สำนักงานคณะกรรมการการอุดมศึกษา

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รายงานวิจัยฉบับสมบูรณ์

โครงการ Production of synthesis fuel from products of fermentation process and process for fuel oil quality improvement
(การผลิตน้ำมันเชื้อเพลิงสังเคราะห์จากผลิตภัณฑ์ที่ได้จากกระบวนการหมักผลิตผลทางการเกษตรและกระบวนการปรับปรุงคุณภาพน้ำมันเชื้อเพลิง)

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กรกฎาคม 2551

สัญญาเลขที่ MRG4980053

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สนับสนุนโดยสำนักงานคณะกรรมการการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย

การผลิตน้ำมันเชื้อเพลิงสังเคราะห์จากผลิตภัณฑ์ที่ได้จากกระบวนการหมักผลิตผลทางการเกษตรและกระบวนการปรับปรุงคุณภาพน้ำมันเชื้อเพลิง

งานวิจัยนี้เกี่ยวข้องกับวิธีการเพิ่มปริมาณเอทานอลในน้ำมันแก๊สโซลีนสำหรับเครื่องยนต์ทั่วไปที่ไม่ต้องทำการปรับแต่ง ควบคู่กับการปรับปรุงคุณภาพของน้ำมันเชื้อเพลิงไปพร้อมกัน การทำปฏิกิริยาอีเทอริฟิเคชันโดยตรงของน้ำมันที่ได้จากกระบวนการฟลูอิไดซ์คาตาไลติกแคร้กกิ้ง (FCC) ด้วยเอทานอล ที่อุณหภูมิ 343 เคลวิน ในเครื่องปฏิกรณ์แบบอัดความดัน ภายใต้ความดัน 0.8 เมกะปลาสคาล โดยใช้ตัวเร่งปฏิกิริยาที่ใช้อยู่ในเชิงพาณิชย์สองชนิดได้แก่ เบต้า-ซีโอไลท์และแอมเบอร์ลิส 16 เป็น โดยทั่วไปสารโอเลฟินส์ที่ว่องไวในน้ำมันที่ได้จากกระบวนการฟลูอิไดซ์คาตาไลติกแคร้กกิ้งมีจำนวนคาร์บอนอยู่ในช่วง 5-7 อะตอมเป็นส่วนใหญ่ กระบวนการอีเทอริฟิเคชันโดยตรงของน้ำมันที่ได้จากกระบวนการฟลูอิไดซ์คาตาไลติกแคร้กกิ้งด้วยเอทานอลมีจุดเด่นคือ น้ำมันแก๊สโซลีนมีปริมาณเพิ่มขึ้นอย่างมีประสิทธิผลด้วยการเติมอีเทอร์ที่ผลิตจากเอทานอลซึ่งเป็นพลังงานที่สร้างขึ้นใหม่ได้ อีกทั้งน้ำมันที่ผ่านการทำปฏิกิริยาอีเทอริฟิเคชันแล้ว จะมีออกเทนสูงขึ้น ขณะที่ค่าความดันไอของสารผสมและปริมาณโอเลฟินส์ลดลง โดยค่าความดันไอของ FCC แก๊สโซลีนที่ผ่านการทำปฏิกิริยาอีเทอริฟิเคชันแล้วมีค่าน้อยกว่าแก๊สโซฮอล์ ซึ่งชี้ให้เห็นว่าน้ำมันที่ผ่านกระบวนการดังกล่าวมีความเหมาะสมสำหรับการใช้ในประเทศเขตร้อนหรือในช่วงฤดูร้อนมากกว่าแก๊สโซฮอล์ อย่างไรก็ตามน้ำมันดังกล่าวมีค่าออกเทนต่ำกว่าแก๊สโซฮอล์เล็กน้อยเมื่อใช้ตัวเร่งปฏิกิริยาแอมเบอร์ลิส 16 โดยเมื่อพิจารณาถึงชนิดของตัวเร่งปฏิกิริยา พบว่าเบต้า-ซีโอไลท์เหมาะสมกับปฏิกิริยานี้มากกว่าแอมเบอร์ลิส 16 โดยเบต้า-ซีโอไลท์ ไม่เพียงแต่ให้การเร่งปฏิกิริยาการเกิดของอีเทอร์ที่สูงกว่าเท่านั้น ยังทำให้เกิดปฏิกิริยาการเกิดไอโซเมอร์โดยปราศจากการเกิดเป็นสารอะโรมาติกส์ประเภทเบนซีน จึงให้ค่าออกเทนและความสามารถในการทดแทนด้วยพลังงานที่สร้างขึ้นใหม่ได้สูงขึ้น รวมถึงให้ค่าความดันไอของสารผสมที่ต่ำกว่า

Production of Synthesis Fuel from Products of Fermentation Process and Process for Fuel Oil Quality Improvement.

