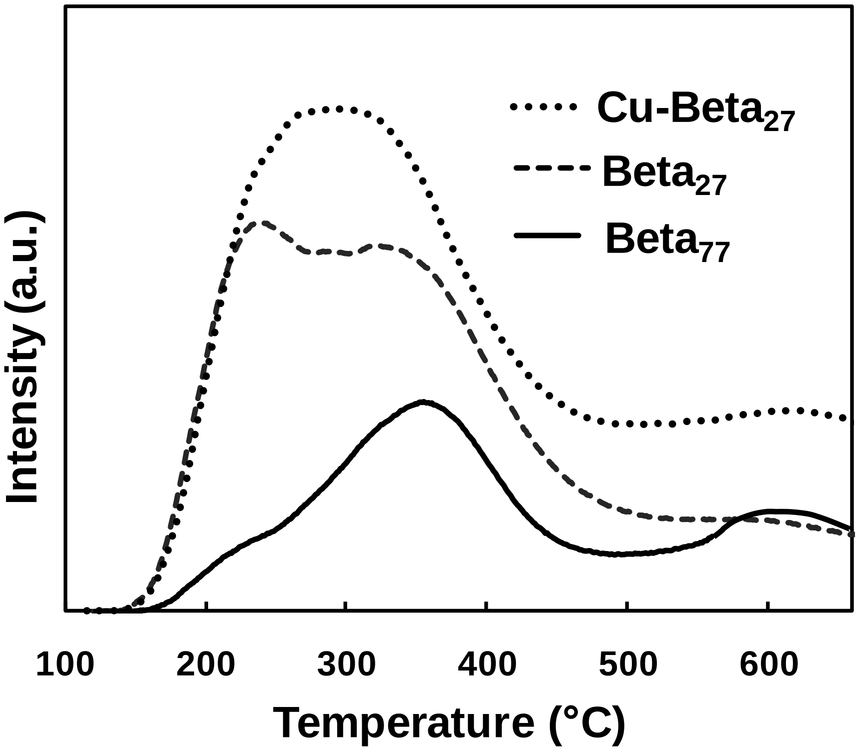


Figure 4.4 NH_3-TPD results of different catalysts.

The NH_3-TPD profiles of Cu-Beta$_{27}$, Beta$_{27}$, and Beta$_{77}$ are shown in Fig. 4.4. Comparing the NH_3-TPD profiles between Beta$_{77}$ and Beta$_{27}$, it can be revealed that the total acidity (determined by total area of the graph) decreases with increasing Si/Al. This manner is as expected since the acid site in zeolite is generally formed on the Si-O-A1 linkage of the zeolite framework. In addition, a decrease of weak acidity is more pronounced compared with the strong acidity. It is worth to note that both the weak and strong acid sites are active for etherification reaction; however weak acid is more stable due to less carbon formation (Kim et al. 2003). The Cu-Beta$_{27}$ catalyst can increase both weak and strong acid sites. It is found that the reaction that requires strong acid (over 400 °C) rather than weak acid is the skeletal isomerization as observed by Woo et al. (1996) and Escalante et al. (1997) for skeletal of n-butene to iso-butene. However, in this study, the major decreased olefins are reactive and non-reactive branched olefins rather than linear olefins. It is known that the reaction involving positional isomerization is faster than skeletal isomerization (Modhera et al. 2009). Stronger acid catalyst and/or higher operating temperature would be needed for skeletal isomerization compared to those for positional or double bond shift isomerization. The increase of olefins conversion could therefore be presumably arisen from isomerization among branched olefin to reactive olefins, which could be further reacted by etherification with ethanol.

4.3.4 Comparison of olefin reduction techniques

Since operating condition among various techniques are different and the amount of olefins in the FCC gasoline feedstock among various studies are varied in a wide range ca. 25-61 vol.% as shown in Table 4.4, therefore, comparison performances of olefin reduction among different techniques might be difficult. As a consequence it is worth to provide the necessary data, such as operating temperature and pressure, catalyst, feed and product composition, to give an overall idea in order to clarify characteristics and advantages of each process.

Table 4.4 Comparison of olefin reduction techniques.

			Olefins (vol%)			**Aromatics (vol%)**			**RON**		
Reaction	**References**	**Catalyst, operating *T* and *P***	**initial**	**final**	**change (%)**	**initial**	**final**	**change (%)**	**initial**	**final**	**change**
Hydroisomerization	Fan et al. (2005a)	β/ZSM-5 composite, 315°C, 2.0 MPa	41.1	9.9	-75.9	17.4	29.3	+68.4	91.7	92.1	+0.4
	Fan et al. (2005b)	SAPO-11/MOR/β/ZSM, 300°C, 2.0 MPa	41.7	6.3	-84.9	17.1	21.4	+25.1	91.7	86.3	-5.4
Non-hydrogenation	Zubin et al. (2007)	BPyC-AlCl$_3$ ionic liquid[1], 25°C, N.A.[2]	42.5	28.0	-34.1	15.7	18.1	+15.3	91.3	90.5	-0.8
	Ding et al. (2007)	kaolin/γ-Al$_2$O$_3$/ZSM-5, 400°C, 0.1 MPa	43.5	18.7[3]	-56.8	14.4	33.7[3]	+134.0	92.1	~92[4]	~0[4]
	Li et al. (2007)	Ni/W/SiO$_2$.Al$_2$O$_3$, 170°C, 2.5 MPa	51.0	25.6	-49.8	19.1	37.1	+94.2	88.6	89.1	+0.5
	Lihua and Jinshen (2008)	Ni,Mo/β-zeolite, 140°C, 2.0 MPa	60.9	33.0	-45.8	12.2	29.1	+138.5	92.0	95.0	+3.0
Etherification with ethanol	Kiatkittipong et al. (2008)	β-zeolite (Si/Al=40), 70°C, 0.8 MPa	25.7	13.9	-45.9	17.0	16.9	-0.6	88.0	94.1	+6.1
20 vol% (This study)	Kiatkittipong et al. (2011)	Cu-β-zeolite (Si/Al=27), 70°C, 0.8 MPa	24.8	9.3	-62.4	20.5	20.7	+1.0	88.0	94.8	+6.8

[1] BPyC = 1-butylpyrinium chloride

[2] N.A. = not available

[3] Determined from Fig. 2 of Ding et al. (2007) with optimal kaolin/γ-Al$_2$O$_3$ ratio of 1.5

[4] Ding et al. (2007) reported preserving of gasoline RON

The ability of etherification with ethanol for reducing olefins in FCC gasoline is compared with current techniques of hydroisomerization and non-hydrogenation as summarized in Table 4.4. It can be seen that hydroisomerization, which is usually accompanied with aromatization, can diminish the olefins at the highest extent (84.9% of olefins reduction). However, the process would suffer from the loss of RON if compensation by an increase of aromatics compound is not enough.

Non-hydrogenation was proposed instead of hydroisomerization in case when low-cost hydrogen is unavailable. However, as presented in Table 4.4, non-hydrogenation shows much lower degree of olefin reduction than that of hydroisomerization process. In addition, the RON obtained from hydroisomerization or non-hydrogenation strongly depends upon the degree of olefins reduction and aromatization. Therefore, to compromise the olefins and aromatic content under the restriction limit (18 vol.% for olefins and 35 vol.% for aromatics) it is necessary to consider the RON value preserved in the gasoline as well.

From the study, it is summarized that etherification with ethanol shows an intermediate performance between hydroisomerization and non-hydrogenation process as indicated by reduction of olefin. Moreover, the change of aromatic compounds can be negligible. It is worth to note that the change in vol.% of olefin and aromatic compounds in case of etherification shown here was calculated by excluding from the dilution effect of ethanol substitution. In addition, the process shows the improvement of RON which is obtained from generated ether compounds and unreacted ethanol remaining in the gasoline. Therefore we could claim here that self-etherification of FCC gasoline with ethanol catalyzed by Cu-Beta$_{27}$ catalyst is one of promising processes for reducing olefins with effective increasing RON and renewability of the gasoline.

4.4 Summary

The etherification of FCC gasoline with ethanol is a promising technology for gasoline upgrading by efficient reduction of olefin content accompanying with quality improvement. The Beta-zeolite with Si/Al of 27 modified by ion-exchanged with Cu shows an outstanding performance; it provides high ethanol conversion and olefin consumption e.g. 55.1 and 62.4%, respectively, in case of 20% ethanol in feed. By increasing the ethanol fraction in feed up to 30 vol.%, the reaction could be further enhanced. Higher ethanol conversion means ethanol could be higher supplemented into gasoline and less free ethanol remaining. Lower ethanol left in gasoline results in lower blending Reid vapor pressure (bRvp). Comparison to other techniques for reducing olefin content in FCC gasoline, etherification with ethanol catalyzed by Cu-Beta catalyst provides intermediate values of olefin reduction between the hydroisomerization and non-hydrogenation process. However, our proposed technique could effectively improve RON without an increase of aromatic content.

CHAPTER 5

Conclusion and Recommendation

5.1 Conclusion

A novel process for fuel oil quality improvement by replacing with renewable resource including ethanol and glycerol derivative were explored in this study. Self-etherification reaction is proposed as an alternative way for upgrading FCC gasoline, which is the main contribution of olefins when it is blended with gasoline pool.

Self-etherified FCC gasolines with ethanol are beneficial over typical olefin reduction process i.e. hydroisomerization and aromatization in term of RON improvement without an increase of aromatic content. Moreover, the self-etherification process overcomes the drawbacks of gasoline with direct ethanol blend (so called "gasohol"). FCC etherification with ethanol gave a higher potential for utilization of ethanol as a fuel extender than direct blending for conventional engine which was limited at some ethanol contents, i.e. 10-20 vol.% (E10-E20). With broad range of ethers production, RON increased comparably to FCC with direct ethanol blend while bRvp was effectively lower. Comparing between two catalysts used, Beta-zeolite was a more suitable catalyst than Amberlyst 16 because it offered products with higher RON and higher ethanol conversion. Beta-zeolite with Si/Al ratio of 27 shows greater activity toward the FCC etherification with ethanol compared to Beta-zeolite with Si/Al of 42 and 77. The Beta-zeolite with Si/Al of 27 modified by ion-exchanged with Cu (Cu-Beta$_{27}$) shows an outstanding performance; it provides high ethanol conversion and olefin consumption of 55.1 and 62.4%, respectively, in case of 20% ethanol in feed. With increasing ethanol substitution ratio up to 30 vol.%, higher amount of ethanol was converted with a conversion of 49.6% and therefore the amounts of remaining olefinic compounds are only 7 vol.% which are much lower than a limiting value regulated by Euro 4 standard at 18 vol.%. Higher ethanol conversion means ethanol could be higher supplemented into gasoline thus higher renewability and less free ethanol remaining. Etherified FCC gasoline with ethanol catalyzed by Cu-Beta$_{27}$ showed significant improvement of RON opposing with a decreased of bRvp which are preference properties. The RON of original FCC gasoline, FCC with direct ethanol blend, and etherified gasoline are 88.0, 97.5 and 98.5 while bRvp are 6.5, 8.0 and 6.1 psi, respectively

The possibility of using self-etherification of FCC gasoline for gasoline quality improvement and increasing renewability was broaden by using glycerol, a by-product of biodiesel production, as fuel extender. In the case of self-etherification with glycerol, Amberlyst 16 gave significantly higher catalytic activity than Beta-zeolite which opposed to the case of ethanol. This implies that glycerol, which is larger, has more branched and more OH groups than ethanol, requires large pore catalyst for the reactants to enter the pores and in turn for desorption of larger molecules of etherification products. Unlike ethanol, free glycerol could not be left in the gasoline. Complete conversion of glycerol can be obtained with reaction system containing 84 cm^3 of FCC gasoline, 16 cm^3 of glycerol and 10 g of catalyst carried out at 70 °C for 10 h. The etherified FCC gasoline with glycerol showed higher RON (90.1) and lower bRvp (4.5) than original FCC gasoline. The distillation temperature of etherified FCC gasoline increased in all volume percents evaporated with similar shape to original FCC gasoline.

5.2 Recommendation

It is recommended that additional works such as development of an industrial-scale process for the self-etherification reaction and studies of the process economics should be further investigated.

For the industrial-scale application, the experiment on continuous operation in pilot scale is necessary. A Cu-Beta$_{27}$ catalyst would be packed in a column. The plot of reaction performance with time on stream should be investigated.

For the process economic point of view, when comparing to direct ethanol blending (gasohol), of course, the self-etherification with ethanol might seem to be inferior due to it requires a further step of the reaction, which therefore resulting in an increase of a direct capital and operating cost. However, an indirect cost e.g. social and health impact is also needed to be considered as our process gives a green fuel. From this study, it was proven that self-etherification process can enhance the use of ethanol in gasoline in the derived form of ethers with higher quality (i.e. lower olefins content and bRvp than that of gasohol and original gasoline). Firstly, considering in term of fuel quality, not only the emission at end pipe, is the evaporative emission also lower. As known that gasohol which has high blending vapor pressure can cause higher evaporative emission. This emission can become dominate the total emission. As such, the direct cost of evaporative fuel loss and indirect cost of end pipe and evaporative emission on human health and ecological system affected from using gasohol should be also taken into account for comparison reason. Secondly, our process shows an increase in the renewability of ethanol use for gasoline substitution over gasohol. The obvious benefits are such as 1) decrease of fossil fuel used and hence gaining carbon credit 2) decrease crude oil import leading to higher energy security and lower trade deficit and 3) increase occupational in the agricultural sector.

In the case of self-etherification with glycerolthe price of glycerol will be anticipated much lower than ethanol in the near future due to drastically demand of biodiesel production. As a consequence, using glycerol instead of ethanol could become more economical. However, testing with real system is required in case of glycerol ethers due to currently a few researches have been done.

References

Agarwal, A.K. 2007. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Progress in Energy and Combustion Science, **33**: 233-271.

Ancillotti, F., Mauri, M.M., and Pescarollo, E. 1977. Ion exchange resin catalyzed addition of alcohols to olefins. Journal of Catalysis, **46**: 49-57.

Aronov, D.M., and Noreiko, L.M. 1967. Basic requirements for automotive gasoline quality. Chemistry and Technology of Fuels and Oils, **3**: 359-362.

Assabumrungrat, S., Kiatkittipong, W., Praserthdam, P., and Goto, S. 2003. Simulation of pervaporation membrane reactors for liquid phase synthesis of ethyl tert-butyl ether from tert-butyl alcohol and ethanol. Catalysis Today, **79-80**: 249-257.

Assabumrungrat, S., Kiatkittipong, W., Sevitoon, N., Praserthdam, P., and Goto, S. 2002. Kinetics of liquid phase synthesis of ethyl tert-butyl ether from tert-butyl alcohol and ethanol catalyzed by β-zeolite supported on monolith. International Journal of Chemical Kinetics, **34**: 292-299.

Baeck, S.H., and Lee, W.Y. 1998. Dealumination of Mg-ZSM-22 and its use in the skeletal isomerization of 1-butene to isobutene. Applied Catalysis A: General, **168**: 171-177.

Balcerowiak, W. 1997. Speciation analysis of sulfonic groups of cation exchanger using thermogravimetry. Reactive and Functional Polymers, **33**: 323-327.

Boonthamtirawuti, O., Kiatkittipong, W., Arpornwichanop, A., Praserthdam, P., and Assabumrungrat, S. 2009. Kinetics of liquid phase synthesis of tert-amyl ethyl ether from tert-amyl alcohol and ethanol over Amberlyst 16. Journal of Industrial and Engineering Chemistry, **15**: 451-457.

Boz, N., Dogu, T., Murtezaoglu, K., and Dogu, G. 2004. Effect of hydrogen ion-exchange capacity on activity of resin catalysts in tert-amyl-ethyl-ether synthesis. Applied Catalysis A: General, **268**: 175-182.

Caetano, N.S., Loureiro, J.M., and Rodrigues, A.E. 1994. MTBE synthesis catalysed by acid ion exchange resins: Kinetic studies and modeling of multiphase batch reactors. Chemical Engineering Science, **49**: 4589-4604.

Canizares, P. and Carrero, A. 2000. Comparative study of the catalytic properties of ferrierite zeolite exchanged with alkaline earth metals in the skeletal isomerization of n-butene. Catalysis Letters, **64**: 239–246

Collignon, F., Mariani, M., Moreno, S., Remy, M., and Poncelet, G. 1997. Gas phase synthesis of MTBE from methanol and isobutene over dealuminated zeolites. Journal of Catalysis, **166**: 53-66.

Colombo, F., Corl, L., Dalloro, L., and Delogu, P. 1983. Equilibrium constant for the methyl tert-butyl ether liquid-phase synthesis by use of UNIFAC. Industrial and Engineering Chemistry Fundamentals, **22**: 219-223.

Corma, A., Gonzalez-Alfaro, V., and Orchilles, A.V. 1999. The role of pore topology on the behaviour of FCC zeolite additives. Applied Catalysis A: General, **187**: 245-254.

Cruz, V.J., Izquierdo, J.F., Cunill, F., Tejero, J., Iborra, M., and Fitรฉ, C. 2005. Acid ion-exchange resins catalysts for the liquid-phase dimerization/etherification of isoamylenes in methanol or ethanol presence. Reactive and Functional Polymers, **65**: 149-160.

Dasari, M.A., Kiatsimkul, P.P., Sutterlin, W.R., and Suppes, G.J. 2005. Low-pressure hydrogenolysis of glycerol to propylene glycol. Applied Catalysis A: General, **281**: 225-231.

de Menezes, E.W., and Cataluna, R. 2008. Optimization of the ETBE (ethyl tert-butyl ether) production process. Fuel Processing Technology, **89**: 1148-1152.

Demirbas, A. 2007. Progress and recent trends in biofuels. Progress in Energy and Combustion Science, **33**: 1-18.

Ding, Y., Liang, J., Fan, Y., Wang, Y., and Bao, X. 2007. Synergisms between matrices and ZSM-5 in FCC gasoline non-hydrogenating upgrading catalysts. Catalysis Today, **125**: 178-184.

Dirk-Faitakis, C.B., and Chuang, K.T. 2004. Simulation Studies of Catalytic Distillation for Removal of Water from Ethanol Using a Rate-Based Kinetic Model. Industrial and Engineering Chemistry Research, **43**: 762-768.

Dogu, T., Aydin, E., Boz, N., Murtezaoglu, K., and Dogu, G. 2003. Diffusion Resistances and Contribution of Surface Diffusion in TAME and TAEE Production Using Amberlyst-15. International Journal of Chemical and Reaction Engineering, **1**: ArticleA6

Duarte, C., and Loureiro, J.M. 2004. Effect of adsorption on residue curve maps for heterogeneous catalytic distillation systems. Industrial and Engineering Chemistry Research, **43**: 3242-3250.

Escalante, D., Mendez, B., Hernandez, G., Lopez, C.M., Machado, F.J., Goldwasser, J., and De Ramรญrez Agudelo, M.M. 1997. The skeletal isomerization of 1-butene over Zn-silicoaluminophosphate molecular sieves. Catal. Lett., **47**: 229-233.

Fan, Y., Bao, X., and Shi, G. 2005a. Hβ/HZSM-5 composite carrier supported catalysts for olefins reduction of FCC gasoline via hydroisomerization and aromatization. Catal. Lett., **105**: 67-75.

Fan, Y., Bao, X., Lei, D., Shi, G., Wei, W., and Xu, J. 2005b. A novel catalyst system based on quadruple silicoaluminophosphate and aluminosilicate zeolites for FCC gasoline upgrading. Fuel, **84**: 435-442.

Fan, Y., Bao, X., Shi, G., Wei, W., and Xu, J. 2004. Olefin reduction of FCC gasoline via hydroisomerization aromatization over modified HMOR/HZSM-5/Hβ composite carriers. Applied Catalysis A: General, **275**: 61-71.

Ferreira, M.V., and Loureiro, J.M. 2004. Number of actives sites in TAME synthesis: Mechanism and kinetic modeling. Industrial and Engineering Chemistry Research, **43**: 5156-5165.

Ferreira, M.V., Ribeiro, A.M., and Loureiro, J.M. 2007. Experimental and simulation studies of TAME synthesis in a fixed-bed reactor. Industrial and Engineering Chemistry Research, **46**: 1105-1113.

Fite, C., Iborra, M., Tejero, J., Izquierdo, J.F., and Cunill, F. 1994. Kinetics of the liquid-phase synthesis of ethyl tert-butyl ether (ETBE). Industrial and Engineering Chemistry Research, **33**: 581-591.

Francoisse, O., and Thyrion, F.C. 1991. Kinetics and mechanism of ethyl tert-butyl ether liquid-phase synthesis. Chemical Engineering and Processing, **30**: 141-149.

French, R., and Malone, P. 2005. Phase equilibria of ethanol fuel blends. Fluid Phase Equilibria, **228-229**: 27-40.

Gicquel, A., and Torck, B. 1983. Synthesis of methyl tertiary butyl ether catalyzed by ion-exchange resin. Influence of methanol concentration and temperature. Journal of Catalysis, **83**: 9-18.

Gomez, C., Cunill, F., Iborra, M., Izquierdo, F. and Tejero, J. 1997. Experimental Study of the Simultaneous Synthesis of Methyl tert-Butyl Ether and Ethyl tert-Butyl Ether in Liquid Phase. Industrial and Engineering Chemistry Research, **36**: 4756-4762.

Gupta, V.P. 1995. Glycerine ditertiary butyl ether preparation, ARCO Chemical Technology, L.P.

Harmer, M.A., and Sun, Q. 2001. Solid acid catalysis using ion-exchange resins. Applied Catalysis A: General, **221**: 45-62.

Hu, T., Chen, J., Wang, H., Ma, J., and Wei, M. 2006. Influence of shaped and modified Hβ zeolite on etherification of FCC light gasoline. Microporous and Mesoporous Materials, **94**: 283-287.

Izquierdo, J.F., Cunill, F., Vila, M., Tejero, J., and Iborra, M. 1992. Equilibrium constants for methyl tert-butyl ether liquid-phase synthesis. Journal of Chemical and Engineering Data, **37**: 339-343.

Jensen, K.L., and Datta, R. 1995. Ethers from ethanol. 1. Equilibrium thermodynamic analysis of the liquid-phase ethyl tert-butyl ether reaction. Industrial and Engineering Chemistry Research, **34**: 392-399.

Johnson, D.T., and Taconi, K.A. 2007. The glycerin glut: Options for the value-added conversion of crude glycerol resulting from biodiesel production. Environmental Progress, **26**: 338-348.

Karinen, R.S., and Krause, A.O.I. 2000. A novel tertiary ether. Synthesis of 3-methoxy-3-methylheptane from 2-ethyl-1-hexene and methanol. Catal. Lett., **67**: 73-79.

Karinen, R.S., and Krause, A.O.I. 2001. Kinetic model for the etherification of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene with methanol. Industrial and Engineering Chemistry Research, **40**: 6073-6080.

Karinen, R.S., and Krause, A.O.I. 2006. New biocomponents from glycerol. Applied Catalysis A: General, **306**: 128-133.

Karinen, R.S., Linnekoski, J.A., and Krause, A.O.I. 2001. Etherification of C5- and C8-alkenes with C1-to C4-alcohols. Catalysis Letters, **76**: 81-87.

Katsobashvili, Y.R., Golosov, S.A., and Sheftelevich, Y.L. 1967. Effect of fractional composition and residual content of aromatic hydrocarbons on the stability of fuels. Chemistry and Technology of Fuels and Oils, **3**: 234-236.

Kesling, H.S., Karas, L.J., and Liotta, F.J. 1994. Diesel fuel, ARCO Chemical Technology, L.P.

Kiatkittipong, W., Assabumrungrat, S., Praserthdam, P., and Goto, S. 2002. A pervaporation membrane reactor for liquid phase synthesis of ethyl tert-butyl ether from tert-butyl alcohol and ethanol. Journal of Chemical Engineering of Japan, **35**: 547-556.

Kiatkittipong, W., Thipsunet, P., Goto, S., Chaisuk, C., Praserthdam, P., and Assabumrungrat, S. 2008. Simultaneous enhancement of ethanol supplement in gasoline and its quality improvement. Fuel Processing Technology, **89**: 1365-1370.

Kiatkittipong, W., Yoothongkham, K., Chaisuk, C., Praserthdam, P., Goto, S., and Assabumrungrat, S. 2009. Self-etherification process for cleaner fuel production. Catalysis Letters, **128**: 154-163.

