รายงานวิจัยฉบับสมบูรณ์

โครงการ Selection and Design of Glycerol Ethers Production for Renewable Fuel
(การเลือกและออกแบบระบบผลิตสารประกอบกลีเซอรอลอีเทอร์เพื่อใช้เป็นเชื้อเพลิงทดแทน)

โดย ผู้ช่วยศาสตราจารย์ ดร. วรพล เกียรติกิตติพงษ์ และคณะ

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สัญญาเลขที่ MRG5180163

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย และสำนักงานคณะกรรมการการอุดมศึกษา
(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกว. และสกอ.ไม่จำเป็นต้องเห็นด้วยเสมอไป)

กิตติกรรมประกาศ

ขอขอบคุณสำนักงานกองทุนสนับสนุนการวิจัย (สกว.) สำนักงานคณะกรรมการการอุดมศึกษา (สกอ.) และสถาบันวิจัยและพัฒนา มหาวิทยาลัยศิลปากร ที่ให้การสนับสนุนงานวิจัยนี้ ขอขอบคุณ ศาสตราจารย์ ดร.สุทธิชัย อัสสะบำรุงรัตน์ ที่ปรึกษาโครงการที่กรุณาให้คำแนะนำที่มีค่าเป็นอย่างยิ่งเสมอมา ขอขอบคุณ ศาสตราจารย์ ดร.ปิยะสาร ประเสริฐธรรม หัวหน้าศูนย์เชี่ยวชาญเฉพาะทางด้านคาตาไลซิสและวิศวกรรมปฏิกิริยาที่ใช้ตัวเร่งปฏิกิริยา ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ที่ให้การสนับสนุนในการใช้เครื่องมือในการวิเคราะห์ต่างๆ และบริษัทไทยออยล์ จำกัด (มหาชน) ที่ได้อนุเคราะห์สารตัวอย่าง FCC แก๊สโซลีนเพื่อใช้ในงานวิจัย ตลอดจนต้นสังกัดของผู้วิจัย ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์และเทคโนโลยีอุตสาหกรรม มหาวิทยาลัยศิลปากร ที่เอื้อเฟื้อสถานที่และให้เวลาผู้วิจัยในการทำวิจัยเป็นอย่างดี

Abstract

Project Code: MRG5180163

Project Title: Selection and design of glycerol ethers production for renewable fuel

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Project Period: 24 months

Glycerol, a major by-product of biodiesel production, was employed as a fuel extender in this study. The study can be divided into two main section i.e. 1) glycerol ethers synthesis from glycerol etherification with *tert*-butyl alcohol (TBA) in reactive distillation, and 2) self-etherification of fluidized catalytic cracking (FCC) gasoline and glycerol.

For the first section, firstly, the equilibrium thermodynamic analysis is investigated by applying three group contribution methods i.e. Joback's, Benson's and Gani's to determine the equilibrium composition by minimizing Gibbs free energy approach. Gani's group contribution method provides the best agreement with the experimental results. Secondly, the kinetic parameter determination was performed to fit with the experimental results carried out in an autoclave reactor. The Langmuir-Hinshelwood based on activity model shows the best reaction rate description. Furthermore, the obtained kinetic rate expressions are also well verified with independent experimental results in fixed bed reactors reported in literature. Finally, the production of glycerol ethers in reactive distillation (RD) is investigated. The suitable RD configuration consists of 6 rectifying stages and 6 reaction stages without stripping stage. The simulations are in good agreement with the experimental results.

For self-etherification in the second section, the process was originally investigated by etherifying the entire (FCC) gasoline with glycerol. The reactions were carried out in a pressurized liquid phase reactor in the presence of three different catalysts (i.e. Amberlyst 16, Amberlyst 15, and β-zeolite) at 70 °C and 2.6 MPa with a volume ratio of FCC gasoline to glycerol ratio of 84:16 for 10 h. The catalytic activity could be ordered as Amberlyst 16 > Amberlyst 15 >> β-zeolite. The properties of FCC and etherified FCC products were determined by the standard analysis of research octane number (RON), blending Reid vapor

pressure (bRvp), distillation temperature following the standard methods of ASTM D-2699, ASTM D-5191 and ASTM D-86, respectively. It was found that the olefin content decreased opposing with increasing of octane number due to ethers of glycerol formation and the etherified gasoline product has lower bRvp than that of original FCC gasoline. The process of FCC gasoline etherification with glycerol showed great environmental benefits; in addition, ethers produced renewably from glycerol could extend the gasoline volume.

Keywords: Glycerol, Renewable energy, Etherification, Reactive distillation, FCC gasoline

บทคัดย่อ

รหัสโครงการ: MRG5180163

ชื่อโครงการ: การเลือกและออกแบบระบบผลิตสารประกอบกลีเซอรอลอีเทอร์
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ระยะเวลาโครงการ: 24 เดือน

งานวิจัยนี้ได้นำกลีเซอรอลซึ่งเป็นผลิตภัณฑ์พลอยได้จากการผลิตไบโอดีเซลมาใช้เป็นเชื้อเพลิงทดแทน การศึกษาสามารถแบ่งได้เป็น 2 ส่วนหลักได้แก่ การผลิตสารประกอบอีเทอร์จากกลีเซอรอลและเทอร์เชียรี บิวทิล แอลกอฮอล์ในหอกลั่นแบบมีปฏิกิริยา และปฏิกิริยาการเกิดอีเทอร์ในตัวของแก๊สโซลีนจากกระบวนการฟลูอิไดซ์คะตะไลติกแครกกิงและกลีเซอรอล

สำหรับการผลิตอีเทอร์จากกลีเซอรอลและเทอร์เชียรี บิวทิล แอลกอฮอล์โดยหอกลั่นแบบมีปฏิกิริยา ในลำดับแรกเป็นการพิจารณาสมดุลทางอุณหพลศาสตร์ โดยวิธีกรุ๊ปคอนทริบิวชัน 3 วิธีได้แก่ วิธีของโจแบค วิธีของเบนสัน และวิธีของกานี ถูกนำมาใช้ในการทำนายองค์ประกอบสารที่ภาวะสมดุลโดยวิธีการหาค่าพลังงานอิสระของกิบส์ที่ต่ำที่สุด ซึ่งพบว่าวิธีของกานีสามารถทำนายองค์ประกอบสารที่ภาวะสมดุลได้ดีที่สุด ลำดับต่อมาเป็นการหาค่าพารามิเตอร์ทางจลนพลศาสตร์ของปฏิกิริยาโดยทำการทดลองในเครื่องปฏิกรณ์ชนิดอัดแรงดัน โดยพบว่าแบบจำลองของแลงเมียล์-ฮินเชลวูดซึ่งอธิบายในรูปแอคติวิตีสามารถอธิบายผลการทดลองได้เหมาะสมที่สุด อีกทั้งค่าพารามิเตอร์ทางจลนพลศาสตร์ที่ได้ยังอธิบายผลการทดลองในเครื่องปฏิกรณ์แบบเบดนิ่งจากผู้วิจัยอื่นได้ดี ในลำดับสุดท้ายเป็นการผลิตกลีเซอรอลอีเทอร์ในหอกลั่นแบบมีปฏิกิริยา พบว่ารูปแบบของหอกลั่นแบบมีปฏิกิริยาที่เหมาะสมที่สุดประกอบด้วยชั้นเรคติฟายอิงจำนวน 6 ชั้น ชั้นการเกิดปฏิกิริยาจำนวน 6 ชั้น และไม่มีชั้นสตริปปิง โดยผลจากแบบจำลองสอดคล้องกับการยืนยันด้วยผลการทดลองเป็นอย่างดี

ส่วนที่สองเป็นการศึกษาปฏิกิริยาการเกิดอีเทอร์ในตัวของแก๊สโซลีนจากกระบวนการฟลูอิไดซ์คะตะไลติก แครกกิงและกลีเซอรอลซึ่งทำการทดลองในเครื่องปฏิกรณ์ชนิดอัดแรงดันที่อุณหภูมิ 70 องศาเซลเซียส ความดัน 2.6 เมกะปาสคาล สัดส่วนแก๊สโซลีนต่อกลีเซอรอล 84:16 เป็นเวลา 10 ชั่วโมง พบว่าตัวเร่งปฏิกิริยาแอมเบอร์ลิสต์ 16 เป็นตัวเร่งปฏิกิริยาที่ดีกว่าแอมเบอร์ลิสต์ 15 และเบต้าซีโอไลต์ ทำการวิเคราะห์คุณสมบัติของน้ำมันโดยทำการทดสอบหาค่าออกเทนวิจัย ค่าความดันไอของ Reid และ

ค่าอุณหภูมิการกลั่นตามมาตรฐาน ASTM D-2699, ASTM D-5191 และ ASTM D-86 ตามลำดับ โดยพบว่าน้ำมันผลิตภัณฑ์มีปริมาณโอเลฟินส์ลดลง ค่าออกเทนสูงขึ้นและค่าความดันไอของสารผสมมีค่าต่ำลงเมื่อเทียบกับแก๊สโซลีนตั้งต้นซึ่งเป็นคุณสมบัติตามที่ต้องการ ผลิตภัณฑ์เชื้อเพลิงที่ได้มีปริมาณมากขึ้นซึ่งเป็นส่วนที่มาจากการใช้พลังงานหมุนเวียนและคุณสมบัติที่ได้ยังเป็นมิตรกับสิ่งแวดล้อมมากขึ้นอีกด้วย

คำหลัก: กลีเซอรอล พลังงานหมุนเวียน ปฏิกิริยาการผลิตอีเทอร์ หอกลั่นแบบมีปฏิกิริยา แก๊สโซลีนจากกระบวนการฟลูอิไดซ์คะตะไลติกแครกกิง

Nomenclature

a_i	activity of species *i*, dimensionless
E_a	activation energy, kJ mol^{-1}
F_i	molar flow rate of species *i*, mol min^{-1}
G^{tot}	total Gibbs free energy, kJ mol^{-1}
ΔH	standard enthalpy change of reaction, kJ mol^{-1}
$k_{j\mathrm{a}}$	forward rate constant of reaction *j* th for activity based model, mol s^{-1} kg^{-1}
$k_{-j\mathrm{a}}$	backward rate constant of reaction *j* th for activity based model, mol s^{-1} kg^{-1}
$k_{j\mathrm{x}}$	forward rate constant of reaction *j* th for mole fraction based model, mol s^{-1} kg^{-1}
$k_{-j\mathrm{x}}$	backward rate constant of reaction *j* th for mole fraction based model, mol s^{-1} kg^{-1}
$K_{j\mathrm{a}}$	equilibrium constant of reaction *j* th for activity base, dimensionless
$K_{j\mathrm{x}}$	equilibrium constant of reaction *j* th for mole fraction base, dimensionless
K_w	sorption constant, dimensionless
M	number of data points
n_i	number of mole of species *i*, mol
n^{tot}	total number of moles, mol
N_{Rec}	number of tray in rectifying section
N_{Rxn}	number of tray in reaction section
N_{Strip}	number of tray in stripping section
r	reaction rate, mol s^{-1} kg^{-1}
R	gas constant, J mol^{-1} K^{-1}

ΔS	standard entropy change of reaction, J mol^{-1} K^{-1}
t	reaction time, s
T	temperature, K
W	catalyst weight, kg
x_i	mole fraction of *i* th component, dimensionless

Greek letters

γ_i	activity coefficient of species *i* estimated by UNIFAC method, dimensionless
μ_i	chemical potential of species *i*,
μ_i^0	standard chemical potential of species *i*,

Subscript

a	activity base
x	mole fraction base
exp	experimental data
eq	equilibrium
i	species *i*
j	for *j* th reaction

Abbreviations

DTBG	di *tert*-butyl ether of glycerol
G	glycerol
IB	isobutylene

LH	Langmuir-Hinshelwood kinetic model
LH-A	Langmuir-Hinshelwood based on activity model
MTBG	mono *tert*-butyl ether of glycerol
PL	Power law model
PL-A	Power law based on activity model
PL-X	Power law based on mole fraction model
TBA	*tert*-butyl alcohol
tert	tertiary
TTBG	tri *tert*-butyl ether of glycerol

Executive Summary

Introduction

Biodiesel is a world-recognized renewable fuel for fossil diesel substitution. Since the demand of biodiesel increases rapidly, glycerol (the major by-product from biodiesel production) is expected to be oversupplied in the near future (Zhou et al., 2008). Therefore, many researches attempt to utilize glycerol in several approaches.

Etherification of glycerol is a process for cetane improving production. The product from glycerol etherification consists of mono-, di- and tri-tert-ether of glycerol. Di- and tri-tert-butyl ethers of glycerol are usable as potential cetane enhancement for diesel fuels due to their good blending properties with diesel fuel and high cetane number (David, 1940; Olah, 1996). Regarding this reaction, isobutylene (IB) reacts with glycerol in the presence of acid catalyst to form a mixture of mono-, di- and tri-tert-butyl ethers of glycerol (called MTBG, DTBG and TTBG, respectively) (Karinen et al., 2006, Klepacova et al. 2005; 2007). Klepacova et al. (2006) studied the etherification of glycerol with tert-butyl alcohol (TBA) over ion-exchange resin catalyst (Amberlyst 15, 31, 35, 119) and reported the optimal condition at 75ºC in the presence of Amberlyst 15; furthermore, the excess of TBA has a positive effect on the yield of ethers. It is noted that the use of TBA instead of IB is recently of interest since the latter is typically derived from non-renewable crude oil and become limited (Rihko and Krause, 1996) while TBA is a by-product from propylene oxide production (Quitain et al., 1999). Nevertheless, until now, no research has been investigated the thermodynamic and kinetic of etherification of glycerol and TBA. Moreover, since the reaction is limited by thermodynamic equilibrium, employing reactive distillation for simultaneous product or by-product removal are beneficial in the view of equilibrium shifting.

Although ethers of glycerol are mainly studied as diesel fuel additives, Karinen and Krause (2006) reported that they also offered high octane numbers. Octane numbers for the mixture of ethers from IB and glycerol were reported to be 112–128 of BRON and 91– 99 of BMON (Wessendorf, 1995), therefore it offers as an alternative for conventional octane enhancer such as, ETBE (Assabumrungrat et al., 2002; 2003, Kiatkittipong et al., 2003) and TAEE (Boonthamtirawuti et al., 2009). FCC gasoline containing several C_4-C_8 reactive olefins which are promising sources for etherification. On the contrary, these olefins content should be eliminated or minimized before using

as a gasoline in the environment viewpoint. Our previous works studied etherification of FCC gasoline with ethanol. The process 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 bRvp and amount of olefins content (Kiatkittipong et al. 2008; 2009). The using broad range of ethers production by self-etherification of FCC gasoline and glycerol for gasoline quality improvement is challenged.

The aim of this research is to produce glycerol ethers as renewable fuel with fuel quality improvement. The study can be divided into two main section i.e. 1) glycerol ethers synthesis from glycerol etherification with TBA in reactive distillation, and 2) self-etherification of FCC gasoline and glycerol.

For the production of glycerol ethers as cetane enhancer by etherification with TBA, firstly, the equilibrium thermodynamic analysis is investigated by applying three group contribution methods i.e. Joback's, Benson's and Gani's to determine the equilibrium composition by minimizing Gibbs free energy approach. Secondly, the kinetic parameter determination was performed to fit with the experimental results carried out in an autoclave reactor. The obtained kinetic parameters are used to investigate the ethers production from glycerol and TBA in reactive distillation.

For self-etherification of FCC gasoline and glycerol, the process was investigated by etherifying the entire FCC gasoline with glycerol catalyzed by three commercial catalysts; i.e. Amberlyst 16, Amberlyst 15 and β-zeolite. The properties of etherified gasoline product; i.e., research octane number (RON) and blending Reid vapor pressure (bRvp), distillation temperature and composition of FCC gasoline etherified were analyzed and compared to the original FCC gasoline.

Experimental

Apparatus

For thermodynamic and kinetic studies; the experiments were carried out in an autoclave reactor as shown in Fig. 1(a). The mixture was stirred by using turbine at the maximum speed for minimizing the external mass transfer resistance. 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.

For the reactive distillation study (Fig. 1(b)); the reactive distillation set-up consists of a four-neck round bottom flask with a mantle heater served as the reboiler, the vacuum-insulated column and the condenser. The column is divided into three sections of rectifying, reaction and stripping. Catalysts packed in the stainless steel mesh were placed inside the column to allow the simultaneous reaction along with the product separation.

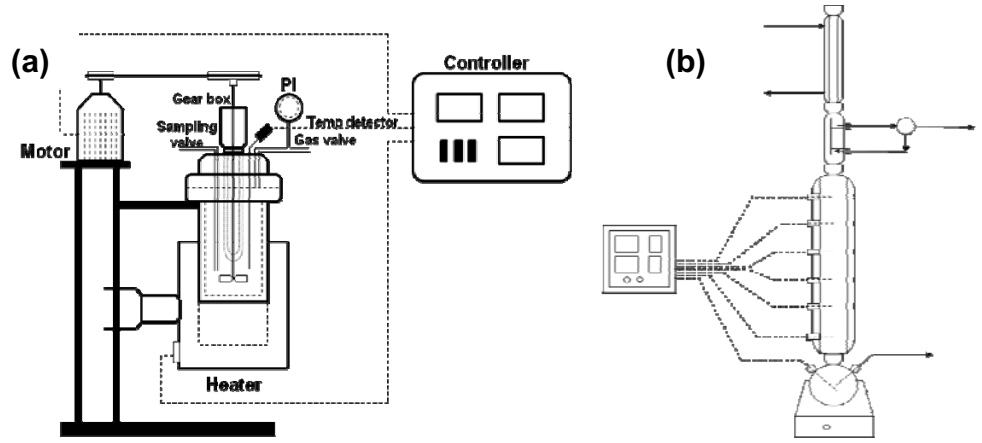

Fig. 1. Schematic diagram of (a) autoclave reactor and (b) reactive distillation

Analysis

Chemical compositions of a liquid sample were analyzed by using a gas chromatograph, Shimadzu GC 14B with hydrogen flame ionization detector. 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.

Results and Discussion

Part 1: Glycerol ethers synthesis from glycerol etherification with TBA in reactive distillation

Equilibrium thermodynamic analysis

Equilibrium reaction of glycerol with TBA was studied by minimizing the Gibbs free energy. The effect of temperature on the etherification of glycerol with TBA in term of glycerol conversion was illustrated in Fig. 2.

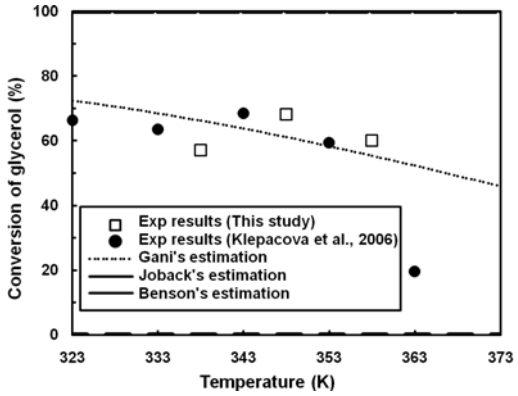

Fig. 2 Effect of reaction temperature on equilibrium conversion of glycerol from simulation and experiment.

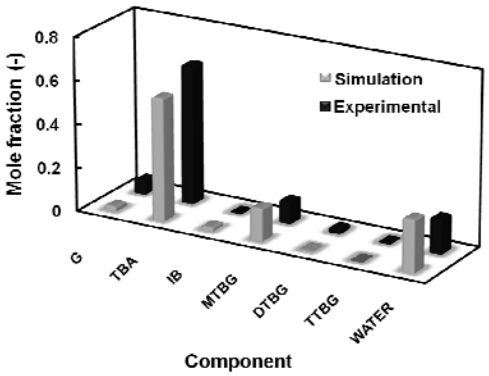

Fig. 3 Equilibrium composition obtained from the simulation using Gani's group contribution and the experiment at 348 K.

The simulation results were compared with the experimental results in this study as well as the results reported by Klepáčová et al. (2005, 2006). TBA was fed in excess at a constant molar ratio of TBA to glycerol of 4:1. Only Gani's group contribution method showed good agreement with the experimental results in term of glycerol equilibrium conversion and equilibrium composition as shown in Figs. 2 and 3, respectively.

Kinetic parameter determination

The reactions taking place in the direct etherification of glycerol and TBA can be summarized as follows

$$\text{Glycerol} + \text{TBA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{MTBG} + \text{H}_2\text{O} \quad (1)$$

$$\text{MTBG} + \text{TBA} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{DTBG} + \text{H}_2\text{O} \quad (2)$$

$$\text{DTBG} + \text{TBA} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{TTBG} + \text{H}_2\text{O} \quad (3)$$

Comparing among the different models i.e. Langmuir-Hinshelwood based on activity (LH-A) and Power law model based both activity and mole fraction based (PL-A and PL-X), LH-A appeared to be the best model to fit the experimental results. Fig. 4 shows the mole changes with time at T = 358 K which are in good fitting with LH-A model. The expressions of the rate constants and the activation energy of LH-A model are summarized in Table 1.

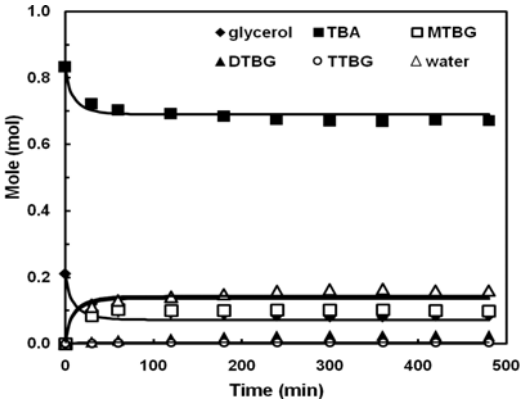

Fig. 4 Mole changes with time at 358 K (catalyst weight = 1.025 g, G:TBA = 1:4, 5 bar)

Table 1. Kinetic rate constants from LH-A model.

Rate constant	E_a (kJ mole^{-1})
k_1 = exp(31.872-8690/T)	82.15
k_2 = exp(32.659-10624/T)	88.33
k_3 = exp(7.6561-4189/T)	34.83

Reactive distillation study

Simulations of the etherification of glycerol and TBA in the reactive distillation (RD) were then carried out using RADFRAC model in the Aspen Plus. From the simulation, the optimum design for the reactive distillation is 6 rectifying and 6 reactions without stripping stage. An experiment was carried out at the suitable configuration obtained from the simulation. The liquid mole fraction of each component at each stage inside the reactive distillation and the temperature profile were shown in Fig. 5. Clearly, the vapor liquid equilibrium stages ensure that water is produced and excess TBA exists in the top of the column. Furthermore, the products i.e. MTBG, DTBG and TTBG are in the bottom stream.

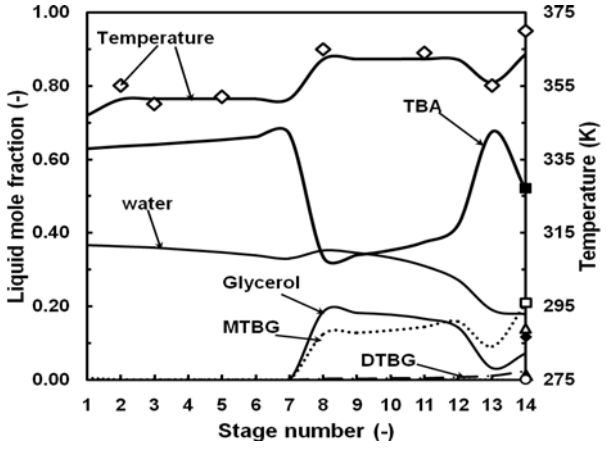

Fig. 5 Mole fraction and temperature profiles along the column at standard operating condition.

Part 2: Self-etherification of FCC gasoline and glycerol

Catalyst and operating condition screening

The reactivity of catalysts could be ordered as Amberlyst 16 > Amberlyst 15 >> β-zeolite; importantly, only Amberlyst 16 gave a complete conversion of glycerol after 10 h of reaction. Fig. 6 compares the amount of iso-olefinic compounds in original FCC gasoline and etherified FCC gasoline. It can be seen that small iso-olefins; i.e. C_4-C_6 iso-olefins are decreased after etherification reaction; however, larger atomic number of iso-olefins, e.g. C_7 iso-olefins are almost constant or slightly increased.