This research concerns the method for increasing ethanol supplement in gasoline without modification of conventional engine with improve gasoline quality simultaneously. The direct etherification of FCC gasoline with ethanol were carried out at 343 K in a pressurized liquid phase reactor at 0.8 MPa and catalyzed by two commercial catalysts, i.e., Beta-zeolite and Amberlyst 16. Typically, the reactive olefins available in FCC gasoline are mainly in a range of C_5-C_7 compounds. The process of FCC gasoline etherification with ethanol has several benefits. Firstly, the gasoline volume is effectively increased by adding ethers produced from ethanol which is renewable. Secondly, the etherified gasoline product has higher octane number with lower bRvp and amount of olefins content. The bRvp of etherified FCC gasoline was found to be lower than that of gasohol, indicating that the gasoline from this process is more suitable than gasohol especially for the tropical zone or in summer. However, the octane number of etherified FCC gasoline catalyzed by Amberlyst 16 is slightly lower than that of gasohol. Beta-zeolite was a more suitable catalyst than Amberlyst 16 for the etherification of FCC gasoline with ethanol because not only a better catalytic activity for etherification, but some isomerization also occurred without aromatization to benzene and therefore it offered products with higher RON and gasoline renewability with lower bRvp.

Executive Summary

Introduction

Ethanol, one of biofuels, is a renewable energy source for alleviate the oil crisis and global climate change. Carbon dioxide produced from ethanol combustion is not considered as a global warming contributor since it is carbon neutral. Ethanol can be blended directly into gasoline (called "gasohol"); however, many recent researches reported disadvantages of the gasohol. The overall air pollutant emissions from the use of gasohol are usually higher than those from the use of conventional gasoline because its high blending Reid vapor pressure (bRvp) leads to higher evaporative emissions. Ethanol-derived ethers can overcome the drawbacks of gasoline with direct ethanol blend. Ethers/gasoline fuel shows less volatility than gasohol. Commercially, ETBE and TAEE can be produced by etherification of ethanol with isobutene (IB) and isoamylene (IA), olefinic compounds, respectively. However, their productions are unlikely to meet demands of oxygenate ethers. Heavier reactive olefins should be considered as additional reactants for ether production.

FCC gasoline contains substantial amount of reactive olefinic compounds. On the contrary, these olefinic compounds also should be diminished in order to meet the new mandatory of gasoline composition which allowed the olefin content not to exceed 18 vol% following the Euro-4 gasoline composition. By etherifying the entire FCC gasoline, the bRvp of the gasoline could be reduced together with an increase of gasoline volume and octane number. The success of the process was reported by Pescarollo et al. (1993), who etherified FCC light gasoline with methanol and recently by Hu et al. (2005). However, no work has focused on direct etherification of FCC gasoline with ethanol which is a more environmental friendly process.

In this study, the process for fuel oil quality improvement was investigated by etherifying the entire FCC gasoline with ethanol catalyzed by commercial catalysts, i.e., Amberlyst 16 and β-zeolite. The process is expected to give a higher potential for utilization of ethanol as a fuel extender than the case with direct blending for conventional engine which is limited at some ethanol contents, i.e., 10 vol% (E10). The fuel characteristics of FCC etherified gasoline and FCC with direct ethanol blend were compared with those of gasohol (E10) which is a standard commercial fuel.

Experimental

Figure 1 shows schematic diagram of the experimental apparatus. The reaction system consisted of 20 and 80 cm^3 (or 30:70 cm^3) of FCC gasoline and ethanol, respectively and 10 g of catalyst (Amberlyst 16 or β-zeolite with Si/Al=40) was carried out at 70 ^oC for 10 h under a pressure of 0.8 MPa. The mixture was stirred by using turbine at the maximum speed of 1163 rpm for all experiments 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.

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

From the analysis, the fraction of total olefins in the FCC gasoline feed was about 25 vol%. Most olefins were in a range of C_5-C_7 hydrocarbons. Table 1 provided the properties of various gasolines, i.e., FCC gasoline, commercial gasohol with 10 vol% ethanol (E 10), FCC gasoline with direct ethanol blend and FCC gasoline etherified with pure ethanol.

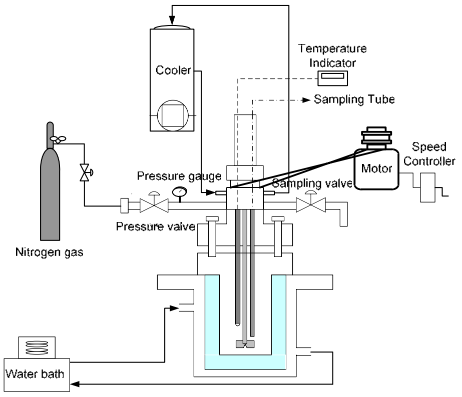

Figure 1. Schematic diagram of the experimental apparatus.