Kiatkittipong, W., Suwanmanee, S., Laosiripojana, N., Praserthdam, P., Assabumrungrat, S. 2010. Cleaner gasoline production by using glycerol as fuel extender. Fuel Processing Technology, **91**: 456-460

Kiatkittipong, W., Wongsakulphasatch, S., Tintan, N., Laosiripojana, N., Praserthdam, P., Assabumrungrat, S. 2011. Gasoline upgrading by self-etherification with ethanol on modified beta-zeolite. Fuel Processing Technology, **92**: 1999-2004

Kim, J.W., Kim, D.J., Han, J.U., Kang, M., Kim, J.M., and Yie, J.E. 2003. Preparation and characterization of zeolite catalysts for etherification reaction. Catalysis Today, **87**: 195-203.

Kitchaiya, P., and Datta, R. 1995. Ethers from ethanol. 2. Reaction equilibria of simultaneous tert-amyl ethyl ether synthesis and isoamylene isomerization. Industrial and Engineering Chemistry Research, **34**: 1092-1101.

Kiviranta-Paakkonen, P., Struckmann, L.K., Linnekoski, J.A., and Krause, A.O.I. 1998. Dehydration of the Alcohol in the Etherification of Isoamylenes with Methanol and Ethanol. Industrial and Engineering Chemistry Research, **37**: 18-24.

Kiviranta-Paakkonen, P.K., Struckmann nee Rihko, L.K., Linnekoski, J.A., and Krause, A.O.I. 1998. Dehydration of the Alcohol in the Etherification of Isoamylenes with Methanol and Ethanol. Industrial and Engineering Chemistry Research, **37**: 18-24.

Klepacova, K., Mravec, D., and Bajus, M. 2005. Tert-Butylation of glycerol catalysed by ion-exchange resins. Applied Catalysis A: General, **294**: 141-147.

Klepacova, K., Mravec, D., and Bajus, M. 2006. Etherification of glycerol with tert-butyl alcohol catalysed by ion-exchange resins. Chemical Papers, **60**: 224-230.

Klepacova, K., Mravec, D., Kaszonyi, A., and Bajus, M. 2007. Etherification of glycerol and ethylene glycol by isobutylene. Applied Catalysis A: General, **328**: 1-13.

Li, L., Zhai, Y., Zhang, J., Wang, J., and Yu, T. 2007. A new catalyst for the non-hydrogenation reduction of olefins. Petroleum Science and Technology, **25**: 427-441.

Lihua, L., and Jinshen, Z. 2008. Olefin reduction of FCC naphtha using -zeolite catalyst in the absence of hydrogen. Petroleum Science and Technology, **26**: 144-152.

Linnekoski, J.A., Krause, A.O., and Rihko, L.K. 1997. Kinetics of the Heterogeneously Catalyzed Formation of tert-Amyl Ethyl Ether. Industrial and Engineering Chemistry Research, **36**: 310-316.

Linnekoski, J.A., Krause, A.O.I., and Struckmann, L.K. 1998. Etherification and hydration of isoamylenes with ion exchange resin. Applied Catalysis A: General, **170**: 117-126.

Lippa, A.J. 2006. Software fuel volatility measurement. Software Fuel Volatility Measurement.

Magyar, S., Hancsok, J., and Kallo, D. 2005. Hydrodesulfurization and hydroconversion of heavy FCC gasoline on PtPd/H-USY zeolite. Fuel Processing Technology, **86**: 1151-1164.

Melero, J.A., Vicente, G., Morales, G., Paniagua, M., Moreno, J.M., Roldan, R., Ezquerro, A., and Perez, C. 2008. Acid-catalyzed etherification of bio-glycerol and isobutylene over sulfonic mesostructured silicas. Applied Catalysis A: General, **346**: 44-51.

Modhera, B., Chakraborty, M., Parikh, P.A., and Bajaj, H.C. 2009. 1-hexene isomerization over nano-crystalline zeolite Beta: Effects of metal and carrier gases on catalytic performance. Catal. Lett., **132**: 168-173.

Nieminen, V., Kumar, N., Datka, J., Paivarinta, J., Hotokka, M., Laine, E., Salmi, T., and Murzin, D.Y. 2003. Active copper species in 1-butene skeletal isomerization: Comparison between copper-modified MCM-41 and Beta catalysts. Microporous and Mesoporous Materials, **60**: 159-171.

Niu, X., Song, Y., Xie, S., Liu, S., Wang, Q., and Xu, L. 2005. Synthesis and catalytic reactivity of MCM-22/ZSM-35 composites for olefin aromatization. Catal. Lett., **103**: 211-218.

Niven, R.K. 2005. Ethanol in gasoline: Environmental impacts and sustainability review article. Renewable and Sustainable Energy Reviews, **9**: 535-555.

Noureddini, H. 2000. Process for producing biodiesel fuel with reduced viscosity and a cloud point below 32 °F, Board of Regents of the University of Nebraska.

Oktar, N., Murtezaoglu, K., Dogu, G., Gonderten, I., and Dogu, T. 1999. Etherification rates of 2-methyl-2-butene and 2-methyl-1-butene with ethanol for environmentally clean gasoline production. Journal of Chemical Technology and Biotechnology, **74**: 155-161.

Perry, R., and Gee, I.L. 1995. Vehicle emissions in relation to fuel composition. Science of the Total Environment, **169**: 149-156.

Pescarollo, E., Trotta, R., and Sarathy, P.R. 1993. Etherify light gasolines. Hydrocarbon Processing, **72**: 53-56.

Pimentel, D. 1991. Ethanol fuels: Energy security, economics, and the environment. Journal of Agricultural and Environmental Ethics, **4**: 1-13.

Prior, J.M.V., and Loureiro, J.M. 2001. Residual thermodynamic properties in reactor modeling. Chemical Engineering Science, **56**: 873-879.

Ren, Y.J., and Li, S. 2008. The effect of lanthanum and niobium on additives for olefins reduction of FCC gasoline. Catalysis Letters, **121**: 85-89.

Richter, M., Krisnandi, Y.K., Eckelt, R., and Martin, A. 2008. Homogeneously catalyzed batch reactor glycerol etherification by CsHCO3. Catalysis Communications, **9**: 2112-2116.

Rihko, L.K., and Krause, A.O.I. 1993. Reactivity of isoamylenes with ethanol. Applied Catalysis A, General, **101**: 283-295.

Rihko, L.K., and Krause, A.O.I. 1996. Etherification of FCC light gasoline with methanol. Industrial and Engineering Chemistry Research, **35**: 2500-2507.

Rihko, L.K., Linnekoski, J.A., and Krause, A.O.I. 1994. Reaction equilibria in the synthesis of 2-methoxy-2-methylbutane and 2-ethoxy-2-methylbutane in the liquid phase. Journal of Chemical and Engineering Data, **39**: 700-704.

Słomkiewicz, P.M. 1997. Isomerization of C-4 alkenes catalysed by macroporous ion exchange resin. Reactive and Functional Polymers **33**: 299-304.

Sow, B., Hamoudi, S., Hassan Zahedi-Niaki, M., and Kaliaguine, S. 2005. 1-butanol etherification over sulfonated mesostructured silica and organo-silica. Microporous and Mesoporous Materials, **79**: 129-136.

Szklo, A., Schaeffer, R., and Delgado, F. 2007. Can one say ethanol is a real threat to gasoline? Energy Policy, **35**: 5411-5421.

Umar, M., Patel, D., and Saha, B. 2009. Kinetic studies of liquid phase ethyl tert-butyl ether (ETBE) synthesis using macroporous and gelular ion exchange resin catalysts. Chemical Engineering Science, **64**: 4424-4432.

Umar, M., Saleemi, A.R., and Qaiser, S. 2008. Synthesis of ethyl tert-butyl ether with tert-butyl alcohol and ethanol on various ion exchange resin catalysts. Catalysis Communications, **9**: 721-727.

Vila, M., Cunill, F., Izquierdo, J.-F., Tejero, J., and Borra, M. 1993. Equilibrium constants for ethyl tert-butyl ether liquid-phase synthesis. Chemical Engineering Communications, **124**: 223-232.

Vlasenko, N.V., Kochkin, Y.N., and Puziy, A.M. 2006. Liquid phase synthesis of ethyl-tert-butyl ether: The relationship between acid, adsorption and catalytic properties of zeolite catalysts. Journal of Molecular Catalysis A: Chemical, **253**: 192-197.

Wang, M., Saricks, C., and Wu, M. 1997. Fuel-Cycle Fossil Energy Use and Greenhouse Gas Emissions of Fuel Ethanol Produced from U.S. Midwest Corn.

Wang, M., Wu, M., and Huo, H. 2007. Life-cycle energy and greenhouse gas emission impacts of different corn ethanol plant types. Environmental Research Letters, **2**: 024001.

Wessendorf, R. 1995. Glycerinderivate als Kraftstoffkomponenten. Erdoel & Kohle, Erdgas, Petrochemie, **48**: 138-143.

Woo, H.C., Lee, K.H., and Lee, J.S. 1996. Catalytic skeletal isomerization of n-butenes to isobutene over natural clinoptilolite zeolite. Applied Catalysis A: General, **134**: 147-158.

Wu, M., Wu, Y., and Wang, M. 2006. Energy and emission benefits of alternative transportation liquid fuels derived from switchgrass: A fuel life cycle assessment. Biotechnology Progress, **22**: 1012-1024.

Zhang, P., Guo, X., Guo, H., and Wang, X. 2007. Study of the performance of modified nano-scale ZSM-5 zeolite on olefins reduction in FCC gasoline. Journal of Molecular Catalysis A: Chemical, **261**: 139-146.

Zhang, T., and Datta, R. 1995a. Ethers from ethanol. 3. Equilibrium conversion and selectivity limitations in the liquid-phase synthesis of two tert-hexyl ethyl ethers. Industrial and Engineering Chemistry Research, **34**: 2237-2246.

Zhang, T., and Datta, R. 1995b. Ethers from ethanol. 4. Kinetics of the liquid-phase synthesis of two tert-hexyl ethyl ethers. Industrial and Engineering Chemistry Research, **34**: 2247-2257.

Zhang, T., and Datta, R. 1996. Ethers from ethanol - 5. Equilibria and kinetics of the coupled reaction network of liquid-phase 3-methyl-3-ethoxy-pentane synthesis. Chemical Engineering Science, **51**: 649-661.

Zhang, T., Jensen, K., Kitchaiya, P., Phillips, C., and Datta, R. 1997. Liquid-Phase Synthesis of Ethanol-Derived Mixed Tertiary Alkyl Ethyl Ethers in an Isothermal Integral

Packed-Bed Reactor. Industrial and Engineering Chemistry Research, **36**: 4586-4594.

Zholobenko, V., Garforth, A., Dwyer, J. 1997. TGA-DTA study on calcination of zeolitic catalysts. Thermochimica Acta **294**: 39-44

Zhou, C.H., Beltramini, J.N., Fan, Y.X., and Lu, G.Q. 2008. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. Chemical Society Reviews, **37**: 527-549.

APPENDIX

LIST OF PUBLICATIONS

Journal publications:

1) Worapon Kiatkittipong*, Piyaporn Thipsunet, Shigeo Goto, Choowong Chaisuk, Piyasan Praserthdam and Suttichai Assabumrungrat. 2008. Simultaneous enhancement of ethanol supplement in gasoline and its quality improvement. Fuel Processing Technology, 89: 1365-1370. (Impact factor 2010 = 2.781)
2) Worapon Kiatkittipong*, Khamron Yoothongkham, Choowong Chaisuk, Piyasan Praserthdam, Shigeo Goto and Suttichai Assabumrungrat. 2009. Self-etherification process for cleaner fuel production. Catalysis Letters, 128: 154-163. (Impact factor 2010 = 1.907)
3) Worapon Kiatkittipong*, Suwimol Wongsakulphasatch, Nattapon Tintan, Navadol Laosiripojana, Piyasan Praserthdam and Suttichai Assabumrungrat. 2011. Gasoline upgrading by self-etherification with ethanol on modified beta-zeolite. Fuel Processing Technology, 92: 1999-2004 (Impact factor 2010 = 2.781)

FUEL PROCESSING TECHNOLOGY 89 (2008) 1365–1370

available at www.sciencedirect.com

www.elsevier.com/locate/fuproc

Simultaneous enhancement of ethanol supplement in gasoline and its quality improvement

Worapon Kiatkittipong[a,*], *Piyaporn Thipsunet*[b], *Shigeo Goto*[c], *Choowong Chaisuk*[a], *Piyasan Praserthdam*[b], *Suttichai Assabumrungrat*[b]

[a]*Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand*
[b]*Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand*
[c]*Department of Chemical Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan*

ARTICLE INFO

Article history:
Received 19 November 2007
Received in revised form 8 June 2008
Accepted 24 June 2008

Keywords:
Fuel
FCC gasoline
Ethanol
Etherification
Octane number
Blending Reid vapor pressure

ABSTRACT

Ethanol and ethanol derivatives are attractive renewable energy resources nowadays. Even though ethanol can be blended directly into gasoline (called "gasohol"), many recent researches have reported disadvantages of gasohol. Apart from immiscibility and corrosion problems, overall air pollutant emissions from the use of gasohol are usually higher than those from the use of conventional gasoline because of its higher blending Reid vapor pressure (bRvp). Ethers derived from ethanol may overcome these drawbacks. Direct etherification of FCC gasoline with ethanol was investigated in this work. The reactions were carried out in a pressurized liquid phase reactor at 0.8 MPa and catalyzed by two commercial catalysts, i.e., β-zeolite and Amberlyst 16. The bRvp of etherified FCC gasoline was found to be lower than that of gasohol (20 vol.% ethanol), indicating that the gasoline from this process is more suitable than gasohol especially for the tropical zone or in summer. The decrease of bRvp was due to the consumptions of both ethanol and olefins. In case of β-zeolite catalyst, ethanol conversion was 36.3% while olefins content was decreased from 25.7 to 13.9 vol.%. However, as expected, etherified FCC gasoline gave slightly lower RON than gasohol. It was found that β-zeolite was a more suitable catalyst than Amberlyst 16 for the etherification of FCC gasoline with ethanol because it offered products with higher RON and higher ethanol conversion.

1. Introduction

Recent environmental regulations have resulted in significant changes in the formulation of transportation fuels. An oxygenated compound is a key component to be added to gasoline for pollution reduction and improvement of combustion efficiency, thereby reducing CO content and hydrocarbon emissions from exhaust pipe. Consequently, the use of oxygenated compounds has increased rapidly.

Oxygenated compounds can be divided into two groups: 1) alcohols, e.g. methanol and ethanol, and 2) alcohol derivatives like ethers, e.g. methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME) and *tert*-amyl ethyl ether (TAEE). The etherification of methanol and C_4–C_5 alkenes has been studied relatively widely. The kinetic expression and thermodynamic equilibrium were reported for MTBE [1] and TAME [2] production. The mechanisms generally proposed for the reactions are of Langmuir–Hinshelwood type [2,3] and of Eley–Rideal type [4,5]. However, the use of MTBE has already been forbidden in 25 states of USA [6,7] and many countries because it may contaminate underground water. Japan has ceased to use MTBE though official specifica-

---

[*] *Corresponding author*. Tel./fax: +66 3421 9368.
E-mail address: kworapon@su.ac.th (W. Kiatkittipong).

0378-3820/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.fuproc.2008.06.007

tions continue to allow a 7% volume limit [8]. Moreover, methanol and methanol derivatives such as MTBE and TAME are not favorable in an environmental view point because they are mostly derived from natural gas whose production may contribute to global warming.

Ethanol, one of biofuels, is a renewable energy source for alleviate the oil crisis and global climate change. Carbon dioxide produced from ethanol combustion is not considered as a global warming contributor since it is carbon neutral. Ethanol can be blended directly into gasoline (called “gasohol”); however, many recent researches reported disadvantages of the gasohol. One of good reviews on the effect of ethanol in gasoline is reported by Niven [9]. The overall air pollutant emissions from the use of gasohol are usually higher than those from the use of conventional gasoline because its high blending Reid vapor pressure (bRvp) leads to higher evaporative emissions. Ethanol-derived ethers can overcome the drawbacks of gasoline with direct ethanol blend. Ethers/gasoline fuel shows less volatility than gasohol. Therefore, ethers derived from ethanol still have drawn a number of research activities. Commercially, ETBE and TAEE can be produced by etherification of ethanol with isobutene (IB) and isoamylene (IA), olefinic compounds, respectively. Several reports on the production of ETBE and TAEE have focused on liquid phase synthesis in various types of reactor such as continuous stirred tank reactor [10–12], semi-batch reactor [13] and plug flow reactor [14]. Normally, this etherification can be catalyzed by a strongly acidic macro-porous cation-exchange resin, e.g. Amberlyst 15 [12,13,15], Amberlyst 16 [11,14,16,17], Amberlyst 35 [18–20], Purolite 275 [21], Smopex-101 [22], Dowex M32 [14], and Bayer K-2631 [23]. Equilibrium limitations for this reaction may be possibly overridden by special multifunctional reactor configurations [24,25]. Many simulation and reactor modeling also investigated for the etherification reaction [26,27]. Alternative routes for synthesis of ethers were also currently explored. In our previous studies, ETBE and TAEE were produced from reactions between ethanol and *tert*-butyl alcohol (TBA), a major by-product of propylene oxide production, and *tert*-amyl alcohol (TAA), a major component of fusel oil which is a by-product obtained from biomass fermentation, respectively [28–31].

Heavier reactive olefins have been considered as additional reactants for ether production. Various C_6 and C_8 olefins were etherified with methanol [19,22,32–34]. 3-Methoxy-3-methyl heptane was firstly synthesized by 2-ethyl-1-hexene and methanol [20] or selective dimerization of 1-butene, and then further etherified with methanol [35].

FCC gasoline contains substantial amount of reactive olefinic compounds. By etherifying the entire FCC gasoline, the bRvp of the gasoline could be reduced together with an increase of gasoline volume and octane number. The success of the process was reported by Pescarollo et al. [36], who etherified FCC light gasoline with methanol. The improvements in octane number and volume by reducing olefinicity and bRvp of the gasoline were reported. Rihko and Krause [37] studied the etherification of FCC light gasoline with methanol catalyzed by Amberlyst 16 in a temperature range of 323–353 K. In the kinetic study, the formation of l-methyl-l-methoxy cyclopentane was found to be twice as fast as the formation of C_6 methyl ethers.

Recently, Hu et al. [38] studied the same reaction over various zeolite catalysts. The activities were ordered as: Hβ>HMOR>HZSM-5. The influences of shaped and modified Hβ zeolite were also investigated.

However, no work has focused on direct etherification of FCC gasoline with ethanol which is a more environmental friendly process. The process is expected to give a higher potential for utilization of ethanol as a fuel extender than the case with direct blending for conventional engine which is limited at some ethanol contents, i.e., 10 vol.% (E10). The decrease of olefin content to less than 18 vol.% following the Euro 4 gasoline composition is anticipated.

In this study, the process for fuel oil quality improvement was investigated by etherifying the entire FCC gasoline with ethanol catalyzed by commercial catalysts, i.e., Amberlyst 16 and β-zeolite. The fuel characteristics of FCC etherified gasoline and FCC with direct ethanol blend were compared with those of gasohol (E10) which is a standard commercial fuel.

2. Experimental

2.1. *Chemicals*

FCC gasoline is cut off from a catalytic cracking unit of an oil refinery. Its compositions are given in Table 1. Ethanol (99 vol.%) and other chemicals needed in the experiment are analytical grade. All chemicals were used without further purification.

Table 1 – Compositions of FCC gasoline in volume percent

Carbon number	*n*-Paraffins	*i*-Paraffins	Olefins	Naphtenes	Aromatics	Total
C4	0.435	0.268	1.976	0	0	2.679
C5	1.054	8.109	8.739	0.112	0	18.014
C6	0.816	7.759	6.856	1.821	0.333	17.584
C7	0.766	0.18	6.097	3.023	2.373	18.439
C8	0.932	4.805	1.129	3.737	4.979	15.582
C9	0.28	3.991	0.655	2.522	4.944	12.391
C10	0.249	3.214	0.218	0.564	2.782	7.026
C11	0.133	1.33	0	0.21	1.26	2.933
C12	0.046	0.135	0	0.049	0.31	0.54
C13	0.014	0	0	0	0	0.014
Total	4.726	35.79	25.67	12.038	16.98	95.204

Table 2 – Physical properties of catalysts

Catalysts	Surface area (m^2/g)	Particle size (μm)	Pore diameter (nm)	Pore volume (cm^3/g)
Amberlyst 16	45	700	20	1.82
β-zeolite	625	45	0.58	0.129

2.2. Catalysts

Amberlyst 16 and β-zeolite with Si/Al=40 (H^+ form) used in this study were purchased from Chemica Fluka and Tosoh (Japan), respectively. The catalysts were dried overnight in an oven at 383 K before use. The physical properties of the catalysts were shown in Table 2.

2.3. Apparatus

Etherification of FCC gasoline with ethanol was carried out in a cylindrical shape autoclave reactor as shown in Fig. 1. The volume of reactor was 100 cm^3 with reactor height of 8 cm and outside and inside diameters of 5 and 4 cm, respectively. The turbine was used to stir the mixture. A valve for liquid sampling and a port for the thermocouple were installed at the top. The mixture was stirred by using turbine at the maximum speed of 1163 rpm for all experiments. At this speed, the effect of external mass transfer resistance could be neglected [31]. The reactor was maintained at a constant temperature by circulating hot water in jackets.

2.4. Analysis

Chemical compositions of a liquid sample were analyzed by using a gas chromatograph, Shimadzu GC 14B with hydrogen flame ionization detector. The separation column was a DB-1 capillary column and He was used as a carrier gas with a flow rate of 1 $cm^3\ min^{-1}$. The analysis was done by injecting 1 μl of sample in the column. The injector temperature and the detector temperature were set at 250 and 300 °C, respectively. One ramp of the column temperature was programmed from 40 °C (isotherm during 5 min) to 260 °C with a temperature ramp rate of 10 °C min^{-1} and kept at the final temperature of 260 °C for 5 min. The standard analysis of Research Octane Number (RON), blending Reid vapor pressure (bRvp) and the distillation temperature were carried out by following the standard methods of ASTM D-2699, ASTM D-5191 and ASTM D-86, respectively.

2.5. Operation procedure

The reaction system consisted of 80 cm^3 of FCC gasoline, 20 cm^3 of ethanol and 10 g of catalyst and was carried out at 70 °C for 10 h under a pressure of 0.8 MPa. After run, the reactor was cooled down to reach a room temperature before opening the reactor and collecting the sample in order to prevent the evaporation loss.

3. Results and discussion

3.1. Etherification of FCC gasoline with ethanol

Table 1 shows the compositions of FCC gasoline. The fraction of total olefins was about 25 vol.%. Most olefins were in a range of C_5–C_7 hydrocarbons. Table 3 provided the properties of various gasolines, i.e., FCC gasoline, commercial gasohol with 10 vol.% ethanol (E10), FCC gasoline with direct ethanol blend at 20 vol.% and FCC gasoline etherified with pure ethanol.

As shown in Table 3, originally, FCC gasoline has lower Research Octane Number than the specifications of regular (RON=91) and premium (RON=95) gasolines. It is worthy to note that a commercial process may blend this FCC fraction with high octane number fraction obtained from isomerization or aromatization. However, FCC quality improvement by converting olefins which have high atmospheric reactivity and volatility to ethers with higher octane number could also decrease demand of aromatics which are more environmentally benign.

Compared to original FCC gasoline, FCC with direct ethanol blend significantly increased RON but unfortunately its bRvp also increased dramatically. Although the bRvp value did not exceed the specification of E10, lower bRvp could be more favorable for preventing vapor lock especially in hot countries. As shown in Table 3, FCCs etherified with ethanol by using both Amberlyst 16 and β-zeolite catalysts could effectively decrease the values of bRvp because the reactive olefins in FCC gasoline and ethanol were converted to ethers which have lower bRvp. However, the etherified gasoline showed slightly lower octane number than FCC with direct ethanol blend because ethanol has higher value of octane number (RON=118) than ethers, i.e., ETBE (RON=118), TAEE (RON=105), *tert*-hexyl-ethyl-ether (THEE) (RON=110).