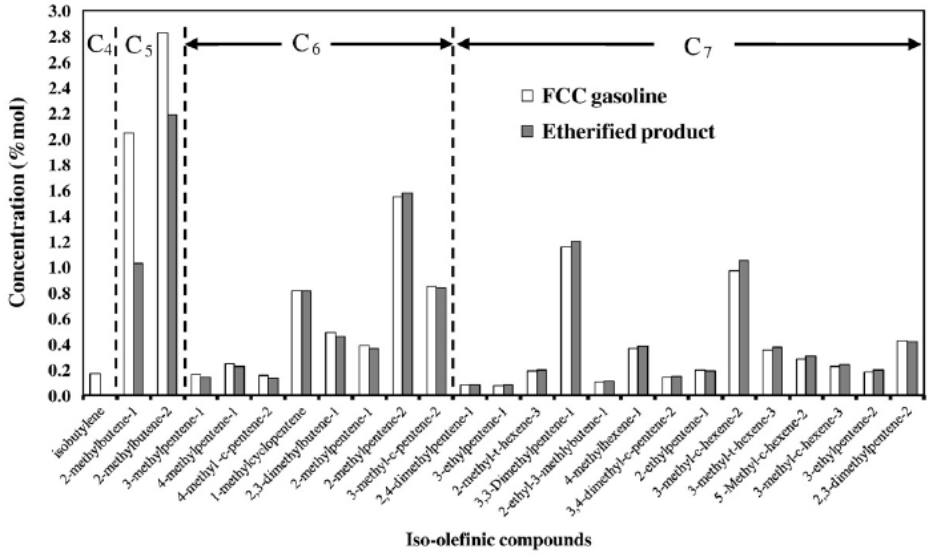

Fig. 6 Iso-olefinic compounds of FCC gasoline and FCC etherified product.

RON and bRvp of etherification products are shown in Table 2. The higher RON of FCC etherified product than that of original FCC gasoline implied that RON of ethers product is higher than that of olefinic compounds. Furthermore, since olefinic compounds were consumed during the reaction, the bRvp of etherified FCC decrease from 6.5 psia to 4.5 psia. The reduction of bRvp is beneficial especially for near tropical countries or in the summer period.

Table 2 Comparison of gasoline properties.

	Original FCC gasoline	Etherified FCC gasoline with glycerol
RON	88.0	90.1
bRvp (psia)	6.5	4.5
Density (g/cm^3)	0.7186	0.7403

Conclusion

This research studies the glycerol etherification for fuel quality improvement which can be divided into two main parts. The first part involved glycerol etherified with *tert*-butyl alcohol catalyzed by Amberlyst 15 in reactive distillation. The equilibrium study demonstrated that among three group contribution methods (i.e. Joback, Benson and Gani group contribution method), Gani's group contribution method estimated the nearest Gibbs free energy comparing to available database. The estimated equilibrium conversion and product distribution at reaction temperature in a range of 338-358 K showed good agreement with that obtained by experimental results from this study and as reported in the literature. The Langmuir-Hinshelwood activity based model which takes into account the effect of water adsorption is the best kinetic model to fit the experimental results. The obtained kinetic parameters were also well verified with the independent experiments in fixed bed reactor from the literature. Lastly, both simulation and experimental studies in reactive distillation indicated that the suitable configuration consists of 6 rectifying stages and 6 reaction stages without stripping stage.

For the second part, the etherification of FCC gasoline with glycerol in the presence of acid catalysts was found to be a promising process for gasoline quality improvement as well as utilizing of glycerol as fuel extender. The catalytic activity could be ordered as Amberlyst 16 > Amberlyst 15 >> β-zeolite. The etherified FCC gasoline with glycerol showed higher research octane number (RON) and lower blending Reid vapor pressure (bRvp) which are preference properties.

CHAPTER I

INTRODUCTION

Nowadays, global warming and energy crisis are recognized as the most global severe problems and the transportation is a significant part of this concern. Biodiesel is an alternative fuel that is chemically produced from the reaction of vegetable oil or animal fat with alcohol (i.e. methanol or ethanol). The great advantage of biodiesel is its "carbon neutral" in term of CO_2 releasing since the CO_2 emitted from the combustion of biodiesel is considered to be recyclable by planting. However, for every 9 kg of biodiesel produced, about 1 kg of crude glycerol is formed as by-product (Dasari et al., 2005; Richter et al., 2008). As the biodiesel production is increasing exponentially, the crude glycerol produced from the transesterification has also been generated in a large quantity carrying thus become oversupply (Johnson et al., 2007; Zhou et al., 2008).

Etherification of glycerol is a process for cetane improving production. The product from glycerol etherification consists of mono-, di- and tri-*tert*-ether of glycerol. Di- and tri-*tert*-butyl ethers of glycerol are usable as potential cetane enhancement for diesel fuels due to their good blending properties with diesel fuel and high cetane number (David, 1940; Olah, 1996). In addition, due to the presence of oxygen in their structure, it might decrease carbon monoxide and particulate matter emission from the incomplete combustion. Karinen and Krause (2006) studied the etherification of glycerol with iso-butylene (IB) over Amberlyst 35 ion-exchange resin catalyst and reported the optimal condition for enhancing the highest selectivity with initial IB to glycerol molar ratio of 3 at the temperature of 80ºC. Klepacova *et al*. (2005; 2007) reported that large-pore zeolite H-Y catalyst showed the highest glycerol conversion (88.7%) after 8 h; however the formation of tri-*tert*-butyl ether of glycerol was sterically hindered. It is known that Amberlysts 15 and 35 are promising catalysts for the

production of di- and tri-*tert*-butyl ether of glycerol. Melero *et al*. (2008) reported the achievement of glycerol conversions up to 100% with the combined selectivities towards di- and tri-*tert*-butyl ethers of glycerol over 92% after 4 h of reaction using arenesulfonic-acid-modified SBA-15 at 75ºC and IB to glycerol molar ratio of 4. Klepacova *et al*. (2006) studied the etherification of glycerol with *tert*-butyl alcohol (TBA) over ion-exchange resin catalyst (Amberlyst 15, 31, 35, 119) and reported the optimal condition at 75ºC in the presence of Amberlyst 15; furthermore, the excess of TBA has a positive effect on the yield of ethers. It is noted that the use of TBA instead of IB is recently of interest since the latter is typically derived from non-renewable crude oil and become limited (Rihko and Krause, 1996) while TBA is a by-product from propylene oxide production (Quitain *et al*., 1999). In addition, TBA was also previously employed instead of IB for the production of conventional oxygenated ethers i.e. ETBE (Assabumrungrat *et al*., 2002; 2003; Kiatkittipong *et al*., 2002), TAEE (Boonthamtirawuti *et al*., 2009).

Recently, the application of reactive distillation for etherification of glycerol, either in the presence or absence of fatty acids with C4-C5 alcohols e.g. iso-butyl alcohol, TBA and iso-amyl alcohol have been patented (Morgan 2008). Water produced from the etherification (and esterification in the presence of fatty acid) is removed from the reaction section as a distillate, thereby achieves higher conversion. Products i.e. mono-, di and tri-triol ethers (along with fatty acid esters) are obtained as bottom products. Ozbay et al. (2010) investigated the etherification of glycerol and TBA in fixed bed reactor catalyzed by Amberlyst-15, -16 and -35, Nafion-SAC-13 and γ-alumina. Among these catalysts, Amberlyst 15 showed the highest activity while Amberlyst 16 showed the highest selectivity of di-ethers. Nevertheless, until now, no research has been investigated the thermodynamic and kinetic of etherification of glycerol and TBA. Typically, the thermodynamic properties can be estimated by the first-order group contribution method such as Joback and Reid

(Joback and Reid 1987), Klincewicz and Reid (1984), the second-order group contribution by Benson (1958; 1976), and Gani (Constantinou and Gani, 1994; Abildskov *et al.*, 1996) and the third-order (Marrero and Gani, 2001). The purpose of each higher order terms is to provide more structural information unavailable in the lower order terms.

Although ethers of glycerol are mainly studied as diesel fuel additives, Karinen and Krause (2006) reported that they also offered high octane numbers. Octane numbers for the mixture of ethers from IB and glycerol were reported to be 112–128 of BRON and 91– 99 of BMON (Wessendorf, 1995), therefore it offers as an alternative for conventional octane enhancer. However, as shown above, until now, the research works are limited with only two etherification agents; i.e. IB and TBA for the etherification with glycerol.

FCC gasoline containing several C_4-C_8 reactive olefins which are promising sources for etherification. On the contrary, these olefins content should be eliminated or minimized before using as a gasoline in the environment viewpoint. The etherification of entire FCC gasoline has been successfully experimented with methanol (Pescarollo et al., 1993; Rihko and Krause, 2006; Hu et al., 2006) and ethanol (Kiatkittipong et al., 2008; 2009). Rihko and Krause (1996) employed Amberlyst 16 for etherification of light FCC gasoline with methanol and reported that TAME is the main ether observed in the products. Hu et al. (2006) presented that H-β zeolite showed higher conversion and catalytic stability than other catalysts including H-MOR, H-ZSM5 and cation exchange resin D005 for FCC etherification with methanol. Kiatkittipong et al. (2008) studied etherification of FCC gasoline with ethanol over β-zeolite and Amberlyst 16 and reported that β-zeolite is the suitable catalyst for this reaction since it offered products with higher RON and ethanol conversion as well as lower blending Reid vapor pressure (bRvp). We previously indicated that the cold start problem is not occurred even in low bRvp, according to the satisfied drivability index (Kiatkittipong et al., 2009). In the present work, the possibility of using broad range of ethers

production by self-etherification of FCC gasoline and glycerol for gasoline quality improvement was firstly challenged.

Objectives

1. To estimate the missing properties of ether products from etherification glycerol with tert-butyl alcohol using different group contribution methods.
2. To determine the kinetic parameters for the synthesis of ethers from glycerol and tert-butyl alcohol in batch reactor.
3. To produce tert-butyl ethers of glycerol in reactive distillation and investigate the effect of operating conditions on the performance of a reactive distillation.
4. Enhance the potential for utilization of glycerol as a fuel extender with quality improvement simultaneously by self-etherification with FCC gasoline.

CHAPTER II

THEORY

2.1 Biodiesel

Biodiesel is a nonpetroleum-based fuel that consists of alkyl esters derived from either the trans-esterification of triglycerides (TGs) or the esterification of free fatty acids (FFAs) with alcohols. Biodiesel is called the environmentally friendly biofuel since it provides a means to recycle carbon dioxide. In other words, biodiesel does not contribute to global warming. As a point of comparison, pure biodiesel (B100) releases about 90% of the energy that normal diesel does, and hence, its expected engine performance is nearly the same in terms of engine torque and horsepower. The transesterification reaction is shown in Fig. 2.1. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side (Hoydonckx *et al*. 2004).

Among the alcohols used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and NaOH catalyst is easily dissolved in it. The reaction can be catalyzed by alkalis, acids, or enzymes. Industrially, NaOH and KOH are preferred due to their wide availability and low cost.

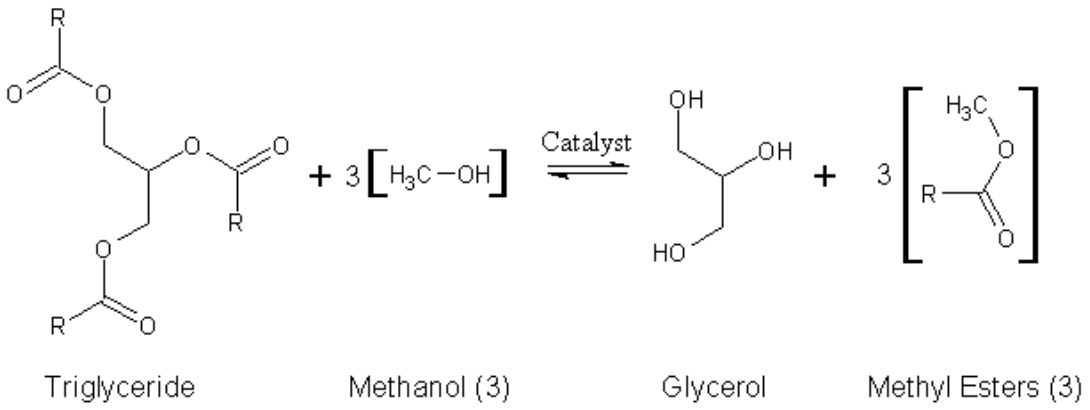

Fig. 2.1 Transesterification of triglycerides with alcohol.

Cetane number (CN) is widely used as diesel fuel quality parameter. The number relates to the ignition delay (the period that occurs between the start of fuel injection and the start of combustion). Since there are hundreds of components in diesel fuel, with each having a different cetane quality, the overall cetane number of the diesel is the average cetane quality of all the components. Generally, diesel engines run well with a cetane number from 40 to 51. Biodiesel from vegetable oil sources have been recorded as having a cetane number range of 48 to 61 (Romas *et al*. 2009). Biodiesel cetane number depends on the feedstock used for its production. The longer the fatty acid carbon chains and the more saturated molecules has higher the cetane number (Demirbas 2005; Knothe *et al*. 1998). Fuels with higher cetane number which have shorter ignition delays provide more time for the fuel combustion process to be completed. Hence, higher speed diesels operate more effectively with higher cetane number fuels. Premium diesel may have additives to improve cetane number and lubricity, detergents to clean the fuel injectors and minimize carbon deposits, water dispersants, and other additives depending on geographical and seasonal needs. Dimethyl ether may prove advantageous as a future diesel fuel as it has a high cetane number (Jang and Bae 2009). The 2-Ethyhexyl nitrate (2-EHN) (Bornemann *et al*. 2002) or di-*tert*-butyl peroxide (Clothier *et al*. 2000) can be added to diesel oil to improve ignition and boost cetane number.

2.2 Etherification of glycerol

Glycerol has numerous applications in different industrial processes. One of the interesting processes is glycerol ethers synthesis. A number of studies on the preparation of glycerol ethers from glycerol with isobutylene or *tert*-butyl alcohol by using different catalytic systems have been reported (Noureddini *et al*. 1998; Klepacova *et al*. 2005; Klepacova *et al*. 2006; Karinen *et al*. 2006). The reactions are shown in Fig. 2.2. However, an isobutylene source is limited to catalytic cracking or stream cracking fractions therefore ether products still partly base on fossil. Isobutylene is also a valuable reagent as use as a starting material in other chemical industries. Since *tert*-butyl alcohol is a major by-product in the ARCO process for the manufacture of propylene oxide (Matouq *et al.* 1993), it can provide an alternative route for the ethers synthesis (Matouq *et al*. 1996).

Tert-butyl alcohol had been proved as an alternative reagent instead of isobutylene to react with ethanol for ETBE production (Goto *et al*. 1999). TBA can directly react with glycerol, or indirectly dehydrated to isobutylene and then react with glycerol. However, in the case of etherification with glycerol using *tert*-butyl alcohol as an etherification agent, the reaction gave lower di- and tri-ethers yield than that of using isobutylene. This might be influenced from water formation from TBA dehydration which inhibit the catalytic activity of ion-exchange resin catalysts (Klepakova *et al*. 2006).

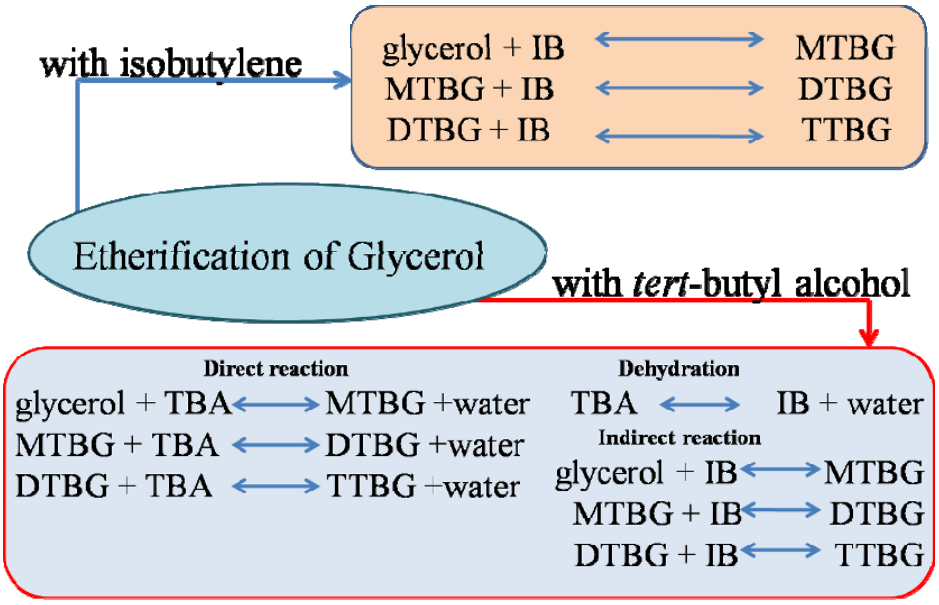

Fig 2.2 Etherification of glycerol with isobutene and *tert*-butyl alcohol

2.3 Conventional reactor versus reactive distillation

A conventional configuration for a chemical process usually involves two steps of chemical reaction and subsequent separation as shown in Fig. 2.3. In the chemical reaction step, reactants are brought into contact with solid catalysts at appropriate process conditions in one or more reactors. The stream leaving the reactor section then goes to one or more separation steps where unconverted reactants are separated from the reaction products and the inerts. The unconverted reactants, in some cases, may be recycled to the reaction section. When a substantial amount of inerts are present in the system, at least two separation units for separation of high purity product and for separation of the unconverted reactants from the inerts are required. The separation process by distillation is typically chosen.

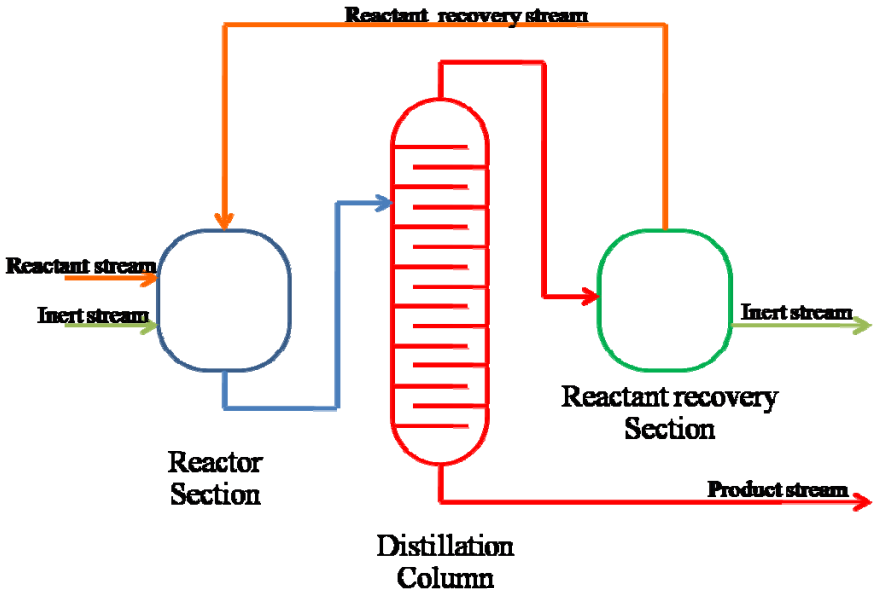

Fig. 2.3 Conventional process involving reaction followed by separation.

Reactive distillation is combination of reaction and separation in one single. Reactive distillation can eliminate conversion limitations of equilibrium control reaction by continuous removal of products from the reaction. Reactive distillation has been applied to many esterification, hydrolysis process and the formation of fuel oxygenates in chemical and petrochemical industries. Reactive distillation was first used by the chemical and petrochemical industry in esterification process to separate reaction product from reactant to increase product yields (Venkataraman *et al*. 1990). Applications of commercial reactive distillations can be found in many processes as reported in literature methyl acetate process (Fuchigami 1989), ethyl *tert*-butyl ether (Assabumrungrat *et al*. 2004), on pilot scale ethyl acetate process (Lai *et al*. 2007).

2.4.1 Reactive distillation configurations

The flow diagram of the reactive distillation is shown in Fig. 2.4. The middle section of the column is the reactive section. For a non-azeotropic chemical system,

separation of the inerts takes place in the rectifying section and the purification of the product takes place in the stripping section.

The reactive distillation column contains both the catalyst contact device and the distillation device. A reaction occurs in the catalyst contact device and then the reacting phase passes to the distillation device for vapor/liquid contact and separation. For both configurations, a rectification section may be located above the reactive distillation section of the column and a stripping section may be located below it, depending upon purity specifications.

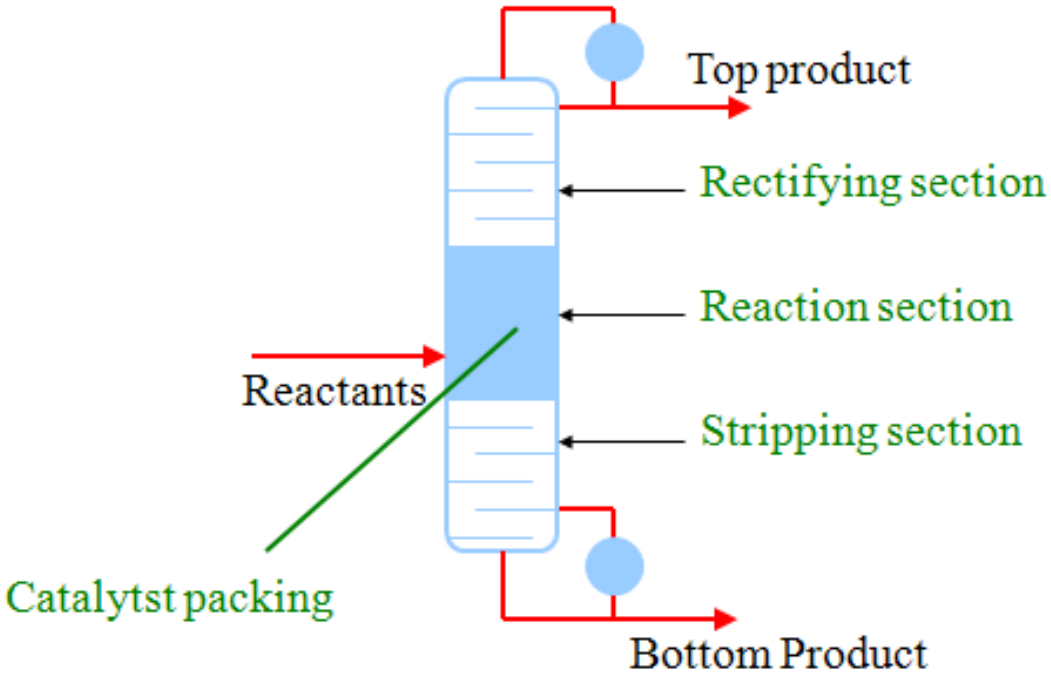

Fig. 2.4 Concept of reactive distillation

2.4.2 Advantages of reactive distillation

Application of reactive distillation to a catalytic chemical reaction using solid catalysts offers many advantages compared to a conventional process as summarized below:

4.2.1 Two process steps, i.e. separation and reaction, can be carried out in the same device. Such integration leads to lower costs in pumps, piping and instrument.

4.2.2 The heat released from the reaction can be used for vaporization of liquid, leading to savings of energy costs by the reduction of reboiler duties.

4.2.3 Product selectivity can be improved due to a fast removal of reactants or products from the reaction zone. By this, the probability of consecutive reactions, which may occur in the sequential operation mode, is lowered.

4.2.4 If the reaction zone in the reactive distillation column is placed above the feed point, poisoning of the catalyst can be avoided. This leads to longer catalyst lifetime compared to conventional systems.

CHAPTER III

LITERATURE REVIEW

This chapter contains the research reviews of etherification of glycerol with *tert*-butyl alcohol, the kinetic models of ethers and esters production, group contribution methods and application of reactive distillation for ethers production.

3.1 Production of *tert*-butyl ether of glycerol

Tert-Butyl ethers of glycerol with high content of di-ethers and especially tri-ethers are known as potential oxygenates to diesel fuels (diesel, biodiesel and their mixtures). These oxygenate ethers can reduce the emissions and mainly particulate matters (Noureddini *et al*. 1998). When glycerol is etherified with isobutene or *tert*-butyl alcohol, some or all of the hydroxyl groups in the glycerol molecule react. Thus, depending on the extent of etherification, up to five ether isomers may be formed (as shown in Fig. 3.1): two monosubstituted monoethers (3-*tert*-butoxy-1,2-propanediol (a) and 2-*tert*-butoxy-1,3-propanediol (b)), two disubstituted diethers (1,3-di-*tert*-butoxy-2-propanol (c) and 2,3-di-*tert*-butoxy-1-propanol (d)) and one trisubstituted triether (1,2,3-tri-*tert*-butoxy propane(e)).