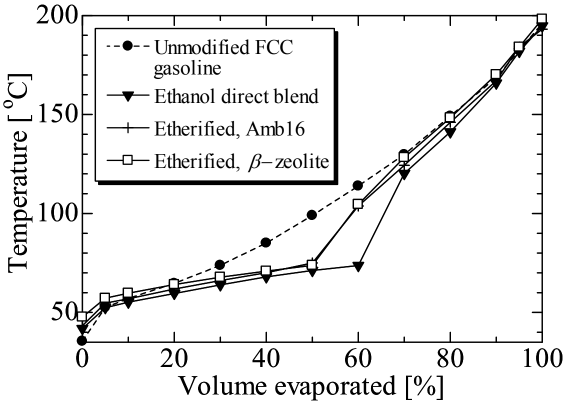

Figure 2. Distillation curves from ASTM D-86 tests.

As shown in Table 1, originally, a research octane number (RON) of original FCC gasoline was 88 which was lower than that of the specification of regular gasolines (RON = 91). FCC with direct ethanol blend in 20 and 30 vol% showed RON up to 94.8 and 97.9, respectively. However, unfortunately their bRvp also increased dramatically. It should be noted that although the bRvp value does not exceed the specification of E10, lower bRvp can be more favorable for preventing evaporative loss and vapor lock especially in hot countries. FCCs etherified with ethanol by using both Amberlyst 16 and β-zeolite catalysts can effectively decrease the values of bRvp because the reactive olefins in FCC gasoline and ethanol are converted to ethers which have lower bRvp.

Table 1. Comparison of gasoline properties.

Properties	FCC Gasoline	Gasohol E10	20 vol% Ethanol			30 vol% Ethanol		
			Direct blend	Etherified Gasoline		Direct blend	Etherified Gasoline	
				Amb 16	β-zeolite		Amb 16	β-zeolite
RON	88	95	94.8	93	94.1	97.9	96.9	98.2
bRvP(psi)	6.5	< 9	7.441	7.05	5.657	8.0	7.24	6.58
Density(g/cm^3)	0.683	0.749	0.735	0.739	0.745	0.735	0.739	0.745
Viscosity(Pa s)	$6.09x10^{-4}$	$5.05x10^{-4}$	$6.20x10^{-4}$	$5.27x10^{-4}$	$6.18x10^{-4}$	$6.03x10^{-4}$	$5.92x10^{-4}$	$5.0x10^{-4}$
DI (°F)	1168	< 1250	1143	1175	1182	N.D.	N.D.	N.D.

Comparing the RON between ethanol direct blended and etherified gasolines, the gasoline etherified by Amberlyst 16 shows slightly lower octane number than FCC with direct ethanol blend because ethanol has higher value of octane number (RON = 118) than ethers, i.e., ETBE (RON = 118), TAEE (RON = 105), *tert*-hexyl-ethyl-ether (THEE) (RON = 110). However, etherified gasoline catalyzed by β-zeolite shows similar RON to that of ethanol direct blended gasoline and slightly higher than that of etherified gasoline catalyzed by Amberlyst 16. The β-zeolite gave higher value of octane number, probably due to the possible isomerization and some aromatizations. The percentages of the olefins reduction were 33.6 and 45.7% in the cases of Amberlyst 16 and β-zeolite, respectively. The remaining olefins were lower than that of the Euro-4 standard limitation of 18 vol%. It can be concluded that β-zeolite is a more suitable catalyst for the etherification of FCC gasoline with ethanol compared to Amberlyst 16.

For other gasoline properties, the density and the viscosity of the etherified gasoline are close to those of the commercial gasohol.

The distillation curves from ASTM D-86 test shown in Figure 1 indicate that the presence of ethanol both in gasoline with direct ethanol blend and etherified gasoline with some unreacted ethanol increased initial boiling point (IBP). Compared with the unmodified FCC gasoline, the distillation temperature in all vol% evaporated and final distillation temperatures decrease in the case of gasoline with direct ethanol blend. On the contrary, in the case of FCC etherified gasoline, the distillation temperatures are lower than those of the unmodified FCC gasoline in the range of 20-80 vol% evaporated (T20-T80) and then become comparably or higher than those of the unmodified FCC gasoline. These may imply that distillation temperatures of ethanol-existing fuels are dependent on the evaporation of ethanol and its amount.