Comparison between two catalysts indicated that β-zeolite catalyst showed higher catalytic activity than Amberlyst 16 as observed by its higher ethanol conversion, and therefore the value of bRvp was lower. In addition, RON of the etherified

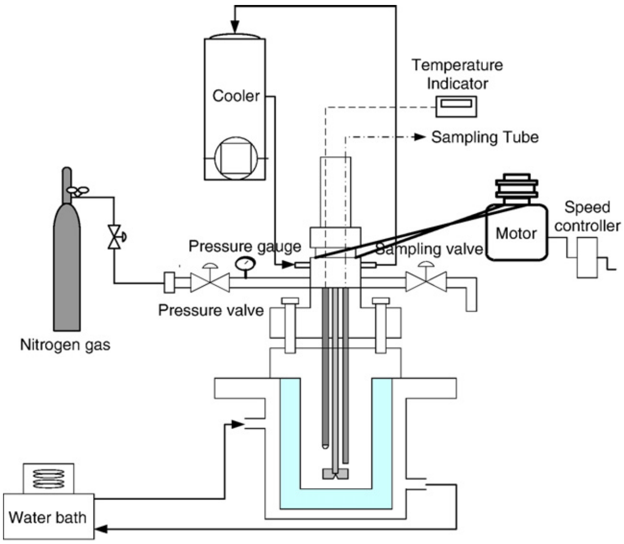


Fig. 1 – Schematic diagram of the experimental apparatus.

Table 3 – Comparison of gasoline properties

	FCC gasoline	Commercial gasohol (E10)	FCC with ethanol direct blend	Etherified FCC gasoline	
				Amberlyst 16	β-zeolite
RON	88	95	94.8	93	94.1
bRvp (psia)	6.5	<9	7.44	7.05	5.65
Density (g cm^{-3})	0.6828	0.7485	0.7346	0.7388	0.7448
Viscosity (Pa s)	6.09×10^{-4}	5.05×10^{-4}	6.20×10^{-4}	5.27×10^{-4}	6.18×10^{-4}
Ethanol conversion (%)	–	–	0	29.3	36.3
Olefins reduction (%)	–	–	0	33.6	45.7

gasoline catalyzed by β-zeolite was higher than that of Amberlyst 16. It should be noted that β-zeolite gave higher value of octane number, probably due to the possible isomerization and some aromatizations [39–41]. Noted that the remaining ethanol content was marginal, increasing the ethanol content within this operating condition might give the ethanol remaining higher than the conventional engine specification. The percentages of the olefins reduction were 33.6 and 45.7% in the cases of Amberlyst 16 and β-zeolite, respectively. Although the performance of olefins reduction via etherification was inferior than that via hydroisomerization and aromatization which previously reported by Fan et al. [40,41], the remaining olefins were lower than that of the Euro 4 standard limitation. It can be concluded that β-zeolite is a more suitable catalyst for the etherification of FCC gasoline with ethanol compared to Amberlyst 16.

For other gasoline properties, the density and the viscosity of the etherified gasoline are close to those of the commercial gasohol. The distillation curves from ASTM D-86 test shown in Fig. 2 indicate that the presence of ethanol both in gasoline with direct ethanol blend and etherified gasoline with some unreacted ethanol increased initial boiling point (IBP). Compared with the unmodified FCC gasoline, the distillation temperature in all volume percents evaporated and final distillation temperatures decrease in the case of gasoline with direct ethanol blend. On the contrary, in the case of FCC etherified gasoline, the distillation temperatures are lower than those of the unmodified FCC gasoline in the range of 20–80 vol.% evaporated and then become comparably or higher than those of the unmodified FCC gasoline. These may imply that distillation temperatures of ethanol-existing fuels are dependent on the evaporation of ethanol and its amount.

Comparing between gasoline with direct ethanol blend and etherified gasoline, because of the presence of ethers rather than olefins and ethanol, the distillation temperature is higher for the etherified gasoline. These results can also be confirmed with the decrease of the bRvp as shown in Table 3, i.e. with higher conversion of ethanol in the case of β-zeolite, the distillation temperatures are higher than those of Amberlyst 16. Although the change in bRvp affected the distillation temperature through the whole temperature range, the most effect appeared at the front end of the curve. Therefore the difference between etherified gasoline catalyzed by β-zeolite and Amberlyst 16 which are two most similar compositions could be observed only at the front end of distillation curve. It is worthy to note that the distillation temperature of FCC with direct ethanol blend at 60 vol.% evaporated is much lower than the others. It may be explained by the differences in boiling point values (ethanol; about 78 °C and gasoline; about 35–200 °C). The results agreed well with those from the study by Hsieh et al. [42] who tested ethanol–gasoline blended fuels in a spark-ignition (SI) engine. Their results showed significantly decrease of the 50% distillation temperature when ethanol was blended with more than 10 vol.% into gasoline whose boiling temperature is in a range of 25–230 °C. Therefore, the process could be satisfied to decrease gasoline volatility which affects not only a vehicle's driveability but also its VOC emissions in both evaporative and end pipe exhaust emissions and it should be noted that this method allows the use of ethanol in gasoline at higher content than does the conventional method with direct blending.

4. Conclusion

The simultaneous operation for FCC gasoline quality improvement and supplement by ethanol was investigated in the heterogeneous catalytic system. Although direct ethanol blend could improve RON of gasoline, bRvp of blending gasoline increased significantly. Etherified FCC gasolines with ethanol increased RON comparably or slightly lower than FCC with direct ethanol blend while bRvp was effectively lower. Therefore, FCC etherification with ethanol gave a higher potential for utilization of ethanol as a fuel extender

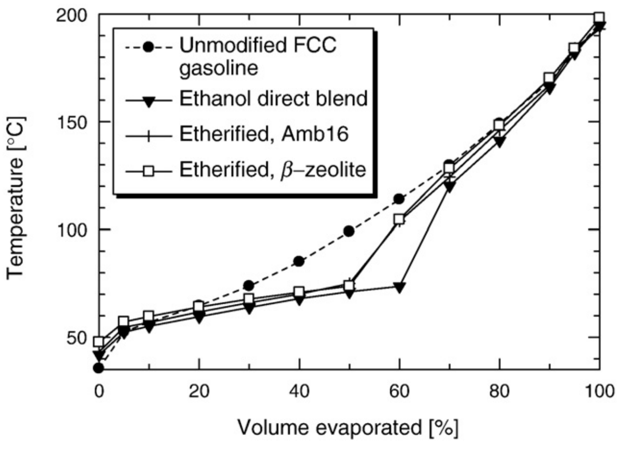


Fig. 2 – Distillation curves from ASTM D-86 tests.

than direct blending for conventional engine which was limited at some ethanol contents, i.e., 10 vol.% (E10). Comparing between two catalysts, it was reported that β-zeolite was a more suitable catalyst for the etherification of FCC gasoline with ethanol because it offered products with higher RON and ethanol conversion with lower bRvp.

Acknowledgement

Financial supports from Silpakorn University Research and Development Institute (SURDI), the Thailand Research Fund and Commission on Higher Education are gratefully acknowledged. The authors also gratefully acknowledged the technical supports from Thai Oil Public Company Limited.

REFERENCES

[1] N.S. Caetano, J.M. Loureiro, A.E. Rodrigues, MTBE synthesis catalysed by acid ion exchange resins: kinetic studies and modeling of multiphase batch reactors, Chem. Eng. Sci. 49 (1994) 4589–4604.

[2] M.V. Ferreira, J.M. Loureiro, Number of actives sites in TAME synthesis: mechanism and kinetic modeling, Ind. Eng. Chem. Res. 43 (2004) 5156–5165.

[3] M.V. Ferreira, A.M. Ribeiro, J.M. Loureiro, Experimental and simulation studies of TAME synthesis in a fixed-bed reactor, Ind. Eng. Chem. Res. 46 (2007) 1105–1113.

[4] L.K. Rihko, P.K. Kiviranta-Paakkonen, A.O.I. Krause, Kinetic model for the etherification of isoamylenes with methanol, Ind. Eng. Chem. Res. 36 (1997) 614–621.

[5] R.L. Piccoli, H.R. Lovisi, Kinetic and thermodynamic study of the liquid-phase etherification of isoamylenes with methanol, Ind. Eng. Chem. Res. 34 (1995) 510–515.

[6] ACE-American coalition for ethanol, ACE: State by state handbook 2006, , 2006 Available at: www.ethanol.org.

[7] A. Szklo, R. Schaeffer, F. Delgado, Can one say ethanol is a real threat to gasoline? Energy Policy 35 (2007) 5411–5421.

[8] Japanese regulation values of automobile fuels (in Japanese). Available at http://www.env.go.jp/air/car/nenryou/kisei.pdf.

[9] R.K. Niven, Ethanol in gasoline: environmental impacts and sustainability, Renew. Sust. Energ. Rev. 9 (2005) 535–555.

[10] P. Kiviranta-Paakkonen, L.K. Struckmann, J.A. Linnekoski, A.O.I. Krause, Dehydration of the alcohol in the etherification of isoamylenes with methanol and ethanol, Ind. Eng. Chem. Res. 37 (1998) 18–24.

[11] J.A. Linnekoski, P. Kiviranta-Paakkonen, A.O.I. Krause, Simultaneous isomerization and etherification of isoamylenes, Ind. Eng. Chem. Res. 38 (1999) 4563–4570.

[12] N. Oktar, K. Murtezaoglu, G. Dogu, I. Gonderten, T. Dogu, Etherification rates of 2-methyl-2-butene and 2-methyl-1-butene with ethanol for environmentally clean gasoline production, J. Chem. Technol. Biotechnol. 74 (1999) 155–161.

[13] P. Kitchaiya, R. Datta, Ethers from ethanol. 2. Reaction equilibria of simultaneous *tert*-amyl ethyl ether synthesis and isoamylene isomerization, Ind. Eng. Chem. Res. 34 (1996) 1092–1101.

[14] L.K. Rihko, A.O.I. Krause, Reactivity of isoamylene with ethanol, Appl. Catal. A-Gen. 101 (1993) 283–295.

[15] R.S. Karinen, J.A. Linnekoski, A.O.I. Krause, Etherification of C_5- and C_8-alkenes with C_1- to C_4-alcohols, Catal. Lett. 76 (2001) 81–87.

[16] L.K. Rihko, J.A. Linnekoski, A.O.I. Krause, Reaction equilibria in the synthesis of 2-methoxy-2-methylbutane and 2-ethoxy-2-methylbutane in the liquid phase, J. Chem. Eng. Data 39 (1994) 700–704.

[17] J.A. Linnekoski, A.O.I. Krause, L.K. Rihko, Kinetics of the heterogeneously catalyzed formation of *tert*-amyl ethyl ether, Ind. Eng. Chem. Res. 36 (1997) 310–316.

[18] R.S. Karinen, A.O.I. Krause, New biocomponents from glycerol, Appl. Catal. A-Gen. 306 (2006) 128–133.

[19] R.S. Karinen, M.S. Lylykangas, A.O.I. Krause, Reaction equilibrium in the isomerization of 2,4,4-trimethyl pentenes, Ind. Eng. Chem. Res. 40 (2001) 1011–1015.

[20] R.S. Karinen, A.O.I. Krause, A novel tertiary ether. Synthesis of 3-methoxy-3-methylheptane from 2-ethyl-1-hexene and methanol, Catal. Lett. 67 (2000) 73–79.

[21] V.J. Cruz, J.F. Izquierdo, F. Cunill, J. Tejero, M. Iborra, C. Fité, Acid ion-exchange resins catalysts for the liquid-phase dimerization/etherification of isoamylenes in methanol or ethanol presence, React. Funct. Polym. 65 (2005) 149–160.

[22] R.S. Karinen, A.O.I. Krause, Kinetic model for the etherification of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene with methanol, Ind. Eng. Chem. Res. 40 (2001) 6073–6080.

[23] C. Gomez, F. Cunill, M. Iborra, F. Izquierdo, J. Tejero, Experimental study of the simultaneous synthesis of methyl *tert*-butyl ether and ethyl *tert*-butyl ether in liquid phase, Ind. Eng. Chem. Res. 36 (1997) 4756–4762.

[24] D. Varisli, T. Dogu, Simultaneous production of *tert*-amyl ethyl ether and *tert*-amyl alcohol from isoamylene–ethanol–water mixtures in a batch-reactive distillation column, Ind. Eng. Chem. Res. 44 (2005) 5227–5232.

[25] N. Boz, T. Dogu, Reflux–recycle–reactor for high yield and selectivity in TAME and TAEE production, AICHE J. 51 (2005) 631–640.

[26] J.M.V. Prior, J.M. Loureiro, Residual thermodynamic properties in reactor modeling, Chem. Eng. Sci. 56 (2001) 873–879.

[27] C. Duarte, J.M. Loureiro, Effect of adsorption on residue curve maps for heterogeneous catalytic distillation systems, Ind. Eng. Chem. Res. 43 (2004) 3242–3250.

[28] S. Assabumrungrat, W. Kiatkittipong, N. Srivitoon, P. Praserthdam, S. Goto, Kinetics of liquid phase synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol catalyzed by supported β-zeolite, Int. J. Chem. Kinet. 34 (2002) 292–299.

[29] S. Assabumrungrat, W. Kiatkittipong, P. Praserthdam, S. Goto, Simulation of pervaporation membrane reactors for liquid phase synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol, Catal. Today 79-80 (2003) 249–257.

[30] W. Kiatkittipong, S. Assabumrungrat, P. Praserthdam, S. Goto, Pervaporative membrane reactor for liquid phase synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol catalyzed by β-zeolite, J. Chem. Eng. Jpn. 35 (2002) 547–556.

[31] O. Boonthamtirawuti, W. Kiatkittipong, S. Assabumrungrat, A. Arpornwichanop, P. Praserthdam, Kinetics of liquid phase synthesis of *tert*-amyl ethyl ether from *tert*-amyl alcohol and ethanol over Amberlyst 16. J. Ind. Eng. Chem. (in press) Article in press.

[32] S. Wang, J.A. Guin, Catalytic activity of silica supported sulfated zirconia catalysts for liquid phase etherification of C_6 olefins with alcohols, Fuel Process. Technol. 84 (2003) 135–146.

[33] J. Snelling, C.W. Curtis, Y.K. Park, Synthesis of higher carbon ethers from olefins and alcohols I. Reactions with methanol, Fuel Process. Technol. 83 (2003) 219–234.

[34] L.K. Rihko-Struckmann, R.S. Karinen, A.O.I. Krause, K. Jakobsson, J.R. Aittamaa, Process configurations for the production of the 2-methoxy-2,4,4-trimethylpentane—a novel gasoline oxygenate, Chem. Eng. Process. 43 (2004) 57–65.

[35] R.S. Karinen, A.O.I. Krause, E.Y.O. Tikkanen, T.T. Pakkanen, Catalytic synthesis of a novel tertiary ether 3-methoxy-3-methyl heptane from 1-butene, J. Mol. Catal. A-Chem. 152 (2000) 253–255.

[36] E. Pescarollo, R. Trotta, P.R. Sarathy, Etherify light gasolines, Hydrocarb. Process. 73 (1993) 53–60.

[37] L.K. Rihko, A.O.I. Krause, Etherfication of FCC light gasoline with methanol, Ind. Eng. Chem. Res. 35 (1996) 2500–2507.

[38] T. Hu, J. Chen, H. Wang, J. Ma, M. Wei, Influence of shaped and modified Hβ zeolite on etherification of FCC light gasoline, Microporous Mesoporous Mat. 94 (2006) 295–303.

[39] Y. Fan, X. Bao, G. Shi, W. Wei, J. Xu, Olefin reduction of FCC gasoline via hydroisomerization aromatization over modified HMOR/HZSM-5/Hβ composite carriers, Appl. Catal. A-Gen. 275 (2004) 61–71.

[40] Y. Fan, X. Bao, G. Shi, Hβ/HZSM-5 composite carrier supported catalysts for olefins reduction of FCC gasoline via hydroisomerization and aromatization, Catal. Lett. 105 (2005) 67–75.

[41] Y. Fan, X. Bao, D. Lei, G. Shi, W. Wei, J. Xu, A novel catalyst system based on quadruple silicoaluminophosphate and aluminosilicate zeolites for FCC gasoline upgrading, Fuel. 84 (2005) 435–442.

[42] W.D. Hsieh, R.H. Chen, T.L. Wu, T.H. Lin, Engine performance and pollutant emission of an SI engine using ethanol–gasoline blended fuels, Atmos. Environ. 36 (2002) 403–410.

Catal Lett
DOI 10.1007/s10562-008-9717-9

Self-Etherification Process for Cleaner Fuel Production

Worapon Kiatkittipong · Khamron Yoothongkham · Choowong Chaisuk · Piyasan Praserthdam · Shigeo Goto · Suttichai Assabumrungrat

Received: 3 August 2008 / Accepted: 29 September 2008

Abstract The process of fluidized catalytic cracking (FCC) gasoline self-etherification with ethanol has several benefits. Firstly, the gasoline volume is effectively increased by adding ethers produced from ethanol which is renewable. Secondly, the etherified gasoline product has higher octane number with lower blending Reid vapor pressure (bRvp) and amount of olefins content. Two catalysts; i.e., Amberlyst 16 and Beta-zeolite are used for etherification in this study. The bRvp of etherified FCC gasoline is lower than that of ethanol direct blend gasoline (called gasohol) and also could be lower than that of original FCC gasoline with moderate ethanol conversion. However, the octane number of etherified FCC gasoline catalyzed by Amberlyst 16 is slightly lower than that of gasohol. Beta-zeolite is a more suitable catalyst than Amberlyst 16 for the etherification of FCC gasoline with ethanol because not only a better catalytic activity for etherification, but some isomerization also occurs without aromatization. Therefore it offers improved gasoline products with higher research octane number and gasoline renewability with lower bRvp than that of gasohol. Olefins and ethanol conversions increase with increasing ethanol ratio in feed. Nevertheless, ethanol feed ratio is limited specification of distillation temperatures which are dependent on the evaporation of ethanol and its amount. The cold start problem might not be occurred even in low bRvp as proven by satisfied drivability index.

Keywords Fluidized catalytic cracking gasoline · Olefin reduction · Octane enhancement · Self-etherification · Beta-zeolite · Amberlyst 16

1 Introduction

At the moment, transport fuel is mainly derived from fossil and the attention has been focused on biomass derived fuel production. Ethanol is one of the most widely-used renewable liquid fuel and may be among the most suitable choices for use with the existing infrastructure i.e. road, gas station and automobile engine. CO_2 produced from ethanol combustion is not considered as a global warming contributor because it is a part of the carbon cycle and therefore is carbon neutral. Since the CO_2 is recycled to the tissue during plant growth, with modern agriculture, soil organic matter can be built up and therefore net CO_2 can be removed from the atmosphere [1].However, some researchers have severely questioned the claim of its renewability. Pimental [2] claimed that ethanol might not be a renewable energy source. Its overall production system is uneconomic and causes environmental burden. In addition, the important concept of life cycle assessment was illustrated for ethanol production [3, 4]. CO_2 emissions over the life cycle of ethanol production are such that the net greenhouse benefit of low ethanol blends is marginal [5]. Although the advantages of using ethanol for fossil fuel

---

W. Kiatkittipong (✉) · C. Chaisuk
Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University,
Nakhon Pathom 73000, Thailand
e-mail: kworapon@su.ac.th

K. Yoothongkham · P. Praserthdam · S. Assabumrungrat
Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering,
Faculty of Engineering, Chulalongkorn University,
Bangkok 10330, Thailand

S. Goto
Department of Chemical Engineering, Nagoya University,
Chikusa, Nagoya 464-8603, Japan

substitution are controversy, ethanol consumption still extends over the world.

Ethanol can be blended directly into gasoline which is called as gasohol. Flexible-fuel cars can be run on up to 85 vol% (E85) or pure ethanol. However, most of present cars can be run on gasoline blended with lower concentration of ethanol i.e., 10–20 vol%. Therefore the chance of using ethanol as a fuel extender is limited. Furthermore, many recent researches reported disadvantages of the gasohol [6]. With a present standard of engine and the use of catalytic converter, the emissions at the end pipe are relatively small while evaporative emissions have become significant. Evaporative emissions are considered as a loss of fuel which can be occurred from diurnal, running loss, hot soak and refueling [7, 8]. Therefore, some researchers found that the overall air pollutant emissions (exhaust and evaporative emissions) by the use of gasoline-ethanol blend appear to be higher than those posed by conventional gasoline because of its high blending Reid vapor pressure (bRvp) [6]. An ethanol-gasoline mixture also undergoes a phase separation on contact with water which increases the corrosion of steel underground storage tanks, increasing the risk of leakage to surrounding soil. Even though ethanol/gasoline (gasohol) can tolerate significantly higher water content than conventional gasoline before phase separation, the problem on the engine is more serious. Ethanol partitions preferentially into an aqueous phase and therefore causes an off-spec gasoline. Combustion of this partition causes the lean burn effects [8]. Refiners and auto-makers prefer to use ethers to meet the octane number and oxygenate requirement for technical reasons because ethers can overcome the drawbacks of gasoline with direct ethanol blend.

Most of ethers are derived from methanol and ethanol [9–25] and some from butanol [26] and glycerol [27–29]. Although methanol can also be produced from biomass, the production is cost-intensive and therefore it is currently made from natural gas which is more cost-competitive [30]. As a result, ethers derived from ethanol could be the most suitable additives for gasoline extender and octane modifier. The most well-known ethanol-derived ethers are ethyl tertiary butyl ether (ETBE) and tertiary amyl ethyl ether (TAEE). Commercially, ETBE and TAEE can be produced by etherification of ethanol with isobutene (IB) and isoamylene (IA), olefinic compounds, respectively. Several researchers investigated the liquid phase reaction of ETBE synthesis. The kinetic expressions [31–33] and thermodynamic equilibrium were reported [34]. It still has drawn the attention from some researchers [35–39]. For TAEE synthesis, the major isomer of IA is 2-methyl-2-butene (2M2B) which is usually assumed to be in isomerization equilibrium with 2-methyl-1-butene (2M1B). Rihko and Krause [40] found that 2M1B was more reactive than 2M2B which is in good agreement with other researches [41, 42]. There are a number of studies focusing on etherification of 2M1B and 2M2B with ethanol in both kinetics [43, 44] and the reaction equilibrium [45, 46].

Unconventional routes for ethers synthesis were also previously investigated. *tert*-Butyl alcohol (TBA), a major by-product of propylene oxide production, and *tert*-amyl alcohol (TAA), a major component of fusel oil which is a by-product obtained from biomass fermentation were employed as a reactant with ethanol for ETBE and TAEE synthesis, respectively [47–53]. However, unfortunately, the productions of ETBE and TAEE via these olefinic compounds i.e., IB, IA or alcohols i.e., TBA, TAA are unlikely to meet demands of oxygenate ethers. Heavier reactive olefins should be considered as additional reactants for ether production. 3-Methoxy-3-methylheptane was firstly investigated by etherified 2-Ethyl-1-hexene with methanol [54]. Consequently, etherification of C5- and C8-alkenes i.e., 2-methyl-1-butene and C8–2,4,4-trimethyl-1-pentene, respectively, with different C1- to C4-alcohols was studied [55].

FCC light gasoline is a potential valuable feedstock of reactive olefins for production of oxygenated ethers. On the contrary, these olefinic compounds are among the most photochemical reaction components of hydrocarbon emissions from automotive engines which strongly affect on ground ozone level. Therefore they should be diminished also in order to meet the new mandatory of gasoline composition which allows the olefin content not to exceed 20 or 18 vol% as regulated by the International charter on clean fuels and Euro 4 standard, respectively. Pescarollo et al. [56] studied the etherification of the entire light FCC gasoline with methanol. IA conversion was 68.8% close to thermodynamic equilibrium while conversions of C_6 and C_7 reactive olefins were 42.9% and 23.2%, respectively. Simultaneous improvements in octane number and gasoline volume with reductions in olefinicity, atmospheric reactivity and bRvp of gasoline were obtained. Similar reaction was also studied by using Amberlyst 16, a cation-exchange resin, as a catalyst in a temperature range of 50–80 °C [57]. They reported the initial etherification rates and thermodynamic limitations for the reaction of methanol with the C_5 and C_6 olefinic compounds. The equilibrium constants of C_6 olefins etherified with ethanol were lower than those of IA, C_5 olefins. Various zeolites were investigated on FCC light gasoline etherified by methanol. The activities were ordered as: $H\beta > HMOR > HZSM\text{-}5$. H$\beta$ also showed higher catalytic stability than other catalysts for the production of TAME [58].