Klepacova *et al*. (2005) studied etherification of glycerol with isobutylene or *tert*-butyl alcohol the liquid phase catalyzed by strong acid ion exchange resins of Amberlyst type and by two large-pore zeolites H-Y and H-Beta. In the case of using isobutylene, the highest glycerol conversion of 100% was obtained over both strong acid macroreticular ion-exchange resin A-35 and A-15 at 60°C. However, higher temperature (90°C) causes considerable drop in conversion and yield of desired di-ethers and tri-ethers. The obtained yield is 39.2% in the case of A-35 while 10.8% in the case of A-15. This is become the higher reaction temperature supports some side reactions show below.

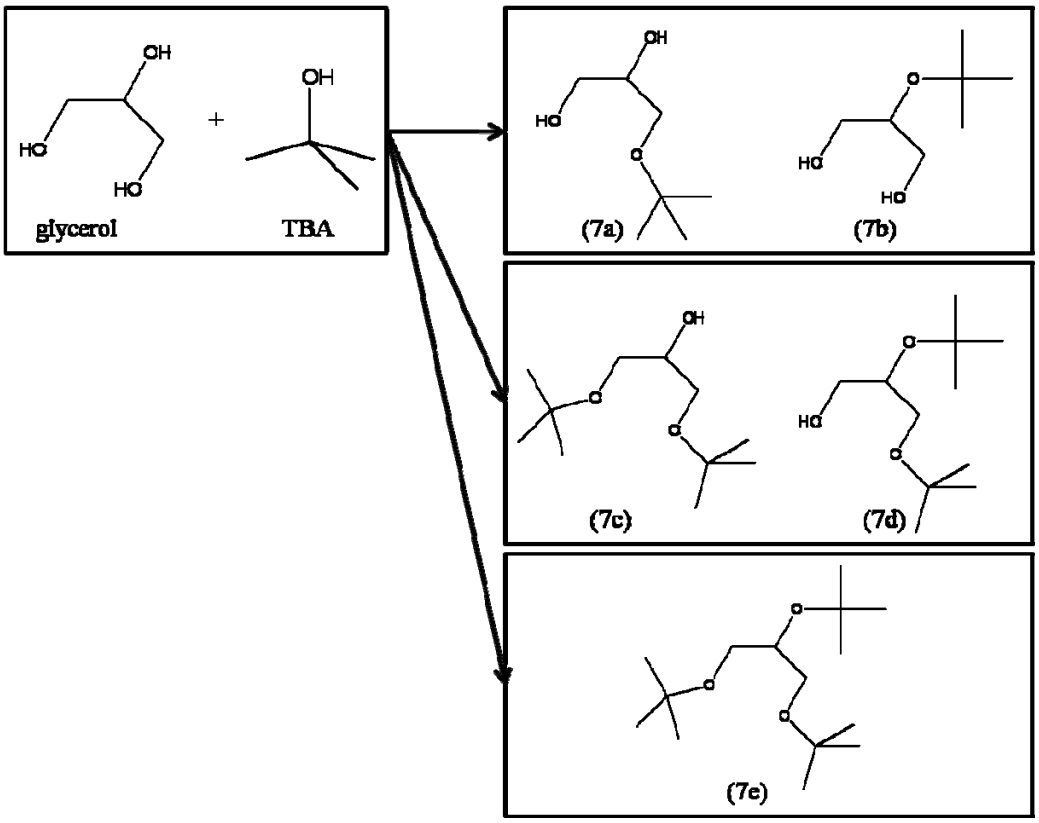

Fig. 3.1 Reaction scheme for the etherification of glycerol with *tert*-butyl alcohol.

The formation of diisobutylenes (DIB) by dimerisation of isobutylene could be occursed when molar ratio of isobutylene to glycerol was over 4:1. Zeolites H-Y and H-Beta provides lower selectivity than ion-exchange resins. Tri-*tert*-butyl ether of glycerol (TTBG) is not formed over H-Beta zeolite because of steric hindrance. The higher amount of lower oligomers of isobutylene (di-isobutylenes) was formed over H-Beta at 90°C. In the case of using *tert*-butyl alcohol, glycerol conversions at 60°C were 86% and 79% while yield of desired di-ethers and tri-ethers were 14.8% and 13.4% in the cases of A-35 and A-15, respectively. The lower in conversion and yield in case of using *tert*-butyl alcohol comparing with isobutylene might because water formation by dehydration of *tert*-butyl alcohol which can deactivate the catalysts.

Klepacova *et al*. (2006) further emphasized on the investigation of Amberlyst type ion exchange resin i.e., Amberlyst 15, Amberlyst 35, Amberlyst 31 and Amberlyst 119. The most suitable catalysts for *tert*-butylation of glycerol are the ion-exchange resins with a high degree of crosslinking i.e., Amberlyst 15 or Amberlyst 35. These catalysts have large pores which allow the formation of voluminous molecules of glycerol *tert*-butyl ethers. The optimal reaction temperature is 75°C, the glycerol conversion was 87.8 % on catalyst Amberlyst 35 (more acid) and 68.4 % on Amberlyst 15 when *tert*-butyl alcohol was an etherification agent. The conversion of glycerol and the yield of ethers have increased with higher mole ratio n(TBA)/n(G). Water present in the reaction system has an inhibition effect on glycerol *tert*-butylation. The best results were reached when isobutylene was used as etherification agent (XG = 100 %, Yield of di- and tri-ethers is 91.6 % for A-15 and 90.8 % for A-35). No water was formed during this reaction. The higher swelling capacity was shown by ion exchange resins with gel structure A-31 and A-119 because the degree of crosslinking is very low, but their pores are too narrow also after the swelling, so the reaction runs slowly and with difficulty.

Karinen *et al*. (2006) studied the etherification of glycerol with isobutene in liquid phase with acidic ion exchange resin catalyst (A-35). To increase the selectivity of the reaction towards the ethers and to hinder the formation of hydrocarbons it is required that the reaction should be carried out above 70°C with isobutene and glycerol near stoichiometric ratio. Excess of isobutene enhances the oligomerisation reaction whereas and the excess of glycerol increases the viscosity of the reaction mixture. High viscosity affect the mass transfer between liquid solution and catalyst therefore the reaction rate was limited. In a typical 7 h experiment, complete or almost complete conversion of glycerol was achieved at reaction temperatures above 70°C when the initial isobutylene/glycerol ratio was 3 or higher.

Addition of *tert*-butyl alcohol to the reaction mixture can hinder the oligomerisation reactions and eliminate the mass transfer limitations therefore improves the selectivity and yield. The formation of tri-ether is favoured when the initial isobutene/glycerol molar ratio is high. The optimal conditions for the formation of the di-ether are stoichiometric initial molar ratio of isobutene/glycerol and 80°C, and at low conversion level as well as with low initial isobutene/glycerol molar ratio the mono-ethers are the main products. C8 alkenes are the main products in the oligomerisation reaction. The fraction of C12 and C16 hydrocarbons decreases when the reaction is carried out at high temperatures or if the selectivity is controlled by adding *tert*-butyl alcohol to the reaction mixture.

Klepacova *et al*. (2007) investigated the influence of catalyst, and temperature on the etherification of glycerol with isobutylene in the liquid phase catalysed by strong acid ion-exchange resins of Amberlyst type (A-15 and A-35), p-toluenesulfonic acid and by two large-pore zeolites H-Y and H-Beta. The highest glycerol conversion 88.7% was achieved over zeolite H-Y after 8 h. Reaction over H-Beta zeolite runs faster with high selectivity to di-ethers, but formation of tri *tert*-butyl ethers of glycerol was sterically hindered. The highest amount of tri-ethers was observed over A-35. In the case of ion-exchange resins A-35 gives about 10% higher initial rate than A-15. From the technological point of view the zeolites are not convenient as catalysts for studied reaction because of their easy deactivation and higher price to that of ion-exchange resins. The homogeneous catalyst (p- toluenesulfonic acid) provides better results in di-ethers formation. The most appropriate temperature for etherification of glycerol is 60°C because the reaction rate is sufficient with high conversion and selectivity to ethers. The concentration of glycerol decrease as temperature increases, showing that the side reaction of isobutylene dimerisation became the preferred reaction at higher temperatures and longer reaction times.

Melero et al. (2008) investigated the etherification of glycerol with isobutylene over different sulfonic acid modified mesostructured silicas such as Propylsulfonic-acid-functionalized mesostructured silica (Pr- SBA-15) and Arenesulfonic-acid-functionalized mesostructured silica (Ar-SBA- 15). Sulfonic-acid-functionalized mesostructured silicas have demonstrated an excellent catalytic behavior in the etherification of glycerol with isobutylene to yield tert-butylated derivates.

It is worthy to note that although the above literatures are mainly studied these ethers as diesel fuel additives; high octane numbers for the mixture of ethers has been reported (112-128(BRON) and 91-99(MBON)).

3.2 Kinetic mechanism models of esters and ethers production

The kinetic models of etherification and esterification catalyzed by ion-exchange resins were classified in Langmuir-Hinshelwood model (LH model), Eley-Rideal model (ER model) and Pseudo Homogenous model (PH model or PL model). For high polar reaction media, the PH model has been successful used to estimated kinetic parameter (Sanz *et al*. 2004; Steinigeweg and Gmehling 2004; Jiménez *et al*. 2002) However, the PH model does not considering in sorption effect of the different species (reactants and products) into the catalyst (ion-exchange resin). The LH model and ER model consider the sorption effect in their kinetic model. For LH model, the basic idea mechanism is that all reactants are adsorbed on the catalyst surface before chemical reaction takes place. The ER model is applied when the reaction takes place between an adsorbed and a non-adsorbed reactant. Fig. 3.2 shows the difference between LH model and ER model mechanism. For ER mechanism, firstly an atom adsorbs onto the surface of catalyst (Fig. 3.2-a) and another atom passes by which interacts with the one on the surface (Fig. 3.2-b). Finally, a molecule is formed and then desorbs (Fig.

3.2-c). But for LH mechanism, two atoms adsorb onto the surface of catalyst (Fig. 3.2-d). Two atoms diffuse across the surface and interact when they are close (Fig. 3.2-e). Finally, a molecule is formed which desorbs from catalyst surface (Fig. 3.2-f).

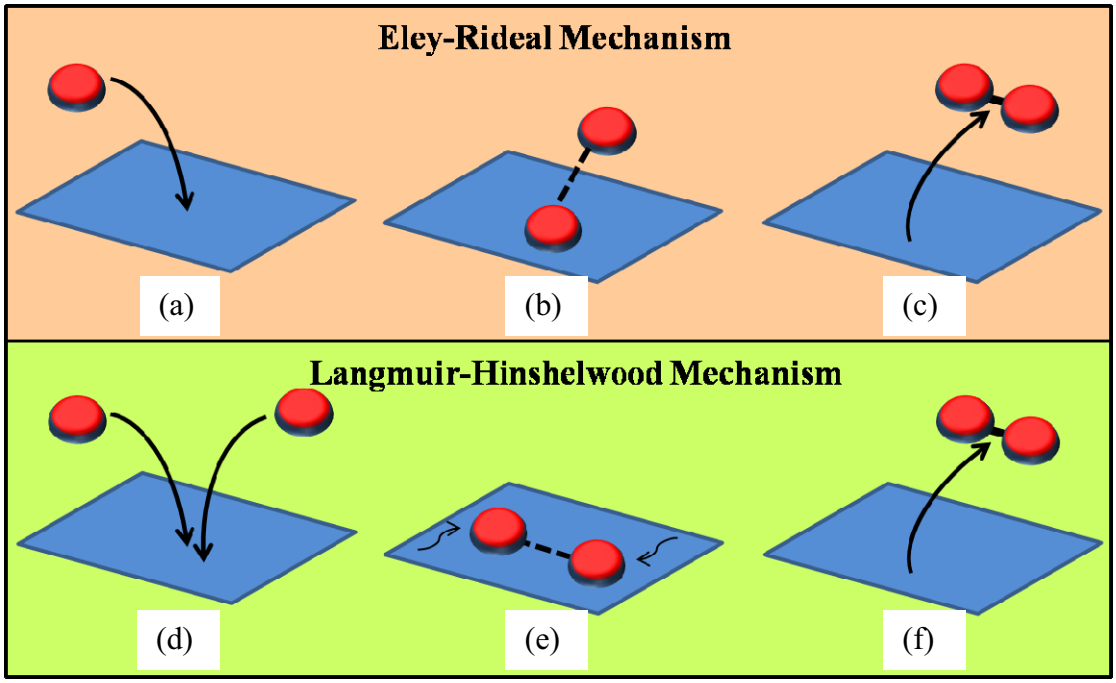

Fig. 3.2 Eley-Rideal and Langmuir-Hinshelwood mechanism.

Delgado *et al*. (2007) was investigated esterification of lactic acid and ethanol in the presence of the commercial ion-exchange resin Amberlyst 15. Experimental kinetic data of the esterification and the hydrolysis reactions were correlated simultaneously with the Langmuir–Hinshelwood (LH) and pseudo-homogeneous (PH) models. The non-ideality of the liquid phase was considered by using activities instead of mole fractions. The activity coefficients of the components in the liquid phase were calculated by using the UNIQUAC equation. The equilibrium constant was calculated from the component composition at equilibrium. The kinetic parameters of the PH and LH models were obtained by reduction of the experimental kinetic data to minimizing the objective function using the Simplex–Nelder–Mead method. A fourth order Runge-Kutta method was used to solve the differential

equation. The quality of the curve fitting was evaluated through the mean relative deviation. The LH model gave the best agreement with the kinetic experimental data. The activation energy of esterification and hydrolysis reactions were found to be 52.29 and 56.05 kJ mol^{-1}.

Zhang *et al*. (2004) studied the esterification of lactic acid with ethanol in the presence of five difference ion-exchange resins. Two simplified mechanisms based on LH model were compared by correlating the experimental data. The LH mechanism model were classified in mechanism A and B. Mechanism A assumes that ethanol and water adsorbed much stronger than other components in the esterification solution, so the adsorption of ethyl lactate and lactic acid was neglected. For mechanism B, it was assumed that lactic acid and water had the strongest adsorption than ethyl lactate and ethanol. The rate equation for mechanism A described more accurately the experimental data than mechanism B. Therefore, the former was more reliable for this kind of esterification reaction.

Karinen and Krause (2001) investigated etherification of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene with methanol catalyzed by a novel Smopex-101. The LH model which the adsorption of alkenes is assumed to be weak relative to methanol and ether show the activation energies obtained for the etherification of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene were 86 and 80 kJ mol^{-1}. An equally good fit was obtained with the ER model, which assumes that the alkenes react without adsorption. In both models the adsorption constants for methanol and ether are of the same order of magnitude. This constitutes a significant difference from the modeling results obtained with conventional ion-exchange resin catalysts and can be explained by the nature of the polymer matrixes.

Mao *et al*. (2007) investigated the etherification of methanol with 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B) catalyzed by the macroporous cation-exchange resin (D005II). The activity coefficients were estimated by Wilson method. There

were three mechanisms adopted for simulating reaction rate equations, containing homogeneous reaction mechanism (PH model), LH mechanism model and ER mechanism model. The equations based on the LH mechanism model were found to get the best fit with the experimental data. The results showed that the experimental data for thermodynamics agreed with the theoretical predications well, and the activation energy was 88.1 and 102.1 kJ mol^{-1} for the etherification of 2M1B and 2M2B, respectively, by kinetic calculation.

3.3 Group contribution method

A group contribution method is a technique to estimate and predict thermodynamic and other properties from molecular structures. Their advantages are that they need no experimental data, and since organic compounds used in chemical industry. Group contribution methods can be applied to really a great number of substances. However, first order group contribution methods cannot distinguish among structural isomers, because the isomers have the same number and kind of groups. The second order groups have been introduced into the group contribution equation.

Benson *et al*. (1976) had proposed additives of molecular properties. It is shown that the zero-order approximation is equivalent to the law of additive of atomic properties, the first-order approximation to the law of additives of bond properties, the second-order approximation to the law of additives of group properties. The results showed agreements for the various rules and certain extensions and limitations. The estimation of bond dissociation energies is possible with the additives rules as are the thermodynamic properties of free radicals. The conclusion showed that for C_p and $S°$ (ideal gases), the additives of atomic properties works to about ±2 cal $mole^{-1}K^{-1}$, while the additives of bond properties is usually

good to about ±1 cal mole^{-1}K^{-1}. The latter also estimates H_f^0 to about ±3 kcal mole^{-1}. The group additives relation is generally obeyed to within ±0.5 cal mole^{-1}K^{-1} for C_p and $S°$ and about ±0.6 kcal mole^{-1} for H_f^0.

George *et al*. (1976) used Ambrose, Joback and Chueh-Swanson definitions of group contributions and modified to account for the location of the functional groups in the molecule for predicting the auto ignition temperature (AIT) of pure components. The result proposed that the method can predict the auto ignition temperature of pure components only from the knowledge of the molecular structure, with an average error of 2.8 % and a correlation coefficient of 0.98.

Iwai *et al*. (1999) introduced the second order of group contribution method for calculate normal boiling point of many substance. This method showed the absolute average error of the normal boiling points of 1.24 K. The proposed method can distinguish the normal boiling points of alkane isomers well. The saturated vapor pressures have been calculated using the present second order groups. The absolute average percent errors are 6.0, 3.6, and 6.0% at T_b−50, Tb and T_b+50, respectively.

Constantinou and Gani (2004) had reported the expectation of higher order of group contribution method should be more correct than lower order group contribution method. The methods for prediction of normal boiling point, normal melting point, critical pressure, critical temperature, critical volume, standard enthalpy of vaporization, standard Gibbs energy, and standard enthalpy of formation at 298 K were investigated. This research showed the distinguish among isomers. Compared to the currently-used methods-first order method, this technique (Gani's method) demonstrates significant improvements in accuracy and applicability.

Mavrovouniotis (2004) had presented for the estimation of the standard Gibbs energies of formation of biochemical compounds (and hence the equilibrium constants of biochemical reactions) from the contributions of groups. The method employs a large set of groups and special corrections. The contributions were estimated via multiple linear regressions, using screened and weighted literature data. For most of the data employed, the error is less than 2 kcal mol^{-1}. The method provides a useful first approximation to Gibbs energies and equilibrium constants in biochemical systems.

Rajagopal *et al*. (2005) estimated the standard enthalpy of formation, by Benson's group contribution, and by semi-empirical molecular simulation methods compared with experimental data. Benson's method can estimate hydrocarbon enthalpies satisfactorily. The Benson's estimates of enthalpies of free radicals superior to the molecular simulation parameterization method (PM3) and are less accurate than the specialized computationally intensive PM3-family correlation (PM3-FC) method. The estimation of enthalpies for hydrocarbon radicals is substantially improved by a linear correlation of estimated values from semi-empirical molecular simulation method PM3 with experimental data. The radical enthalpies are now comparable to molecular simulated PM3-FC estimates. The hydrocarbon cations were divided into classes and estimated enthalpies found by adding Benson's enthalpy of radicals to the average ionization energy for the class. These predictions have an average absolute deviation of 8.6 kcal mol^{-1}. The proposed correlations effectively predict the standard enthalpy of formation of hydrocarbons, free radicals and carbocations. This methodology can be readily implemented in simulation programs to estimatethermo chemical properties of hydrocarbons, free radicals and carbocations and to improve the design and optimization of hydroprocessing units reducing costly hydrogen consumption.

Dalmazzone *et al.* (2006) applied Benson's second order groups, for the prediction of critical temperatures and enthalpies of vaporization of covalent compounds. The results were compared to the most common existing first or second order group contribution methods. The overall precision for T_c predictions of 381 compounds is 5.8 K, which better than Constantinou of 9.2 K and Joback of 23.6 K. It also precise for prediction of ΔH_{vap} of 319 compounds at 298 K and at the normal boiling point. Furthermore, group contribution may now be used for the computation of gas phase properties, T_c, and ΔH_{vap} at any temperature lower than T_c.

3.4 Ethers production in reactive distillation

Reactive distillation was proposed in the late 1910s, the first commercial practice started in about 1980s. The integration of separation and reaction process in a one unit can improves the conversion of chemical reactants and the selectivity of the desired products, by shifting the chemical equilibrium boundaries, accelerating reactions, reducing by-products, and overcoming azeotropic limitations. Nowadays, reactive distillation is one of favor process for liquid phase synthesis of octane-enhance for gasoline such as Methyl *tert*-Butyl Ether (MTBE), Tertiary Amyl Methyl Ether (TAME), Ethyl *tert*-Butyl Ether (ETBE), Tertiary Amyl Ethyl Ether (TAEE). Recently, many researches showed the use of MTBE is tendency to pollute underground water. It is a pending legislation to use of MTBE in many states in US. TAEE or ETBE are the most potential octane enhancer to replace MTBE.

Matouq *et al*. (1996) reported that reactive distillation column was efficient to separate ETBE from an aqueous solution and homogenous catalyst. Catalysts such as $NaHSO_4$, H_2SO_4 fail to synthesis ETBE because the dehydration of TBA was dominant. Quitain *et al*. (1999a) studied a continuous synthesis of ETBE from TBA and bio-ethanol (2.5

mol% ethanol in aqueous solution) catalyzed by Amberlyst 15 in reactive distillation column. At standard operating condition, 60 mol% ETBE can be obtained in the distillate and almost pure water was in the residue. The conversion of TBA and ETBE selectivity are 99.9 and 35.9 %, respectively. Aiouache and goto (2004) studied etherification of TAEE in reactive distillation column inserted by a zeolite NaA membrane tube. Assabumrungrat *et al*. (2004) investigated the synthesis of ETBE from a liquid phase reaction between *tert*-butyl alcohol and ethanol in reactive distillation catalyzed by β-zeolite with three compositions (Si/Al ratio=13, 36 and 55). The reactive distillation column packed with β-zeolite shows better performance than that packed with the commercial Amberlyst 15. It is obviously due to the better performance of β-zeolite as reported by previous work (Assabumrungrat *et al*. 2002). The effect of various operating parameters for both types of catalysts follows the same trend.

3.5 Etherification with entire FCC gasoline

However, as shown in the literature, olefinic reactants are mostly limited as isobutene and isoamyleme.

FCC gasoline containing several C_4-C_8 reactive olefins which are promising sources for etherification. On the contrary, these olefins content should be eliminated or minimized before using as a gasoline in the environment viewpoint. The etherification of entire FCC gasoline has been successfully experimented with methanol (Pescarollo et al., 1993; Rihko and Krause, 2006; Hu et al., 2006) and ethanol (Kiatkittipong et al., 2008; 2009).

Pescarollo et al. (1993) had investigated etherify FCC light gasoline with methanol. The higher ether can be produced from reaction between reactive olefins and methanol. The result showed olefins conversions are lower with larger atomic number of olefins. The conversion of isobutene is 84.2%, isopentene is 68.8% as closely approaches thermodynamic

equilibrium. Rihko and Krause (1996) employed Amberlyst 16 for etherification of light FCC gasoline with methanol and reported that TAME is the main ether observed in the products. Hu et al. (2006) presented that H-β zeolite showed higher conversion and catalytic stability than other catalysts including H-MOR, H-ZSM5 and cation exchange resin D005 for FCC etherification with methanol.

Our previous works studied etherification of FCC gasoline with ethanol. The process 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 bRvp and amount of olefins content (Kiatkittipong et al. 2008; 2009). Comparing between β-zeolite and Amberlyst 16, β-zeolite is the suitable catalyst for this reaction since it offered products with higher RON and ethanol conversion as well as lower blending Reid vapor pressure (bRvp). We previously indicated that the cold start problem is not occurred even in low bRvp, according to the satisfied drivability index (Kiatkittipong et al. 2009).

CHAPTER IV

RESEARCH PROCEDURE

This chapter describes the research procedures for glycerol ethers production for renewable fuel. Both simulation and experiment were performed in the part of synthesis of *tert*-butyl ethers from glycerol and *tert*-butyl alcohol in reactive distillation. Some difference in the experimental procedure in the part of self-etherification of FCC gasoline was expressed.