Comparing between gasoline with direct ethanol blend and etherified gasoline, because of the presence of ethers rather than olefins and ethanol, the distillation temperature is higher for the etherified gasoline. These results can also be confirmed with the decrease of the bRvp as shown in Table 1, i.e. with higher conversion of ethanol in the case of β-zeolite, the distillation temperatures are higher than those of Amberlyst 16. The distillation temperature of FCC with direct ethanol blend at 60 vol% evaporated (T60) is much lower than the others. It may be explained by the differences in boiling point values (ethanol; about 78 °C and gasoline; about 35-200 °C).

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

$$DI = (1.5 \times T10) + (3 \times T50) + T90 \qquad (1)$$

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

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

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

Therefore, the process could be satisfied to decrease gasoline volatility which affects not only a vehicle's driveability but also its VOC emissions in both evaporative and end pipe exhaust emissions and it should be noted that this method allows the use of ethanol in gasoline at higher content than does the conventional method with direct blending.

Conclusion

The simultaneous operation for FCC gasoline quality improvement and supplement by ethanol was investigated in the heterogeneous catalytic system. Although direct ethanol blend could improve RON of gasoline, bRvp of blending gasoline increased significantly. Etherified FCC gasolines with ethanol increased RON comparably or slightly lower than FCC with direct ethanol blend while bRvp was effectively lower. Therefore, FCC etherification with ethanol gave a higher potential for utilization of ethanol as a fuel extender than direct blending for conventional engine which was limited at some ethanol contents, i.e., 10 vol% (E10). Comparing between two catalysts, it was reported that β-zeolite was a more suitable catalyst for the etherification of FCC gasoline with ethanol because it offered products with higher RON and ethanol conversion with lower bRvp.

CHAPTER I

INTRODUCTION

1.1 Motivations

Nowadays, global warming and energy crisis are recognized as the most global severe problems. Worldwide energy consumption has increased 17 fold in the last century. The emissions of CO_2, SO_2 and NO_x from fossil fuel combustion are major causes of atmospheric pollution (Ture et al., 1997). By the middle of this century, world petroleum reserves are estimated to be depleted at the present rate of consumption (Sheehan et al., 1997; Demirbas, 2007). Transportation sector is a primary consumer of petroleum fuels which are mostly diesel and gasoline at the present.

Ethanol is one of the most widely used as a renewable liquid fuel for solving the global climate change and oil crisis. Since it is a renewable energy, CO_2 produced from ethanol combustion is not considered as a global warming contributor because it is a part of the carbon cycle and therefore is carbon neutral. In addition, with modern agricultural, soil organic matter will build up and therefore net removal of CO_2 from the atmosphere (Agarwal, 2007). Ethanol may be the most potential utilization of existing infrastructure, i.e., road, gas station and vehicles. Ethanol can be blended directly into gasoline which is called as “gasohol”. Flexible-fuel cars can be run on up to 85 vol% (E85) or pure ethanol. However, most of present car can be run on gasoline restricted blended with some ethanol content, i.e. 10-20 vol%. Therefore the chance of using ethanol as a fuel extender is limited. Furthermore, many recently researches reported the disadvantages of the gasohol. With presently standard of engine and the use of catalytic converter make the emissions at the end pipe are relatively small while evaporative emissions have become significant. Evaporative emissions are considered as a loss of fuel which can be occurred from diurnal, running loss, hot soak and refueling (French and Malone, 2005). Therefore, some researchers found that the overall air pollutant emissions from using gasohol were usually higher than those from using conventional gasoline because of its high blending Reid vapor pressure (bRvp) (Niven, 2005). The evaporative emission of ethanol blend might be serious especially for the tropical zone or in summer.

Ethanol-derived ethers can overcome the drawbacks of gasoline with direct ethanol blend. Ethers/gasoline fuel shows less volatility than gasohol. Therefore, ethers derived from ethanol still have drawn a number of research activities. The most well-known ethanol derivatives ethers, ethyl tert-butyl ether (ETBE) and tert-amyl ethyl ether (TAEE) are commercially produced by etherification of ethanol with isobutene (IB) and isoamylene (IA), olefinic compounds, respectively. Refiners and auto-makers also prefer to use ethers to meet the octane number and oxygenate requirement for technical reasons. ETBE and TAEE were employed for replace methyl tertiary butyl ether (MTBE) which was introduced as gasoline additives since 1979 with two main reasons. Firstly, the use of MTBE has already been forbidden in 25 states of USA (ACE, 2006; Szklo et al., 2007) and many countries because it may contaminate underground water. Japan has ceased to use MTBE though official specifications continue to allow a 7% volume limit (Japanese regulation values of automobile fuels). Secondly, MTBE is derived from the reaction of methanol with isobutene (IB). Although methanol can be also produced from biomass, the production is cost-intensive and therefore it currently made from natural gas which is more cost competitiveness (Demirbas, 2007). Therefore, methanol and methanol derivatives such as MTBE are not favorable in an environmental view point because their contribution on a global warning potential.