Conversions of olefins in FCC gasoline by hydroisomerization and aromatization have been recently investigated by many researchers [59–63]. The loss of octane number from olefin reduction was compensated by the formation of iso-paraffins and aromatics. This process is beneficial in the viewpoint of olefin reduction; though aromatic compounds which have a greater tendency to emit unburned hydrocarbons [64] might be produced.

However, the previous processes for upgrading FCC gasoline are still based on non-renewable energy. To enhance the renewability of gasoline, ethanol could be more partly substituted into gasoline with quality improvement aspects as illustrated in our preliminary work [65]. In this study, the entire FCC gasoline was fed with ethanol in a molar ratio of 80:20 and 70:30. The gasoline composition, olefin and ethanol conversion, and the amount of ethers production were clarified. The gasoline properties i.e., RON, bRvp, distillation temperature (IBP, T10, T50, T90 and FBP), estimated minimum cold start temperature and drivability index were compared between original FCC gasoline, commercial E10 gasohol, FCC with direct blend of ethanol and etherified FCC gasoline. Aspect of catalyst characterization on catalytic activity was also discussed.

2 Experimental

2.1 Chemicals

FCC gasoline is cut off from a catalytic cracking unit of an oil refinery. Ethanol (99 vol%) and other chemicals needed in the experiment were analytic grade. All chemicals were used without further purification.

2.2 Catalysts

The ion exchange resin catalyst, Amberlyst 16 and the strong acid solid catalyst, Beta-zeolite with Si/Al = 40 (H^+ form) were selected for this study. Amberlyst 16 and Beta-zeolite were purchased from Fluka and Tosoh (Japan), respectively. The catalysts were dried overnight in an oven at 110 °C before use. The properties of the catalysts are shown in Table 1. The acidity of the catalysts and pore size were reported by the producer. BET surface area of the catalysts was measured by Micromeritics ASAP 2020. A sample of 0.3 g was degassed at 300 °C for 3 h and the amount of N_2 adsorption was recorded. The thermogravimetric analysis (TGA) curves were obtained in flowing air on SDT Q600 (TA instruments) with a temperature increasing rate of 5 °C/min in the range of 30–1,000 °C.

Table 1 Properties of catalysts

Catalysts	Surface area (m^2/g)	Pore diameter (nm)	Acidity (mmol H^+/g)
Amberlyst 16	45	20	5.0
Beta-zeolite	625	0.58	1.03

2.3 Apparatus

The reaction was carried out in a cylindrical shape autoclave reactor as shown in Fig. 1. The 100 cm^3 reactor was maintained at a constant temperature by circulating hot water in jackets. The turbine was used to stir the mixture at the maximum speed of 1163 rpm by a speed controller in all experiments to minimize the external mass transfer resistance [52]. A valve for liquid sampling and a port for the thermocouple were installed at the top.

2.4 Analysis

In gasoline investigations, the compounds called "PIANO" consisting of paraffins, isoparaffins, aromatics, naphthenes and olefins were determined with the amount of the oxygenates. They were analyzed by an FID gas chromatograph with a Supelco capillary column. The analysis was done by injecting 1 μL of sample in the column. It should be noted that a sample must be centrifuged before the injection in order to separate residue catalyst which can damage the GC column. The injector and detector temperature were 250 °C. The column was heated with three ramps. Firstly, the column was heated from 5 to 65 °C with a ramp rate of 6 °C min^{-1} and holding at 65 °C for 45 min. Afterward, heated to 180 °C, with a ramp rate of 3 °C min^{-1} and holding for 5 min. Finally, the temperature was increased at a ramp rate of 10 °C min^{-1}–200 °C where it was held for 0.5 min. The amount of ethanol was further analyzed

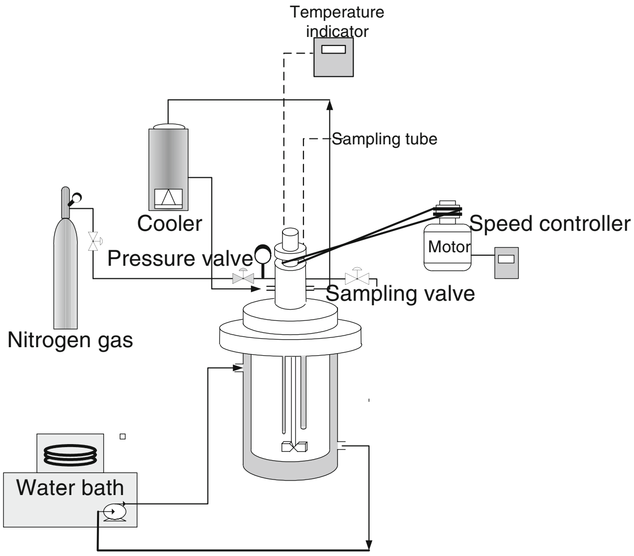


Fig. 1 Experimental apparatus

by Shimadzu GC 14B with hydrogen flame ionization detector. The separation column was a DB-1 capillary column and He was used as a carrier gas. The standard test methods of ASTM D-2699, ASTM D-5191 and ASTM D-86 were employed to determine Research Octane Number (RON), blending Reid vapor pressure (bRvp) and distillation temperature, respectively.

2.5 Operation Procedure

The experiments were carried out at 70 °C for 10 h in the batch reactor. The system was pressurized by N_2 at 0.8 MPa to ensure that all reaction components were in the liquid phase. The reaction system consisted of FCC gasoline and ethanol with a volume ratio of 80:20 and 70:30 with 10 g of catalyst. The samples of feed and product were collected at the initial and final of the experiment. It should be noted that for collecting the final product after run for 10 h, the reactor was cooled down to room temperature before opening the reactor and collecting the sample in order to minimize the evaporation loss.

3 Results and Discussion

3.1 Gasoline Composition and Reaction Activities

The distributions of the hydrocarbon groups present in the FCC gasoline feed are shown in Table 2. Most olefins were in a range of C_5 through C_7 hydrocarbons. The fraction of total olefins was about 25 vol%. Table 3 provides the gasoline composition, olefins conversion and ethanol

Table 2 Compositions of FCC gasoline in volume percent

Carbon number	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	Total
n-Paraffins	0.435	1.054	0.816	0.766	0.932	0.28	0.249	0.133	0.046	0.014	4.726
i- Paraffins	0.268	8.109	7.759	0.18	4.805	3.991	3.214	1.33	0.135	0	35.79
Olefins	1.976	8.739	6.856	6.097	1.129	0.655	0.218	0	0	0	25.67
Naphthenes	0	0.112	1.821	3.023	3.737	2.522	0.564	0.21	0.049	0	12.038
Aromatics	0	0	0.333	2.373	4.979	4.944	2.782	1.26	0.31	0	16.98
Total	2.679	18.014	17.584	18.439	15.582	12.391	7.026	2.933	0.54	0.014	95.204

Table 3 Gasoline composition, olefins conversion and ethanol conversion of FCC gasoline with different treatments (FCC: ethanol volumetric ratio = 80:20)

Component	FCC gasoline (g)	Ethanol (g)	20 vol% Ethanol		
			Direct blend (g)	Etherified gasoline	
				Amberlyst 16 (g)	Beta-zeolite (g)
Olefins					
-C4	1.76	–	1.76	0.92	0.86
-C5	8.85	–	8.85	6.15	5.1
-C6	5.69	–	5.69	4.42	3.54
-C7	4.54	–	4.54	3.56	2.73
-C8	1.09	–	1.09	0.29	0.28
-C9	0.44	–	0.44	0.29	0.29
-C10	0.35	–	0.35	0	0.15
Other hydrocarbon	54.84	–	54.84	55.79	55.08
Oxygenates					
-Ethanol	0	22.44	22.44	15.87	14.29
-Ether	0	–	–	12.71	17.68
Total	77.56	22.44	100	100	100
C4 Olefins conversion (−)	–	–	0	0.48	0.51
C5 Olefins conversion (−)	–	–	0	0.31	0.42
C6 Olefins conversion (−)	–	–	0	0.22	0.38
C7 Olefins conversion (−)	–	–	0	0.22	0.40
Ethanol conversion (−)	–	–	0	0.29	0.36

conversion of FCC gasolines directly blended and etherified with ethanol with a volume ratio of 80:20. Since pure ethanol was supplemented into the FCC gasoline with 20 vol% (~22.4 wt%) for both cases, the amount of final gasoline product was increased. In the case of ethanol direct blend, the amount of each component is constant because the reaction cannot occur without the catalyst. In the cases of etherified gasoline, Amberlyst 16 and Beta-zeolite were used as catalysts. Olefins and ethanol were mainly converted to ethers. Comparing between two catalysts, it was found that Beta-zeolite gives higher ethanol and olefins conversions, resulting in higher ether products. It is worthy to note that olefins conversions are lower with larger atomic number of olefins in both catalysts because large molecular of olefins hardly enters to pores of catalyst [58]. The tendency of these results was similar to that of the etherified FCC gasoline with methanol experimented by Pescarollo et al. [56]. They reported that the conversions of C4, C5, C6, and C7 olefins were 0.84, 0.64, 0.43, and 0.23, respectively. Even though the FCC feed composition and the ratio of alcohol to FCC were different, a simple comparison between the performance of methanol [56] and ethanol (as shown in Tables 3 and 4) for etherification could be noticed. Higher conversion of isobutene (C4) and isoamylene (C5) in FCC with methanol than with ethanol were observed. These results are similar to the individual study of C4 and C5 olefins with alcohol in the literature [40, 45, 66–68]. The activity of ethanol was less than that of methanol as a result of the decrease of dielectric constant or polarity. The value of dielectric constants decreased with increasing of molecular weights of alcohols which were 32.6 and 24.3 for methanol and ethanol, respectively. The more polar component could be preferably adsorbed over the actives sites than the less polar component [55].

However, the comparable or some higher conversions of C6 and C7 olefins with ethanol compared to those with methanol were unexpected. The higher conversion of C6 olefins with ethanol over that with methanol also has been previously observed by Rihko and Krause [57]. These contrasting results might be explained by the study of Cruz et al. [69]. They declared that ethanol can react with alkenes easier than methanol due to the higher acidity of ethanol. The complexity of the system might be related to the complicated mechanism of adsorption over active site. Many components; i.e., alcohol, ether and hydrocarbon having significantly different polarity should play a role; therefore, this issue should be further investigated.

The ratio of FCC gasoline and ethanol was changed to 70:30 and the reaction was carried out at the same operating condition described earlier. The results are summarized in Table 4. Beta-zeolite still shows a better catalyst

Table 4 Gasoline composition, olefins conversion and ethanol conversion of FCC gasoline with different treatments (FCC: ethanol volumetric ratio = 70:30)

Component	FCC gasoline (g)	Ethanol (g)	30 vol% ethanol		
			Direct blend (g)	Etherified gasoline	
				Amberlyst 16 (g)	Beta-zeolite (g)
Olefins					
-C4	1.72	–	1.72	0.78	0.67
-C5	7.72	–	7.72	3.39	3.19
-C6	5.12	–	5.12	3.79	2.28
-C7	3.86	–	3.86	2.07	1.88
-C8	0.94	–	0.94	0.51	0.58
-C9	0.39	–	0.39	0.12	0.17
-C10	0.29	–	0.29	0.22	0.06
Other hydrocarbon	46.81	–	46.81	48.32	47.82
Oxygenates					
-Ethanol	–	33.15	33.15	18.69	16.06
-Ether	–	–	–	22.11	27.29
Total	66.85	33.15	100	100	100
C4 Olefins conversion (–)	–	–	0	0.55	0.61
C5 Olefins conversion (–)	–	–	0	0.56	0.59
C6 Olefins conversion (–)	–	–	0	0.26	0.55
C7 Olefins conversion (–)	–	–	0	0.46	0.51
Ethanol conversion (–)	–	–	0	0.44	0.52

performance than Amberlyst 16. Compared with Table 3, the ethanol conversion and all C4–C7 olefins conversions increased with increasing ethanol fraction in feed. The remaining unreacted ethanol from the case with the feed ratio of 70:30 did not exceed the ethanol content of 15 vol% in the case of Beta-zeolite. Therefore it is not over the gasoline specification of i.e., E15 and E20 which are limited by ethanol content of 15 and 20 vol%, respectively. The effect of gasoline composition in both Tables 3 and 4 are further discussed with the gasoline properties shown in Table 5.

3.2 Gasoline Properties and Their Quality Improvement

Table 5 summarizes the gasoline properties comparison. FCCs with direct ethanol blend at 20 and 30 vol% increased RON from original of 88 up to 94.8 and 97.9, respectively. However, unfortunately their bRvp also increased dramatically. As shown experimentally, FCCs etherified with ethanol by using both Amberlyst 16 and Beta-zeolite catalysts can effectively decrease the values of bRvp because the reactive olefins in FCC gasoline and ethanol are converted to ethers which have lower bRvp. FCCs etherified with 30 vol% ethanol both catalyzed by Beta-zeolite and Amberlyst 16 give lower bRvp than FCC with direct ethanol blend at 20 vol%. These results also confirm the increase of ethanol substitution ability into gasoline. Comparing with original FCC gasoline, the bRvp value of etherified gasoline catalyzed by Beta-zeolite is lower or similar in the cases of using 20 and 30 vol%, respectively. These results may strongly depend on the decrease of olefins content and the amount of unreacted ethanol remaining in the solution. Therefore, it is worthy to note that the difference of bRvp between original FCC gasoline and etherified gasoline may not be as significant as that of bRvp between FCC with direct ethanol blend and etherified gasoline. The decrease in bRvp reduces the evaporative loss of fuel hence preventing vapor lock in summer. As known that too low bRvp might cause a cold start problem, however, it might not be in this case as it was proven by minimum cold start temperature and drivability index (DI) which will be discussed later.

Comparing the RON between ethanol directly blended and etherified gasolines, the gasoline etherified by Amberlyst 16 shows slightly lower octane number than ethanol directly blended gasoline because ethanol has higher value of octane number (RON = 118) than ethers, e.g., ETBE, TAEE and *tert*-hexyl-ethyl-ether (THEE) whose RON are 118, 105, and 110, respectively. However, the gasoline etherified using Beta-zeolite as catalyst shows similar RON to that of ethanol direct blended gasoline and slightly higher than that of etherified gasoline catalyzed by Amberlyst 16.

Table 5 Comparison of gasoline properties

Properties	ASTM standard	FCC gasoline	Gasohol E10	20 vol% ethanol			30 vol% ethanol		
				Direct blend	Etherified gasoline		Direct blend	Etherified gasoline	
					Amberlyst 16	Beta-zeolite		Amberlyst 16	Beta-zeolite
RON	D-2699	88.0	95.0	94.8	93.0	94.1	97.9	96.9	98.2
bRvP (psi)	D-5191	6.5	<9.0	7.441	7.05	5.657	8.0	7.24	6.58
Density (g/cm^3)		0.683	0.749	0.735	0.739	0.745	0.735	0.739	0.745
Viscosity × 10^6 (g_f.s/cm^2)		6.213		6.325	5.374	6.310	6.152	6.035	5.160
Distillation	D-86								
Temperature °C (°F)									
IBP		35.5(95.9)		41.9(107.4)	43.3(109.9)	47.7(117.9)			
T 10		57.1(134.8)	<70(158)	55.2(131.4)	56.9(134.4)	59.7(139.5)			
T 50		99.0(210.2)	70–110(158–338)	70.2(158.4)	75.0(167)	73.8(164.9)	N.D	N.D	N.D
T 90		168.7(335.7)	<170(338)	165.9(330.6)	167.1(332.8)	170.2(338.4)			
FBP		196.0(384.8)	<200(392)	194.7(382.5)	193.1(379.6)	198.2(388.8)			
Driveability index, DI °C (°F)		631(1168)	<677(1250)	617(1143)	635(1175)	638(1182)			
Estimated minimum cold start temperature °C (°F)		−6.7(19.9)	–	−8.1(17.42)	−6.9(19.58)	−5.1(22.82)			

Fan et al. [59] found that Beta-zeolite was an effective catalyst for upgrading FCC gasoline via isomerization and some aromatizations. However, fortunately the amounts of aromatic are not increased in the case of FCC gasoline etherified with Beta-zeolite (not shown here). As the amounts of aromatic are not increased, there is no greater tendency in damage to elastomers and increased of toxic aromatic emissions as unburned hydrocarbons. Therefore, the enhancement of octane number in the case of FCC etherified by Beta-zeolite is not from etherification reaction only but also from isomerization. In addition, Corma et al. [70] studied various zeolites as catalysts for the cracking of *n*-heptane, a model molecule of gasoline range. When using Beta-zeolite as a catalyst, the ratio of isobutene to *n*-butene and isopentene to *n*-pentene products were 1.27 and 2.0, respectively. Therefore, ether products may not be possibly limited by the amount of reactive olefins originally present in gasoline, the reactive olefins could be further obtained via cracking by Beta-zeolite.

In the case of Amberlyst 16, Slomkiewicz et al. [71] reported that Amberlyst showed high catalytic activity for double bond isomerization or the *cis-/trans*-transformation. However, the isomerization from linear olefin to branched olefin is much more difficult because the reaction normally required significantly higher temperature at which Amberlyst could not resist [72].

Apart from bRvp which represents the volatility property of gasoline, T10, T50, and T90 (D-86 temperature at 10, 50 and 90 vol%, respectively) and drivability index are key motor gasoline specifications in the US. The distillation temperature (IBP, T10, T50, T90, and FBP) and drivability index are also provided in Table 5. Initial boiling point (IBP) increased with the presence of ethanol both in gasoline with direct ethanol blend and etherified gasoline with some unreacted ethanol. Comparing with unmodified FCC gasoline, T10, T50, T90, and FBP decrease in the case of gasoline with direct ethanol blend and etherified with Amberlyst 16. While in the case of etherified with Beta-zeolite, the distillation temperature decreases only for T10 and T50. IBP and T10 effects cold starting ability and inversely vapor lock problem. Increase these front end distillation temperature may increase minimum cold start temperature while decrease the possibility of vapor lock. The minimum cold start temperature could be estimated by the empirical relation as [73] Minimum cold start temperature (°C) $= 5.62\sqrt{\mathrm{T10}-40}-30$.

As shown in Table 5, the estimated minimum cold start temperature of etherified gasoline did not pose a cold start problem comparing to original FCC gasoline. However, the appropriate values strongly depend on the regional and seasonal of their used.

From the above results, these may imply that distillation temperatures of ethanol containing fuels are dependent on the evaporation of ethanol and its amount. These results can also be confirmed with the decrease of the bRvp as shown in the Table 5, i.e., with higher ethanol converted, the distillation temperatures in the case of Beta-zeolite seem to be higher than those of Amberlyst 16 and ethanol directly blended, respectively. It is worthy to note that T50 of FCC-ethanol blend is marginal with the specification value of gasohol E10, it is possibly that blending with higher amount of ethanol i.e., 30 vol% may make the T50 off specs. Therefore, the distillation temperature test of ethanol 30 vol% was not performed but the available results are enough for discussion.

A drivability index (DI) has been developed to predict cold-start and warm-up drivability. The drivability index, DI is defined as follows [8, 74].

$$\mathrm{DI} = (1.5 \times \mathrm{T10}) + (3 \times \mathrm{T50}) + \mathrm{T90} \tag{1}$$

When oxygenate are present in the gasoline, the DI could be corrected as follows [75]

$$\mathrm{DI} = (1.5 \times \mathrm{T10}) + (3 \times \mathrm{T50}) + \mathrm{T90} + 20 \times \mathrm{wt\%\ oxygen} \tag{2}$$

Drivability index provides the relationship between drivability and distillation properties. T10 represents the gasoline ability to vaporize rapidly and enable cold starting. T50 and T90 represent the heavier gasoline components' ability to vaporize as the engine warms up and be burnt during combustion. Therefore, lower values of DI generally result in better cold-start and warm-up performance; however, low DI can indicate poor drivability in that the combustion is too rich of stoichiometry [75]. Therefore once good drivability is achieved, there is no benefit to further lowering the DI [76].

As shown in Table 5, DI values of FCC gasoline and those of etherified FCC gasoline do not show considerable difference, however, the values of DI of the gasoline products are in the satisfied range of the gasoline specification.

3.3 Aspect of Catalyst Characterization on Catalytic Activity

Linnekoski et al. [44] investigated the etherification and hydration of isoamylene catalyzed by ion exchange resin. Addition of only small amount of water resulted in significantly dropped in ethanol and olefins conversion [44]. Karinen et al. [55] reported that water reacted to tertiary alcohol at an early stage relative to the other reactions. This is because the higher acidity of water compared to that of ethanol resulted in the increasing of basic solvated proton which lowers activity as previously mentioned in the literature [77–79]. In our experiments, although both catalysts were dried at 110 °C overnight, the remaining water adsorbed in the pore of catalyst might be examined by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA).

TGA and DTGA of Amberlyst 16 were investigated as shown in Figs. 2 and 3, respectively. The weight loss of Amberlyst 16 at the temperature lower than 200 °C are almost 10 wt% which should be corresponding to the amount of water desorption [80, 81]. The consecutive mass loss step of Amberlyst 16 might be the thermal desulfonation [80]. The final peak at 470 °C of DTGA (Fig. 3) might be the thermooxidative decompositions of a polymers matrix [80] which corresponds well with high intensity exothermic as shown in Fig. 2.

On the contrary, insignificant weight loss at the temperature lower than 200 °C can be observed in the case of Beta-zeolite as shown in Fig. 4, indicating traces of water desorption. Thermal analysis also revealed desorption of precursor component such as organic template [81] i.e., at the temperature of 420 and 560 °C. The DTGA in Fig. 5 showed corresponding well of intense exothermic heat. However, it should be noted that weight loss and exothermic heat were much more pronounced in the case of Amberlyst 16. This TGA results also confirm the higher thermal stability of Beta-zeolite than that of Amberlyst 16.

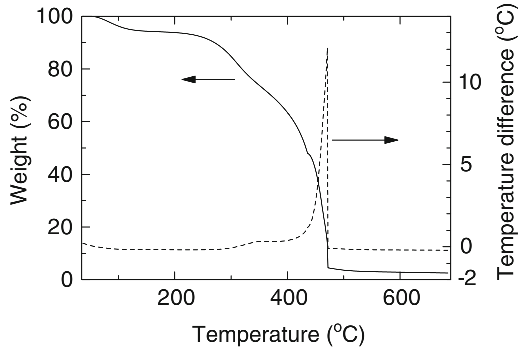


Fig. 2 Thermogravimetric analysis (TGA) of Amberlyst 16

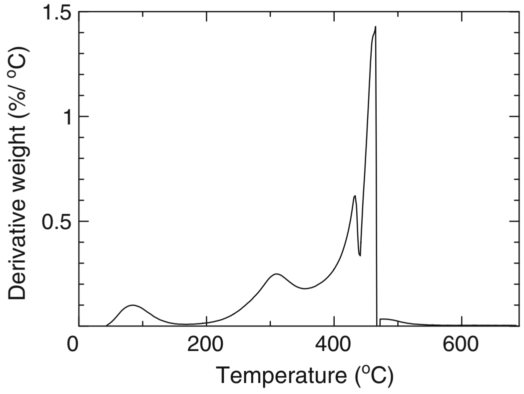


Fig. 3 Differential thermogravimetric analysis (DTGA) of Amberlyst 16

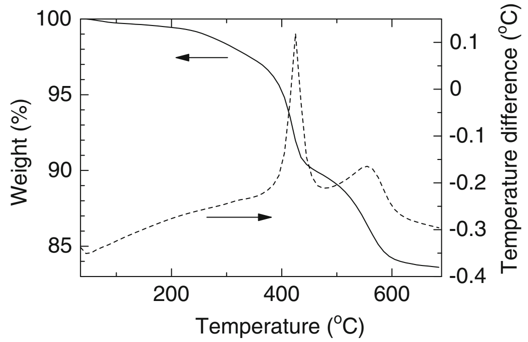


Fig. 4 Thermogravimetric analysis (TGA) of Beta-zeolite

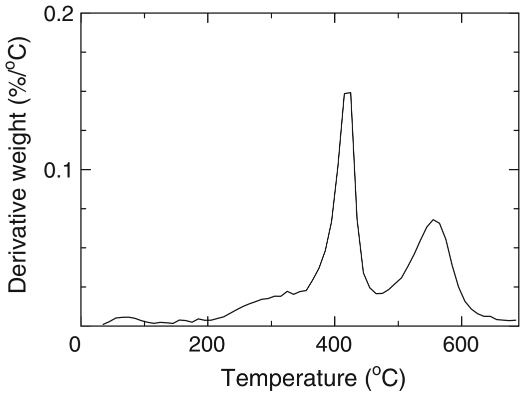


Fig. 5 Differential thermogravimetric analysis (DTGA) of Beta-zeolite

Therefore, it can be concluded here that Beta-zeolite is a more suitable catalyst for upgrading FCC gasoline with ethanol compared to Amberlyst 16. For other gasoline properties, the density and the viscosity of the etherified gasoline are close to those of the commercial gasohol.