1. Theoretical analysis

Gibbs free energy minimization

Due to the component of ether products are not appearing in Aspen Plus data base so the new components must be specified and added to Aspen Plus program. The various group contribution methods were applied to estimate the missing properties are Joback's method, Gani's method and Benson's method. The group contribution methods can be classified into first order and second order. The Aspen Plus program allow user to add the functional group for each component include the method of group contribution. The equilibrium reactoin of etherification of glycerol with *tert*-butyl alcohol were considering by minimization of Gibbs free energy approach. The total Gibbs free energy of the system is defined as

$$G^{tot} = \sum_{i=1}^{k} n_i \mu_i \qquad (4.1)$$

The chemical potential of species i (μ_i) for non-ideal solution can be presented by

$$\mu_i = \overline{\mu}_i^{o} + RT \ln(x_i) + RT \ln(\gamma_i) = \overline{\mu}_i^{o} + RT \ln(a_i) \qquad (4.2)$$

The activity coefficient of species *i* (γ_i) can be calculated using the UNIFAC method. Substituting Eq. (2) into Eq. (1) offers:

$$G^{tot} = \sum_{i=1}^{k} n_i \bar{\mu}_i^0 + \sum_{i=1}^{k} n_i RT \ln(a_i)$$

$$= \sum_{i=1}^{k} n_i \bar{\mu}_i^0 + \sum_{i=1}^{k} n_i RT \ln\left(\frac{\gamma_i N_i}{N^{tot}}\right) \quad (4.3)$$

For minimizing the objective function (G^{tot}), the approaches method for minimization Gibbs free energy problem is Lagrange multipliers (Nichita *et al*. 2002; Jarungthammachote and Dutta 2008).

Reaction pathway

The reactions taking place in the direct etherification of glycerol and TBA can be summarized as follows

$$\text{Glycerol + TBA} \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} \text{MTBG + } H_2O \quad (4.4)$$

$$\text{MTBG + TBA} \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} \text{DTBG + } H_2O \quad (4.5)$$

$$\text{DTBG + TBA} \underset{k_{-3}}{\overset{k_3}{\longleftrightarrow}} \text{TTBG + } H_2O \quad (4.6)$$

For the indirect reaction, TBA is firstly dehydrated to IB and water.

$$\text{TBA} \underset{k_{-4}}{\overset{k_4}{\longleftrightarrow}} \text{IB + } H_2O \quad (4.7)$$

IB from dehydration reaction is further reacted with glycerol as follows

$$\text{Glycerol + IB} \underset{k_{-5}}{\overset{k_5}{\longleftrightarrow}} \text{MTBG} \quad (4.8)$$

$$\text{MTBG + IB} \underset{k_{-6}}{\overset{k_6}{\longleftrightarrow}} \text{DTBG} \quad (4.9)$$

$$\text{DTBG + IB} \underset{k_{-7}}{\overset{k_7}{\longleftrightarrow}} \text{TTBG} \quad (4.10)$$

The equilibrium constants are defined as

$$K_j = \frac{k_j}{k_{-j}} \tag{4.11}$$

To determine the equilibrium parameters (K_1, K_2 and K_3), several of group contribution methods i.e. Benson, Joback and Gani were used to estimate the missing properties of ethers products. Equilibrium constants in term of activity (abbreviated as K_{ja}) are defined as

$$K_{ja} = \frac{\prod_{i=product} a_i}{\prod_{i=reactant} a_i} \tag{4.12}$$

The equilibrium constant based on mole fraction can be calculated by the relation in Eqs. 13-15.

$$a_i = \gamma_i x_i \tag{4.13}$$

$$K_{ja} = \frac{\prod_{i=product} a_i}{\prod_{i=reactant} a_i} = \frac{\prod_{i=product} \gamma_i x_i}{\prod_{i=reactant} \gamma_i x_i}$$

$$K_{ja} = \left[\frac{\prod_{i=product} \gamma_i}{\prod_{i=reactant} \gamma_i}\right]\left[\frac{\prod_{i=product} x_i}{\prod_{i=reactant} x_i}\right] = K_{jx}\left[\frac{\prod_{i=product} \gamma_i}{\prod_{i=reactant} \gamma_i}\right] \tag{4.14}$$

then $$K_{jx} = K_{ja} \Big/ \left[\frac{\prod_{i=product} \gamma_i}{\prod_{i=reactant} \gamma_i}\right] \tag{4.15}$$

2. Kinetic study

2.1 Chemical and catalysts

Table 4.1 give the supplier name of chemical and catalyst. FCC gasoline was obtained from the catalytic cracking unit of local oil refinery; its compositions are given in Table 4.2. Before use, the catalysts were dried overnight in an oven at 110°C. The physical properties of these three catalysts are presented in Table 4.3.

Table 4.1 Chemical and catalyst used in the study

Chemical and catalyst	Purity (%)	Supplier
Glycerol	99.5	Ajax chemical
tert-butyl alcohol	99.5	Ajax chemical
MTBG	99.5	Merck
FCC gasoline	-	Thai Oil
Amberlyst 15	-	Chemika Fluka
Amberlyst 16	-	Chemika Fluka
β-zeolite	-	Tosoh

Table 4.2 Composition of FCC gasoline in volume percent

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

Table 4.3 Physical properties of catalysts

	Surface area (m^2 / g)	Particle size (μm)	Pore diameter (nm)	Pore volume (cm^2/g)
Amberlyst 16	45	700	20	1.82
Amberlyst 15	53	600-850	30	0.40
β-zeolite	625	45	0.58	0.129

2.2 Batch reactor apparatus and experimental procedure

Kinetic study of the etherification of glycerol and *tert*-butyl alcohol used Amberlyst-15 as a catalyst was carried out in an autoclave reactor as shown in Figure 4.1. Autoclave reactor was maintained at a constant temperature by heating jacket with temperature controller around the reactor chambers. For both thermodynamic and kinetic study; 16 ml of glycerol, 83 ml of *tert*-butyl alcohol and 1.025 g of catalysts (A-15) were added into the reactor together at room temperature. The solution was pressurized by N_2 gas to 5 bar to prevent vaporization of liquid solutions and heated to the desired reaction temperature. Liquid samples (0.5 cm^3) were taken for analysis at 0, 30, 60, 90, 120, 180, 240, 300, 360, 420, 480 mins. Firstly, the effect of reaction time and stirred speed on equilibrium reaction were investigated to maintain the equilibrium reaction. Finally, the reaction time were set at 480 minute and stirred at about 600 rpm for all reaction to investigate equilibrium reaction and determine the kinetic parameters.

For self-etherification study, the reaction system containing 84 cm^3 of FCC gasoline, 16 cm^3 of glycerol and 10 g of catalyst was carried out at 70 °C for 10 h under a N_2 pressure of 2.6 MPa. Prior to the reaction, the mixture was separated into two liquid phases since glycerol and FCC gasoline are insoluble in each other. Hence, no sampling was taken

during 10 h of reaction as it could not be assured that the sample would well stand for the mixture and its phase (Karinen and Krause, 2006). After reaction, the reactor was cooled down to the room temperature before collecting the sample from the reactor in order to prevent the evaporation loss. It is noted that the gasoline sample was centrifuged to separate catalyst from the solution before further analysis.

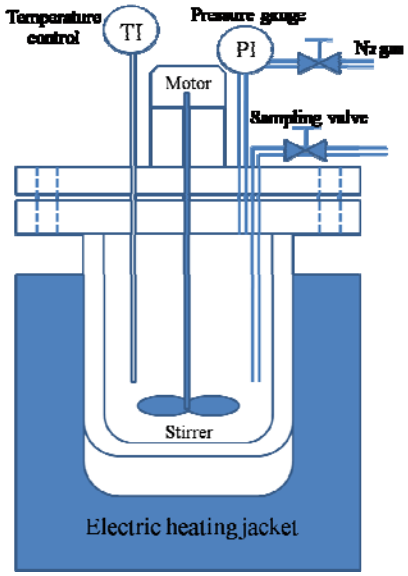

Fig. 4.1 Schematic diagram of the autoclave reactor.

2.3 Sample analysis

The analysis was carried out using gas chromatography (GC). The operating condition of the GC is shown in Table 4.4. A 0.025 microliter of sample was injected into the GC column.

Table 4.4 Operating conditions of gas chromatography

Gas chromatography Shimadzu GC14B	
Operating conditions	
Detector	FID
Carrier gas	Nitrogen (N_2)
Carrier gas (bar)	30
Capillary column	HP-INNOWAX
Length of column (m)	30
Injection temperature (C)	300
Column temperature (C)	40-240 (hold 5 min)
Heating rate (C/min)	10
Detector temperature (C)	150

For the part of self-etherification of FCC gasoline, the liquid reaction products were analyzed in PIANO (paraffins, isoparaffins, aromatics, naphthenes and olefins) by FID gas chromatography using a Supelco capillary column. The condition of gas chromatography was followed from our previous study (Kiatkittipong et al., 2009). The standard analysis of Research Octane Number (RON), blending Reid vapor pressure (bRvp) and distillation temperature were carried out by following the standard methods of ASTM D-2699, ASTM D-5191 and ASTM D-86, 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 Reactive distillation study

Reactive distillation study was performed on both experiment and simulation. The reactive distillation set-up consists of a four-neck round bottom flask with a mantle heater served as the reboiler, the vacuum-insulated column and the condenser as shown in Figure

4.2. The column is divided into three sections of rectifying, reaction and stripping. Catalysts packed in the stainless steel mesh were placed inside the column to allow the simultaneous reaction along with the product separation. The stainless steel mesh saddles were used as the packing materials in the stripping section of the column and the six thermocouples were connected along the column height to measure the temperature profiles inside the column. A coolant was circulated in the condenser located at the top. The reflux ratio was controlled by a solenoid valve with a multi-timer.

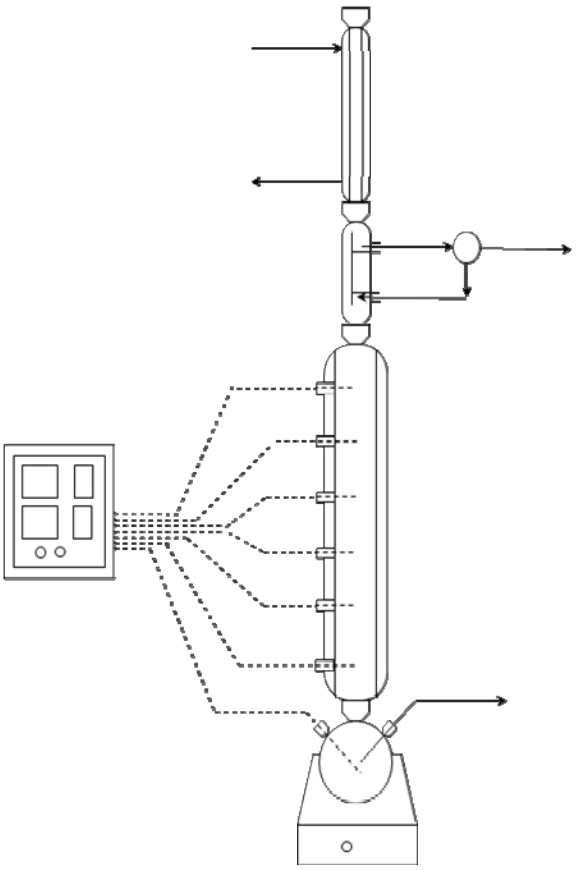

Fig. 4.2 Schematic diagram of reactive distillation

CHAPTER V

RESULTS AND DISCUSSION

Part I: Glycerol ethers synthesis from glycerol etherification with TBA in reactive distillation

5.1 Equilibrium thermodynamic analysis

Three types of group contribution methods i.e. Joback's method (Joback and Reid 1987), Gani's method (Constantinou and Gani 1994; Marrero and Gani 2001) and Benson's method (Benson and Buss 1985; Benson 1976) were applied to calculate the Gibbs free energy of formation. The values of Gibbs free energy of formation are illustrated in Table 5.1. Since the values of Gibbs free energy of the ether products are not available, the values of other available oxygenated ethers were referred for comparison. It was found that Gani's method showed the lowest percent deviation compared with the other methods. Equilibrium reaction of glycerol with TBA was studied by minimizing the Gibbs free energy. The effect of temperature on the etherification of glycerol with TBA in term of glycerol conversion was illustrated in Fig. 5.1. The simulation results were compared with the experimental results in this study as well as the results reported by Klepáčová *et al.* (2005, 2006). TBA was fed in excess at a constant molar ratio of TBA to glycerol of 4:1. Only Gani's group contribution method showed good agreement with the experimental results in term of glycerol equilibrium conversion and equilibrium composition as shown in Figs. 5.1 and 5.2, respectively. It can be seen that the glycerol conversion at equilibrium decreases with increasing reaction temperature since the overall reaction is exothermic. The equilibrium constants based on both activity and concentration of glycerol etherification obtained from the Arrhenius' plots are summarized in Table 5.2.

Table 5.1 Summary of Gibbs free energy values estimated from Aspen Plus compared with those from database.

Name	G_f (kJ mol^{-1})				Deviation (%)		
	Joback	Benson	Gani	database	Joback	Benson	Gani
MTBG	-370.18	-369.64	-388.19	-	-	-	-
DTBG	-301.84	-318.50	-356.33	-	-	-	-
TTBG	-233.50	-269.07	-269.59	-	-	-	-
TBA	-151.18	-157.03	-180.70	-177.60	-14.87	-11.57	1.74
IB	62.09	96.90	59.41	58.08	6.90	66.84	2.29
Glycerol	-438.52	-417.35	-446.67	-447.10	-1.92	-6.65	-0.09
ETBE	-102.52	-103.43	-110.93	-121.70	-15.76	-15.01	-8.84
MTBE	-110.94	-103.78	-107.10	-117.50	-5.58	-11.67	-8.84

Table 5.2 Equilibrium constants estimated by Aspen Plus program.

reaction	**Rate constant**
r_1	$K_{1a} = \exp(-7.52+2095/T)$
	$K_{1x} = \exp(-5.15+1523/T)$
r_2	$K_{2a} = \exp(-11.68+2573/T)$
	$K_{2x} = \exp(-10.31+1857/T)$
r_3	$K_{3a} = \exp(-15.08+2573/T)$
	$K_{3x} = \exp(-17.44+3315/T)$

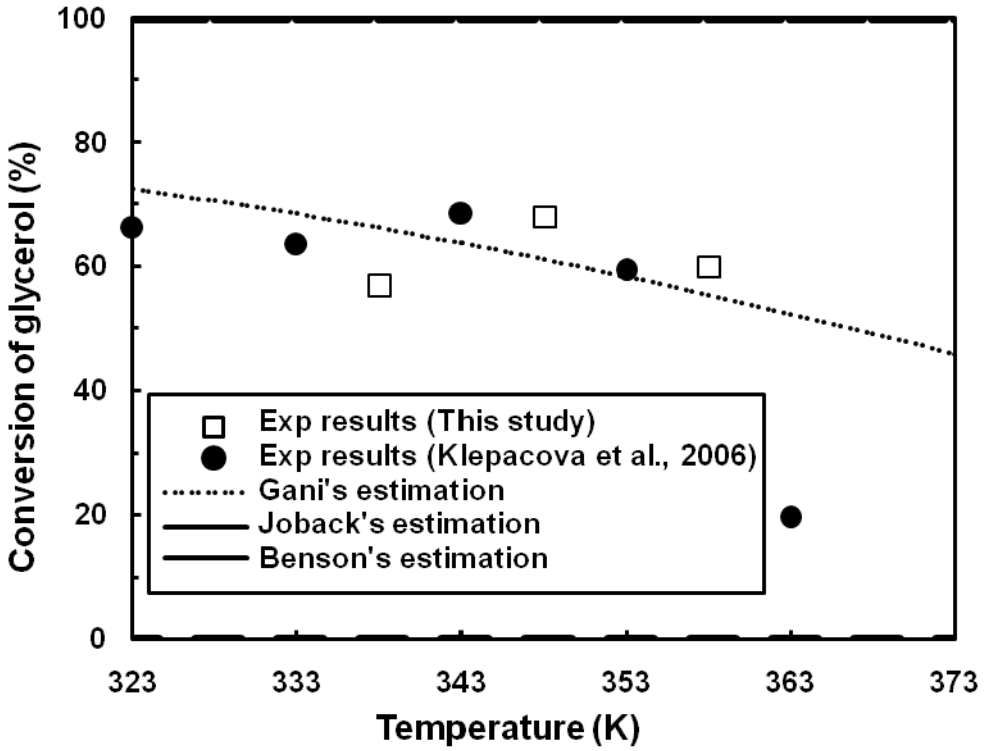

Fig. 5.1 Effect of reaction temperature on equilibrium conversion of glycerol from simulation and experiment.

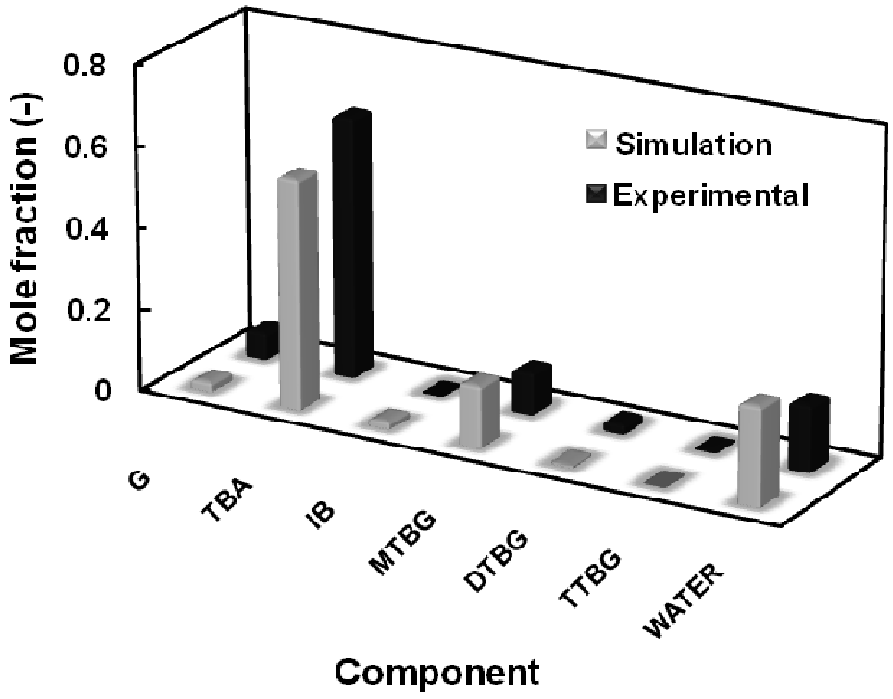

Fig. 5.2 Equilibrium composition obtained from the simulation using Gani's group contribution and the experiment at 348 K.

5.2 Kinetic study

Regarding the study of the external mass transfer effect over the catalyst (Amberlyst 15), the conversion increased with increasing the speed of stirrer and leveled off at the speed level of 600 rpm (the results are not shown here), indicating the negligible of external mass transfer at this stirrer speed. Therefore, the speed of 600 rpm was used throughout the experiments.

5.2.1 Development of mathematical models

The reverse reaction in Eq. (4.7) and the forward reactions in Eqs. (4.8) to (4.10) were neglected since the operating pressure in this study was at 5 bar (and only small amount of IB can be dissolved in the liquid solution at this condition). It was also confirmed by our experimental results that the concentration of IB in liquid mixture was relatively small. The experimental results were fitted with two kinetic models; Langmuir-Hinshelwood (LH) and Power Law (PL) based on both activities (a_i) and mole fraction (x_i). The rate expressions of consecutive reaction pathway of Eqs. (4.4) to (4.6) and TBA dehydration (Eq. 4.7) could be written in term of activity as

$$r_{1a} = k_{1a}\left[\frac{a_G a_{TBA} - a_{MTBG} a_{water}/K_{1a}}{(1+K_{wa}a_{water})^Z}\right] \quad (5.1)$$

$$r_{2a} = k_{2a}\left[\frac{a_{MTBG} a_{TBA} - a_{DTBG} a_{water}/K_{2a}}{(1+K_{wa}a_{water})^Z}\right] \quad (5.2)$$

$$r_{3a} = k_{3a}\left[\frac{a_{DTBG} a_{TBA} - a_{TTBG} a_{water}/K_{3a}}{(1+K_{wa}a_{water})^Z}\right] \quad (5.3)$$

$$r_{4a} = k_{4a}\left[\frac{a_{TBA}}{(1+K_{wa}a_{water})^Z}\right] \quad (5.4)$$

where Z=0 for Power Law (PL) model and Z=1 for Langmuir-Hinshelwood (LH) model. The kinetic parameters of TBA dehydration over Amberlyst 15 reported by (Yang *et al*. 2000) were employed in this study as shown below.

$$k_{4a} = \exp(15.451 - 10325/T) \quad (5.5)$$

$$k_{4c} = \exp(15.39 - 10270/T) \quad (5.6)$$

$$K_{wa} = \exp(-36.456 + 7646/T) \quad (5.7)$$

$$K_{wc} = \exp(-35.62 + 7530/T) \quad (5.8)$$

Note that the ion-exchange capacity for Amberlyst 15 is 4.4 [mol-H (kg dry resin)$^{-1}$].

By performing material balances for a batch reactor, the following expressions are obtained.

$$-\frac{dm_{\mathrm{TBA}}}{dt} = \frac{dm_{\mathrm{H_2O}}}{dt} = W(r_1 + r_2 + r_3 + r_4) \quad (5.9)$$

$$-\frac{dm_{\mathrm{Glycerol}}}{dt} = \frac{dm_{\mathrm{MTBG}}}{dt} + \frac{dm_{\mathrm{DTBG}}}{dt} + \frac{dm_{\mathrm{TTBG}}}{dt} = W(r_1 + r_2 + r_3) \quad (5.10)$$

$$\frac{dm_{\mathrm{MTBG}}}{dt} = W(r_1) \quad (5.11)$$

$$\frac{dm_{\mathrm{DTBG}}}{dt} = W(r_2) \quad (5.12)$$

$$\frac{dm_{\mathrm{TTBG}}}{dt} = W(r_3) \quad (5.13)$$

The best-fitted kinetic parameters were purposed by minimizing the relative root mean square deviation (RMSD) values as expressed by

$$RMSD_i = \frac{1}{M}\sqrt{\sum_{t=1}^{M}\left(\frac{\left(x_{i,t} - x_{i,\exp,t}\right)}{\left(x_{i,\exp,t}\right)}\right)^2} \quad (5.14)$$

5.2.2 Kinetic parameter determination

The experiments were carried out at three temperature levels to investigate the kinetic parameters. The mathematical models and equilibrium constants from the previous section were used to determine the kinetic parameters. Comparing among the different models i.e. Langmuir-Hinshelwood based on activity (LH-A) and Power law model based both activity and mole fraction based (PL-A and PL-X), LH-A appeared to be the best model to fit the

experimental results providing the lowest of RMSD as shown in Fig. 5.3. Figs. 5.4-5.6 show the mole changes with time at T = 338, 348 and 358 K, respectively which are in good fitting with LH-A model. Although PL model was slightly inferior to LH for fitting with the etherification of glycerol and TBA, the rate expression in PL model is still needed in some software applications (Vadapalli & Seader, 2001; Dhale *et al*., 2004; Bhatia *et al*., 2007; Carlos *et al*., 2010).

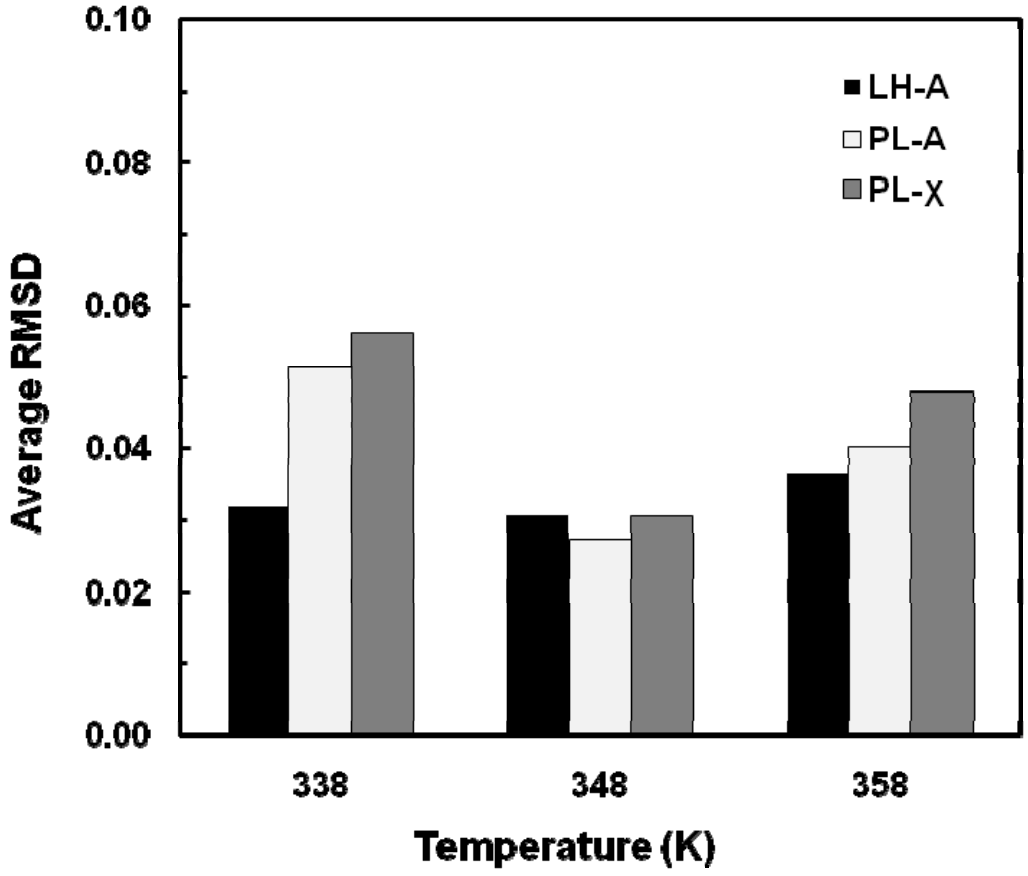

Fig. 5.3 Average RMSD values of PL and LH kinetic models for both activity and mole fraction at various temperatures.