Alternative routes for ETBE and TAEE syntheses were also currently explored. In the previous studies, ETBE and TAEE were produced by reaction between ethanol and *tert*-Butyl alcohol (TBA) which is a major by-product of propylene oxide production or TAA is a major component of fusel oil, a byproduct obtained from biomass fermentation, respectively (Assabumrungrat et al., 2002, 2003, 2004; Kiatkittipong et al., 2003; Sahapatsombud et al., 2007; Boonthamtirawuti et al., 2008). However, unfortunately, the productions of ETBE and TAEE via these olefinic compounds, i.e. IA, IB or alcohols, i.e. TBA, TAA are unlikely to meet demands of oxygenate ethers. Heavier reactive olefins should be considered as additional reactants for ether production.

FCC gasoline is a potential valuable feedstock of reactive olefins for production of oxygenates ethers. On the contrary, these olefinic compounds also should be diminished in order to meet the new mandatory of gasoline composition which allowed the olefin content not to exceed 18 vol% following the Euro III gasoline composition. Pescarollo et al. (1993) studied etherifying the entire FCC gasoline with methanol. Simultaneous improvements in octane number and gasoline volume with reducing olefinicity, atmospheric reactivity and bRvp of gasoline were obtained.

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

1.2 Objectives

1. Enhance the potential for utilization of ethanol as a fuel extender than the case with direct blending for conventional engine with quality improvement simultaneously.
2. Screen the suitable catalyst for the etherification of FCC gasoline with ethanol.

CHAPTER II

THEORY

This chapter contributes some background information necessary for of the fuel oil quality improvement by the etherification of FCC gasoline with ethanol. The detail of gasoline properties (octane number, bRvp and distillation temperature), oxygenated compound and FCC gasoline were provided.

2.1 Gasoline properties

2.1.1 Octane number

Octane number represents the resistance of gasoline to premature detonation when exposed to heat and pressure in the combustion chamber of an internal-combustion engine. Premature detonation is indicated by knocking or pinging noises that occur as the engine operates. The octane number of a sample of fuel is determined by burning the gasoline in an engine under controlled conditions, e.g., spark timing, compression, engine speed, and load, until a standard level of knock occurs. At present three systems of octane rating are used in the United States. Two of these, the research octane number (RON) and motor octane numbers (MON), are determined by burning the gasoline in an engine under different, but specified, conditions. Usually the MON is lower than the RON. The third octane rating, which federal regulations require on commercial gasoline pumps, is an average of research octane and motor octane.

Octane is measured relative to a mixture of isooctane (2,2,4-trimethylpentane, an isomer of octane) and n-heptane which octane number are 100 and 0, respectively. An 87-octane gasoline, for example, has the same knock resistance as a mixture of 87 vol-% isooctane and 13 vol% n-heptane. This does not mean that the gasoline actually should contain these chemicals in these proportions. However, it has the same autoignition resistance as the describe mixture.

2.1.2 Reid vapor pressure (Rvp)

Vapor pressure is an important physical property of volatile liquids. It is the pressure that a vapor exerts on its surroundings. For volatile petroleum products, vapor pressure is used as an indirect measure of evaporation rate. The most commonly used method for crude oils was the Reid vapor pressure (Rvp), as determined by ASTM method i.e., Standard Test Method for Vapor Pressure of Petroleum Products D-323 (Reid Method) or D-5191 (Mini method) (ASTM, 1996a). These test methods determine vapor pressure at 37.8 ^{o}C (100 ^{o}F) of petroleum products and crude oils with initial boiling point above 0 ^{o}C (32 ^{o}F). Then the pressure developed by gasoline vapors is measured in units of pounds per square inch (psi) or kilopascals (kPa). The methods differ in the design of the apparatus, including the design of the test chamber.

2.1.3 Distillation temperature

The distillation temperature (or namely, distillation profile or distillation curve) can be tested following ASTM D 86 – Test Method for Distillation of Petroleum Products. Gasoline is a mixture of many different compounds, each having its own boiling point and vapor-forming characteristics. Thus gasolines show a boiling range covering a temperature spread from the initial boiling point (IBP) to the final boiling point (FBP). A sample of 100 ml is placed in a round bottom flask and heated at a specified rate. Temperatures are recorded when the first drop is collected (IBP), at recovered volumes of 5 ml, every subsequent 10 ml interval to 90 ml, 95 ml and at the end of the test (end point). Temperatures for each incremental volume percentage evaporated can be obtained by correcting for any sample loss during the test.