In summary, etherification of FCC gasoline enhances the possibility of ethanol substitution and therefore its renewability without increasing gasoline volatility. Olefinic compound was consumed in the reaction process which lessens cost for the refining industry to limit total gasoline olefins following the regulations without octane loss.

It is recommended that additional works such as development of an industrial-scale process for the self-etherification reaction, studies of the nature of the catalytic reaction, and studies of the process economics should be further investigated.

4 Conclusion

Although ethanol direct blend increased RON of FCC gasoline, the value of bRvp became also significantly higher. Etherification of FCC gasoline with ethanol decreased the bRvp significantly and could be possibly lower than that of original FCC gasoline. Beta-zeolite was a more suitable catalyst than Amberlyst 16 for upgrading FCC gasoline. This was due to the higher of catalytic activity for etherification, ethanol could be converted more and therefore increased the renewability of the gasoline while olefinic compounds could be decreased to meet the Euro 4 standard. Normally, the FCC etherified gasoline might give slightly lower of RON compared to ethanol direct blend because RON of ethers were usually lower than that of ethanol. However, Beta-zeolite also showed a catalytic activity of isomerization reaction, RON of the gasoline product was enhanced. The etherified gasoline also showed satisfactions in term of minimum cold start temperature and driveability index. Therefore, the process allows the use of ethanol to substitute in gasoline at higher content than conventional method with direct blending and more suitable gasoline properties can be obtained.

Acknowledgment Financial supports from Silpakorn University Research and Development Institute, the Thailand Research Fund and Commission on Higher Education are gratefully acknowledged. We also thank the technical supports from Thai Oil Public Company Limited.

References

1. Agarwal AK (2007) Prog Energy Combust Sci 33:233
2. Pimentel D (1991) J Agric Environ Ethics 4:1
3. Wang M, Wu M, Huo H (2007) Environ Res Lett 2 Article Number: 024001
4. Wu M, Wu Y, Wang M (2006) Biotechnol Prog 22:1012
5. Wang M, Saricks C, Wu M (1997) Fuel-cycle energy use and greenhouse gas emissions of fuel ethanol produced from US Midwest Corn. Argonne National Laboratory, Argonne, IL
6. Niven RK (2005) Renew Sust Energy Rev 9:535
7. Automobile Emissions: An Overview, Office of Mobile Sources, United States Environmental Protection Agency, EPA 400-F-92–007, August 1994
8. French R, Malone P (2005) Fluid Phase Equilib 228:2
9. Caetano NS, Loureiro JM, Rodrigues AE (1994) Chem Eng Sci 49:4589
10. Piccoli RL, Lovisi HR (1995) Ind Eng Chem Res 34:510
11. Rihko LK, Kiviranta-Paakkonen PK, Krause AOI (1997) Ind Eng Chem Res 36:614
12. Kiviranta-Paakkonen P, Struckmann LK, Linnekoski JA, Krause AOI (1998) Ind Eng Chem Res 37:18
13. Linnekoski JA, Kiviranta-Paakkonen P, Krause AOI (1999) Ind Eng Chem Res 38:4563
14. Karinen RS, Krause AOI (2001) Ind Eng Chem Res 40:6073
15. Ferreira MV, Loureiro JM (2004) Ind Eng Chem Res 43:5156
16. Ferreira MV, Ribeiro AM, Loureiro JM (2007) Ind Eng Chem Res 46:1105
17. Gomez C, Cunill F, Iborra M, Izquierdo F, Tejero J (1997) Ind Eng Chem Res 36:4756
18. Varisli D, Dogu T (2005) Ind Eng Chem Res 44:5227
19. Boz N, Dogu T (2005) AIChE J 51:631
20. Prior JMV, Loureiro JM (2001) Chem Eng Sci 56:873
21. Duarte C, Loureiro JM (2004) Ind Eng Chem Res 43:3242
22. Ancilloti F, Fattore V (1998) Fuel Process Technol 57:163
23. Menezes EW, Cataluña R, Samios D, Silva R (2006) Fuel 85:2567
24. Silva R, Cataluña R, Menezes EW, Samios D, Piatnicki CMS (2005) Fuel 84:951
25. Menezes EW, Cataluña R (2008) Fuel Process Technol. doi: 10.1016/j.fuproc.2008.05.006
26. Sow B, Hamoudi S, Zahedi-Niaki MH, Kaliaguine S (2005) Microporous Mesoporous Mater 79:129
27. Karinen RS, Krause AOI (2006) Appl Catal A: Gen 306:128
28. Klepacova K, Mravec D, Bajus M (2005) Appl Catal A: Gen 294:141
29. Richter M, Krisnandi UK, Eckelt R, Martin A (2008) Catal Commun 9:2112
30. Demirbas A (2007) Prog Energy Combust Sci 33:1
31. Francoisse O, Thyrion FC (1991) Chem Eng Process 30:141
32. Fite C, Iborra M, Tejero J, Izquierdo J, Cunill F (1994) Ind Eng Chem Res 33:581
33. Zhang T, Jensen K, Kitchaiya P, Phillips C, Datta R (1997) Ind Eng Chem Res 36:4586
34. Jensen KL, Datta R (1995) Ind Eng Chem Res 34:392
35. Dirk-Faitakis BC, Chuang KT (2004) Ind Eng Chem Res 43:762
36. Oh JH, Park SJ (2005) J Ind Eng Chem 11:456
37. Micek-Ilnicka A (2006) J Mol Catal A 260:170
38. Vlasenko NV, Kochkin YN, Puziy AM (2006) J Mol Catal A 253:192
39. Han KJ, Oh JH, Park SJ (2007) J Ind Eng Chem 13:360
40. Rihko LK, Krause AOI (1993) Appl Catal A: Gen 101:283
41. Oktar N, Murtezaoglu K, Dogu G, Gonderten I, Dogu T (1999) J Chem Technol Biot 74:155
42. Boz N, Dogu T, Murtezaoglu K, Dogu G (2004) Appl Catal A: Gen 268:175
43. Linnekoski JA, Krause AOI, Rihko LK (1997) Ind Eng Chem Res 36:310
44. Linnekoski JA, Krause AOI, Struckmann LK (1998) Appl Catal A: Gen 170:117
45. Rihko LK, Linnekoski JA, Krause AOI (1994) J Chem Eng Data 39:700
46. Kitchaiya P, Datta R (1996) Ind Eng Chem Res 34:1092
47. Assabumrungrat S, Kiatkittipong W, Srivitoon N, Praserthdam P, Goto S (2002) Int J Chem Kinet 34:292
48. Assabumrungrat S, Kiatkittipong W, Praserthdam P, Goto S (2003) Catal Today 79–80:249
49. Kiatkittipong W, Assabumrungrat S, Praserthdam P, Goto S (2002) J Chem Eng Jpn 35:547
50. Aiouache F, Goto S (2003) Chem Eng Sci 58:2056
51. Aiouache F, Goto S (2003) Chem Eng Sci 58:2456
52. Boonthamtirawuti O, Kiatkittipong W, Assabumrungrat S, Arpornwichanop A, Praserthdam PJ (2008) Ind Eng Chem (in press)
53. Umar M, Saleemi AR, Qaiser S (2008) Catal Commun 9:721
54. Karinen RS, Krause AOI (2000) Catal Lett 67:73
55. Karinen RS, Linnekoski JA, Krause AOI (2001) Catal Lett 76:81
56. Pescarollo E, Trotta R, Sarathy PR (1993) Hydrocarb Process 73:53
57. Rihko LK, Krause AOI (1996) Ind Eng Chem Res 35:2500
58. Hu T, Chen J, Wang H, Ma J, Wei M (2006) Microporous Mesoporous Mater 94:295
59. Fan Y, Bao X, Shi G, Wei W, Xu J (2004) Appl Catal A: Gen 275:61
60. Fan Y, Bao X, Shi G (2005) Catal Lett 105:67
61. Peiqing Z, Xiangsheng W, Xinwen G, Hongchen G, Leping Z, Yongkang H (2004) Catal Lett 92:63
62. Niu X, Song Y, Xie S, Liu S, Wang Q, Xu L (2005) Catal Lett 103:211
63. Ren YJ, Li S (2008) Catal Lett 121:85
64. Perry R, Gee IL (1995) Sci Total Environ 169:149
65. Kiatkittipong W, Thipsunet P, Goto S, Chaisuk C, Praserthdam P, Assabumrungrat S (2008) Fuel Process Technol. doi:10.1016/j.fuproc.2008.06.007

66. Colombo F, Cori L, Dallora L, Delogu P (1983) Ind Eng Chem Fundam 22:219
67. Izquierdo JF, Cunill F, Vila M, Tejero J, Iborra M (1992) J Chem Eng Data 37:339
68. Vila M, Cunill F, Izquierdo JF, Tejero J, Iborra M (1993) Chem Eng Commun 124:223
69. Cruz VJ, Izquierdo JF, Cunill F, Tejero J, Iborra M, Fite C (2005) React Funct Polym 65:149
70. Corma A, González-Alfaro V, Orchillés AV (1999) Appl Catal A: Gen 187:245
71. Slomkiewicz PM (1997) React Funct Polym 33:299
72. Harmer MA, Sun Q (2001) Appl Catal A: Gen 221:45
73. Aronov DM, Noreiko LM (1967) Chem Technol Fuels Oils 3:359
74. Magyar S, Hancsok J, Kallo D (2005) Fuel Process Technol 86:1151
75. Lippa AJ, (2006). Software fuel volatility measurement. US Patent 7,059,313
76. http://www.chevron.com/products/ourfuels/prodserv/fuels/documents/Motor_Fuels_Tch_Rvw_complete.pdf
77. Ancilotti F, Mauri F, Pescarollo E (1977) J Catal 46:49
78. Ancilotti F, Mauri F, Pescarollo E, Romagnoni L (1978) J Mol Catal 4:7
79. Gicquel A, Torck B (1983) J Catal 83:9
80. Balcerowiak W (1997) React Funct Polym 33:323
81. Zholobenko V, Garforth A, Dwyer J (1997) Thermochim Acta 294:39

Fuel Processing Technology 92 (2011) 1999–2004

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Gasoline upgrading by self-etherification with ethanol on modified beta-zeolite

Worapon Kiatkittipong [a,*], Suwimol Wongsakulphasatch [a], Nattapon Tintan [a], Navadol Laosiripojana [b], Piyasan Praserthdam [c], Suttichai Assabumrungrat [c]

[a] Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand
[b] The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand
[c] Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

ARTICLE INFO

Article history:
Received 19 March 2011
Received in revised form 21 May 2011
Accepted 31 May 2011
Available online 25 June 2011

Keywords:
Modified beta zeolite
Renewable energy
Olefins reduction
Etherification
FCC gasoline

ABSTRACT

This research studied the modification of beta-zeolite for self-etherification process of fluidized catalytic cracking (FCC) gasoline and ethanol. The catalytic activity of reducing olefins in FCC gasoline accompanied with higher ethanol substitution was evaluated; moreover, the influences of Si/Al ratio in beta zeolite and the addition of copper (Cu) or magnesium (Mg) in the beta zeolite on the reaction performance were also investigated. It was found that the beta zeolite with Si/Al ratio of 27 (beta$_{27}$) can enhance higher ethanol conversion than those of 42 and 77. In addition, the modification of beta$_{27}$ by Cu (Cu-beta$_{27}$) can further improve the ethanol conversion from 38.2% (beta$_{27}$) to 55.1%, and the olefin content reduction from 46.2% (beta$_{27}$) to 62.4%. The improvement of the catalytic activity also enhances the obtained gasoline properties i.e. lower blending Reid vapor pressure (bRvp) and higher research octane number (RON).

1. Introduction

Fluid catalytic cracking (FCC) of gasoline is the main contribution of olefins when it is blended with gasoline pool. Such olefinic compounds usually present in an unstable form, which are easily oxidized by photochemical reaction, leading to an increase of ground ozone level. Hence the amounts of olefinic compounds are enforced to have a limiting upper value of 18 vol.% as regulated by Europe IV vehicle standard of unleaded gasoline. Several studies on selective hydrogenation for olefins reduction have been proposed and some of them have already been performed the pilot-scale operations; however, this technique is still facing problems with low gasoline yield and loss in research octane number (RON) [1,2]. Converting olefins in FCC gasoline by hydroisomerization and aromatization was therefore developed and was succeeded in reducing the loss of octane number from olefin reduction due to compensation by the formation of iso-paraffins and aromatics [1,3–5]. However, this process has to be operated at a high temperature between 270 and 370 °C with pure hydrogen at the pressure of 2.0–3.0 MPa. A catalyst modification for non-hydrogenation reduction of olefins, which is known as a process without hydrogen supply in feed, has been proposed as it is especially beneficial for the refineries where hydro-treating is limited or low-cost hydrogen could not be provided [6]. The products from the non-hydrogenation provide similar RON or slightly higher than those obtained from the original FCC gasoline [6–8]. The operating temperatures of non-hydrogenation reduction of olefins in this operation are normally in the range of 170–400 °C.

Since most conventional techniques are usually operated at relatively high temperatures and it is difficult to achieve higher RON as well as the process does not increase a renewability of gasoline, etherification reaction is proposed as an alternative way for upgrading FCC gasoline [9]. By etherifying the entire FCC gasoline, the olefin content and bRvp of the gasoline could be reduced with an increase of gasoline yield, octane number and oxygen content. The etherification of the entire FCC gasoline has been successfully experimented with methanol [10–13]. Rihko and Krause [11] employed Amberlyst 16 for etherification of light FCC gasoline with methanol. Tert-amyl methyl ether (TAME), producing from iso-amylene (C_5-olefinic compounds), was observed to be the main ether products. Hu et al. [13] investigated various catalysts i.e. beta-, MOR-, ZSM5-zeolite and D005 cationic exchange resin for FCC etherification with methanol. They reported that beta-zeolite provides the highest conversion and catalytic stability. In addition, instead of methanol, the FCC process could also employ the renewable reagents i.e. ethanol [9,14] and glycerol [15]. An advantage of using such renewable reagents is that they are more environmentally friendly, which can partially reduce the global warming from gasoline utilization. Kiatkittipong et al. [9] studied FCC gasoline upgrading by etherification with ethanol. The use of ethanol in the etherification process can overcome the constraint of using ethanol as fuel extender by direct blending method (as well known as “gasohol”) which is limited at ca. 10–20 vol.% for non-flex fuel engine. Moreover, this process can decrease evaporative loss by reducing gasoline volatility. Considering the catalytic performance, beta-zeolite was found to enhance better catalytic activity than Amberlyst 16 since it provides not only higher

---

[*] Corresponding author. Tel./fax: +66 3421 9368.
E-mail address: kworapon@su.ac.th (W. Kiatkittipong).

0378-3820/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.fuproc.2011.05.024

Table 1
Compositions of FCC gasoline (vol.%).

Carbon number	n-Paraffins	i-Paraffins	Olefins	Naphtenes	Aromatics	Total
C4	0.215	0.111	1.208	0	0	1.534
C5	0.996	7.691	6.693	0	0	15.380
C6	1.102	11.764	7.053	1.631	0.323	21.874
C7	0.794	7.146	7.246	2.564	2.230	19.980
C8	1.059	5.953	0.688	2.230	4.608	14.538
C9	0.391	3.030	1.937	2.827	5.079	14.264
C10	0.257	2.620	0	0.137	5.563	8.577
C11	0.281	0.829	0	0.087	0.766	1.864
C12	0.077	0.446	0	0.205	0.909	1.637
Total	5.072	39.591	24.825	9.681	20.478	99.647

ethanol and olefin conversion but also gives higher RON with lower blending Reid vapor pressure (bRvp). A satisfied drivability index showed that no cold start problem occurs even at low bRvp [14]. However, it is worth to note that in the case of FCC etherified with glycerol, Amberlyst 16 expresses much higher catalytic activity than that of beta-zeolite. The explanation is possibly due to the fact that the glycerol derived ethers products are larger and more obstructed than ethanol derived ether, which may not suit to the pore structure of zeolite [15]. The demand of oxygenated ethers is usually limited by the reaction of C_4 and C_5 reactive olefins. Recently, several studies have been investigating the synthesis of these ethers in different routes i.e. ethanol derived ethers such as ethyl *tert*-butyl ether (ETBE) and *tert*-amyl ethyl ether (TAEE) [17–20], and glycerol derived ethers [16]. When employing the whole FCC gasoline as olefins sources for etherification, so called “self-etherification”, the wide range of ethers production by FCC self-etherification with ethanol [9,14] and glycerol [15] could effectively enhance the RON and sustain the demand of oxygenated ethers.

According to our previous works on the etherified FCC gasoline with ethanol, the amount of remaining olefinic compounds in the products are in compliance with the limiting values regulated by Euro IV standard [9,14]; however, converting the rest olefinic compounds would be beneficial both in terms of olefins reduction and enhanced ethanol substitution in gasoline. It is known from previous studies that only tertiary olefins (double bond attached to a tertiary carbon) are reactive for etherification [21–23]. Moreover, the etherification reactions are strongly limited by the thermodynamics. Many studies on the thermodynamics of various ethanol etherification reactions with e.g. C_4-isobutene [24,25], C_5-isoamylene [21] and various C_6 reactive olefins [23,26] have been published. The equilibrium conversion from the experiments [27] agrees well with their theoretical calculation [23], where ETBE formation is substantially higher than that of 2-ethoxy-2-methylpentane and TAEE, respectively. Therefore, higher demand of ethanol to substitute in gasoline by converting to ethers cannot be implemented by only etherification. The idea of this study is to combine the catalytic isomerization of non-reactive olefins to produce a surplus reactive olefins and etherification with ethanol as a synergy for ethanol supplementary in gasoline with olefin reduction. Many researchers have studied on skeletal isomerization especially n-butenes to isobutene, in which various metals e.g. magnesium [28] and copper [29] were loaded on silica-alumina or zeolite supported for skeletal isomerization enhancement. In this study, we focus on the modification of beta-zeolite to achieve higher ethanol and olefin conversions with preferable gasoline properties for enhancing renewability and environmental friendliness of gasoline.

2. Materials and method

2.1. Chemicals

FCC gasoline was obtained from the catalytic cracking unit of an oil refinery; its compositions are given in Table 1. Chemical precursors employed in the study for modifying beta-zeolite are copper nitrate ($Cu(NO_3)_2.2.5H_2O$) and magnesium chloride ($MgCl_2.6H_2O$) supplied from Ajax Finechem Ltd. Commercial beta-zeolite with Si/Al = 27 in the form of Na^+ (mean particle size of 3–6 μm) was purchased from Tosoh company, Japan.

2.2. Catalyst modification

2.2.1. Removal of Na^+ from beta-zeolite

Beta-zeolite was exchanged into H^+ form by dissolving 10 g of beta-zeolite in 150 ml of 1 M NH_4Cl aqueous solution at 80 °C for 5 h. The exchanged process was performed for 3 times. After that beta-zeolite was washed with deionized water for 3 times. The beta-zeolite was separated by centrifugation and dried at 110 °C for 3 h. At this stage, the obtained crystals were in the NH_4^+ form. Then, the sample was calcined at a temperature of 550 °C under air stream for 6 h to dissociate the ammonium into H^+ form, as NH_3 escapes to the atmosphere and H^+ stays on the catalyst to balance the ionic charge [17].

2.2.2. Dealumination of beta-zeolite

Beta-zeolite was dealuminated by following the procedure reported by Collignon et al. [30], from which 10 g of beta-zeolite was dissolved in 200 ml of 0.5 M HNO_3 solution and stirred at 80 °C for a desired period. The zeolite was then washed with deionized water for several times and dried at 110 °C for 3 h.

2.2.3. Modification by ion exchanging with metal cation

After exchanged beta-zeolite to H^+ form, Hbeta-zeolite was then back exchanged with cations Cu and Mg. The procedure of the back exchange is similar to that reported by Nieminen et al. [29] and Canizares et al. [31], in which 10 g of Hbeta-zeolite was mixed with 150 ml aqueous solution of 0.1 M copper nitrate or 0.5 M aqueous magnesium chloride at 80 °C. Metal-Hbeta-zeolite was then washed

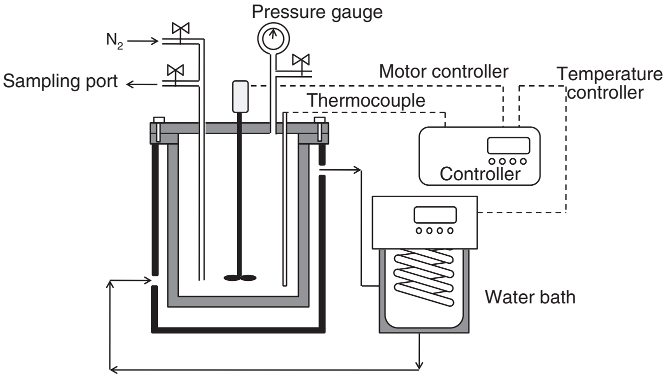


Fig. 1. Schematic diagram of the reactor apparatus.

with deionized water, dried at 110 °C for 12 h and calcined under air flow at 500 °C for 3 h.

2.3. Experimental technique

Etherification of FCC gasoline with glycerol was carried out in a cylindrical shape autoclave reactor as shown in Fig. 1. A valve for liquid sampling and a port for the thermocouple were installed at the top of the reactor. For all experiments, the mixture was stirred by using a turbine at the maximum speed of 1163 rpm since the effect of external mass transfer resistance could be negligible at this stirring speed [9]. The reactor was maintained at a constant temperature by circulating hot water in jackets. The ratio of FCC gasoline:ethanol was varied in vol.% (with total volume of 100 cm^3) and 10 g of catalyst was carried out at 70 °C for 10 h under a pressure of 0.8 MPa. It should be noted that although it is not practical in industrial application, high ratio of catalyst to reactant was applied in this study in order to reach reaction equilibrium within 10 h. After reaction, the reactor was cooled down to room temperature before collecting the sample from the reactor in order to prevent evaporation loss.

2.4. Catalyst characterizations

Structural characteristics of the catalysts were investigated by powder X-ray diffraction (XRD) analysis using a Siemens D5000 diffractometer equipped with CuKα radiation and Ni filter. Its surface area and mean pore diameter were determined by N_2 adsorption (BET method) using a BEL-SORP automated system. Chemical analysis was determined by inductive couple plasma (ICP), Varian: liberty 220. Acidity of catalyst was investigated by Micromeritics 2000 TPD/TPR ammonia-temperature programmed desorption (NH_3-TPD).

2.5. Product analysis

The standard analysis of research octane number (RON), blending Reid vapor pressure (bRvp) and distillation temperature was carried out following the standard methods of ASTM D-2699, ASTM D-5191 and ASTM D-86, respectively.

3. Results and discussion

3.1. Catalyst characterization

The surface area and mean pore diameter of the catalysts with Cu and Mg loading and dealumination are illustrated in Table 2. It can be seen that the catalyst surface area and mean pore diameter decrease with metal loading. The chemical composition of the catalysts is shown in Table 2 in terms of Si/Al molar ratio and metal content (Cu, Mg). Beta-zeolite starting material with Si/Al = 27 was dealuminated to two levels (i.e., Si/Al of 42 and 77) and Cu and Mg were exchanged with H$^+$ in similar level at approximately 1 wt.%.

Fig. 2 shows the XRD patterns of beta-zeolite with different Si/Al ratios and metal loadings. The spectrum of beta-zeolite has characteristic peaks similar to those previously reported in the literature [17]. It is noted that these peaks are also observed in all catalyst samples indicating that the incorporation of metal does not change crystalline structure of the modified beta-zeolite. In addition, no significant peaks of Cu and Mg are observed from the XRD due to low amount of metal loading.