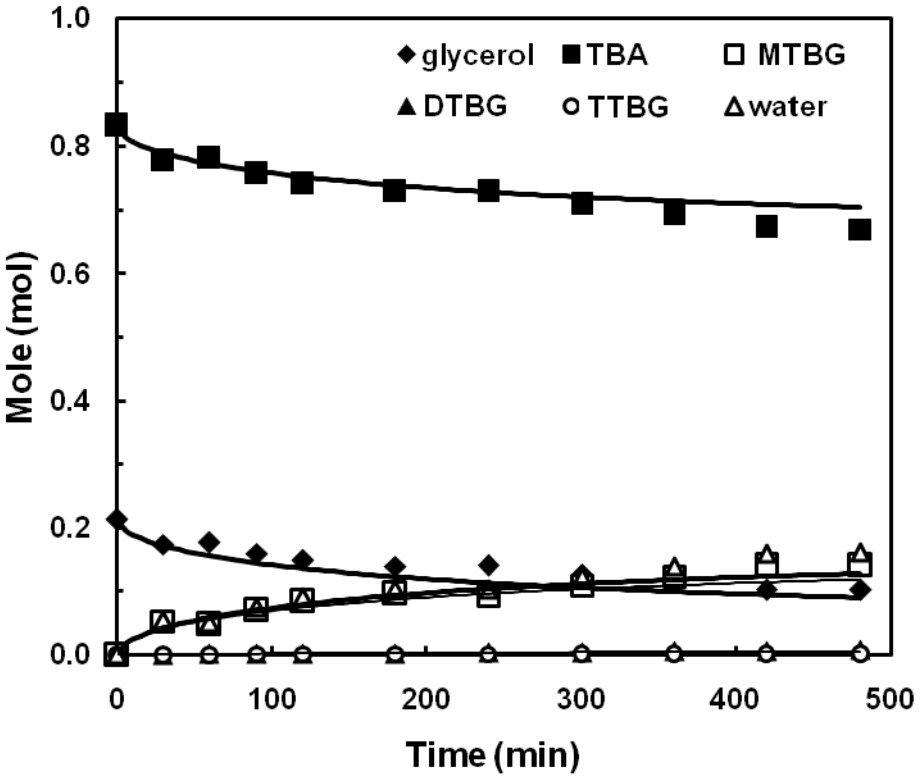

Fig. 5.4 Mole changes with time at 338 K (catalyst weight = 1.025 g, G:TBA = 1:4, 5 bar), (symbols: experimental results, solid lines: LH-A model).

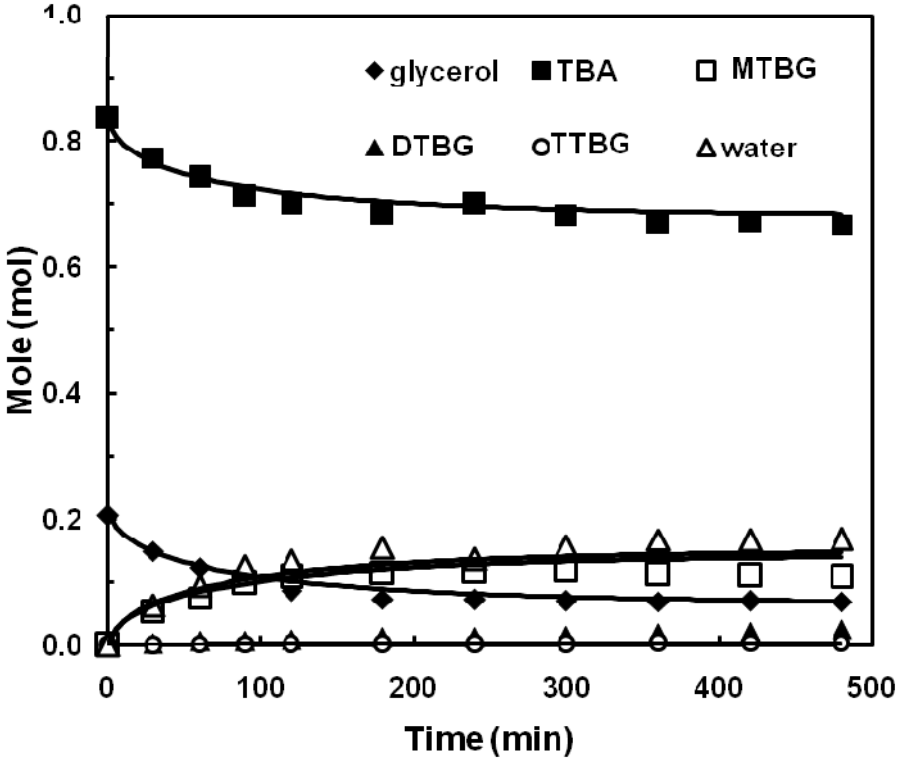

Fig. 5.5 Mole changes with time at 348 K (catalyst weight = 1.025 g, G:TBA = 1:4, 5 bar), (symbols: experimental results, solid lines: LH-A model).

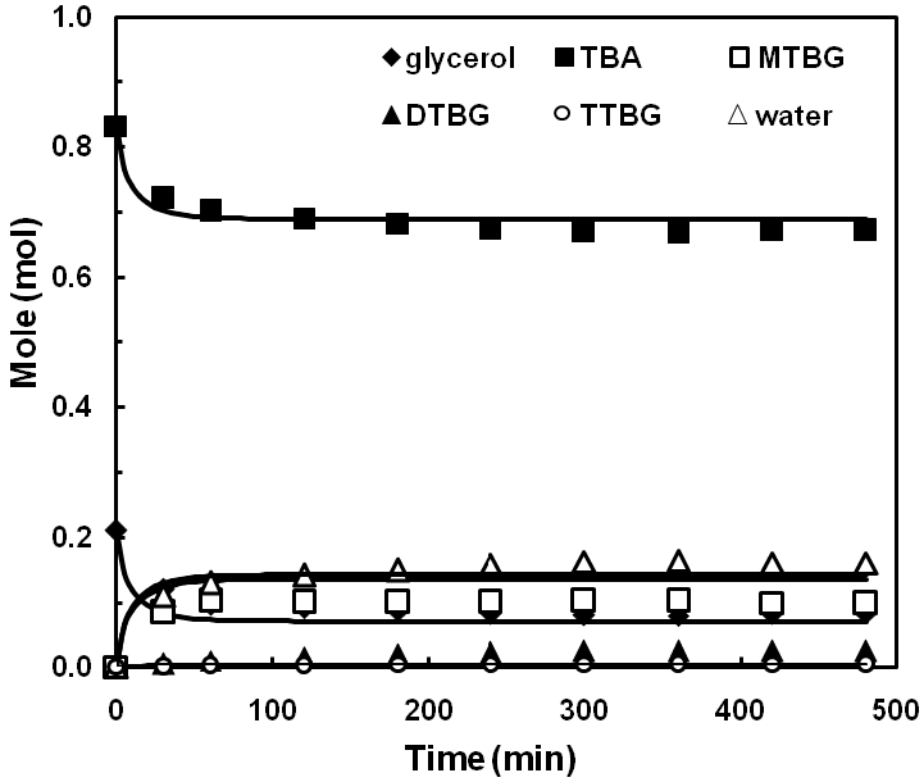

Fig. 5.6 Mole changes with time at 358 K (catalyst weight = 1.025 g, G:TBA = 1:4, 5 bar), (symbols: experimental results, solid lines: LH-A model).

The temperature-dependent rate constants were determined by plotting the relationships according to the Arrhenius's as shown in Figs. 5.7 and 5.8. The sorption equilibrium constant of water as a function of temperature can be determined by Van't Hoff plot as shown in Fig. 5.8. The sorption equilibrium of water decreased with the increase of temperature as regularly observed in the most adsorption processes. The heat of adsorption of water calculated by Eq. (5.15) is 73 kJ mol^{-1} which is slightly higher than the previous reports of 63 and 55 kJ mol^{-1} (Yang *et al*., 1995; Abella *et al*., 1999).

$$K_{vap} = \exp\left[\frac{-\Delta G}{RT}\right] = \exp\left[-\frac{\Delta S}{R} + \frac{\Delta H}{RT}\right] \qquad (5.15)$$

The expressions of the rate constants and the activation energy are summarized in Table 5.3.

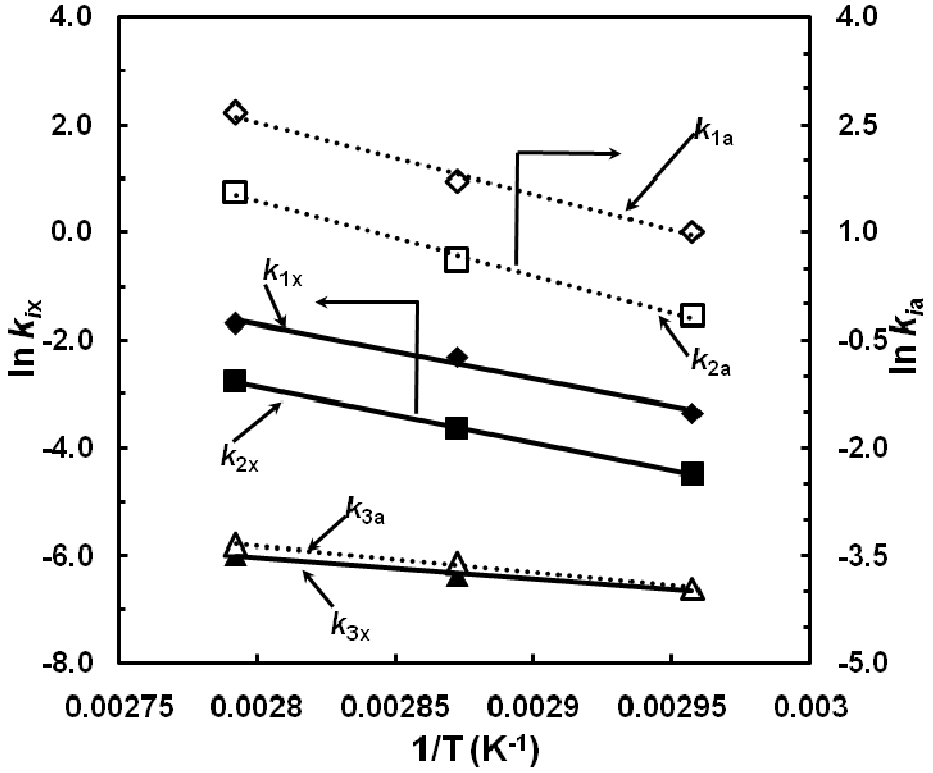

Fig. 5.7 Arrhenius's plots of PL-X (solid lines) and PL-A (dot-dashed lines).

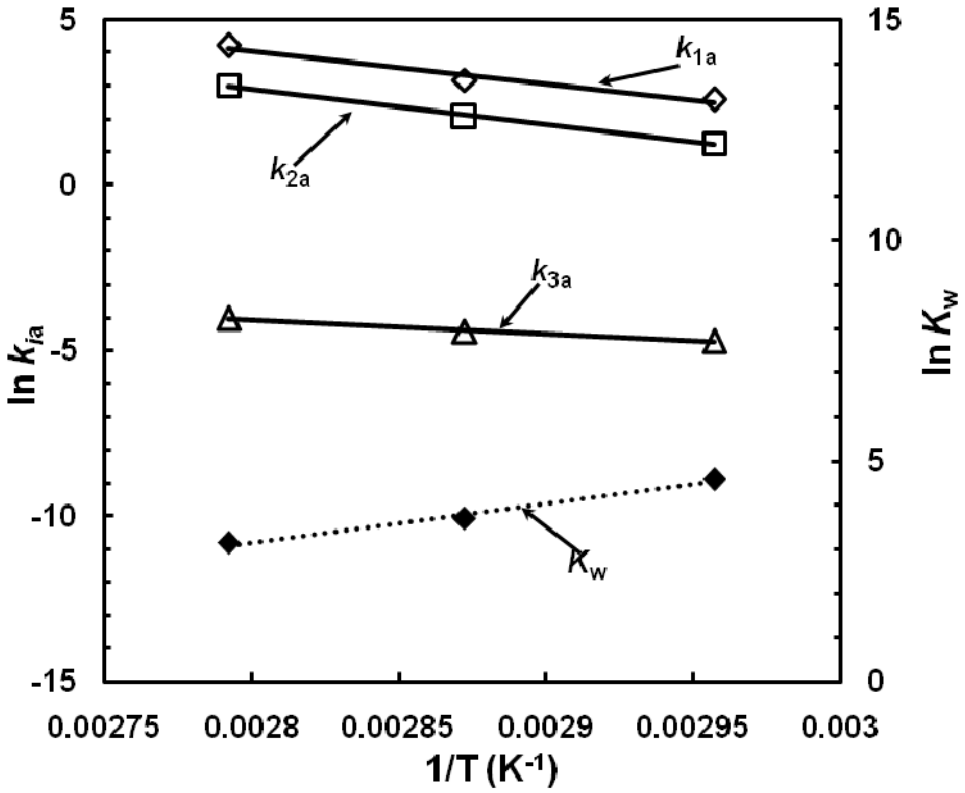

Fig. 5.8 Arrhenius's (solid line) and Van't Hoff plots (dashed line) of LH-A model.

Table 5.3 Kinetic rate constants from PL-A, PL-X and LH-A models.

Model	Rate constant	Activation energy, E_a (kJ mole^{-1})
PL-X	k_1 = exp(26.299-10006/T)	81.77
	k_2 = exp(26.437-10468/T)	88.09
	k_3 = exp(5.0194-3952/T)	32.85
PL-A	k_1 = exp(30.499-9988/T)	83.04
	k_2 = exp(30.629-10425/T)	86.67
	k_3 = exp(7.0013-3704/T)	30.79
LH-A	k_1 = exp(31.872-8690/T)	82.15
	k_2 = exp(32.659-10624/T)	88.33
	k_3 = exp(7.6561-4189/T)	34.83

5.2.3 Validation of purposed kinetic parameters

Recently, Ozbay *et al.*, (2010) performed the experimental study of etherification of glycerol and TBA in a fixed bed reactor. The experimental results with varying operating temperature and space time using Amberlyst 15 as the catalyst were employed to compare with our simulation results. The mathematical models for fixed bed reactor could be derived from material balance and summarized as follows.

Fixed bed reactor model

$$-\frac{dF_{\mathrm{TBA}}}{dW}=\frac{dF_{\mathrm{H_2O}}}{dW}=r_1+r_2+r_3+r_4 \tag{5.16}$$

$$-\frac{dF_{\mathrm{glycerol}}}{dW}=\frac{dF_{\mathrm{MTBG}}}{dW}+\frac{dF_{\mathrm{DTBG}}}{dW}+\frac{dF_{\mathrm{TTBG}}}{dW}=r_1+r_2+r_3 \tag{5.17}$$

$$\frac{dF_{\mathrm{MTBG}}}{dW}=r_1 \tag{5.18}$$

$$\frac{dF_{\mathrm{DTBG}}}{dW} = r_2 \tag{5.19}$$

$$\frac{dF_{\mathrm{TTBG}}}{dW} = r_3 \tag{5.20}$$

As shown in Fig. 5.9, the simulation results agreed well with their experimental results operated in fixed bed reactor with the space time of 18 g s ml^{-1} and glycerol:TBA feed molar ratio of 1:8. Even the space time was increased by 19 times (342 g s ml^{-1}), good agreement of simulation results are still obtained as shown in Fig. 5.10.

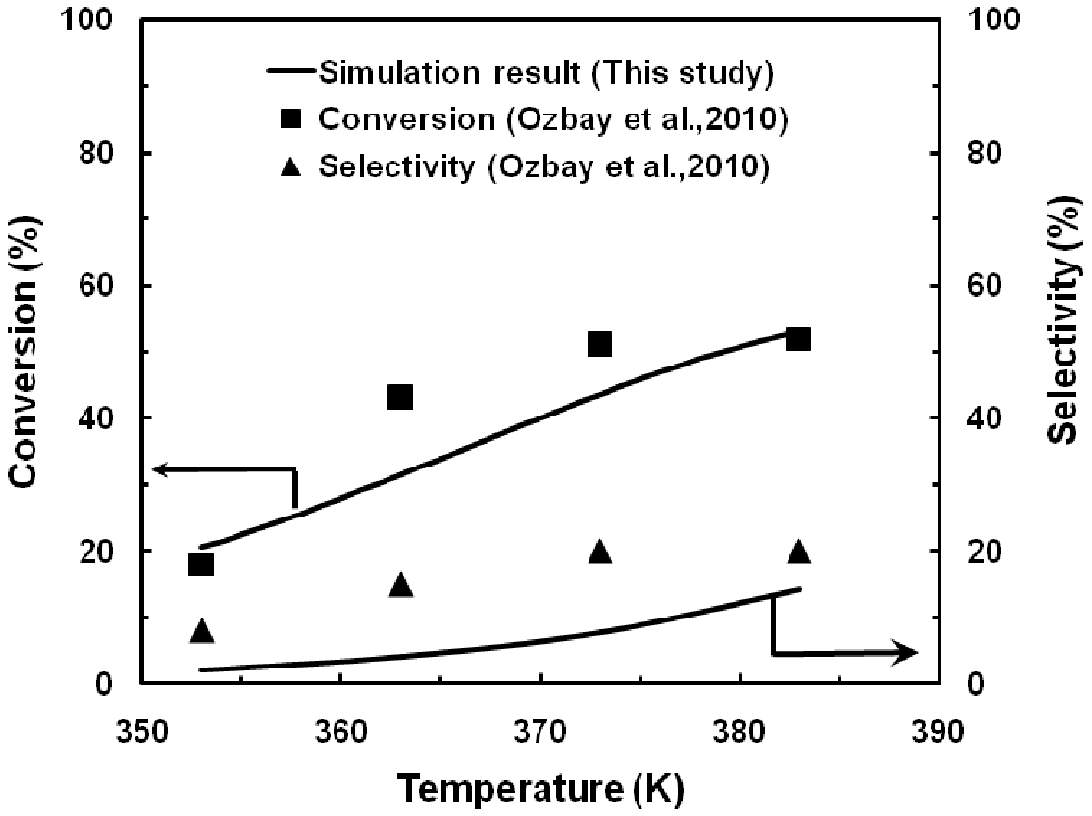

Fig. 5.9 Effect of reaction temperature on fixed bed reactor performance.

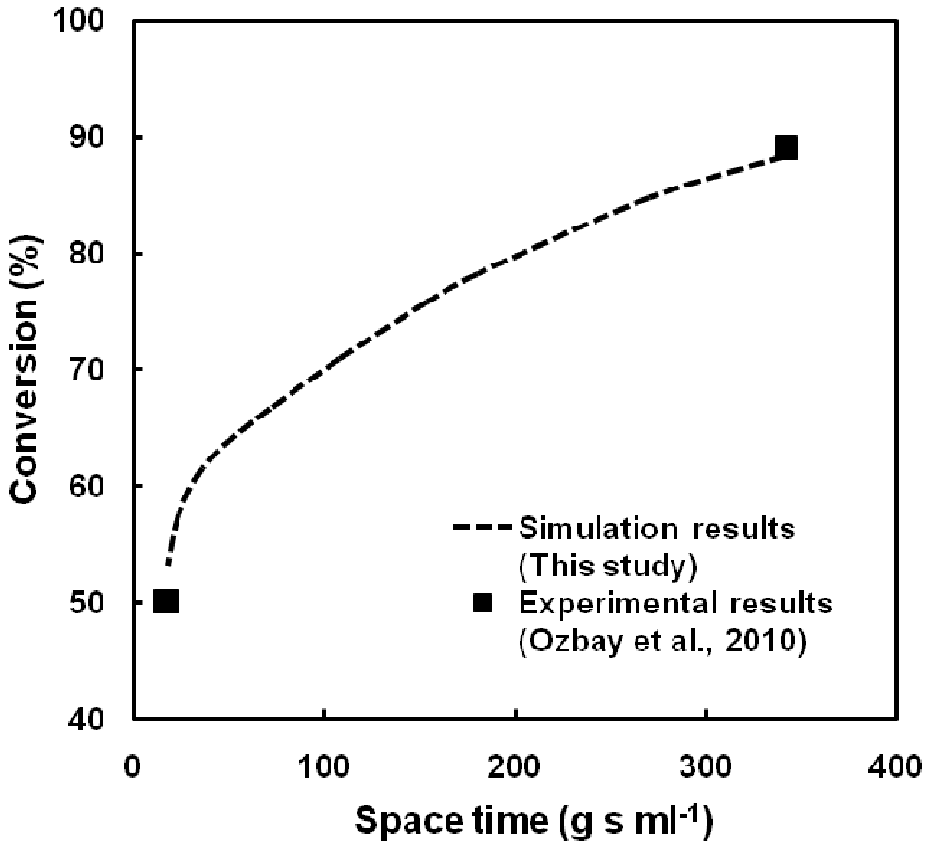

Fig. 5.10 Effect of space time on fixed bed reactor performance.

5.3 Reactive distillation study

Simulations of the etherification of glycerol and TBA in the reactive distillation (RD) were then carried out using RADFRAC model in the Aspen Plus. The obtained LH-A reaction rate from the previous section was employed for investigating the design variables and operating variables. The design variables considered here consist of the number of tray in rectifying (N_{Rec}), reaction (N_{Rxn}) and stripping (N_{Strip}) section. Note that the chemical properties were estimated by Gani's group contribution and the glycerol to TBA feed ratio ($F_{glycerol}/F_{TBA}$) was set at 0.25. The feed stage of heavy reactant, glycerol, was placed on the top of reaction zone and light reactant, TBA, was placed on the lowest of reaction zone.

The desired products i.e. DTBG and TTBG were obtained in the liquid residue. The conversion of glycerol and selectivity of desired products were defined as follows.

$$\text{Conversion of glycerol} = \frac{\text{difference in molar flowrate of inlet and outlet of glycerol}}{\text{feed molar flowrate of glycerol}} \times 100 \quad (36)$$

$$\text{Selectivity of desired products} = \frac{\text{molar flowrate of DTBG and TTBG in residue}}{\text{difference in molar flowrate of inlet and outlet of glycerol}} \times 100 \quad (37)$$

5.3.1 Effect of design variables

The effect of the number of reaction stages (with constant of total catalyst loading) and stripping stages on the reactive distillation performance was shown in Fig. 5.11. Both conversion and selectivity decreased with increasing the number of stripping stage from 0 to 6 stages. This can be explained that the increase of the number of stripping stages causes the slight temperature decreasing in reaction zone and thus decreases the glycerol conversion and the desired products, DTBG and TTBG, which are the consecutive products of further etherification of MTBG.