Distillation data are often represented and specified by the temperature at which a given percentage of the gasoline is evaporated such as T10 (sometimes written T10% or $T_{10\%}$) is the temperature at which 10% volume of the gasoline is evaporated. It is considered preferable and more meaningful to use percentages evaporated rather than temperatures, particularly when carrying out blending calculations.

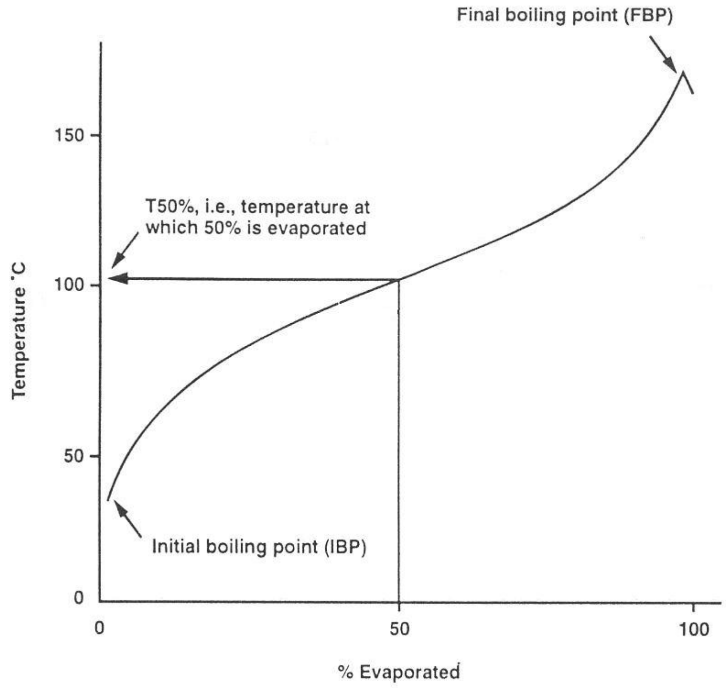

Figure 2.1 ASTM Distillation Curve (Owen and Coley, 1995)

Figure 2.1 shows the ASTM D 86 distillation curve. The distillation characteristics of a gasoline are not always similar to that shown in this figure because the shape is dependent on the blend composition.

2.1.4 Drivability

Driveability Index (DI) has been added to the ASTM specifications to help improve cold start and warm up performance. The drivability of a vehicle has been defined as the degree to which a vehicle starts readily, idles evenly, drives smoothly when cruising and accelerating, and generally responds to the throttle. It is well known that vehicle drivability deteriorates as ambient temperature decreases and, generally speaking, drivers do not expect such a good performance during warm-up of their vehicles in very cold weather.

Drivability malfunctions are caused by variations in mixture strength giving an air-fuel mixture outside the ignitable range in one or more cylinders for a few cycles. When a single point injection or a carbureted engine is cold and the ambient temperature is low, a large proportion of the fuel going forward can be present in the inlet manifold as a liquid film rather than as a vapor. This lack of vaporization gives rise to a hesitation before a burnable mixture reaches the cylinders at the start of acceleration.

The fuel parameters that influence cold weather drivability are not simple and can vary widely from one vehicle to another. An overall drivability index (DI) has been developed in the U.S. where:

$$DI = (0.5 \times T10) + T50 + (0.5 \times T90) \qquad (2.1)$$

This equation has been developed and refined, and a later version for use in the U.S. is as follow;

$$DI = (1.5 \times T10) + (3 \times T50) + T90 \qquad (2.2)$$

This version has been shown to correlate well with driver satisfaction both for hydrocarbon-only gasoline and also when MTBE is present although at the same DI, the hydrocarbon fuels had a higher satisfaction level than gasoline containing MTBE. For fuels representing typical commercial gasoline, Rvp and DI are usually intercorrelated so that meeting low Rvp levels. In order to minimize evaporative emissions can lead to poor cold weather drivability.

2.2 Oxygenated compound

Oxygenates are compounds containing oxygen in a chain of hydrocarbon atoms. They are beneficial to gasoline function in two ways. Firstly, they have higher blending octane number, so they can replace high octane aromatics in the fuel. These aromatics are responsible for disproportionate amounts of CO and hydrocarbon (HC) exhaust emissions which called “aromatic substitution effect”. Oxygenates can also be used in engines without sophisticated engine management systems to move to the lean side of stoichiometry, thus reducing emission of CO and HC. In addition, the advantage of using the oxygenate agents is to reduce smog-forming tendencies of the exhaust gases. However, on vehicles with engine management systems, the higher fuel volume is required to bring the stoichiometry back to the preferred optimum setting.