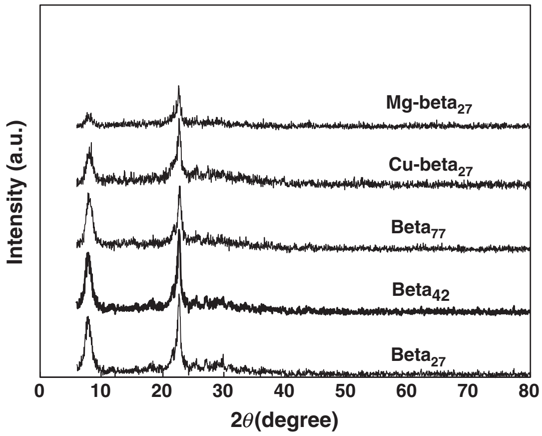


Fig. 2. XRD patterns of beta-zeolite catalyst.

3.2. Catalyst performance

The catalyst performance for etherification of FCC gasoline with ethanol is presented in terms of ethanol conversion as shown in Fig. 3. It can be seen that beta-zeolite with Si/Al of 27 shows a greater activity toward the FCC etherification with ethanol compared to beta-zeolite with Si/Al of 42 and 77. It is noted that ethanol conversion slightly decreases (from 38.0% to 36.3%) with increasing Si/Al ratio from 27 to 42; however, it drastically decreases (from 38% to 21% when Si/Al ratio is increased to 77. The role of copper and magnesium on the reaction performance was investigated as shown in Fig. 3. It was found that the addition of both copper and magnesium into beta-zeolite with Si/Al ratio of 27 (denoted as Cu-beta$_{27}$ and Mg-beta$_{27}$) can significantly enhance the etherification of FCC gasoline with ethanol. The highest ethanol conversion of 55.1% could be obtained with Cu-beta$_{27}$ catalyst at 20 vol.% ethanol. With increasing ethanol substitution ratio up to 30 vol.%, higher amount of ethanol was converted with a conversion of 49.6% as shown in Table 3. The characterization of obtained gasoline products is provided in the next section.

3.3. Characterization of gasoline products

The composition of FCC gasoline (as shown in Table 1) illustrates that the main components of olefins are C_5–C_7 hydrocarbons and about 25 vol.% of olefins are found in gasoline. Table 3 presents the gasoline properties, olefins conversion, and ethanol conversion of FCC gasoline for FCC:ethanol initial feed ratios of 80:20 and 70:30, respectively. It can be seen that the original FCC gasoline has RON of 88 and bRvp of 6.5. The RON increases to 94.8 and 97.9 with ethanol direct blending at 20 and 30 vol.%, respectively; however, bRvp increases up to 7.42 and 8.0. An increase of bRvp induces higher

Table 2
Properties of catalysts.

Catalysts	Si/Al [−][a]	Metal content (Cu, Mg) [wt.%][a]	Surface area [m^2 g^{-1}][b]	Mean pore diameter [nm][b]
Beta$_{27}$	27	–	667	0.59
Beta$_{42}$	42	–	625	0.58
Beta$_{77}$	77	–	563	0.59
Cu-beta$_{27}$	27	0.92	550	0.57
Mg-beta$_{27}$	27	1.04	535	0.53

[a] Determined by ICP.
[b] Determined by BET.

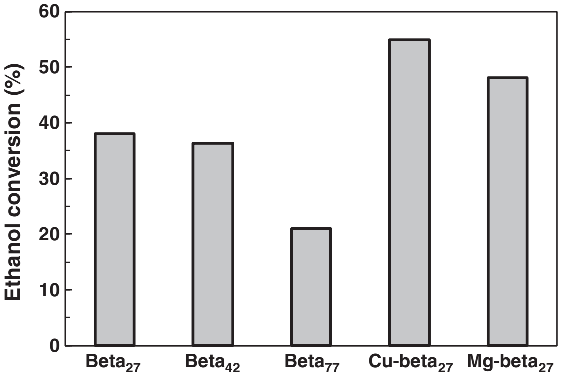


Fig. 3. Ethanol conversion from etherification with FCC gasoline catalyzed by various beta-zeolite based catalysts (FCC gasoline:ethanol = 80:20 by volume).

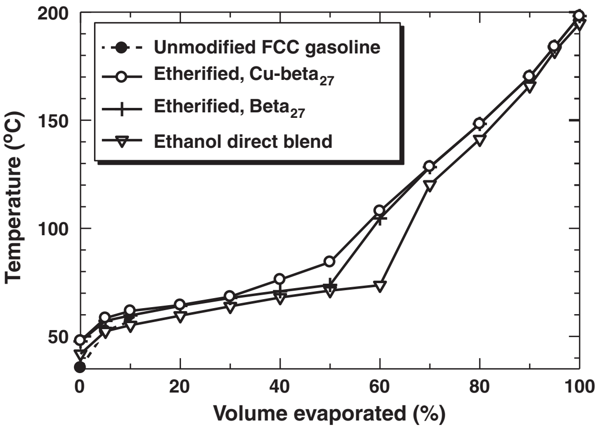


Fig. 4. Distillation temperatures (following the ASTM D-86 standard method).

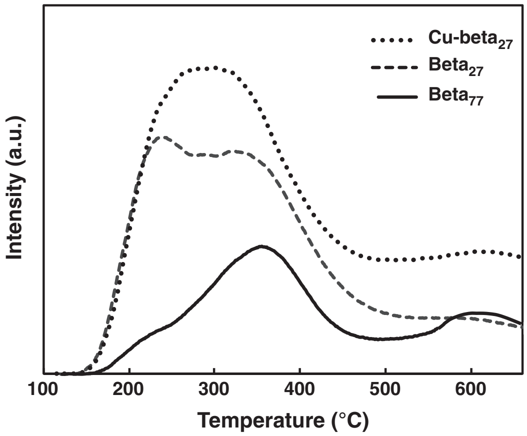


Fig. 5. NH_3-TPD results of different catalysts.

evaporative loss and leads to vapor lock which is not favorable especially in summer or in tropical countries. It is worthy to note that recently more restriction on gasoline volatility is enforced i.e. California Reformulated Gasoline Phase 3 (CaRFG3) regulation with the cap limit of bRvp at 6.4–7.2 seasonally (http://www.arb.ca.gov/fuels/gasoline/carfg3/carfg3.htm). As presented in Table 3, FCC etherified with ethanol by using either beta$_{27}$ or Cu-beta$_{27}$ could effectively decrease the values of bRvp because the olefins in FCC gasoline and ethanol are converted to ethers which have lower bRvp. The main ether product obtained in this study is TAEE, which is similar to the case of etherification of FCC gasoline with methanol as reported by Rihko and Krause [11], where TAME is obtained as a main ether product. The concentration of ethers and some free ethanol remaining in the final products is provided in Table 3. The less free ethanol left in gasoline indicates a higher possibility of using the gasoline in a non-flex fuel engine. The oxygen contents determined from ethanol and ethers left in final product are approximately 6.7–7.0 and 9.6–10.0 wt.% in cases of etherification with 20 and 30 vol.% ethanol, respectively. By incorporating copper in beta$_{27}$ (Cu-beta$_{27}$), the etherification reaction is enhanced as indicated by an increase of ethanol conversion and olefins reduction. It is worthy to note that from the analysis of the olefin distribution, both the amounts of tertiary olefins and non-reactive branched olefins decreased. This will be discussed in more details in the next paragraph. For other gasoline properties, density and viscosity of the etherified gasoline are found to be close to those of the commercial gasohol. When ethanol is increased to 30 vol.%, similar trend to those of 20 vol.% ethanol is observed for all properties studied.

The results of distillation temperatures carried out following the ASTM D-86 standard method are shown in Fig. 4. The direct blending of ethanol significantly changes the distillation curve compared to that of the original FCC gasoline as the distillation temperature is drastically affected at the temperature of 50–60 evaporated volume (T_{50} and T_{60}). Apart from the initial boiling point (IBP), the distillation temperature of direct blending ethanol decreases throughout the percent volume of evaporated gasoline.

In case of FCC gasoline etherified with ethanol using catalyst either Cu-beta$_{27}$ or beta$_{27}$, the gasoline products showed higher values of IBP, T_5, and T_{10} than those of the original FCC gasoline. The higher values of these front end distillation temperatures support the results of lower value of the bRvp, which are in the order of Cu-beta$_{27}$<beta$_{27}$<original FCC gasoline<ethanol direct blending. The least remaining of ethanol from unconverted in etherified gasoline with Cu-beta$_{27}$ makes the most similar distillation curve compared to the original FCC gasoline as shown by the closer distillation temperature in the range of T_{30}–T_{60}. From the

Table 3
Comparison of gasoline properties.

Properties	FCC gasoline	Gasoline E10	20 vol.% Ethanol			30 vol.% Ethanol		
			Direct blend	Etherified gasoline		Direct blend	Etherified gasoline	
				Beta$_{27}$	Cu-beta$_{27}$		Beta$_{27}$	Cu-beta$_{27}$
RON	88	95	94.8	94.2	94.8	97.9	98.2	98.5
bRvP (psi)	6.5	< 9.0	7.42	5.64	5.22	8.0	6.47	6.08
Density (g cm^{-3})	0.683	0.749	0.735	0.745	0.748	0.735	0.745	0.749
Viscosity (Pa s)	6.09×10^{-4}	5.05×10^{-4}	6.20×10^{-4}	6.19×10^{-4}	6.17×10^{-4}	6.03×10^{-4}	5.09×10^{-4}	5.14×10^{-4}
Ethanol conversion (%)			0	38.2	55.1	0	40.3	49.6
Olefins reduction (%)			0	46.2	62.4	0	60.1	68.7
Free ethanol left (wt.%)		Approx .11%	22.4	13.9	10.1	33.1	19.8	16.7
Ethers conc. (wt.%)			0	16.2	22.4	0	22.8	26.2

Table 4
Comparison of olefin reduction techniques.

Reaction	References	Catalyst, operating *T* and *P*	Olefins (vol.%)			Aromatics (vol.%)			RON		
			Initial	Final	Change (%)	Initial	Final	Change (%)	Initial	Final	Change
Hydroisomerization	Fan et al. [1]	β/ZSM-5 composite, 315 °C, 2.0 MPa	41.1	9.9	−75.9	17.4	29.3	+68.4	91.7	92.1	+0.4
	Fan et al. [2]	SAPO-11/MOR/β/ZSM, 300 °C, 2.0 MPa	41.7	6.3	−84.9	17.1	21.4	+25.1	91.7	86.3	−5.4
Non-hydrogenation	Zubin et al. [36]	BPyC-$AlCl_3$ ionic liquid[1], 25 °C, N.A.[2]	42.5	28.0	−34.1	15.7	18.1	+15.3	91.3	90.5	−0.8
	Ding et al. [6]	kaolin/γ-Al_2O_3/ZSM-5, 400 °C, 0.1 MPa	43.5	18.7[3]	−56.8	14.4	33.7[3]	+134.0	92.1	~92[4]	~0[4]
	Li et al. [7]	Ni/W/SiO_2.Al_2O_3, 170 °C, 2.5 MPa	51.0	25.6	−49.8	19.1	37.1	+94.2	88.6	89.1	+0.5
	Lihua and Jinshen [8]	Ni,Mo/β-zeolite, 140 °C, 2.0 MPa	60.9	33.0	−45.8	12.2	29.1	+138.5	92.0	95.0	+3.0
Etherification with ethanol (20 vol.%)	Kiatkittipong et al. [9]	β-zeolite (Si/Al = 40), 70 °C, 0.8 MPa	25.7	13.9	−45.9	17.0	16.9	−0.6	88.0	94.1	+6.1
	Kiatkittipong et al. (this study)	Cu-β-zeolite (Si/Al = 27), 70 °C, 0.8 MPa	24.8	9.3	−62.4	20.5	20.7	+1.0	88.0	94.8	+6.8

[1] BPyC = 1-butylpyrinium chloride.
[2] N.A. = not available.
[3] Determined from Fig. 2 of Ding et al. [6] with optimal kaolin/γ-Al_2O_3 ratio of 1.5.
[4] Ding et al. [6] reported preserving of gasoline RON.

results, we could presume that higher olefin consumption, which are mostly in C_5–C_7 range, might mainly contribute to higher front end distillation temperature while higher ethanol conversion mainly contribute to higher middle range distillation temperature.

The NH_3-TPD profiles of Cu-beta$_{27}$, beta$_{27}$, and beta$_{77}$ are shown in Fig. 5. Comparing the NH_3-TPD profiles between beta$_{77}$ and beta$_{27}$, it can be revealed that the total acidity (determined by total area of the graph) decreases with increasing Si/Al. This manner is as expected since the acid site in zeolite is generally formed on the Si–O–A1 linkage of the zeolite framework. In addition, a decrease of weak acidity is more pronounced compared with the strong acidity. It is worth to note that both the weak and strong acid sites are active for etherification reaction; however weak acid is more stable due to less carbon formation [32]. The Cu-beta$_{27}$ catalyst can increase both weak and strong acid sites. It is found that the reaction that requires strong acid (over 400 °C) rather than weak acid is the skeletal isomerization as observed by Woo et al. [33] and Escalante et al. [34] for skeletal of n-butene to iso-butene. However, in this study, the major decreased olefins are reactive and non-reactive branched olefins rather than linear olefins. It is known that the reaction involving positional isomerization is faster than skeletal isomerization [35]. Stronger acid catalyst and/or higher operating temperature would be needed for skeletal isomerization compared to those for positional or double bond shift isomerization. The increase of olefins conversion could therefore be presumably arisen from isomerization among branched olefin to reactive olefins, which could be further reacted by etherification with ethanol.

3.4. Comparison of olefin reduction techniques

Since operating condition among various techniques is different and the amount of olefins in the FCC gasoline feedstock among various studies is varied in a wide range ca. 25–61 vol.% as shown in Table 4, therefore, comparison performances of olefin reduction among different techniques might be difficult. As a consequence, it is worth to provide the necessary data, such as operating temperature and pressure, catalyst, feed and product composition, to give an overall idea in order to clarify characteristics and advantages of each process. The ability of etherification with ethanol for reducing olefins in FCC gasoline is compared with current techniques of hydroisomerization and non-hydrogenation as summarized in Table 4. It can be seen that hydroisomerization, which is usually accompanied with aromatization, can diminish the olefins at the highest extent (84.9% of olefins reduction). However, the process would suffer from the loss of RON if compensation by an increase of aromatics compound is not enough.

Non-hydrogenation was proposed instead of hydroisomerization in case when low-cost hydrogen is unavailable. However, as presented in Table 4, non-hydrogenation shows a much lower degree of olefin reduction than that of hydroisomerization process. In addition, the RON obtained from hydroisomerization or non-hydrogenation strongly depends upon the degree of olefins reduction and aromatization. Therefore, to compromise the olefins and aromatic content under the restriction limit (18 vol.% for olefins and 35 vol.% for aromatics) it is necessary to consider the RON value preserved in the gasoline as well.

From the study, it is summarized that etherification with ethanol shows an intermediate performance between hydroisomerization and non-hydrogenation process as indicated by reduction of olefin. Moreover, the change of aromatic compounds can be negligible. It is worth to note that the change in vol.% of olefin and aromatic compounds in the case of etherification shown here was calculated by excluding from the dilution effect of ethanol substitution. In addition, the process shows the improvement of RON which is obtained from generated ether compounds and unreacted ethanol remaining in the gasoline. Therefore we could claim here that self-etherification of FCC gasoline with ethanol catalyzed by Cu-beta$_{27}$ catalyst is one of promising processes for reducing olefins with effective increasing RON and renewability of the gasoline.

Conclusion

The etherification of FCC gasoline with ethanol is a promising technology for gasoline upgrading by efficient reduction of olefin content accompanying with quality improvement. The beta-zeolite with Si/Al of 27 modified by ion-exchanged with Cu shows an outstanding performance; it provides high ethanol conversion and olefin consumption e.g. 55.1 and 62.4%, respectively, in case of 20% ethanol in feed. By increasing the ethanol fraction in feed up to 30 vol.%, the reaction could be further enhanced. Higher ethanol conversion means ethanol could be higher supplemented into gasoline and less free ethanol remaining. Lower ethanol left in gasoline results in lower blending Reid vapor pressure (bRvp). Comparison to other techniques for reducing olefin content in FCC gasoline, etherification with ethanol catalyzed by Cu-beta catalyst provides intermediate values of olefin reduction between the hydroisomerization and non-hydrogenation process. However, our proposed technique could effectively improve RON without an increase of aromatic content.

Acknowledgments

Financial supports from Silpakorn University Research and Development Institute, the Thailand Research Fund and Commission on Higher Education are gratefully acknowledged.

References

[1] Y. Fan, X. Bao, G. Shi, Hβ/HZSM-5 composite carrier supported catalysts for olefins reduction of FCC gasoline via hydroisomerization and aromatization, Catalysis Letters 105 (2005) 67–75.

[2] Y.-J. Ren, S. Li, The effect of lanthanum and niobium on additives for olefins reduction of FCC gasoline, Catalysis Letters 121 (2008) 85–89.

[3] Y. Fan, X. Bao, G. Shi, W. Wei, J. Xu, Olefin reduction of FCC gasoline via hydroisomerization aromatization over modified HMOR/HZSM-5/Hβ composite carriers, Applied Catalysis A: General 275 (2004) 61–71.

[4] Y. Fan, X. Bao, D. Lei, G. Shi, W. Wei, J. Xu, A novel catalyst system based on quadruple silicoaluminophosphate and aluminosilicate zeolites for FCC gasoline upgrading, Fuel 84 (2005) 435–442.

[5] P. Zhang, X. Guo, H. Guo, X. Wang, Study of the performance of modified nano-scale ZSM-5 zeolite on olefins reduction in FCC gasoline, Journal of Molecular Catalysis A: Chemical 261 (2007) 139–146.

[6] Y. Ding, J. Liang, Y. Fan, Y. Wang, X. Bao, Synergisms between matrices and ZSM-5 in FCC gasoline non-hydrogenating upgrading catalysts, Catalysis Today 125 (2007) 178–184.

[7] L. Li, Y. Zhai, J. Zhang, J. Wang, T. Yu, A new catalyst for the non-hydrogenation reduction of olefins, Petroleum Science and Technology 25 (2007) (2007) 427–441.

[8] L. Lihua, Z. Jinshen, Olefin reduction of FCC naphtha using β-zeolite catalyst in the absence of hydrogen, Petroleum Science and Technology 26 (2008) 144–152.

[9] W. Kiatkittipong, P. Thipsunet, S. Goto, C. Chaisuk, P. Praserthdam, S. Assabumrungrat, Simultaneous enhancement of ethanol supplement in gasoline and its quality improvement, Fuel Processing Technology 89 (2008) 1365–1370.

[10] E. Pescarollo, R. Trotta, P.R. Sarathy, Etherify light gasolines, Hydrocarb. Process. 73 (1993) 53–60.

[11] L.K. Rihko, A.O.I. Krause, Etherification of FCC light gasoline with methanol, Industrial and Engineering Chemistry Research 35 (1996) 2500–2507.

[12] M. Jun, T.Y. Wen, M. Jun, D. Dan, L. Qiu-Ying, W. Hai-Yan, Etherification performance of transition metals modified β-zeolite catalyst, Petroleum Science and Technology 23 (2005) 1083–1090.

[13] T. Hu, J. Chen, H. Wang, J. Ma, M. Wei, Influence of shaped and modified Hβ zeolite on etherification of FCC light gasoline, Microporous and Mesoporous Materials 94 (2006) 295–303.

[14] W. Kiatkittipong, K. Yoothongkham, C. Chaisuk, P. Praserthdam, S. Goto, S. Assabumrungrat, Self-etherification process for cleaner fuel production, Catalysis Letters 128 (2009) 154–163.

[15] W. Kiatkittipong, S. Suwanmanee, N. Laosiripojana, P. Praserthdam, S. Assabumrungrat, Cleaner gasoline production by using glycerol as fuel extender, Fuel Processing Technology 91 (2010) 456–460.

[16] W. Kiatkittipong, P. Intaracharoen, N. Laosiripojana C. Chaisuk, P. Praserthdam, S. Assabumrungrat, Glycerol ethers synthesis from glycerol etherification with tert-butyl alcohol in reactive distillation, Computers and Chemical Engineering (2011) (doi:10.1016/j.compchemeng.2011.01.016).

[17] S. Assabumrungrat, W. Kiatkittipong, N. Srivitoon, P. Praserthdam, S. Goto, Kinetics of liquid phase synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol catalyzed by supported β-zeolite, International Journal of Chemical Kinetics 34 (2002) 292–299.

[18] S. Assabumrungrat, W. Kiatkittipong, P. Praserthdam, S. Goto, Simulation of pervaporation membrane reactors for liquid phase synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol, Catalysis Today 79–80 (2003) 249–257.

[19] W. Kiatkittipong, S. Assabumrungrat, P. Praserthdam, S. Goto, A pervaporation membrane reactor for liquid phase synthesis of ethyl tert-butyl ether from tert-butyl alcohol and ethanol, Journal of Chemical Engineering of Japan 35 (2002) 547–556.

[20] O. Boonthamtirawuti, W. Kiatkittipong, S. Assabumrungrat, A. Arpornwichanop, P. Praserthdam, Kinetic of liquid phase synthesis of *tert*-amyl ethyl ether from *tert*-amyl alcohol and ethanol over Amberlyst 16, Journal of Industrial and Engineering Chemistry 15 (2009) 451–457.

[21] L.K. Rihko, A.O.I. Krause, Reactivity of isoamylenes with ethanol, Applied Catalysis A: General 101 (1993) 283–295.

[22] P. Kitchaiya, R. Datta, Ethers from ethanol. 2. Reaction equilibria of simultaneous tert-amyl-ethyl ether synthesis and isoamylene isomerization, Industrial and Engineering Chemistry Research 34 (1995) 1092–1101.

[23] T. Zhang, R. Datta, Ethers from ethanol-3, Equilibrium conversion and selectivity limitations in the liquid-phase synthesis of two tert-hexyl ethyl ethers, Industrial and Engineering Chemistry Research 34 (1995) 2237–2246.

[24] M. Vila, F. Cunill, J.-F. Izquierdo, J. Tejero, M. Borra, Equilibrium constants for ethyl tert-butyl ether liquid-phase synthesis, Chemical Engineering Communications 124 (1993) 223–232.

[25] K.L. Jensen, R. Datta, Ethers from ethanol. 1. Equilibrium thermodynamic analysis of the liquid-phase ethyl tert-butyl ether reaction, Industrial and Engineering Chemistry Research 34 (1995) 392–399.

[26] T. Zhang, R. Datta, Ethers from ethanol-5. Equilibria and kinetics of the coupled reaction network of liquid-phase 3-methyl-3-ethoxy-pentane synthesis, Chemical Engineering Science 51 (1996) 649–661.

[27] T. Zhang, K. Jensen, P. Kitchaiya, C. Phillips, R. Datta, Liquid-phase synthesis of ethanol-derived mixed tertiary alkyl ethyl ethers in an isothermal integral packed-bed reactor, Industrial and Engineering Chemistry Research 36 (1997) 4586–4594.

[28] S.Y. Baeck, W.Y. Lee, Dealumination of Mg-ZSM-22 and its use in the skeletal isomerization of 1-butene to isobutene, Applied Catalysis A: General 168 (1998) 171–177.

[29] V. Nieminen, N. Kumar, J. Datka, J. Paivarinta, M. Hotokka, E. Laine, T. Salmi, D.Yu. Murzin, Active copper species in 1-butene skeletal isomerization: comparison between copper-modified MCM-41 and beta catalysts, Microporous and Mesoporous Materials 60 (2003) 159–171.

[30] F. Collignon, M. Mariani, S. Moreno, M. Remy, G. Poncelet, Gas phase synthesis of MTBE from methanol and isobutene over dealuminated zeolites, Journal of Catalysis 166 (1997) 53–66.

[31] P. Canizares, A. Carrero, Comparative study of the catalytic properties of ferrierite zeolite exchanged with alkaline earth metals in the skeletal isomerization of n-butene, Catalysis Letters 64 (2000) 239–246.

[32] J.W. Kim, D.J. Kim, J.U. Han, M. Kang, J.M. Kim, J.E. Yie, Preparation and characterization of zeolite catalysts for etherification reaction, Catalysis Today 87 (2003) 195–203.

[33] H.C. Woo, K.H. Lee, J.S. Lee, Catalytic skeletal isomerization of n-butenes to isobutene over natural clinoptilolite zeolite, Applied Catalysis A: General 134 (1996) 147–158.