The effects of number of rectifying stages are shown in Fig. 5.12. It is noted that the number of stripping stage is set at zero according to the above results. It was found that both conversion and selectivity slightly increased with increasing the number of rectifying stages and become constant with the rectifying stages of 6 stages. This is due to the fact that more water was removed by increasing the number of rectifying stages and therefore high etherification reaction could be enhanced. However, more TBA was also removed to the distillate, hence, the effect of increasing rectifying stages on the reaction performance could not be more pronounced. Figs. 5.11 and 5.12 also show the effect of number of reaction stages. Increasing the number of reaction stages increased the conversion of glycerol and products selectivity since more reaction stages pronounce the etherification by increasing the residence time. From the simulation as shown in Figs 5.11 and 5.12, the optimum design for

the reactive distillation is 6 rectifying and 6 reactions without stripping stage. An experiment was carried out at the suitable configuration obtained from the simulation with a set of operating conditions as shown in Table 5.4. The concentration profiles of the residue were compared with the simulated as shown in Fig. 5.13. The dashed lines represent the simulated results, while the symbols are the data from the experiment. The simulated results were in good agreement with the experimental results and took around 12 hours to achieve the steady state condition. The liquid mole fraction of each component at each stage inside the reactive distillation and the temperature profile were shown in Fig. 5.14. Clearly, the vapor liquid equilibrium stages ensure that water is produced and excess TBA exists in the top of the column. Furthermore, the products i.e. MTBG, DTBG and TTBG are in the bottom stream.

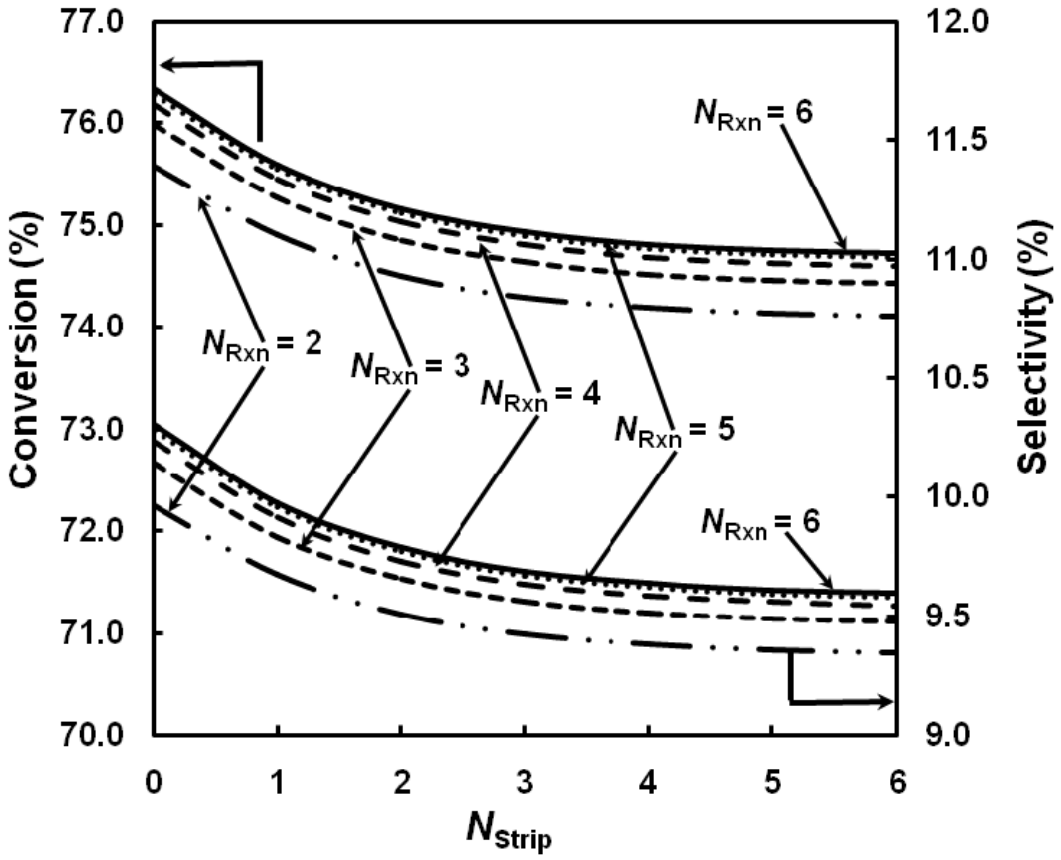

Fig. 5.11 Effect of the number of stripping stages on the conversion and selectivity for various reaction stages (rectifying =6 stage, reflux ratio = 2, heat duty = 80kW).

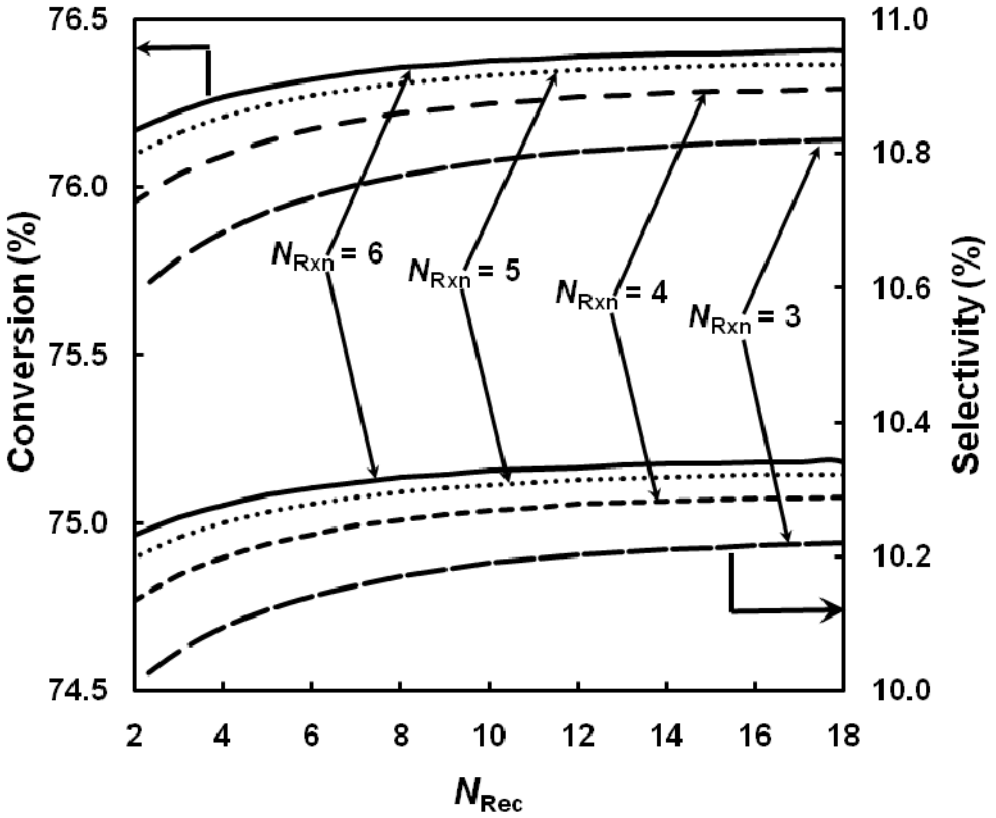

Fig. 5.12 Effect of the number of rectifying stages on the conversion and selectivity for various reaction stages (stripping =1 stage, reflux ratio = 2, heat duty = 80kW).

Table 5.4 Standard operating conditions of reactive distillation

Condition of feed		**Column specification**	
Temperature (K)	298	Rectifying stage	6
Feed flow rate (ml/min)		Reaction stage	6
glycerol	2	Stripping stage	0
tert-butyl alcohol	8	Total catalyst weight (kg)	0.020
Pressure (bar)	1	Heat duty (watt)	80
Feed stage		Reflux ratio (-)	2
glycerol	8		
tert-butyl alcohol	13		

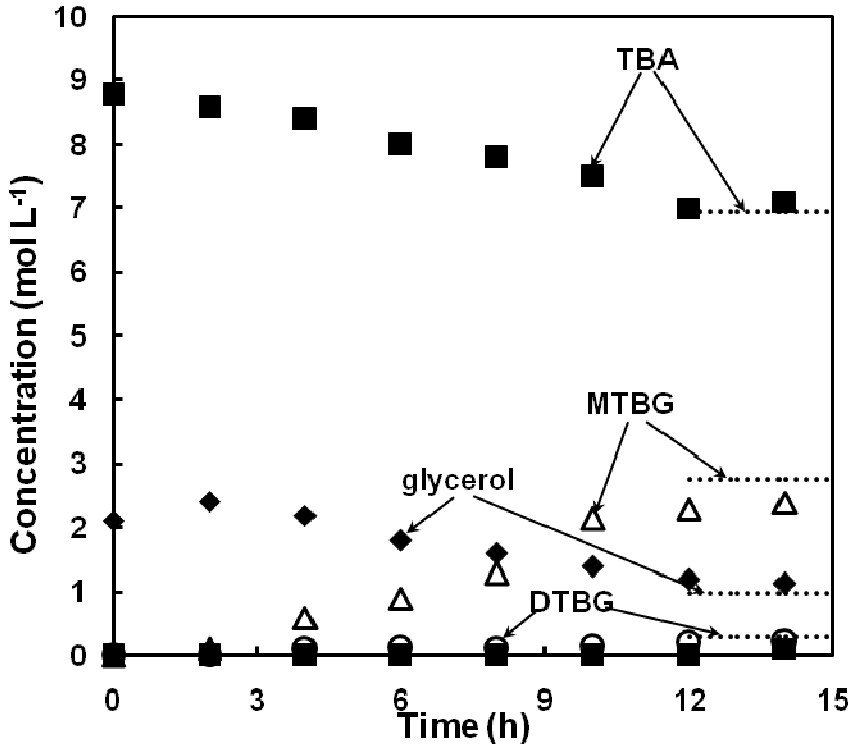

Fig. 5.13 Concentration profiles of bottom product with suitable RD configuration: experiment (symbols) and simulation (dashed line).

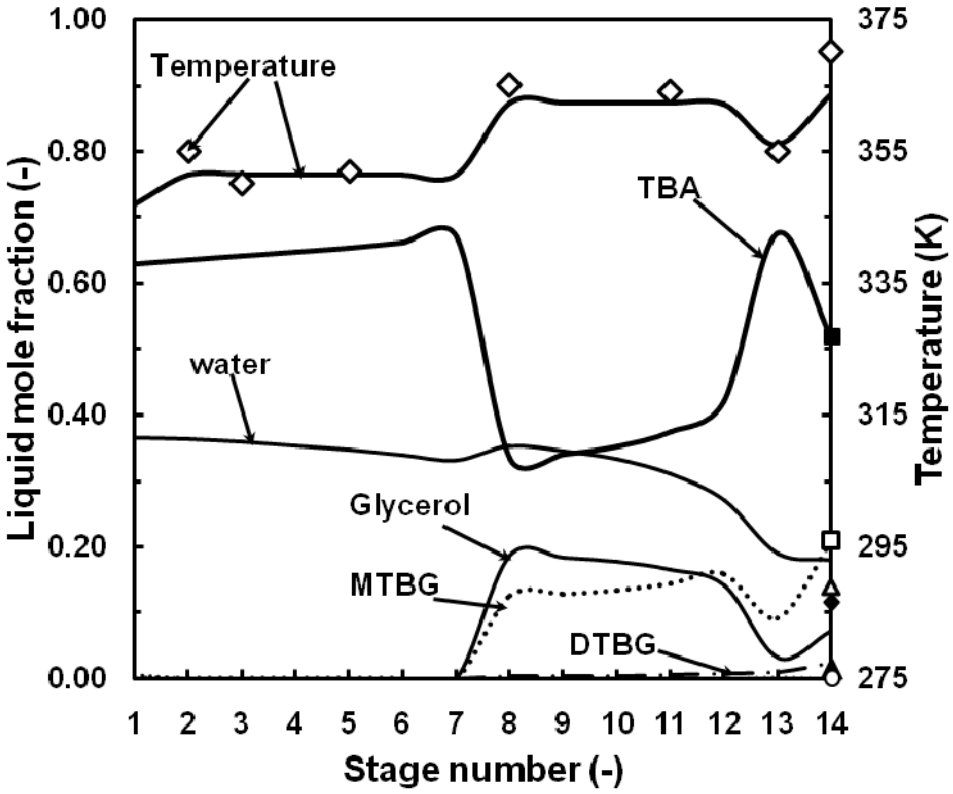

Fig. 5.14 Mole fraction and temperature profiles along the column at standard operating condition.

5.3.2 Effect of reboiler heat duty and reflux ratio

By varying the heat duty and reflux ratio, similar tendencies of conversion and selectivity were obtained as shown in Figs. 5.15(a) and (b). It can be seen that the conversion and selectivity increased initially with increasing reflux ratio before dropping down. This is due to the trade-off in concentration of TBA and water which are major components in distillate. The increase of the reflux ratio increased the concentration of TBA in the reaction section where it can react with glycerol to produce more ethers. However, the increase of reflux ratio increased the concentration of water in the reaction section and lowered the catalytic performance. The effect of heat duty of reboiler on the conversion and selectivity were also presented in Figs. 5.15 (a) and (b). The increase of heat duty increased the conversion and selectivity however this effect becomes smaller at higher heat duty. As the heat duty increased, more glycerol can travel up in to the reactive section and then reacted with TBA. The optimum reflux ratio showed higher value with higher heat duty of reboiler.

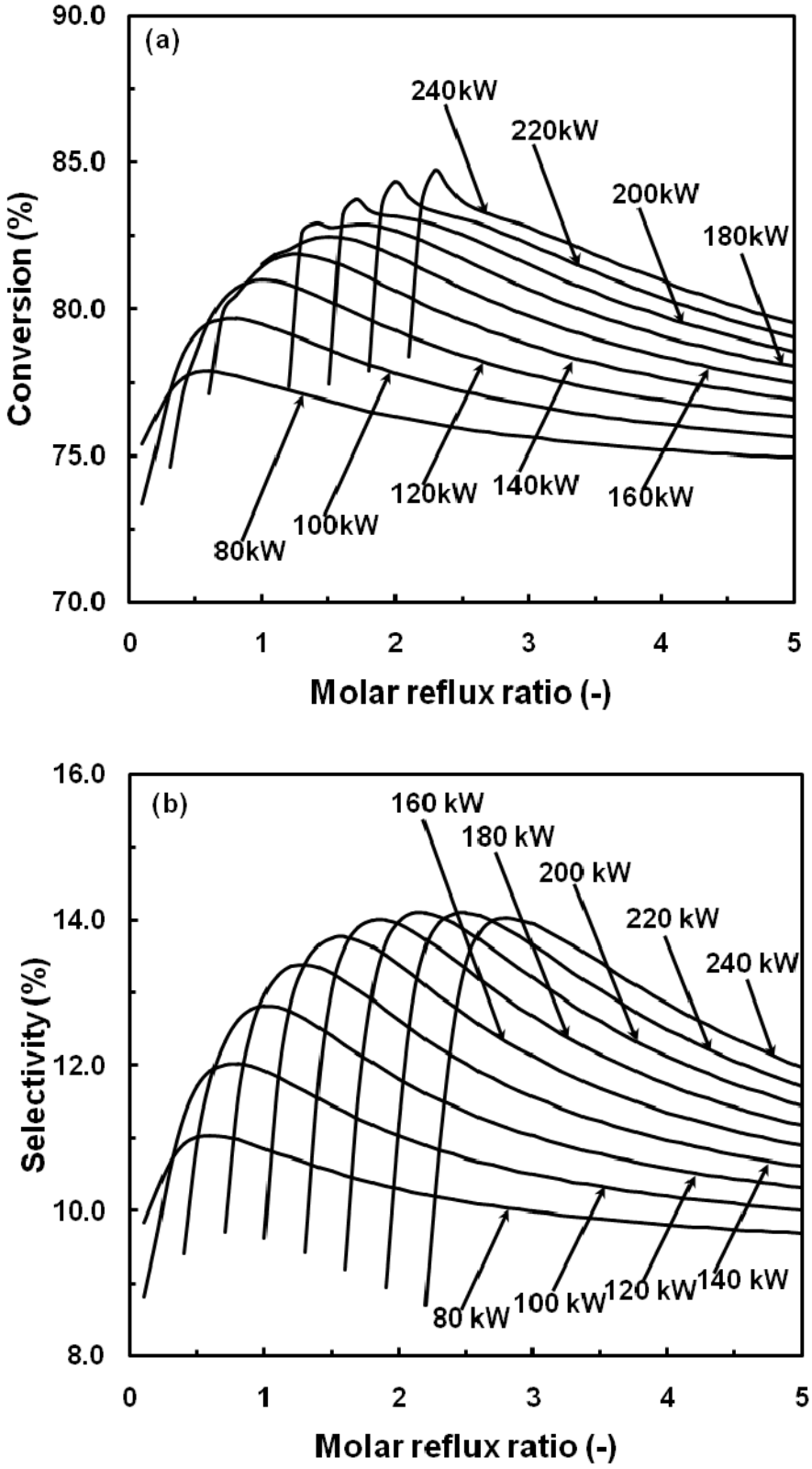

Fig. 5.15 Effect of reflux ratio on (a) glycerol conversion and (b) selectivity at various heat duty of reboiler (6 rectifying stages, 6 reaction stages and without stripping stage).

Part II: Self-etherification of FCC gasoline and glycerol

5.4 Catalyst and operating condition screening

(a) (b)

Fig. 5.16 Mixture of glycerol and FCC gasoline (a) before reaction and (b) after 10 h reaction time in case of incomplete conversion of glycerol.

It should be noted that because of phase separation, no samples were taken during the experiment, since it could not be guaranteed that the sample would well represent the reaction mixture and its phases (Karinen et al., 2006). Figure 5.16 (a) represents two phases separation between glycerol and FCC gasoline before the reaction since glycerol and FCC gasoline are insoluble in each other. Fig. 5.16 (b) shows the mixture after 10 h reaction time in case of incomplete conversion of glycerol. As the reaction proceeds the products accumulate in one or other of the phases according to their solubility. Upper phase has non-polar phase such as hydrocarbons, di-ethers and tri-ether. Lower phase has polar phase such as glycerol and mono-ethers. However, that all components were present in some degree in both phases. The concentration of products and reactants was changing during the reaction. At some stage of the reaction, the two phases dissolve in each other and only one phase remained (Karinen and Krause, 2006). However, in our study the gasoline etherified products are tested for several gasoline properties (e.g. RON, bRvp). The existing of glycerol in gasoline might be harmful

for the testing instrument, therefore the reaction condition which can convert glycerol completely is required.

From our study, it was found that the reactivity of catalysts could be ordered as Amberlyst 16 > Amberlyst 15 >> β-zeolite; importantly, only Amberlyst 16 gave a complete conversion of glycerol after 10 h of reaction. It should be noted that the amounts of glycerol remaining in the cases of Amberlyst 15 and β-zeolite catalysts were difficult to determine since it was immiscible like colloid and attached to a container; in addition, the glycerol left in the gasoline could damage the gasoline testing instruments. Therefore, the glycerol conversions were not calculated and Amberlyst 16 was selected as a suitable catalyst for the reaction.

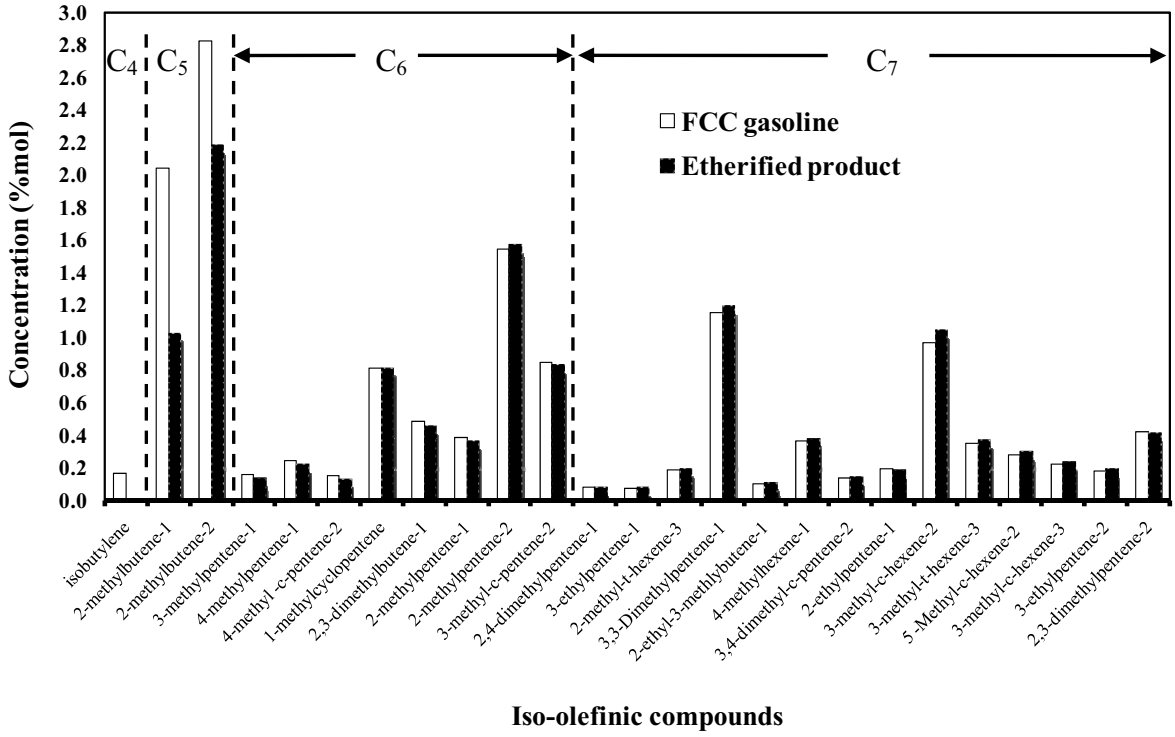

Fig. 5.17 Iso-olefinic compounds of FCC gasoline and FCC etherified product.

Fig. 5.17 compares the amount of iso-olefinic compounds in original FCC gasoline and etherified FCC gasoline. It can be seen that small iso-olefins; i.e. C_4-C_6 iso-olefins are

decreased after etherification reaction; however, larger atomic number of iso-olefins, e.g. C_7 iso-olefins are almost constant or slightly increased. Olefins conversions are lower with larger atomic number of olefins since large molecules of olefins hardly enter into pores of catalyst (Hu et al., 2006). The tendency of these results is in good agreement with that of the etherified FCC gasoline with methanol and ethanol as reported by Pescarollo et al. (1993) and Kiatkittipong et al. (2009), respectively. It should be noted that the isomerization and dimerization between olefinic compounds also occur together with the main etherification, therefore, the calculation to identify the degree of etherification of glycerol based on the changes in olefins become difficult. The slight increase of some large olefins could be due to the presence of the dimerization reaction. In addition, relatively small pore of β-zeolite might be suitable for FCC etherification with methanol (Hu et al., 2006) or ethanol (Kiatkittipong et al, 2008; 2009). However, for larger, more branched and more OH group etherification agent like glycerol, it might require large pore of catalyst for the reactants to enter the pores and in turn for desorption of larger molecules of etherification products. This might be a reason why Amberlyst 15 and 16 gave significantly higher catalytic activity than β-zeolite as observed in this study. Our results also support the results of Klepacova et al. (2005) who studied the etherificaion of IB with glycerol and reported that the large pore of strong acid macroreticular ion-exchange resins gave higher glycerol conversion and selectivity of DTBG and TTBG than that of zeolites and gel type polymer catalysts (with small pore size). In the case of β-zeolite, only MTBG and DTBG were formed while TTBG was not presence. The formation of TTBG might be hindered due to its large molecular size. TTBG could be formed over large-pore H-Y zeolite however with lower selectivity than that over ion exchange resins (Klepacova et al., 2005). However, the difference in the activity between Amberlyst 15 and Amberlyst 16 in this study may need further investigation for the full discussion.

The influences of catalyst amount and operating temperature were also investigated by varying the amount of Amberlyst 16 from 0.5, 5 and 10 g with operating temperature in range of 50-70°C. It was found that the glycerol conversion increased with increasing operating temperature from 50° C to 70°C. Furthermore, glycerol could be completely converted only with 10 g of Amberlyst 16 at temperature of 70°C.

5.5 Characterization of etherification products and FCC gasoline

Research octane number (RON) and blending Reid vapor pressure (bRvp) of etherification products are shown in Table 5.5. It can be seen that the RON of FCC gasoline etherified with glycerol of 90.1 is higher than that of original FCC gasoline (RON=88). Until now, only a few works have reported the octane number of ethers of glycerol, in which the octane number for blending of mixture of mono-, di- and tri-tert-butyl ethers of glycerol was reported to be 112–128 RON and 91– 99 motor octane number (MON) (Wessendorf, 1995). The higher RON of FCC etherified product than that of original FCC gasoline implied that RON of ethers product is higher than that of olefinic compounds. Furthermore, since olefinic compounds were consumed during the reaction, the bRvp of etherified FCC decrease from 6.5 psia to 4.5 psia. The reduction of bRvp is beneficial especially for near tropical countries or in the summer period. It should be noted that the increase of RON in case of etherified with glycerol are different from that with ethanol. In our previous study [36], FCC gasoline was etherified with 20 vol% ethanol catalyzed by Amberlyst 16 and the RON of 93.0 could be obtained. Since the unreacted ethanol can be left in the gasoline therefore the RON of the etherified product also influenced by ethanol remaining which have high octane ($RON_{ethanol}$ = 118). However, in the case of glycerol, this component could not be left in the gasoline, thus the RON improvement might be only from the etherification with glycerol. Negligible increase of etherified product density from original FCC gasoline was observed as shown in Table 5.5.