Table 2.1 Physical properties of oxygenated compounds[a]

Properties	Ethers				Alcohols			
	MTBE	ETBE	TAME	TAEE	TBA	TAA	MeOH	EtOH
CAS No.	1634-04-4	637-92-3	994-05-08	919-94-8	75-65-0	75-85-4	67-56-1	64-17-5
RON[b]	117	118	112	105	94	NA	133	129
MON[c]	101	101	98	95	100	NA	105	102
Mol. Wt.	88.15	102.18	102.18	116.20	74.12	88.15	32.04	46.07
BP(°C)	55.2	67.0	86.0	106.0	82.2	102.0	64.6	78.3
Density (g/mL)	0.741	0.752	0.764	0.761	0.786	0.805	0.791	0.795
Water Solubility (mg/l)	43,000 - 54,300	26,000	20,000	4,000	Miscible	NA	Miscible	Miscible
Blending Rvp (psi)	8	4.7	1.5[d]	1.2[d]	9	NA	40	18
Neat Rvp (psi) 100 °F	7.8	4	2.5	1.2	1.7	NA	NA	2.3
Oxygen(%w)	18.2	15.7	15.7	13.8	21.6	NA	49.9	34.8

a: Multiple sources; The Handbook of MTBE and Other Gasoline Oxygenates, Mealey's MTBE Conference.

b: RON = Research Octane Number simulates fuel performance under low severity engine operation with engine speed 600 rpm.

c: MON = Motor Octane Number simulates more severe operation that might be incurred at high speed or high load with engine speed 900 rpm.

d: Reid Vapor Pressure, Rvp and NA = Not Available

Generally, oxygenates used in gasoline can be classified into two groups; alcohols (C_x-O-H) or ethers (C_x-O-C_y). They have significantly different physical properties as shown in Table 2.1. The vapor pressure, both of blending Rvp and neat Rvp, affects the volatility of the gasoline: the lower vapor pressure gives lower emissions caused by evaporation of the gasoline. In this respect, tertiary ethers are far more suitable oxygenates for gasoline than alcohols.

2.2.1 Alcohol

a) Methanol

Methanol-TBA blend was commercialized by ARCO, under the trade name of Oxynol. The high methanol volatility blending, due to azeotrope formation with HC, caused the refusal of the market. Methanol is one of the reactants to produce MTBE and other methyl ethers. Even though methanol can be produced from renewable source, the production cost still unattractive and therefore presently produced from natural gas.

b) Ethanol

Ethanol can be produced from biomass, such as corn, grain and even agricultural waste which are renewable. In renewable fuels the carbon originates from biomass and does not add to carbon dioxide emissions in the way that fossil fuels do. Since carbon dioxide is a greenhouse gas, this carbon cycle of renewable fuels helps in preventing the accumulation of CO_2 in the atmosphere that leads to the greenhouse effect. However as shown in Table 2.1, the blending vapor pressure of ethanol is quite high, hence increasing the ethanol content in gasoline without other modifications of the gasoline composition leads to greater hydrocarbon emissions and higher ozoneforming potential. Furthermore, at low temperature the separation of the organic and water phases poses a risk.

2.2.2 Ether

The using of the first tertiary ether, methyl tert-butyl ether (MTBE) as oxygenate was first used in commercial gasoline in Italy in 1973 and in the US by ARCO in 1979. Ethers can be derived from fossil fuels such as MTBE and TAME, or partly from renewable fuels such as ETBE and TAEE.

a) MTBE

It is obtained through the reaction of isobutene and methanol. The use of MTBE has grown tremendously since it was introduced in 1973. Recently MTBE has gained considerable negative publicity. After it was detected in ground water in California, the state government passed legislation that prohibits its use in California by the end of the year 2002. Unlike other gasoline components, MTBE is highly soluble in water. With a solubility of 4.3 wt%, it is tens of times more water-soluble than any non-oxygenate component of gasoline. Once it gets into the ground, MTBE travels through the soil into ground water, where it is easily detected even at very low concentrations owing to its distinctive taste and odor. Leaking storage tanks were the main source of the MTBE in soil and ground water in California. MTBE degrades in sunlight, but very slowly in soil or ground water. As MTBE is a relatively new component in the ecosystem, microorganisms have not yet developed the capability to break it down. However, we must bear in mind that some other components of gasoline have been proven far more toxic than MTBE is even suspected of being. For example, MTBE has replaced lead components and, in part, benzene, both of which are known to be toxic and hazardous for human health.