[34] D. Escalante, B. Mendez, G. Hernandez, C.M. Lopez, F.J. Machado, J. Goldwasser, M.M. Raminez de Agudelo, The skeletal isomerization of 1-butene over Zn-silicoaluminophosphate molecular sieves, Catalysis Letters 47 (1997) 229–233.

[35] B. Modhera, M. Chakraborty, P.A. Parikh, H.C. Bajaj, 1-Hexene isomerization over nano-crystalline zeolite beta: Effects of metal and carrier gases on catalytic performance, Catalysis Letters 132 (2009) 168–173.

[36] C. Zubin, M. Shuyun, M. Wei, Synthesis of chloroaluminate ionic liquids and use for olefin reduction in FCC gasoline, Petroleum Science and Technology 25 (2007) 1173–1184.

VITA – WORAPON KIATKITTIPONG

Name	WORAPON KIATKITTIPONG
Position	Assistant Professor
Sex	Male
Nationality	Thai
Address	
(Office)	Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000 Tel: (66)3-421-9364-6 ext. 25613; Fax: (66)3-421-9368
E-mail address	worapon@hotmail.com, kworapon@su.ac.th

Working Experience

August 2006 – present	Assistant Professor
July 2005 – August 2006	Full-time lecturer

Educational Qualification

June 2005	D.Eng., Chemical Engineering, Chulalongkorn University
October 2001	M.Eng., Chemical Engineering, Chulalongkorn University
March 1999	B.Eng., Chemical Engineering, Kasetsart University

International publications

1) **Worapon Kiatkittipong***, Suwimol Wongsakulphasatch, Nattapon Tintan, Navadol Laosiripojana, Piyasan Praserthdam and Suttichai Assabumrungrat, "Gasoline upgrading by self-etherification with ethanol on modified beta-zeolite" Fuel Processing Technology 92 (10) 1999-2004 (2011) (IF-2010 = 2.781)
2) **Worapon Kiatkittipong***, Parinya Intaracharoen, Navadol Laosiripojana, Choowong Chaisuk, Piyasan Praserthdam, Suttichai Assabumrungrat, "Glycerol ethers synthesis from glycerol etherification with tert-butyl alcohol in reactive distillation" Computers and Chemical Engineering 35 (10) 2034-2043 (2011) (IF-2010 = 2.072)
3) W. Khaodee, S. Wongsakulphasatch, **W. Kiatkittipong**, A. Arpornwichanop, N. Laosiripojana, S. Assabumrungrat, "Selection of appropriate primary fuel for hydrogen production for different fuel cell types: Comparison between decomposition and steam reforming" International Journal of Hydrogen Energy 36 (13) 7696-7706 (2011) (IF-2010 = 4.035)
4) Navadol Laosiripojana, **Worapon Kiatkittipong**, Suttichai Assabumrungrat, "Partial oxidation of palm fatty acids over Ce-ZrO_2: Roles of catalyst surface area, lattice oxygen capacity and mobility" AIChE Journal (2011) (Article in press) (IF-2009 = 1.955) (doi:10.1002/aic.12491)

5) Thirasak Pairojpiriyakul, **Worapon Kiatkittipong**, Apinan Soottitantawat, Amornchai Arpornwichanop, Navadol Laosiripojana, Wisitsree Wiyaratn, Eric Coiset and Suttichai Assabumrungrat, “Thermodynamic analysis of hydrogen production from glycerol at energy self-sufficient conditions” The Canadian Journal of Chemical Engineering (2011) (Article in press) (IF-2009 = 0.63) (DOI: 10.1002/cjce.20621)
6) I. Choedkiatsakul, S. Charojrochkul, **W. Kiatkittipong**, W. Wiyaratn, A. Soottitantawat, A. Arpornwichanop, N. Laosiripojana and S. Assabumrungrat, “Performance improvement of bioethanol-fuelled solid oxide fuel cell system by using pervaporation” International Journal of Hydrogen Energy 36 (8) 5067-5075 (2011) (IF-2010 = 4.053)
7) G. Tanarungsun, H. Yamada, T. Tagawa, **W. Kiatkittipong**, P. Praserthdam and S. Assabumrungrat, “Partial oxidation of benzene catalyzed by vanadium chloride in novel reaction–extraction–regeneration system” Chemical Engineering and Processing: Process Intensification , 50 (1) 53-58 (2011) (IF-2009 = 1.742)
8) Vorachatra Sukwattanajaroon, Sumittra Charojrochkul, **Worapon Kiatkittipong**, Amornchai Arpornwichanop, and Suttichai Assabumrungrat, “Performance of Membrane-Assisted Solid Oxide Fuel Cell System Fuelled by Bioethanol” Engineering Journal, 15 (2), 53-66 (2011) (doi:10.4186/ej.2011.15.2.53)
9) Thirasak Pairojpiriyakul, **Worapon Kiatkittipong**, Amornchai Arpornwichanop, Apinan Soottitantawat, Wisitsree Wiyaratn, Navadol Laosiripojana, Eric Coiset and Suttichai Assabumrungrat, “Effect of mode of operation on hydrogen production from glycerol at thermal neutral conditions: Thermodynamic analysis”, International Journal of Hydrogen Energy, 35 (19), 10257-10270 (2010) (IF-2009 = 3.945)
10) P. Piroonlerkgul, **W. Kiatkittipong**, A. Arpornwichanop, A. Soottitantawat, W. Wiyratn, N. Laosiripojana, A.A. Adesina and S. Assabumrungrat “Technical and economic study of integrated system of solid oxide fuel cell, palladium membrane reactor, and CO_2 sorption enhancement unit" Chemical Engineering and Processing: Process Intensification, 49 (10), 1006-1016 (2010) (IF-2009 = 1.742)
11) N. Laosiripojana, **W. Kiatkittipong**, W. Sutthisripok, S. Assabumrungrat “Synthesis of methyl esters from relevant palm products in near-critical methanol with modified-zirconia catalysts” Bioresource Technology, 101 (21), 8416–8423 (2010) (IF-2009 = 4.253)
12) N. Laosiripojana, **W. Kiatkittipong**, S. Charojrochkul, S. Assabumrungrat “Effects of support and co-fed elements on steam reforming of palm fatty acid distillate (PFAD) over Rh-based catalysts” Applied Catalysis A: General, 383 (1-2), 50-57 (2010) (IF-2009 = 3.564)
13) S. Assabumrungrat, P. Sonthisanga, **W. Kiatkittipong**, N. Laosiripojana, A. Arpornwichanop, A. Soottitantawat, W. Wiyaratn, P. Praserthdam “Thermodynamic analysis of calcium oxide assisted hydrogen production from biogas” Journal of Industrial and Engineering Chemistry, 16 (5), 785-789 (2010) (IF-2009 = 1.752).
14) **Worapon Kiatkittipong***, Sirima Suwanmanee, Navadol Laosiripojana, Piyasan Praserthdam and Suttichai Assabumrungrat “Cleaner gasoline production by using glycerol as fuel extender” Fuel Processing Technology, 91 (5), 456-460 (2010) (IF-2009 = 2.321)

15) G. Tanarungsun, H. Yamada, T. Tagawa, **W. Kiatkittipong**, P. Praserthdam and S. Assabumrungrat “Reaction-extraction-regeneration system for highly selective oxidation of benzene to phenol” Chemical Engineering Communications, 197 (8), 1140-1151 (2010) (IF-2009 = 0.586)
16) I. Choedkiatsakul, K. Sintawarayan, T. Prawpipat, A. Soottitantawat, W. Wiyaratn, **W. Kiatkittipong**, A. Arpornwichanop, N. Laosiripojana, S. Charojrochkul and S. Assabumrungrat “Performance assessment of SOFC systems integrated with bio-ethanol production and purification processes” Engineering Journal, 14 (1), 1-14 (2010) (doi:10.4186/ej.2010.13.4.1)
17) P. Piroonlerkgul, W. Wiyaratn, A. Soottitantawat, **W. Kiatkittipong**, A. Arpornwichanop, N. Laosiripojana, S. Assabumrungrat “Operation viability and performance of solid oxide fuel cell fuelled by different feeds” Chemical Engineering Journal, 155 (1-2), 411-418 (2009) (IF- 2009 = 2.816)
18) S. Assabumrungrat, S. Charoenseri, N. Laosiripojana, **W. Kiatkittipong**, P. Praserthdam “Effect of oxygen addition on catalytic performance of Ni/SiO_2.MgO toward carbon dioxide reforming of methane under periodic operation” International Journal of Hydrogen Energy, 34 (15), 6211-6220 (2009) (IF-2009 = 3.945)
19) O. Boonthumtirawuti, **W. Kiatkittipong**, A. Arpornwichanop, P. Praserthdam and S. Assabumrungrat “Kinetic of liquid phase synthesis of *tert*-amyl ethyl ether from *tert*-amyl alcohol and ethanol over Amberlyst 16” Journal of Industrial and Engineering Chemistry, 15 (4), 451-457 (2009) (IF-2009 = 1.752).
20) P. Piroonlerkgul, **W. Kiatkittipong**, A. Arpornwichanop, A. Soottitantawat, W. Wiyaratn, N. Laosiripojana, A.A. Adesina, S. Assabumrungrat “Integration of solid oxide fuel cell and palladium membrane reactor: Technical and economic analysis” International Journal of Hydrogen Energy, 34 (9), 3894-3907 (2009) (IF-2009 = 3.945)
21) **Worapon Kiatkittipong**[*], Khamron Yoothongkham, Choowong Chaisuk, Piyasan Praserthdam, Shigeo Goto and Suttichai Assabumrungrat “Self-etherification process for cleaner fuel production” Catalysis Letters 128 (1-2), 154-163 (2009) (IF-2009 = 2.021)
22) **Worapon Kiatkittipong**, Porntip Wongsuchoto, Prasert Pavasant “Life cycle assessment of bagasse waste management options” Waste Management 29 (5), 1628-1633 (2009) (IF- 2009 = 2.433)
23) Vorapot Kanokkantapong, **Worapon Kiatkittipong**, Bunyarit Panyapinyopol, Porntip Wongsuchoto and Prasert Pavasant “Used lubricating oil management options based on life cycle thinking” Resources Conservation and Recycling, 53 (5), 294-299 (2009) (IF-2009 = 1.987)
24) S. Vivanpatarakij, N. Laosiripojana, **W. Kiatkittipong**, A. Arpornwichanopa, A. Soottitantawat, S. Assabumrungrat “Simulation of solid oxide fuel cell systems integrated with sequential CaO–CO_2 capture unit” Chemical Engineering Journal, 147 (2-3), 336-341 (2009) (IF-2009 = 2.816)
25) A. Arpornwichanop, K. Koomsup, **W. Kiatkittipong**, P. Praserthdam, S. Assabumrungrat “Production of n-butyl acetate from dilute acetic acid and n-butanol

using different reactive distillation systems: Economic analysis" Journal of the Taiwan Institute of Chemical Engineers, 40 (1), 21-28 (2009) (IF-2008 = 1.114)

26) N. Laosiripojana, W. Wiyaratn, **W. Kiatkittipong**, A. Arpornwichanop, A. Soottitantawat and S. Assabumrungrat "Reviews on Solid Oxide Fuel Cell Technology" Engineering Journal, 13 (1), 65-83 (2009) (doi:10.4186/ej.2009.13.1.65)
27) **Worapon Kiatkittipong***, Piyaporn Thipsunet, Shigeo Goto, Choowong Chaisuk, Piyasan Praserthdam and Suttichai Assabumrungrat "Simultaneous enhancement of ethanol supplement in gasoline and its quality improvement" Fuel Processing Technology, 89 (12), 1365-1370 (2008) (IF-2008 = 2.066)
28) G. Tanarungsun, **W. Kiatkittipong**, P. Praserthdam, H. Yamada, T. Tagawa, and S. Assabumrungrat "Hydroxylation of benzene to phenol on Fe/TiO_2 catalysts loaded with different types of second metal" Catalysis Communications, 9 (9), 1886-1890 (2008) (IF-2008 = 2.791)
29) G. Tanarungsun, **W. Kiatkittipong**, P. Praserthdam, H. Yamada, T. Tagawa and S. Assabumrungrat "Ternary metal oxide catalysts for selective oxidation of benzene to phenol" Journal of Industrial and Engineering Chemistry, 14 (5) 596-601 (2008) (IF-2008 = 1.235)
30) **Worapon Kiatkittipong**, Porntip Wongsuchoto, Khanidtha Meewasana and Prasert Pavasant "When to buy new electrical/electronic products?" Journal of Cleaner Production, 16 (13), 1339-1345 (2008) (IF-2008 = 1.362)
31) G. Tanarungsun, **W. Kiatkittipong**, S. Assabumrungrat, H. Yamada, T. Tagawa and P. Praserthdam "Multi transition metal catalysts supported on TiO_2 for hydroxylation of benzene to phenol with hydrogen peroxide" Journal of Industrial and Engineering Chemistry, 13 (5), 870-877 (2007) (IF-2007 = 1.570).
32) G. Tanarungsun, **W. Kiatkittipong**, S. Assabumrungrat, H. Yamada, T. Tagawa and P. Praserthdam "Liquid phase hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by Fe (III)/TiO_2 catalysts at room temperature" Journal of Industrial and Engineering Chemistry, 13 (3), 444-451 (2007) (IF-2007 = 1.570).
33) G. Tanarungsun, **W. Kiatkittipong**, S. Assabumrungrat, H. Yamada, T. Tagawa and P. Praserthdam "Fe (III), Cu (II), V (V)/TiO_2 for hydroxylation of benzene to phenol with hydrogen peroxide at room temperature" Journal of Chemical Engineering of Japan, 40 (5), 415-421 (2007) (IF-2007 = 0.594).
34) **Worapon Kiatkittipong**, Tomohiko Tagawa, Shigeo Goto, Suttichai Assabumrungrat, Kampol Silpasup and Piyasan Praserthdam, "Comparative Study of Oxidative Coupling of Methane Modeling in Various Types of Reactor" Chemical Engineering Journal, 115 (1-2), 63-71 (2005) (4th of TOP 25 Hottest Articles) (IF-2005 = 2.034).
35) **Worapon Kiatkittipong**, Shigeo Goto, Tomohiko Tagawa, Suttichai Assabumrungrat and Piyasan Praserthdam "Simulation of Oxidative Coupling of Methane in Solid Oxide Fuel Cell Type Reactor for C2 Hydrocarbons and Electricity Co-Generation" Journal of Chemical Engineering of Japan, 38 (10), 841-848 (2005) (IF-2005 = 0.519).
36) **Worapon Kiatkittipong**, Tomohiko Tagawa, Shigeo Goto, Suttichai Assabumrungrat and Piyasan Praserthdam "Oxygen transport through LSM/YSZ/LaAlO system for the

use of fuel cell type reactor" Chemical Engineering Journal, 106 (1), 35-42 (2005) (IF-2005 = 2.034).

37) **Worapon Kiatkittipong**, Tomohiko Tagawa, Shigeo Goto, Suttichai Assabumrungrat and Piyasan Praserthdam "Oxidative Coupling of Methane in LSM/YSZ/LaAlO SOFC Reactor" Journal of Chemical Engineering of Japan 37 (12), 1461-1470 (2004) (IF-2004 = 0.515).
38) **Worapon Kiatkittipong**, Tomohiko Tagawa, Shigeo Goto, Suttichai Assabumrungrat and Piyasan Praserthdam "TPD study in LSM/YSZ/LaAlO system for the use of fuel cell type reactor" Solid State Ionics, 166 (1-2), 127-136 (2004) (IF- 2004 = 1.862).
39) Suttichai Assabumrungrat, **Worapon Kiatkittipong**, Piyasan Praserthdam and Shigeo Goto "Simulation of pervaporation membrane reactors for liquid phase synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol" Catalysis Today, 79-80, 249-257 (2003) (IF-2003 = 2.627).
40) **Worapon Kiatkittipong**, Suttichai Assabumrungrat, Piyasan Praserthdam and Shigeo Goto, "A pervaporation membrane reactor for liquid phase synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol", Journal of Chemical Engineering of Japan 35 (6), 547-556 (2002) (IF-2002 = 0.459).
41) Assabumrungrat S, **Kiatkittipong W**, Srivitoon N, Praserthdam P, Goto S, "Kinetics of liquid phase synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol catalyzed by β-zeolite supported on monolith", International Journal of Chemical Kinetics, 34: (5) 292-299, May 2002 (IF-2002 = 1.086)
42) **Worapon Kiatkittipong**, Suttichai Assabumrungrat and Piyasan Praserthdam, "Synthesis of ethyl tert-butyl ether from tert-butyl alcohol and ethanol catalyzed by β-zeolite in pervaporative membrane reactors", Journal of The Institution of Engineers Singapore (Chemical Engineering) vol. 42 (2) 6-10, 2002

VITA – CHOOWONG CHAISUK

Name	CHOOWONG CHAISUK
Position	Assistant Professor
Sex	Male
Nationality	Thai
Address	
(Office)	Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Sanam Chandra Palace Rajamankha Nai Road, Muang, Nakhon Pathom 73000 Tel.: 0-3421-9364-6 Ext 25612; Fax: 0-3421-9368
E-mail address	choowong@su.ac.th, cchaisuk@yahoo.com

Work Experience

2010-Present	Associate Dean (Academic Affairs) of Faculty of Engineering and Industrial Technology, Silpakorn University
2003-Present	Lecturer of Department of Chemical Engineering, Silpakorn University
2003-2008	Head of Department of Chemical Engineering, Silpakorn University

Educational Qualification

1996–2001	D.Eng. in Chemical Engineering, Chulalongkorn University, Bangkok, Thailand
1992–1995	B.Eng. in Chemical Engineering with 2nd class honors, Chulalongkorn University, Bangkok, Thailand

International Publications

1. S. Pisduangdaw, J. Panpranot, **C. Chaisuk**, K. Faungnawakij, and O. Mekasuwandumrong, "Flame sprayed tri-metallic Pt-Sn-X/Al_2O_3 catalysts (X = Ce, Zn, and K) for propane dehydration", **Catal. Commun.**, 12 (12) (2011) 1161-1165.
2. **C. Chaisuk**, A. Wehatoranawee, S. Preampiyawat, S. Netiphat, A. Shotipruk, J. Panpranot, B. Jongsomjit and O. Mekasuwandumrong, "Preparation and characterization of CeO_2/TiO_2 nanoparticles by flame spray pyrolysis", **Ceram. Inter.**, 37 (5) (2011) 1459-1463.
3. **C. Chaisuk**, P. Boonpitak, J. Panpranot and O. Mekasuwandumrong, "Effects of Co dopants and flame conditions on the formation of Co/ZrO_2 nanoparticles by flame spray pyrolysis and their catalytic properties in CO hydrogenation", **Catal. Commun.**, 12 (10) (2011) 917-922.
4. T. Glinrun, O. Mekasuwandumrong, J. Panpranot, **C. Chaisuk** and P. Praserthdam, "Improvement of propane oxidation activity over Pt/Al_2O_3 by the use of mixed

gamma- and chi-Al_2O_3 supports", **React. Kinet. Mech. and Catal.**, 100 (2) (2010) 441-448.

5. S. Pisduangdaw, J. Panpranot, C. Methastidsook, **C. Chaisuk**, K. Faungnawakij, P. Praserthdam and O. Mekasuwandumrong, "Characteristics and catalytic properties of Pt-Sn/Al_2O_3 nanoparticles synthesized by one-step flame spray pyrolysis in the dehydrogenation of propane", **Appl. Cat. A**, 370 (1-2) (2009) 1-6.
6. W. Kiatkittipong, K. Yoothongkham, **C. Chaisuk**, P. Praserthdam, S. Goto and S. Assabumrungrat, "Self-Etherification process for cleaner fuel production", **Catal. Lett.**, 128 (1-2) (2009) 154-163.
7. W. Kiatkittipong, P. Thipsunet, S. Goto, **C. Chaisuk**, P. Praserthdam and S. Assabumrungrat, "Simultaneous enhancement of ethanol supplement in gasoline and its quality improvement", **Fuel Proc. Tech.**, 89 (12) (2008) 1365-1370.
8. T. Burakorn, J. Panpranot, O. Mekasuwandumrong, **C. Chaisuk**, P. Praserthdam and B. Jongsomjit, "Characterization of cobalt dispersed on the mixed nanoscale alumina and zirconia supports", **J. Mater. Proc. Tech.**, 206 (1-3) (2008) 352-358.
9. C. Meephoka, **C. Chaisuk**, P. Samparnpiboon and P. Praserthdam, "Effect of phase composition between nano γ- and χ-Al_2O_3 on Pt/Al_2O_3 catalyst in CO oxidation", **Catal. Commun.**, 9 (4) (2008) 546-550.
10. O. Mekasuwandumrong, P. Tantichuwet, **C. Chaisuk** and P. Praserthdam, "Impact of concentration and Si doping on the properties and phase transformation behavior of nanocrystalline alumina prepared via solvothermal synthesis", **Mater. Chem. Phys.**, 107 (2-3) (2008) 208-214.
11. J. Wiwattanapongpan, O. Mekasuwandumrong, **C. Chaisuk** and P. Praserthdam, "Effect of dopants on the properties of metal-doped zirconia prepared by the glycothermal method", **Ceram. Inter.**, 33 (8) (2007) 1469-1473.
12. P. Praserthdam, **C. Chaisuk**, W. Kongsuebchart, S. Thongyai and S. Kunjara Na Ayudhya, "New concepts in material and energy utilization", **Korean J. Chem. Eng.**, 22 (1) (2005) 115-120.2.
13. N. Kiattisirikul, **C. Chaisuk** and P. Praserthdam, "Nature of the surface species on Ag/Al_2O_3 catalyst in SCR of NO by propene under lean-burn condition through temperature programmed technique", **Catal. Today**, 97 (2-3) (2004) 129-135.
14. S. Sombatchaisak, P. Praserthdam, **C. Chaisuk** and J. Panpranot, "An alternative correlation equation between particle size and structure stability of H-Y zeolite under hydrothermal treatment conditions", **Ind. Eng. Chem. Res.**, 43 (2004) 4066-4072.
15. P. Praserthdam, **C. Chaisuk** and T. Mongkhonsi, "The nature of surface species on modified Pt-based catalysts for the SCR of NO by C_3H_6 under lean-burn condition", **Korean J. Chem. Eng.**, 20 (1) (2003) 32-38.
16. **C. Chaisuk** and P. Praserthdam, "The role of surface species on the SCR of NO by C_3H_6 under lean-burn conditions over platinum catalyst", **React. Kinet. Catal. Lett.**, 78 (1) (2003) 99-105.
17. P. Praserthdam, **C. Chaisuk**, A. Panit and K. Kriwattanawong, "Some aspects about the nature of surface species on Pt-based and MFI-based catalysts for the selective catalytic reduction of NO by propene under lean-burn condition", **Appl. Cat. B**, 38 (3) (2002) 227-241.

18. P. Praserthdam, **C. Chaisuk** and P. Kanchanawanichkun, “Comparative study of coke deposition on catalysts in reactions with and without oxygen”, **Res. Chem. Intermed.**, 24 (5) (1998) 605-612.

VITA – SUTTICHAI ASSABUMRUNGRAT

Name	SUTTICHAI ASSABUMRUNGRAT
Position	Professor
Sex	Male
Nationality	Thai
Status	Married
Address	Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330 Tel: (662) 218-6878-82, FAX (662) 218-6877
Educational Qualification	
November 1996	Ph.D., Chemical Engineering, Imperial College London, UK.
October 1993	M.Sc. (Distinction), Advanced in Chemical Engineering, Imperial College London, UK.
March 1992	B.Eng. (1st Class Honour-Gold medal), Chemical Engineering, Chulalongkorn University
Working Experience	
Nov 1996 – Dec 1998	Full-time lecturer
Dec 1998 – April 2002	Assistant Professor
May 2002 – Sep 2006	Associate Professor
Sep 2006 – present	Professor

International Publications (since 2008)

1) Watcharapong Khaodee, Bunjerd Jongsomjit, Piyasan Praserthdam, Shigeo Goto and Suttichai Assabumrungrat, "Impact of temperature ramp during calcination on characteristics of nano-ZrO_2 and its catalytic activity for isosynthesis" J. Mol. Cat. A, vol. 208 (2008) 35-42 (IF-2008 = 2.814).
2) Hiroshi YAMADA, Tomoaki MIZUNO, Tomohiko TAGAWA, Garun TANARUNGSUN, Piyasan PRASERTHDAM and Suttichai ASSABUMRUNGRAT "Catalyst Regenerator for Partial Oxidation of Benzene in Reaction-Extraction System" Journal of the Japan Petroleum Institute, vol. 51 (2008), 114-117. (IF-2008 = 0.591)
3) N. Laosiripojana, D. Chadwich and S. Assabumrungrat, "Effect of high surface area CeO_2 and Ce-ZrO_2 supports over Ni catalyst on CH_4 reforming with H_2O in the presences of O_2, H_2, and CO_2", Chem. Eng. J., vol. 138 (2008) 264-273 (IF-2008 = 2.813).
4) W. Sangtongkitcharoen, S.Vivanpatarakij, N. Laosiripojana, A. Arpornwichanop and S. Assabumrungrat, "Performance analysis of methanol-fueled solid oxide fuel cell

system incorporated with palladium membrane reactor", Chem. Eng. J., vol. 138 (2008) 436-441 (IF-2008 = 2.813).