Table 5.5 Comparison of gasoline properties

	Original FCC gasoline	**Etherified FCC gasoline with glycerol**
RON	88.0	90.1
bRvp (psia)	6.5	4.5
Density (g/cm^3)	0.7186	0.7403

Fig. 5.18 shows the comparison of distillation curves of original FCC gasoline, etherified FCC gasoline with glycerol (observed from this study) and etherified FCC gasoline with ethanol (Kiatkittipong et al., 2008). Etherified FCC gasoline with glycerol shows higher distillation temperature in all volume percents evaporated than that of original FCC gasoline. The shape of distillation curve of etherified FCC gasoline with glycerol is much more similar to that of original FCC gasoline than that etherified with ethanol. This is due to the complete conversion of glycerol to ethers which have similar properties to gasoline than that of alcohol. The increasing of distillation temperature could support the decreasing of the bRvp of etherified products as shown in Table 5.5 It should be noted that the actual resin content was not determined in this study. The content of potential and actual resins increased with increasing the final boiling point (FBP) of fuels (Kiatkittipong et al., 2008), however, the difference between FBP of original FCC gasoline and etherified products are small (as shown in Fig. 5.18) and therefore the increase of actual resin could be negligible.

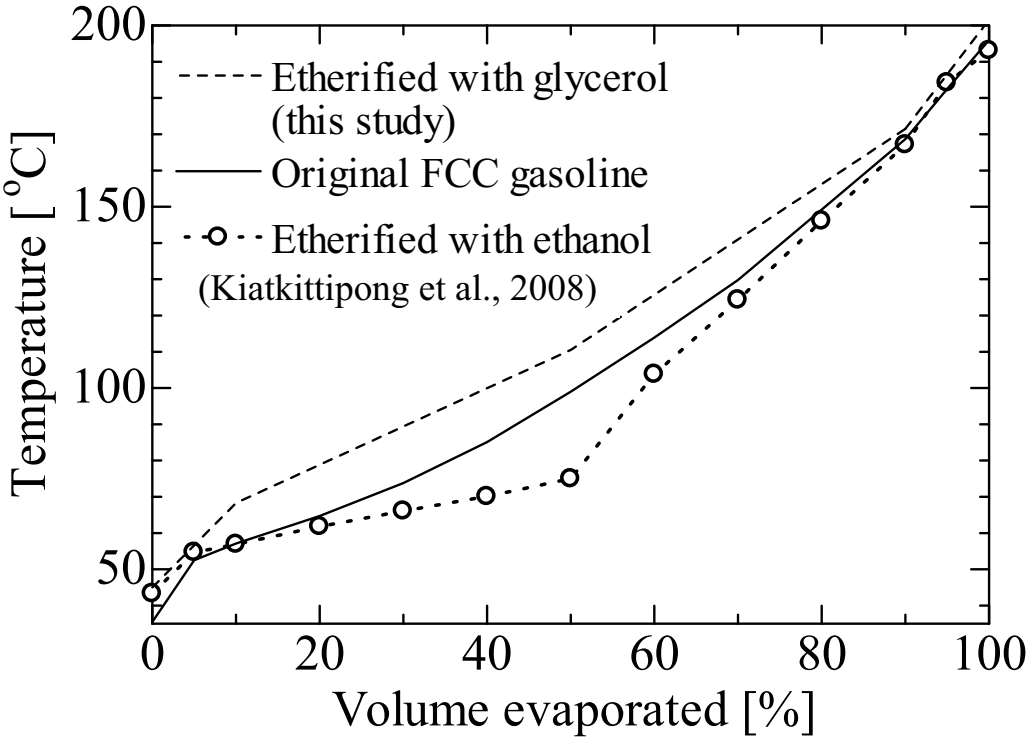

Fig. 5.18 Distillation curve from ASTM D-86 tests.

CHAPTER VI

CONCLUSION

The conclusion of the study can be summarized into two main section i.e. 1) glycerol ethers synthesis from glycerol etherification with tert-butyl alcohol (TBA) in reactive distillation, and 2) self-etherification of fluidized catalytic cracking (FCC) gasoline and glycerol.

6.1 Glycerol ethers synthesis from glycerol etherification with tert-butyl alcohol in reactive distillation.

This section studies the glycerol etherification with tert-butyl alcohol catalyzed by Amberlyst 15 in reactive distillation. From the equilibrium study, it was demonstrated that among three group contribution methods (i.e. Joback, Benson and Gani group contribution method), Gani's group contribution method estimated the nearest Gibbs free energy comparing to available database. The estimated equilibrium conversion and product distribution at reaction temperature in a range of 338-358 K showed good agreement with that obtained by experimental results from this study and as reported in the literature. Three temperature levels of 338, 348, and 358 K were used in the study to obtain the parameters in the Arrhenius' equation of the reaction rate constant and the Van't Hoff equation of water sorption equilibrium. The Langmuir-Hinshelwood activity based model which takes into account the effect of water adsorption is the best kinetic model to fit the experimental results. The obtained kinetic parameters were also well verified with the independent experiments in fixed bed reactor from the literature. Lastly, both simulation and experimental studies in reactive distillation indicated that the suitable configuration consists of 6 rectifying stages and 6 reaction stages without stripping stage.

6.2 Self-etherification of fluidized catalytic cracking (FCC) gasoline and glycerol

The etherification of FCC gasoline with glycerol in the presence of acid catalysts was found to be a promising process for gasoline quality improvement as well as utilizing of glycerol as fuel extender. The catalytic activity could be ordered as Amberlyst 16 > Amberlyst 15 >> β-zeolite. The etherified FCC gasoline with glycerol showed higher research octane number (RON) and lower blending Reid vapor pressure (bRvp) which are preference properties. The distillation temperature of etherified FCC gasoline increased in all volume percents evaporated with similar shape to original FCC gasoline. The suitable operating condition of the reaction was at a FCC gasoline to glycerol volume ratio of 84:16 with operating temperature of 70°C, 10 g of Amberlyst 16 catalyst and 10 h of reaction time.

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Output ที่ได้จากโครงการ

ตีพิมพ์ในวารสารวิชาการระดับนานาชาติที่มีค่า Impact factor

1) **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 (impact factor 2008 = 2.066, 5-year impact factor = 2.684)
2) **Worapon Kiatkittipong***, Parinya Intaracharoen, Navadol Laosiripojana, Choowong Chaisuk, Piyasan Praserthdam and Suttichai Assabumrungrat “Glycerol ethers synthesis from glycerol etherification with *tert*-butyl alcohol in reactive distillation” อยู่ระหว่างการพิจารณาเพื่อตีพิมพ์ในวารสาร Computer & Chemical Engineering (impact factor 2008 = 1.755, 5-year impact factor = 2.431)

การนำเสนอผลงานในการประชุมวิชาการระดับนานาชาติ

1) P. Intaracharoen, P. Ratanakarn, W. Kiatkittipong*, C. Chaisuk, N. Laosiripojana and S. Assabumrungrat “Production of Ether from glycerol: Kinetic Study” International Conference on Chemical & Biomolecular Engineering, National University of Singapore, Singapore, 28-29 Jan, 2010 (oral presentation)
2) S. Suwanmanee, W. Kiatkittipong* and S. Assabumrungrat “Utilization of Glycerol as a Fuel Extender by Etherified with FCC Gasoline” The 2nd Thammasat University International Conference on Chemical, Environmental and Energy Engineering, Swissotel Le Concorde Bangkok Hotel, Bangkok, 3-4 Mar 2009 (oral presentation)
3) Parinya Intaracharoen, Worapon Kiatkittipong*, Piyasan Praserthdam and Suttichai Assabumrungrat “Ether from glycerol: Development of equilibrium thermodynamic model” A Regional Conference on Chemical & Biomolecular Engineering, National University of Singapore, Singapore, 19-20 Dec, 2008 (oral presentation)
4) Parinya Intaracharoen, Worapon Kiatkittipong*, Piyasan Praserthdam and Suttichai Assabumrungrat “Equilibrium thermodynamic analysis of ethers production from glycerol” 15th Regional Symposium on Chemical Engineering (RSCE) in conjunction with 22th Symposium of Malaysian Chemical Engineers (SOMChE) Kuala Lumpur, Malaysia, 2-3 Dec, 2008 (oral presentation)

5) Patomchai Ratanakarn, Worapon Kiatkittipong*, Piyasan Praserthdam and Suttichai Assabumrungrat “Ethyl tert-butyl ether production fed by bio-ethanol in hybrid reactive distillation” 15th Regional Symposium on Chemical Engineering (RSCE) in conjunction with 22th Symposium of Malaysian Chemical Engineers (SOMChE) Kuala Lumpur, Malaysia, 2-3 Dec, 2008 (poster presentation)

การนำเสนอผลงานในการประชุมวิชาการระดับชาติ

1) ปริญญา อินทรเจริญ, วรพล เกียรติกิตติพงษ์*, นวดล เหล่าศิริพจน์, ปิยะสาร ประเสริฐธรรม, สุทธิชัย อัสสะบำรุงรัตน์ “การผลิตสารเพิ่มค่าซีเทนจากกลีเซอรอล : การศึกษาจลนพลศาสตร์ด้วยตัวเร่งปฏิกิริยา Amberlyst 15” การประชุมวิชาการวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย ครั้งที่ 19, เฟลิกซ์ ริเวอร์ แคว รีสอร์ท กาญจนบุรี, 26-27 ตุลาคม 2552 (นำเสนอแบบปากเปล่า)
2) ปริญญา อินทรเจริญ, วรพล เกียรติกิตติพงษ์*, นวดล เหล่าศิริพจน์, ปิยะสาร ประเสริฐธรรม, สุทธิชัย อัสสะบำรุงรัตน์ “การผลิตสารเพิ่มค่าซีเทนจากกลีเซอรอล : การประยุกต์ใช้หอกลั่นแบบมีปฏิกิริยา” การประชุมวิชาการวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย ครั้งที่ 19, เฟลิกซ์ ริเวอร์ แคว รีสอร์ท กาญจนบุรี, 26-27 ตุลาคม 2552 ซึ่งผลงานนี้ได้รางวัลการนำเสนอดีเยี่ยมแบบโปสเตอร์

ภาคผนวก

Appendices

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Cleaner gasoline production by using glycerol as fuel extender

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ABSTRACT

Glycerol, a major by-product of biodiesel production, was employed as a fuel extender in this study. The process was originally investigated by etherifying the entire fluidized catalytic cracking (FCC) gasoline with glycerol. The reactions were carried out in a pressurized liquid phase reactor in the presence of three different catalysts (i.e. Amberlyst 16, Amberlyst 15, and β-zeolite) at 70 °C and 2.6 MPa with a volume ratio of FCC gasoline to glycerol ratio of 84:16 for 10 h. The catalytic activity could be ordered as Amberlyst 16>Amberlyst 15>>β-zeolite. The properties of FCC and etherified FCC products were determined by the standard analysis of Research Octane Number (RON), blending Reid vapor pressure (bRvp), distillation temperature following the standard methods of ASTM D-2699, ASTM D-5191 and ASTM D-86, respectively. It was found that the olefin content decreased opposing with increasing of octane number due to ethers of glycerol formation and the etherified gasoline product has lower bRvp than that of original FCC gasoline. The process of FCC gasoline etherification with glycerol showed great environmental benefits; in addition, ethers produced renewably from glycerol could extend the gasoline volume.

1. Introduction

Nowadays, global warming and energy crisis are recognized as the most global severe problems and the transportation is a significant part of this concern. Biodiesel is an alternative fuel that is chemically produced from the reaction of vegetable oil or animal fat with alcohol (i.e. methanol or ethanol). The great advantage of biodiesel is its "carbon neutral" in term of CO_2 releasing since the CO_2 emitted from the combustion of biodiesel is considered to be recyclable by planting. However, for every 9 kg of biodiesel produced, about 1 kg of crude glycerol is formed as by-product [1,2]. As the biodiesel production is increasing exponentially, the crude glycerol produced from the transesterification has also been generated in a large quantity carrying thus become oversupply [3–5].

Etherification of glycerol is one of the promising processes for oxygenate fuel production [6–8]. Regarding this reaction, isobutylene (IB) reacts with glycerol in the presence of acid catalyst to form a mixture of mono-, di- and tri-tert-butyl ethers of glycerol (called MTBG, DTBG and TTBG, respectively) [9–11]. The use of these ethers can reduce the emissions, mainly particulate matters, carbon oxide, and carbonyl compounds in exhaust gases [6]. Importantly, glycerol ether oxygenates can decrease the cloud point of diesel fuel when combined with biodiesel [12]. Karinen et al. [9] etherified glycerol with IB in liquid phase catalyzed by an acidic ion exchange resin catalyst, Amberlyst 35 and reported that five ethers products; i.e. two of MTBG, two of DTBG and one of TTBG were obtained. Among them, DTBG and TTBG are desired products due to their good blending properties with diesel fuel. Optimal conditions for good selectivity toward ethers were reported to be at IB/glycerol molar ratio of 3 and with the operating temperature of 80 °C. Klepacova et al. [11] studied the reaction between glycerol and IB in the liquid phase catalyzed by Amberlyst 15 and Amberlyst 35, p-toluenesulfonic acid and by two zeolites, H-Y and H-β. They reported that the highest glycerol conversion of 88.7% was achieved over zeolite H-Y after 8 h while Amberlyst 35 gave highest selectivity (DTBG + TTBG). Melero et al. [13] investigated the etherification of glycerol with IB over different sulfonic acid modified mesostructured silicas; i.e. propylsulfonic- and arenesulfonic-acid-functionalized mesostructured silica (Pr- and Ar-SBA-15) and indicated that Ar-SBA-15 provides excellent catalytic behavior in the etherification of glycerol with IB to yield tert-butylated derivates; the product selectivities were ordered as DTBG>TTBG>MTBG. Instead of IB, tert-butyl alcohol (TBA) was recently utilized as an alternative reagent for the production of ethers from glycerol [10,14,15]. We previously reported the employment of TBA instead of IB for the production of common oxygenate ethers such as ethyl tert-butyl ether (ETBE) [16–18] and tert-amyl ethyl ether (TAEE) [19]. Furthermore, Klepacova et al. [10] studied etherification of glycerol with IB or TBA over Amberlyst type, zeolites H-Y and H-β. They reported that zeolites H-Y and H-β provided lower selectivity than ion-exchange resins; in addition, water formation in the case of using TBA as a reagent has an inhibition effect on glycerol tert-

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butylation. The highest yield (approximately 87–88%) for Amberlyst 15 and Amberlyst 35 were obtained at 60 °C when IB was used as etherification agent. Although ethers of glycerol are mainly studied as diesel fuel additives, Karinen and Krause [9] reported that they also offered high octane numbers. Octane numbers for the mixture of ethers from IB and glycerol were reported to be 112–128 of BRON and 91–99 of BMON [20], therefore it offers as an alternative for conventional octane enhancer such as methyl tert-butyl ether (MTBE) [21,22], ETBE [22–26], tert-amyl methyl ether (TAME) [27–29] and TAEE [30–32]. However, as shown above, until now, the research works are limited with only two etherification agents; i.e. IB and TBA for the etherification with glycerol.

FCC gasoline containing several C_4–C_8 reactive olefins which are promising sources for etherification. On the contrary, these olefins content should be eliminated or minimized before using as a gasoline in the environment viewpoint. The etherification of entire FCC gasoline has been successfully experimented with methanol [33–35] and ethanol [36,37]. Rihko and Krause [34] employed Amberlyst 16 for etherification of light FCC gasoline with methanol and reported that TAME is the main ether observed in the products. Hu et al. [35] presented that H-β zeolite showed higher conversion and catalytic stability than other catalysts including H-MOR, H-ZSM5 and cation exchange resin D005 for FCC etherification with methanol. Kiatkittipong et al. [36] studied etherification of FCC gasoline with ethanol over β-zeolite and Amberlyst 16 and reported that β-zeolite is the suitable catalyst for this reaction since it offered products with higher RON and ethanol conversion as well as lower blending Reid vapor pressure (bRvp). We previously indicated that the cold start problem is not occurred even in low bRvp, according to the satisfied drivability index [37].

In the present work, the possibility of using broad range of ethers production by self-etherification of FCC gasoline and glycerol for gasoline quality improvement was firstly illustrated. The process was investigated by etherifying the entire FCC gasoline with glycerol catalyzed by three commercial catalysts; i.e. Amberlyst 16, Amberlyst 15 and β-zeolite. The suitable operating conditions (catalyst type, catalyst amount, and reaction temperature) were primarily screened. From the reaction, the properties of etherified gasoline product; i.e., RON, bRvp, distillation temperature and composition of FCC gasoline etherified were analyzed and compared to the original FCC gasoline.

2. Experimental

2.1. Chemicals

FCC gasoline was obtained from the catalytic cracking unit of local oil refinery; its compositions are given in Table 1. Glycerol AR grade (99.5 vol.%) from QRëC was employed in the study.

Table 1
Composition of FCC gasoline in volume percent.

Carbon number	n-Paraffins	i-Paraffins	Olefins	Naphthenes	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

2.2. Catalysts

Two groups of catalyst; i.e. β-zeolite (Tosoh) and macroreticular cation-exchange resins including Amberlyst 15 and Amberlyst 16 (Chemica Fluka) were used in this study. Before use, the catalysts were dried overnight in an oven at 110 °C. The physical properties of these three catalysts are presented in Table 2.

2.3. Apparatus

Etherification of FCC gasoline with glycerol was carried out in a cylindrical shape autoclave reactor as shown in Fig. 1. The volume of reactor was approximately 100 cm^3 with reactor height of 8 cm and inside diameter of 4 cm. A valve for liquid sampling and a port for the thermocouple were installed at the top of the reactor. The mixture was stirred by using a turbine at the maximum speed of 1163 rpm in all experiments. At this speed, the effect of external mass transfer resistance was found to be negligible [36]. During the reaction, the reactor was maintained at constant temperature by circulating hot water in jackets.

2.4. Analysis

The liquid reaction products were analyzed in PIANO (paraffins, isoparaffins, aromatics, naphthenes and olefins) by FID gas chromatography using a Supelco capillary column. The condition of gas chromatography was followed from our previous study [37]. The standard analysis of Research Octane Number (RON), blending Reid vapor pressure (bRvp) and distillation temperature were carried out by following the standard methods of ASTM D-2699, ASTM D-5191 and ASTM D-86, 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.

2.5. Operation procedure

The reaction system containing 84 cm^3 of FCC gasoline, 16 cm^3 of glycerol and 10 g of catalyst was carried out at 70 °C for 10 h under a N_2 pressure of 2.6 MPa. Prior to the reaction, the mixture was separated into two liquid phases since glycerol and FCC gasoline are insoluble in each other. Hence, no sampling was taken during 10 h of reaction as it could not be assured that the sample would well stand for the mixture and its phase [9]. After reaction, the reactor was cooled down to the room temperature before collecting the sample from the reactor in order to prevent the evaporation loss. It is noted that the gasoline sample was centrifuged to separate catalyst from the solution before further analysis.

3. Results and discussion

According to the composition of original FCC gasoline as shown in Table 1, it contains about 25 vol.% of olefins mainly in C_5 –C_7 hydrocarbons range.

Table 2
Physical properties of catalysts.

	Surface area (m^2/g)	Particle size (μm)	Pore diameter (nm)	Pore volume (cm^2/g)
Amberlyst 16	45	700	20	1.82
Amberlyst 15	53	600–850	30	0.40
β-zeolite	625	45	0.58	0.129

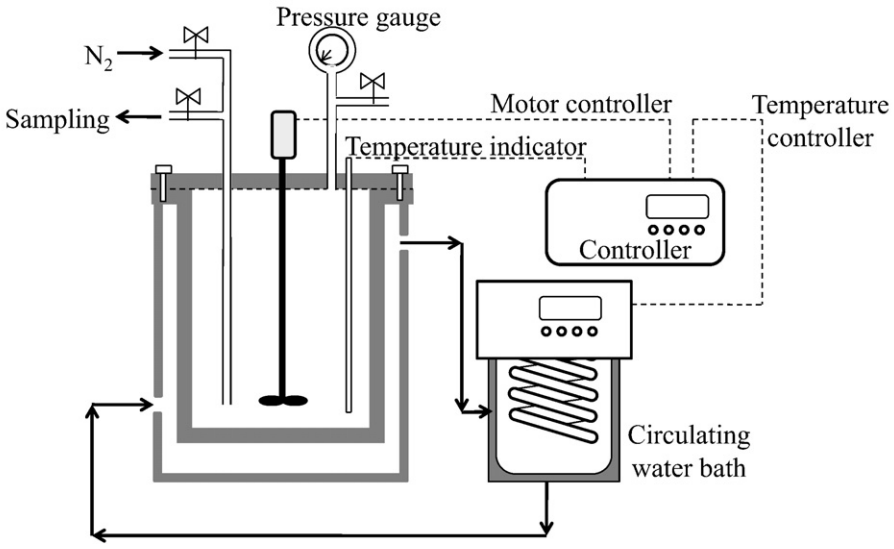

Fig. 1. Schematic diagram of the experimental apparatus.

3.1. Catalyst and operating condition screening

From our study, it was found that the reactivity of catalysts could be ordered as Amberlyst 16>Amberlyst 15>>β-zeolite; importantly, only Amberlyst 16 gave a complete conversion of glycerol after 10 h of reaction. It should be noted that the amounts of glycerol remaining in the cases of Amberlyst 15 and β-zeolite catalysts were difficult to determine since it was immiscible like colloid and attached to a container; in addition, the glycerol left in the gasoline could damage the gasoline testing instruments. Therefore, the glycerol conversions were not calculated and Amberlyst 16 was selected as a suitable catalyst for the reaction.

Fig. 2 compares the amount of iso-olefinic compounds in original FCC gasoline and etherified FCC gasoline. It can be seen that small iso-olefins; i.e. C_4–C_6 iso-olefins are decreased after etherification reaction; however, larger atomic number of iso-olefins, e.g. C_7 iso-olefins are almost constant or slightly increased. Olefins conversions are lower with larger atomic number of olefins since large molecules of olefins hardly enter into pores of catalyst [35]. The tendency of these results is in good agreement with that of the etherified FCC gasoline with methanol and ethanol as reported by Pescarollo et al. [33] and Kiatkittipong et al. [37], respectively. It should be noted that the isomerization and dimerization between olefinic compounds also occur together with the main etherification, therefore, the calculation to identify the degree of etherification of glycerol based on the changes in olefins become difficult. The slight increase of some large olefins could be due to the presence of the dimerization reaction. In addition, relatively small pore of β-zeolite might be suitable for FCC etherification with methanol [35] or ethanol [36,37]. However, for larger, more branched and more OH group etherification agent like glycerol, it might require large pore of catalyst for the reactants to enter the pores and in turn for desorption of larger molecules of

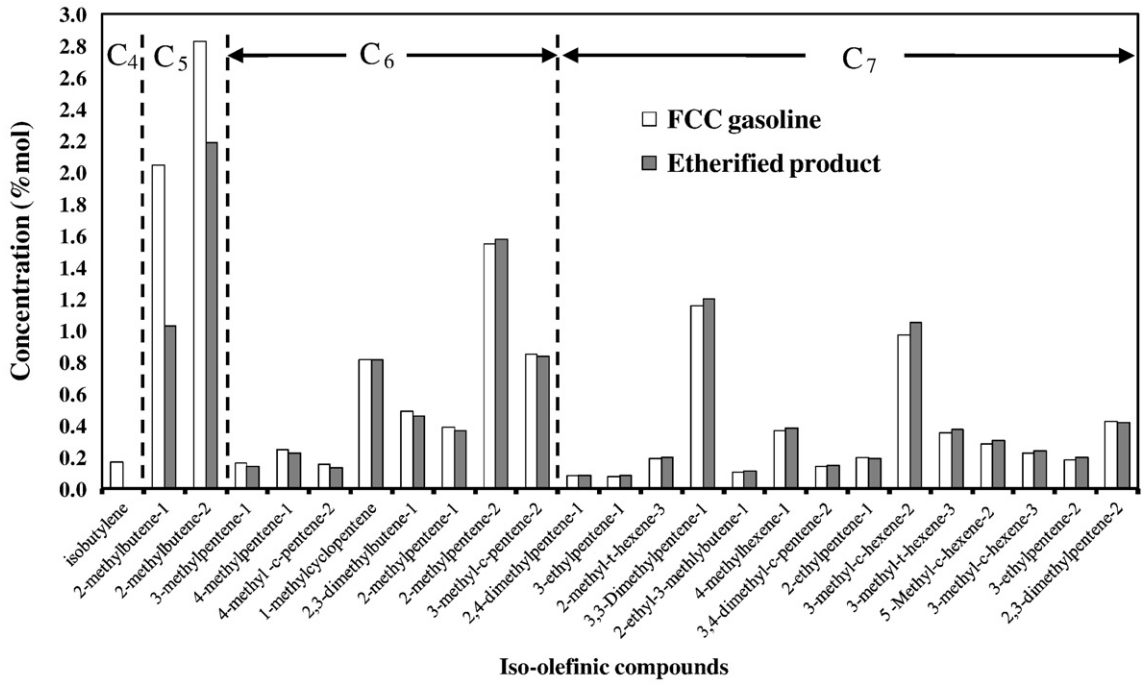

Fig. 2. Iso-olefinic compounds of FCC gasoline and FCC etherified product.

etherification products. This might be a reason why Amberlyst 15 and 16 gave significantly higher catalytic activity than β-zeolite as observed in this study. Our results also support the results of Klepacova et al. [10] who studied the etherification of IB with glycerol and reported that the large pore of strong acid macroreticular ion-exchange resins gave higher glycerol conversion and selectivity of DTBG and TTBG than that of zeolites and gel type polymer catalysts (with small pore size). In the case of β-zeolite, only MTBG and DTBG were formed while TTBG was not presence. The formation of TTBG might be hindered due to its large molecular size. TTBG could be formed over large-pore H-Y zeolite however with lower selectivity than that over ion exchange resins [10]. However, the difference in the activity between Amberlyst 15 and Amberlyst 16 in this study may need further investigation for the full discussion.