5) Amornchai Arpornwichanop, Ukrit Sahapatsombud, Yaneeporn Patcharavorachot and Suttichai Assabumrungrat, "Hybrid Process of Reactive Distillation and Pervaporation for the Production of Tert-Amyl Ethyl Ether", Chinese Journal of Chemical Engineering, vol. 16 (2008) 100-103 (IF-2008 = 0.572).
6) Garun tanarungsun, Worapon Kiatkittipong, Hiroshi Yamada, Tomohiko Tagawa, Piyasan Prasertdam and Suttichai Assabumrungrat, "Hydroxylation of benzene to phenol on Fe/TiO_2 catalysts loaded with different types of second metal", Catal. Commu. Vol. 9 (2008) 1886-1890 (IF-2008 = 2.791).
7) P. Piroonlerkgul, S. Assabumrungrat, N. Laosiripojana and A.A. Adesina, "Selection of appropriate fuel processor for biogas-fuelled SOFC system", Chem. Eng. J., vol. 140 (2008) 241-351 (IF2008 = 2.813).
8) Shivanahalli K Rajesh, Navadol Laosiripojana, Suttichai Assabumrungrat, "High temperature desulphurization using nano-sized ceria adsorbent for SOFC applications", Korean J. of Chemical Engineering, vol.25 (2008) 223-230 (IF-2008 = 0.83).
9) N. Laosiripojana and S. Assabumrungrat, "Kinetic dependencies and reaction pathways in hydrocarbon conversions catalyzed by ceria-based materials", Applied Catalysis B, Vol. 82 (2008) 103-113 (IF-2008 = 4.853).
10) Garun Tanarungsun, Worapon Kiatkittipong, Hiroshi Yamada, Tomohiko Tagawa, Piyasan Prasertdam and Suttichai Assabumrungrat, "Ternary metal oxide catalysts for selective oxidation of benzene to phenol", J. Ind. Eng. Chem., 14 (2008) 596-601 (IF-2008 = 1.235).
11) Amornchai Arpornwichanop, Kittipong Koomsup and Suttichai Assabumrungrat, "Hybrid Reactive Distillation Systems for n-Butyl Acetate Production from Dilute Acetic Acid", J. Ind. Eng. Chem., vol. 14 (2008) 796-803 (IF-2008 = 1.235).
12) A. Arpornwichanop, C. Wiwittanaporn, S. Authayanun and S. Assabumrungrat, "The Use of Dilute Acetic Acid for Butyl Acetate Production in a Reactive Distillation: Simulation and Control Studies", Korean J. Chem. Eng., vol. 25 (2008) 1252-1266 (IF-2008 = 0.83).
13) Worapon Kiatkittipong, Piyaporn Thipsunet, Piyasan Praserthdam, Shigeo Goto, Choowong Chaisuk and Suttichai Assabumrungrat, "Simultaneous enhancement of ethanol supplement in gasoline and its quality improvement", Fuel Processing and Technology, vol. 89 (2008) 1365-1370 (IF-2008 = 2.066).
14) S. Vivanpatarakij, N. Laosiripojana, A. Arpornwichanop and S. Assabumrungrat, "Performance improvement of solid oxide fuel cell system using palladium membrane reactor with different operation modes", Chem. Eng. J., 146 (2009) 112–119 (IF-2009 = 2.816).
15) P. Piroonlerkgul, N. Laosiripojana, A.A. Adesina and S. Assabumrungrat, "Performance of biogas-fed solid oxide fuel cell systems integrated with membrane module for CO_2 removal", Chem. Eng. Process., vol. 48 (2009) 672-682 (IF-2009 = 1.742).

16) S. Assabumrungrat, N. Ruangrassamee, S. Vivanpatarakij, N. Laosiripojana and A. Arpornwichanop, “Influence of stack arrangement on performance of multiple-stack solid oxide fuel cells with non-uniform potential operation” J. Power Sources, vol. 187 (2009) 1-7 (IF-2009 = 3.792).
17) A. Shotipruk, S. Assabumrungrat, P. Pavasant, and N. Laosiripojana, “Reactivity of CeO_2 and Ce-ZrO_2 toward steam reforming of palm fatty acid distillate (PFAD) with co-fed oxygen and hydrogen”, Chem. Eng. Sci., vol. 64 (2009) 459-466 (IF-2009 = 2.136).
18) W. Jamsak, P.L. Douglas, E. Croiset, R. Suwanwarangkul, N. Laosiripojana, S. Charojrochkul and S. Assabumrungrat, “Design of a Thermally Integrated Bioethanol-Fueled Solid Oxide Fuel Cell System Integrated with a Distillation Column”, J. Power Sources, vol. 187 (2009) 190-203 (IF-2009 = 3.792).
19) P. Dokmaingam, S. Assabumrungrat, A. Soottitantawat, I. Sramala, N. Laosiripojana, “Modeling of SOFC with Indirect Internal Reforming Operation: Comparison of Conventional Packed-Bed and Catalytic Coated-Wall Internal Reformer”, Int. J. Hydrogen Energy, vol. 34 (2009) 410-421 (IF-2009 = 3.945).
20) Watcharapong Khaodee, Nicha Tangchupong, Bunjerd Jongsomjit, Piyasan Praserthdama and Suttichai Assabumrungrat, “Investigation of isosynthesis via CO hydrogenation over ZrO_2-CeO_2 mixed oxide catalysts” Catal. Commu., vol. 10 (2009) 494-501 (IF-2009 = 3).
21) Amornchai Arpornwichanop, Kittipong Koomsup, Worapon Kiatkittipong, Piyasan Praserthdam and Suttichai Assabumrungrat, “Production of n-butyl acetate from dilute acetic acid and n-butanol using different reactive distillation systems: Economic analysis”, J. Taiwan Inst. Chem. Engrs., vol. 40 (2009) 21-28 (IF-2008 = 1.114).
22) S. Vivanpatarakij, N. Laosiripojana, W. Kiatkittipong, A. Arpornwichanop, A. Soottitantawat and S. Assabumrungrat, “Simulation of solid oxide fuel cell systems integrated with sequential CaO–CO_2 capture unit”, Chem. Eng. J., vol. 147 (2009) 336–341 (IF-2009 = 2.816).
23) Worapon Kiatkittipong, Khamron Yoothongkham, Choowong Chaisuk, Piyasan Praserthdam, Shigeo Goto and Suttichai Assabumrungrat, “Self-etherification process for cleaner fuel production”, Catalysis Letters., Vol. 128 (2009) 154-163 (IF-2009 = 2.021).
24) P. Piroonlerkgul, W. Kiatkittipong, A. Arpornwichanop, A. Soottitantawat, W. Wiyratn, N. Laosiripojana, A.A. Adesina and S. Assabumrungrat, “Integration of solid oxide fuel cell and palladium membrane reactor: Technical and economic analysis”, Int. J. Hydrogen Energy, 37 (2009) 3894-3907 (IF-2009 = 3.945).
25) P. Dokmaingam, S. Assabumrungrat, A. Soottitantawat and N. Laosiripojana, “Effect of Operating Conditions and Gas Flow Patterns on the System Performances of IIR-SOFC Fueled by Methanol” Int. J. Hydrogen Energy, 34 (2009) 6415-6424 (IF-2009 = 3.945).
26) Suttichai Assabumrungrat, Salinee Charoenseri, Navadol Laosiripojana, Worapon Kiatkittipong, and Piyasan Praserthdam, “Effect of oxygen addition on catalytic performance of carbon dioxide reforming of methane under periodic operation”, Int. J. Hydrogen Energy, 34 (2009) 6211-6220 (IF-2009 = 3.945).

27) Amornchai Arpornwichanop, Nuttapong Chalermpanchai, Yaneeporn Patcharavorachot, Suttichai Assabumrungrat, and Moses Tade, "Performance of an Anode-Supported Solid Oxide Fuel Cell with Direct Internal Reforming of Ethanol", Int. J. Hydrogen Energy, 34 (2009) 7780-7788 (IF-2009 = 3.945).
28) O. Boonthamtirawuti, W. Kiatkittipong, A. Arpornwichanop, P. Praserthdam, S. Assabumrungrat, "Kinetics of Liquid Phase Synthesis of tert-Amyl Ethyl Ether from tert-Amyl Alcohol and Ethanol over Amberlyst 16", J. Ind. Eng. Chem., 15 (2009) 451-457 (IF-2009 = 1.752).
29) Boonrat Pholjaroen, Navadol Laosiripojana, Piyasan Praserthdam and Suttichai Assabumrungrat, "Reactivity of Ni/SiO_2.MgO toward carbon dioxide reforming of methane under steady state and periodic operations" J. Ind. Eng. Chem., 15 (2009) 488-497 (IF-2009 = 1.752).
30) P. Piroonlerkgul, W. Wiyaratn, A. Soottitantawat, W. Kiatkittipong, A. Arpornwichanop, N. Laosiripojana, and S. Assabumrungrat, "Operation viability and performance of SOFC fuelled by different feeds", Chem. Eng. J., 155 (2009) 411-418 (IF-2009 = 2.816).
31) N. Laosiripojana, W. Wiyratn, W. Kiatkittipong, A. Arpornwichanop, A. Soottitantawat, and S. Assabumrungrat, "Reviews on Solid Oxide Fuel Cell Technology", Engineering Journal 13 (2009) 73-90.
32) Garun Tanarungsun, Hiroshi Yamada, Tomohiko Tagawa, Worapon Kiatkittipong, Piyasan Praserthdam and Suttichai Assabumrungrat, "Reaction-Extraction-Regeneration System for Highly Selective Oxidation of Benzene to Phenol" Chemical Engineering Communications, 197 (2010) 1140-1151 (IF-2009 = 0.586).
33) Amornchai Arpornwichanop, Yaneeporn Patcharavorachot, and Suttichai Assabumrungrat, "Analysis of a proton-conducting SOFC with direct internal reforming", Chem. Eng. Sci., 65 (2010) 581-589 (IF-2009 = 2.136)
34) P. Dokmaingam, S. Assabumrungrat, A. Soottitantawat and N. Laosiripojana, "Modeling of tubular-designed SOFC with Indirect Internal Reforming operation (IIR-SOFC) fed by different primary fuels", Journal of Power Sources, 195 (2010) 69-78 (IF-2009 = 3.792).
35) Nicha Tangchupong, Watcharapong Khaodee, Bunjerd Jongsomjit, Navadol Laosiripojana, Piyasan Praserthdam and Suttichai Assabumrungrat, "Effect of calcination temperature on characteristics of sulfated zirconia and its application as a catalyst for isosynthesis" Fuel Proc. Tech., 91 (2010) 121-126 (IF-2009 = 2.321).
36) Watcharapong Khaodee, Nicha Tangchupong, Bunjerd Jongsomjit, Navadol Laosiripojana, Piyasan Praserthdam and Suttichai Assabumrungrat, "Isosynthesis via CO hydrogenation over SO_4-ZrO_2 catalysts", J. Ind. Eng. Chem., 16 (2010) 411-418 (IF-2009 = 1.752).
37) Worapon Kiatkittipong, Sirima Suwanmanee, Navadol Laosiripojana, Piyasan Praserthdam and Suttichai Assabumrungrat, "Cleaner gasoline production by using glycerol as fuel extender", Fuel Proc. Tech., 91 (2010) 456-460 (IF-2009 = 2.321).
38) Yaneeporn Patcharavorachot, Woranee Paengjuntuek, Suttichai Assabumrungrat and Amornchai Arpornwichanop, "Performance evaluation of combined solid oxide fuel

cells with different electrolytes", Int. J. Hydrogen Energy, 35 (2010) 4301-4310 (IF-2009 = 3.945).

39) Issara Choedkiatsakul, Kanokporn Sintawarayan, Tanya Prawpipat, Apinan Soottitantawat, Wisitsree Wiyaratn, Worapon Kiatkittipong,Amornchai Arpornwichanop, Navadol Laosiripojana, Sumittra Charojrochkul and Suttichai Assabumrungrat, "Performance assessment of SOFC systems integrated with bio-ethanol production and purification processes", Engineering Journal 13 (2010) 1-14.

40) P. Dokmaingam, N. Laosiripojana, A. Soottitantawat and S. Assabumrungrat, "Alternative concept for SOFC with direct internal reforming: Benefits from inserting catalyst rod", AIChE J., 56 (2010) 1639-1650 (IF-2009 = 1.955).

41) N. Laosiripojana, W. Sutthisripok, K.P. Lohsoontorn, S. Assabumrungrat, "Reactivity of Ce-ZrO_2 (doped with La-, Gd-, Nb-, and Sm-) toward partial oxidation of liquefied petroleum gas: Its application for sequential partial oxidation/steam reforming", International Journal of Hydrogen Energy, 35 (2010) 6747-6756 (IF-2009 = 3.945).

42) N. Laosiripojana, W. Kiatkittipong, W. Sutthisripok, S. Assabumrungrat, "Synthesis of methyl esters from relevant palm products in near-critical methanol with modified-zirconia catalysts: Effects of catalyst, co-solvent and water formation", Bioresource Technology, 101 (2010) 8416-8423 (IF-2009 = 4.253).

43) Suthida Authayanun, Amornchai Arpornwichanop, Woranee Paengjuntuek, Wisitsree Wiyaratn, and Suttichai Assabumrungrat, "Thermodynamic Study of Hydrogen Production from Crude Glycerol Autothermal Reforming for Fuel Cell Applications", International Journal of Hydrogen Energy, 13 (2010) 6617-6623 (IF-2009 = 3.945).

44) S. Assabumrungrat, P. Sonthisanga, W. Kiatkittipong, N. Laosiripojana, A. Arpornwichanop, A. Soottitantawat, W. Wiyaratn, P. Praserthdam, "Thermodynamic analysis of calcium oxide assisted hydrogen production from biogas", J. Ind. Eng. Chem., 16 (2010) 785-789 (IF-2009 = 1.752).

45) Thirasak Pairojpiriyakul, Worapon Kiatkittipong, Amornchai Arpornwichanop, Apinan Soottitantawat, Wisitsree Wiyaratn, Navadol Laosiripojana, Eric Coiset and Suttichai Assabumrungrat, "Effect of operation modes on hydrogen production from glycerol at energy self-sufficient conditions: Thermodynamic analysis", International Journal of Hydrogen Energy, 35 (2010) 10257-10270 (IF-2009 = 3.945)

46) P. Piroonlerkgul, W. Kiatkittipong, A. Arpornwichanop, W. Wiyaratn, A. Soottitantawat, N. Laosiripojana, A.A. Adesina and S. Assabumrungrat, "Technical and economic study of integrated system of solid oxide fuel cell, palladium membrane reactor, and CO_2 sorption enhancement unit", Chem. Eng. Process., 49 (2010) 1006-1016 (IF-2009 = 1.742).

47) Navadol Laosiripojana, Worapon Kiatkittipong, Suttichai Assabumrungrat, "Effects of support and co-fed elements on steam reforming of palm fatty acid distillate (PFAD) over Rh-based catalysts", Applied Catalysis A: General, 40 (2010) 50-57 (IF-2009 = 3.564).

48) Chartsak Chettapongsaphan, Sumittra Charojrochkul, Suttichai Assabumrungrat, Navadol Laosiripojana, "Catalytic H_2O and CO_2 reforming of CH_4 over perovskite-based $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$: Effects of pre-treatment and co-reactant/CH_4 on its

reforming characteristics", Applied Catalysis A: General, 368 (2010) 194-200 (IF-2009 = 3.564).

49) Navadol Laosiripojana, Weerawan Sutthisripok, Sumittra Charojrochkul, Suttichai Assabumrungrat, "Steam reforming of LPG over Ni and Rh supported on Gd-CeO_2 and Al_2O_3: Effect of support and feed composition", Fuel, 90 (2011) 136-141 (IF-2009 = 3.179).
50) N. Laosiripojana1, S.Charojrochkul, P. Lohsoontorn and S. Assabumrungrat, "Role and advantages of H_2S in catalytic steam reforming over nanoscale CeO_2-based catalysts", J. Catalysis, 276 (2010) 6-15. (IF-2009 = 5.288)
51) Yaneeporn Patcharavorachot, N.P. Brandon, Woranee Paengjuntuek, Suttichai Assabumrungrat, Amornchai Arpornwichanop, "Analysis of Planar Solid Oxide Fuel Cells based on Proton-Conducting Electrolyte", Solid State Ionics, 181 (2010) 1568-1576 (IF-2009 = 2.162)
52) P.Dokmaingam, J.T.S. Irvine, S. Assabumrungrat, S.Charojrochkul, N.Laosiripojana, "Modeling of IT-SOFC with indirect internal reforming operation fueled by methane: Effect of oxygen adding as autothermal reforming", International Journal of Hydrogen Energy, 35 (2010) 13271-13279 (IF-2009 = 3.945).
53) M. Sansernnivet, N. Laosiripojana, S. Assabumrungrat, S. Charojrochkul, "Fabrication of $La_{0.8}Sr_{0.2}CrO_3$-based Perovskite Film via Flame Assisted Vapour Deposition Technique for H_2 production by reforming", Chemical Vapor Deposition, 16 (2011) 311-321 (IF-2009 = 1.829)
54) Suthida Authayanun, Amornchai Arpornwichanop, Yaneeporn Patcharavorachot, Wisitsree Wiyaratn, and Suttichai Assabumrungrat, "Hydrogen Production from Glycerol Steam Reforming for Low- and High-Temperature PEMFCs", International Journal of Hydrogen Energy, 36 (2011) 267-275 (IF-2009 = 3.945).
55) Garun Tanarungsun, Hiroshi Yamada, Tomohiko Tagawa, Worapon Kiatkittipong, Piyasan Praserthdam and Suttichai Assabumrungrat, "Partial Oxidation of Benzene Catalyzed by Vanadium Chloride in Novel Reaction-Extraction-Regeneration System" Chem. Eng. Proc., 50 (2011) 53–58 (IF-2009 = 1.742).
56) Rajesh K Shivanahalli, Navadol Laosiripojana, Suttichai Assabumrungrat, "Thermodynamic analysis for gasification of Thailand rice husk with air, steam, and mixed air/steam for hydrogen-rich gas production", International Journal of Chemical Reactor, 8 (2010) 1-27 (IF-2009 = 0.733).
57) Unalome Wetwatana, Pattaraporn Kim-Lohsoontorn, Suttichai Assabumrungrat, Navadol Laosiripojana, "Catalytic Steam and Autothermal Reforming of Used Lubricating Oil (ULO) over Rh- and Ni-based Catalysts", Industrial & Engineering Chemistry Research, 49 (2010)10981-10985 (IF-2009 = 1.758).
58) N. Laosiripojana, S. Assabumrungrat, "Conversion of poisonous methanethiol to hydrogen-rich gas by chemisorption/reforming over nano-scale CeO_2: The use of CeO_2 as catalyst coating material", Applied Catalysis B: Environmental, Applied Catalysis B: Environmental 102 (2011), pp. 267-275 (IF-2009 = 5.252)
59) Issara Choedkiatsakul, Worapon Kiatkittipong, Wisitsree Wiyaratn, Apinan Soottitantawat, Amornchai Arpornwichanop, Navadol Laosiripojana, Sumittra Charojrochkul and Suttichai Assabumrungrat, "Performance improvement of

bioethanol fuelled solid oxide fuel cell system by using pervaporation”, International Journal of Hydrogen Energy, 36 (2011) 5067-5075 (IF-2009 = 3.945).

60) Somnuk Boributh, Suttichai Assabumrungrat, Navadol Laosiripojana and Ratana Jiraratananon, “Effect of membrane module arrangement of gas-liquid membrane contacting process on CO_2 absorption performance: A modeling study”, J. Mem. Sci., 372 (2011) 75-86 (IF 2009 = 3.203)
61) Vorachatra Sukwattanajaroon, Sumittra Charojrochkul, Worapon Kiatkittipong, Amornchai Arpornwichanop, and Suttichai Assabumrungrat, “Performance of membrane-assisted solid oxide fuel cell system fuelled by bioethanol”, Engineering Journal, 15 (2011) 1-8(IF-2009 = -).
62) W. Khaodee, S. Wongsakulphasatch, W. Kiatkittipong, A. Arpornwichanop, N. Laosiropojana, S. Assabumrungrat, “Selection of appropriate primary fuel for hydrogen production for different fuel cell types: Comparison between decomposition and steam reforming”, International Journal of Hydrogen Energy, 36 (2011) 7696-7706 (IF-2009 = 3.945).
63) Amornchai Arpornwichanop, Manatsana Wasuleewan, Yaneeporn Patcharavorachot, Suttichai Assabumrungrat, “Investigation of a dual-bed autothemal reforming of methane for hydrogen production”, Chemical Engineering Transactions, 25 (2011) 929-934 (IF-2009 = -)
64) Amnart Jantharasuk, Rafiqul Gani, Andrzej Gorak and Suttichai Assabumrungrat, “Methodology for design and analysis of reactive distillation involving multielement systems”, Chem. Eng. Res. Dev., 89 (2011) 1295–1307 (IF-2009 = 1.223).
65) Lida Simasatitkul, Pimpatthar Siricharnsakunchai, Yaneeporn Patcharavorachot, Suttichai Assabumrungrat and Amornchai Arpornwichanop, “Reactive Distillation for Biodiesel Production from Soybean Oil” Korean Journal of Chemical Engineering, accepted October 1, 2010 (IF-2009 = 0.893)
66) N. Laosiripojana, W. Kiatkittipong, W. Sutthisripok, S. Assabumrungrat, “Partial oxidation of palm fatty acids over $Ce\text{-}ZrO_2$: Roles of catalyst surface area, lattice oxygen capacity and mobility”, AIChE J., accepted Oct 22, 2010 (IF-2009=1.955).
67) Wisitsree Wiyaratn, Weerinda Appamana, and Suttichai Assabumrungrat, “Development of $Au/La_{1-x}Sr_xMnO_3$ nanocomposite anode catalyst for further application in solid oxide fuel cell typed reactor”, Journal of Industrial and Engineering Chemistry, in press (IF-2009 = 1.752).
68) Worapon Kiatkittipong, Parinya Intaracharoen, Navadol Laosiripojana, Choowong Chaisuk, Piyasan Praserthdam, Suttichai Assabumrungrat, “Glycerol ethers synthesis from glycerol etherification with tert-butyl alcohol in reactive distillation” Computers and Chemical Engineering 35 (10) 2034-2043 (2011) (IF-2010 = 2.072).
69) Thirasak Pairojpiriyakul, Worapon Kiatkittipong, Amornchai Arpornwichanop, Apinan Soottitantawat, Wisitsree Wiyaratn, Navadol Laosiripojana, Eric Coiset and Suttichai Assabumrungrat, “Thermodynamic analysis of hydrogen production from glycerol at energy self-sufficiency conditions”, Can. J. Chem. Eng., accepted April 14, 2011 (IF-2009 = 0.63)
70) Worapon Kiatkittipong, Suwimol Wongsakulphasatch, Nattapon Tintan, Navadol Laosiripojana, Piyasan Praserthdam and Suttichai Assabumrungrat, “Gasoline

upgrading by self-etherification with ethanol on modified beta-zeolite" Fuel Processing Technology 92 (10) 1999-2004 (2011) (IF-2010 = 2.781)

71) Somnuk Boributh, Suttichai Assabumrungrat, Navadol Laosiripojana and Ratana Jiraratananon, "A modeling study on the effects of membrane characteristics and operating parameters on physical absorption of CO_2 by hollow fiber membrane contactor", J. Mem. Sci., accepted June 20, 2011 (IF 2009 = 3.203)