The influences of catalyst amount and operating temperature were also investigated by varying the amount of Amberlyst 16 from 0.5, 5 and 10 g with operating temperature in range of 50–70 °C. It was found that the glycerol conversion increased with increasing operating temperature from 50 °C to 70 °C. Furthermore, glycerol could be completely converted only with 10 g of Amberlyst 16 at temperature of 70 °C.

3.2. Characterization of etherification products and FCC gasoline

Research octane number (RON) and blending Reid vapor pressure (bRvp) of etherification products are shown in Table 3. It can be seen that the RON of FCC gasoline etherified with glycerol of 90.1 is higher than that of original FCC gasoline (RON = 88). Until now, only a few works have reported the octane number of ethers of glycerol, in which the octane number for blending of mixture of mono-, di- and tri-tert-butyl ethers of glycerol was reported to be 112–128 RON and 91–99 motor octane number (MON) [20]. The higher RON of FCC etherified product than that of original FCC gasoline implied that RON of ethers product is higher than that of olefinic compounds. Furthermore, since olefinic compounds were consumed during the reaction, the bRvp of etherified FCC decrease from 6.5 psia to 4.5 psia. The reduction of bRvp is beneficial especially for near tropical countries or in the summer period. It should be noted that the increase of RON in case of etherified with glycerol are different from that with ethanol. In our previous study [36], FCC gasoline was etherified with 20 vol.% ethanol catalyzed by Amberlyst 16 and the RON of 93.0 could be obtained. Since the unreacted ethanol can be left in the gasoline therefore the RON of the etherified product also influenced by ethanol remaining which have high octane ($RON_{ethanol} = 118$). However, in the case of glycerol, this component could not be left in the gasoline, thus the RON improvement might be only from the etherification with glycerol. Negligible increase of etherified product density from original FCC gasoline was observed as shown in Table 3.

Fig. 3 shows the comparison of distillation curves of original FCC gasoline, etherified FCC gasoline with glycerol (observed from this study) and etherified FCC gasoline with ethanol [36]. Etherified FCC gasoline with glycerol shows higher distillation temperature in all volume percents evaporated than that of original FCC gasoline. The shape of distillation curve of etherified FCC gasoline with glycerol is much more similar to that of original FCC gasoline than that etherified with ethanol. This is due to the complete conversion of glycerol to ethers which have similar properties to gasoline than that of alcohol. The increasing of distillation temperature could support the decreasing of the bRvp of etherified products as shown in Table 3. It should be noted that the actual resin content was not determined in this study. The content of potential and actual resins increased with increasing the final boiling point (FBP) of fuels [38], however, the difference between FBP of original FCC gasoline and etherified products are small (as shown in Fig. 3) and therefore the increase of actual resin could be negligible.

Table 3
Comparison of gasoline properties.

	Original FCC gasoline	Etherified FCC gasoline with glycerol
RON	88.0	90.1
bRvp (psia)	6.5	4.5
Density (g/cm^3)	0.7186	0.7403

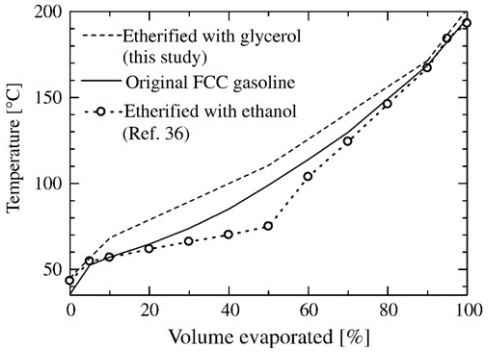

Fig. 3. Distillation curve from ASTM D-86 tests.

4. Conclusion

The etherification of FCC gasoline with glycerol in the presence of acid catalysts was found to be a promising process for gasoline quality improvement as well as utilizing of glycerol as fuel extender. The catalytic activity could be ordered as Amberlyst 16>Amberlyst 15>>β-zeolite. The etherified FCC gasoline with glycerol showed higher research octane number (RON) and lower blending Reid vapor pressure (bRvp) which are preference properties. The distillation temperature of etherified FCC gasoline increased in all volume percents evaporated with similar shape to original FCC gasoline. The suitable operating condition of the reaction was at a FCC gasoline to glycerol volume ratio of 84:16 with operating temperature of 70 °C, 10 g of Amberlyst 16 catalyst and 10 h of reaction time.

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Glycerol ethers synthesis from glycerol etherification with *tert*-butyl alcohol in reactive distillation

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Abstract

The paper presents the study of glycerol etherification with *tert*-butyl alcohol catalyzed by Amberlyst 15 in reactive distillation. Firstly, the equilibrium thermodynamic analysis is investigated by applying three group contribution methods i.e. Joback's, Benson's and Gani's to determine the equilibrium composition by minimizing Gibbs free energy approach. Gani's group contribution method provides the best agreement with the experimental results. Secondly, the kinetic parameter determination was performed to fit with the experimental results carried out in an autoclave reactor. The Langmuir-Hinshelwood based on activity model shows the best reaction rate description. Furthermore, the obtained kinetic rate expressions are also well verified with independent experimental results in fixed bed reactors reported in literature. Finally, the production of glycerol ethers in reactive distillation (RD) is investigated. The suitable RD configuration consists of 6 rectifying stages and 6 reaction stages without stripping stage. The simulations are in good agreement with the experimental results.

Keywords: Etherification, kinetic, equilibrium conversion, group contribution, *tert*-butyl ether of glycerol, reactive distillation

1. Introduction

Biodiesel is a world-recognized renewable fuel for fossil diesel substitution. Since the demand of biodiesel increases rapidly, glycerol (the major by-product from biodiesel production) is expected to be oversupplied in the near future (Zhou *et al*., 2008). Therefore, many researches attempt to utilize glycerol in several approaches.

Etherification of glycerol is a process for cetane improving production. The product from glycerol etherification consists of mono-, di- and tri-*tert*-ether of glycerol. Di- and tri-*tert*-butyl ethers of glycerol are usable as potential cetane enhancement for diesel fuels due to their good blending properties with diesel fuel and high cetane number (David, 1940; Olah, 1996). In addition, due to the presence of oxygen in their structure, it might decrease carbon monoxide and particulate matter emission from the incomplete combustion. Karinen and Krause (2006) studied the etherification of glycerol with iso-butylene (IB) over Amberlyst 35 ion-exchange resin catalyst and reported the optimal condition for enhancing the highest selectivity with initial IB to glycerol molar ratio of 3 at the temperature of 80ºC. Klepacova *et al*. (2005; 2007) reported that large-pore zeolite H-Y catalyst showed the highest glycerol conversion (88.7%) after 8 h; however the formation of tri-*tert*-butyl ether of glycerol was sterically hindered. It is known that Amberlysts 15 and 35 are promising catalysts for the production of di- and tri-*tert*-butyl ether of glycerol. Melero *et al*. (2008) reported the achievement of glycerol conversions up to 100% with the combined selectivities towards di- and tri-*tert*-butyl ethers of glycerol over 92% after 4 h of reaction using arenesulfonic-acid-modified SBA-15 at 75ºC and IB to glycerol molar ratio of 4. Klepacova *et al*. (2006) studied the etherification of glycerol with *tert*-butyl alcohol (TBA) over ion-exchange resin catalyst (Amberlyst 15, 31, 35, 119) and reported the optimal condition at 75ºC in the presence of Amberlyst 15; furthermore, the excess of TBA has a positive effect on the yield of ethers. It is noted that the use of TBA instead of IB is recently of interest since the latter is typically

derived from non-renewable crude oil and become limited (Rihko and Krause, 1996) while TBA is a by-product from propylene oxide production (Quitain *et al*., 1999). In addition, TBA was also previously employed instead of IB for the production of conventional oxygenated ethers i.e. ETBE (Assabumrungrat *et al*., 2002; Kiatkittipong *et al*., 2002; Assabumrungrat *et al*., 2004), TAEE (Boonthamtirawuti *et al*., 2009).

Recently, the application of reactive distillation for etherification of glycerol, either in the presence or absence of fatty acids with C4-C5 alcohols e.g. iso-butyl alcohol, TBA and iso-amyl alcohol have been patented (Morgan 2008). Water produced from the etherification (and esterification in the presence of fatty acid) is removed from the reaction section as a distillate, thereby achieves higher conversion. Products i.e. mono-, di and tri-triol ethers (along with fatty acid esters) are obtained as bottom products. Ozbay et al. (2010) investigated the etherification of glycerol and TBA in fixed bed reactor catalyzed by Amberlyst-15, -16 and -35, Nafion-SAC-13 and γ-alumina. Among these catalysts, Amberlyst 15 showed the highest activity while Amberlyst 16 showed the highest selectivity of di-ethers. Nevertheless, until now, no research has been investigated the thermodynamic and kinetic of etherification of glycerol and TBA. Typically, the thermodynamic properties can be estimated by the first-order group contribution method such as Joback and Reid (Joback and Reid 1987), Klincewicz and Reid (1984), the second-order group contribution by Benson (1958; 1976), and Gani (Constantinou and Gani, 1994; Abildskov *et al.*, 1996) and the third-order (Marrero and Gani, 2001). The purpose of each higher order terms is to provide more structural information unavailable in the lower order terms.

The aim of this research is to analyze the reaction equilibrium and determine the kinetic parameters of ethers production from TBA and glycerol in liquid-phase. The equilibrium simulation was based on the minimization of Gibbs free energy. The obtained

kinetic parameters from this study are used to investigate the ethers production from glycerol and TBA in reactive distillation (RD).

2. Theoretical analysis

2.1 Gibbs free energy minimization

The chemical equilibriums at constant temperature and pressure were calculated based on the minimization of Gibbs free energy. The total Gibbs free energy of the system is defined as

$$G^{tot} = \sum_{i=1}^{k} n_i \mu_i \quad (1)$$

The chemical potential of species *i* (μ_i) for non-ideal solution can be presented by

$$\mu_i = \overline{\mu}_i^0 + RT\ln(x_i) + RT\ln(\gamma_i) = \overline{\mu}_i^0 + RT\ln(a_i) \quad (2)$$

The activity coefficient of species *i* (γ_i) can be calculated using the UNIFAC method. Substituting Eq. (2) into Eq. (1) offers:

$$G^{tot} = \sum_{i=1}^{k} n_i \overline{\mu}_i^0 + \sum_{i=1}^{k} n_i RT ln(a_i)$$

$$= \sum_{i=1}^{k} n_i \overline{\mu}_i^0 + \sum_{i=1}^{k} n_i RT ln(\frac{\gamma_i n_i}{n^{tot}}) \quad (3)$$

For minimizing the objective function (G^{tot}), the approaches method for minimization Gibbs free energy problem is Lagrange multipliers (Nichita *et al*. 2002; Jarungthammachote and Dutta 2008).

2.2 Reaction pathway

The reactions taking place in the direct etherification of glycerol and TBA can be summarized as follows

$$\text{Glycerol + TBA} \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} \text{MTBG + } H_2O \quad (4)$$

$$\text{MTBG + TBA} \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} \text{DTBG + } H_2O \quad (5)$$

$$k_3$$

$$\text{DTBG} + \text{TBA} \underset{k_{-3}}{\overset{}{\longleftrightarrow}} \text{TTBG} + H_2O \quad (6)$$

For the indirect reaction, TBA is firstly dehydrated to IB and water.

$$\text{TBA} \underset{k_{-4}}{\overset{k_4}{\longleftrightarrow}} \text{IB} + H_2O \quad (7)$$

IB from dehydration reaction is further reacted with glycerol as follows

$$\text{Glycerol} + \text{IB} \underset{k_{-5}}{\overset{k_5}{\longleftrightarrow}} \text{MTBG} \quad (8)$$

$$\text{MTBG} + \text{IB} \underset{k_{-6}}{\overset{k_6}{\longleftrightarrow}} \text{DTBG} \quad (9)$$

$$\text{DTBG} + \text{IB} \underset{k_{-7}}{\overset{k_7}{\longleftrightarrow}} \text{TTBG} \quad (10)$$

The equilibrium constants are defined as

$$K_j = \frac{k_j}{k_{-j}} \quad (11)$$

To determine the equilibrium parameters (K_1, K_2 and K_3), several of group contribution methods i.e. Benson, Joback and Gani were used to estimate the missing properties of ethers products. Equilibrium constants in term of activity (abbreviated as K_{ja}) are defined as

$$K_{ja} = \frac{\prod_{i=product} a_i}{\prod_{i=reactant} a_i} \quad (12)$$

The equilibrium constant based on mole fraction can be calculated by the relation in Eqs. 13-15.

$$a_i = \gamma_i x_i \quad (13)$$

$$K_{ja} = \frac{\prod_{i=\text{product}} a_i}{\prod_{i=\text{reactant}} a_i} = \frac{\prod_{i=\text{product}} \gamma_i x_i}{\prod_{i=\text{reactant}} \gamma_i x_i}$$

$$K_{ja} = \left[\frac{\prod_{i=\text{product}} \gamma_i}{\prod_{i=\text{reactant}} \gamma_i}\right]\left[\frac{\prod_{i=\text{product}} x_i}{\prod_{i=\text{reactant}} x_i}\right] = K_{jx}\left[\frac{\prod_{i=\text{product}} \gamma_i}{\prod_{i=\text{reactant}} \gamma_i}\right] \quad (14)$$

then $K_{jx} = {K_{ja}} \Big/ \left[\frac{\prod_{i=\text{product}} \gamma_i}{\prod_{i=\text{reactant}} \gamma_i}\right]$ (15)

3. Experimental

Glycerol (99.5 %) and TBA (99.5 %) were purchased from Ajax chemical. Amberlyst 15, the strong acid ion exchange resin and having macro reticular pore, was used as the catalyst. Prior the reaction, the catalyst was dried overnight in the oven at 383 K. For thermodynamic and kinetic studies; the experiments were carried out in an autoclave reactor as shown in Fig. 1(a). The jacket reactor was maintained at the constant temperature by using the electric heater with the temperature controller. From the reaction, the samples were analyzed by the gas chromatograph (GC 14B, Shimadzu Corp.) with a capillary column of HP-INNOWAX (30 m x 0.32 mm x 0.5 μm). The temperature of injector and detector are 573 and 423 K, respectively. It is noted that the temperature programmed was applied by setting the initial column temperature at 313 K with the ramping rate of 10 K min^{-1} to the final column temperature of 513 K and holding for 5 min. For the reactive distillation study (Fig. 1(b)); the reactive distillation set-up consists of a four-neck round bottom flask with a mantle heater served as the reboiler, the vacuum-insulated column and the condenser. The column is divided into three sections of rectifying, reaction and stripping. Catalysts packed in the stainless steel mesh were placed inside the column to allow the simultaneous reaction along with the product separation. The stainless steel mesh saddles were used as the packing materials in the stripping section of the column and the six thermocouples were connected along the column height to measure the temperature profiles inside the column. A coolant was circulated in the condenser located at the top. The reflux ratio was controlled by a solenoid valve with a multi-timer.

4. Results and discussion

4.1 Equilibrium thermodynamic analysis

Three types of group contribution methods i.e. Joback's method (Joback and Reid 1987), Gani's method (Constantinou and Gani 1994; Marrero and Gani 2001) and Benson's method (Benson and Buss 1985; Benson 1976) were applied to calculate the Gibbs free energy of formation. The values of Gibbs free energy of formation are illustrated in Table 1. Since the values of Gibbs free energy of the ether products are not available, the values of other available oxygenated ethers were referred for comparison. It was found that Gani's method showed the lowest percent deviation compared with the other methods. Equilibrium reaction of glycerol with TBA was studied by minimizing the Gibbs free energy. The effect of temperature on the etherification of glycerol with TBA in term of glycerol conversion was illustrated in Fig. 2. The simulation results were compared with the experimental results in this study as well as the results reported by Klepáčová *et al.* (2005, 2006). TBA was fed in excess at a constant molar ratio of TBA to glycerol of 4:1. Only Gani's group contribution method showed good agreement with the experimental results in term of glycerol equilibrium conversion and equilibrium composition as shown in Figs. 2 and 3, respectively. It can be seen that the glycerol conversion at equilibrium decreases with increasing reaction temperature since the overall reaction is exothermic. The equilibrium constants based on both activity and concentration of glycerol etherification obtained from the Arrhenius' plots are summarized in Table 2.

4.2 Kinetic study

Regarding the study of the external mass transfer effect over the catalyst (Amberlyst 15), the conversion increased with increasing the speed of stirrer and leveled off at the speed

level of 600 rpm (the results are not shown here), indicating the negligible of external mass transfer at this stirrer speed. Therefore, the speed of 600 rpm was used throughout the experiments.

4.2.1 Development of mathematical models

The reverse reaction in Eq. (7) and the forward reactions in Eqs. (8) to (10) were neglected since the operating pressure in this study was at 5 bar (and only small amount of IB can be dissolved in the liquid solution at this condition). It was also confirmed by our experimental results that the concentration of IB in liquid mixture was relatively small. The experimental results were fitted with two kinetic models; Langmuir-Hinshelwood (LH) and Power Law (PL) based on both activities (a_i) and mole fraction (x_i). The rate expressions of consecutive reaction pathway of Eqs. (4) to (6) and TBA dehydration (Eq. 7) could be written in term of activity as

$$r_{1a} = k_{1a}\left[\frac{a_G a_{TBA} - a_{MTBG} a_{water}/K_{1a}}{(1+K_{wa}a_{water})^z}\right] \quad (16)$$

$$r_{2a} = k_{2a}\left[\frac{a_{MTBG} a_{TBA} - a_{DTBG} a_{water}/K_{2a}}{(1+K_{wa}a_{water})^z}\right] \quad (17)$$

$$r_{3a} = k_{3a}\left[\frac{a_{DTBG} a_{TBA} - a_{TTBG} a_{water}/K_{3a}}{(1+K_{wa}a_{water})^z}\right] \quad (18)$$

$$r_{4a} = k_{4a}\left[\frac{a_{TBA}}{(1+K_{wa}a_{water})^z}\right] \quad (19)$$

where Z=0 for Power Law (PL) model and Z=1 for Langmuir-Hinshelwood (LH) model. The kinetic parameters of TBA dehydration over Amberlyst 15 reported by (Yang *et al*. 2000) were employed in this study as shown below.

$$k_{4a} = \exp(15.451 - 10325/T) \quad (20)$$

$$k_{4c} = \exp(15.39 - 10270/T) \quad (21)$$

$$K_{wa}=\exp(-36.456+7646/T) \quad (22)$$

$$K_{wc}=\exp(-35.62+7530/T) \quad (23)$$

Note that the ion-exchange capacity for Amberlyst 15 is 4.4 [mol-H (kg dry resin)$^{-1}$].

By performing material balances for a batch reactor, the following expressions are obtained.

$$-\frac{dm_{\mathrm{TBA}}}{dt}=\frac{dm_{\mathrm{H_2O}}}{dt}=W(r_1+r_2+r_3+r_4) \quad (24)$$

$$-\frac{dm_{\mathrm{Glycerol}}}{dt}=\frac{dm_{\mathrm{MTBG}}}{dt}+\frac{dm_{\mathrm{DTBG}}}{dt}+\frac{dm_{\mathrm{TTBG}}}{dt}=W(r_1+r_2+r_3) \quad (25)$$

$$\frac{dm_{\mathrm{MTBG}}}{dt}=W(r_1) \quad (26)$$

$$\frac{dm_{\mathrm{DTBG}}}{dt}=W(r_2) \quad (27)$$

$$\frac{dm_{\mathrm{TTBG}}}{dt}=W(r_3) \quad (28)$$

The best-fitted kinetic parameters were purposed by minimizing the relative root mean square deviation (RMSD) values as expressed by

$$RMSD_i=\frac{1}{M}\sqrt{\sum_{t=1}^{M}\left(\frac{\left(x_{i,t}-x_{i,\exp,t}\right)}{\left(x_{i,\exp,t}\right)}\right)^2} \quad (29)$$

4.2.2 Kinetic parameter determination

The experiments were carried out at three temperature levels to investigate the kinetic parameters. The mathematical models and equilibrium constants from the previous section were used to determine the kinetic parameters. Comparing among the different models i.e. Langmuir-Hinshelwood based on activity (LH-A) and Power law model based both activity and mole fraction based (PL-A and PL-X), LH-A appeared to be the best model to fit the experimental results providing the lowest of RMSD as shown in Fig. 4. Figs. 5-7 show the mole changes with time at T = 338, 348 and 358 K, respectively which are in good fitting

with LH-A model. Although PL model was slightly inferior to LH for fitting with the etherification of glycerol and TBA, the rate expression in PL model is still needed in some software applications (Vadapalli & Seader, 2001; Dhale *et al*., 2004; Bhatia *et al*., 2007; Carlos *et al*., 2010).

The temperature-dependent rate constants were determined by plotting the relationships according to the Arrhenius's as shown in Figs. 8 and 9. The sorption equilibrium constant of water as a function of temperature can be determined by Van't Hoff plot as shown in Fig. 9. The sorption equilibrium of water decreased with the increase of temperature as regularly observed in the most adsorption processes. The heat of adsorption of water calculated by Eq. (30) is 73 kJ mol^{-1} which is slightly higher than the previous reports of 63 and 55 kJ mol^{-1} (Yang *et al*., 1995; Abella *et al*., 1999).

$$K_{wa} = \exp\left[\frac{-\Delta G}{RT}\right] = \exp\left[-\frac{\Delta S}{R} + \frac{\Delta H}{RT}\right] \qquad (30)$$

The expressions of the rate constants and the activation energy are summarized in Table 3.

4.2.3 Validation of purposed kinetic parameters

Recently, Ozbay *et al*., (2010) performed the experimental study of etherification of glycerol and TBA in a fixed bed reactor. The experimental results with varying operating temperature and space time using Amberlyst 15 as the catalyst were employed to compare with our simulation results. The mathematical models for fixed bed reactor could be derived from material balance and summarized as follows.

Fixed bed reactor model

$$-\frac{dF_{\mathrm{TBA}}}{dW} = \frac{dF_{\mathrm{H_2O}}}{dW} = r_1 + r_2 + r_3 + r_4 \qquad (31)$$

$$-\frac{dF_{\mathrm{glycerol}}}{dW} = \frac{dF_{\mathrm{MTBG}}}{dW} + \frac{dF_{\mathrm{DTBG}}}{dW} + \frac{dF_{\mathrm{TTBG}}}{dW} = r_1 + r_2 + r_3 \qquad (32)$$