b) TAME

It is obtained by reacting methanol with two of C_5 iso-olefins, 2-methyl-2-butene, 2M2B, and 2-methyl-1-butene, 2M1B. The third C_5 iso-olefin, 3-methyl-1-butene is completely inert toward the reaction with methanol. The TAME potential capacity is strictly related to the reactive isoamylenes present in the light gasoline catalytic cracking plants. An additional minor contribution to TAME capacity can arise from C_5 coming from naphtha steam cracking for ethylene manufacture, after a selective hydrogenation to remove dienes. Although TAME may solver the problem of water contaminant over MTBE as its significant lower in water solubility. It derived from methanol which currently still derived from natural gas as mention earlier.

c) ETBE and TAEE

The ethyl ether, ETBE and TAEE are produced by the addition of ethanol to isobutene and reactive isoamylenes, respectively. Ethyl ethers show similarly blending octane properties that methyl ethers while lower in bRvp and water solubility which are more favorable. Presently, TAEE is not in the market, while ETBE is produced in several countries, mainly in retrofit MTBE units, with similar yields and selectivity.

2.3 FCC and FCC Gasoline

Fluidized Catalytic Cracking (FCC) unit, is a primary conversion unit in most integrated refineries. It can convert heavier oils, such as heavy gas oil or vacuum gas oil into lighter products such as the liquefied petroleum gas (LPG), gasoline and diesel. The process employs a finely solid catalyst made by aerating the ground powder of an alumina-silica gel. In newer designs, a very active zeolite-based was employed as a catalyst in a short-contact time vertical or upward sloped pipe called the "riser". Pre-heated feed is sprayed into the base of the riser and contacts with extremely hot fluidized catalyst at 665 to 760 °C. The hot catalyst vaporizes the feed and catalyzes the cracking reactions that break down the high molecular weight oil into lighter components. Heavy residue contains higher amount of conradson carbon residue and poisonous metal i.e., sodium and nickel are strongly effect on the catalyst deactivation. Coke and tar are formed on the catalyst by the cracking. These are burned from the catalyst with air during the regeneration part of cycle. Both cracking and regenerative cycle are continuous. Separation of the catalyst from gases or vapors after the reaction and regeneration processes is done by cyclone separators. Good catalyst circulation is a key factor in FCC unit reliability.

Table 2.2 shows a composition stream from fluidized bed catalytic cracking unit optimized for the maximum production of middle distillates.

Table 2.2 Fluidized bed catalytic cracking adjusted for maximum production of middle distillates typical yield (Chauvel and Lefebvre , 1989).

Products	**% Weight of feedstock**
C_{2-}	4.4
C_3 cut	2.7
C_4 cut	4.9
C_5 cut	5.0
Gasoline	27.5
Light gas oil	43.0
Residue (heavy fuel oil)	8.5
Coke (burned in the unit)	4.0
Total	100.0

The effluent gasoline from the FCC unit has the reactive olefins that can be etherified with ethanol to produce the ethers. The reactive olefins present in FCC gasoline and their corresponding ethers formed by ethanol addition are shown as follows;

Reactive olefins	**B.P., °C**	**Ethylic ethers**
C4		
Isobutene	-6.3	2-methyl-2-ethoxy propane (ETBE)
C5		
2-methyl-2-butene	31.1	2-methyl-2-ethoxy butane (TAEE)
2-methyl-l-butene	38.6	2-methyl-2-ethoxy butane (TAEE)
C6		
2-methyl-l-pentene	62.0	2-methyl-2-ethoxy pentane
2-methyl-2-pentene	67.3	2-methyl-2-ethoxy pentane
cis-3-methyl-2-pentene	67.7	3-methyl-3-ethoxy pentane
trans-3-methyl-2-pentene	70.4	3-methyl-3-ethoxy pentane
2-ethyl-l-butene	64.7	3-methyl-3-ethoxy pentane
2,3-dimethyl-l-butene	53.6	2,3-dimethyl-2-etoxy butane
2,3-dimethyl-2-butene	73.2	2,3-dimethyl-2-etoxy butane
l-methylcyclopentene	75.5	l-methyl-l-ethoxy cyclopentane

C7

2-methyl-l-hexene	92.0	2-methyl-2-ethoxy hexane
2-methyl-2-hexene	95.2	2-methyl-2-ethoxy hexane
cis-3-methyl-2-hexene	97.3	3-methyl-3-ethoxy hexane
trans-3-methyl-2-hexene	95.2	3-methyl-3-ethoxy hexane
cis-3-methyl-3-hexene	95.4	3-methyl-3-ethoxy hexane
trans-3-methyl-3-hexene	93.5	3-methyl-3-ethoxy hexane
2-ethyl-l-pentene	94.0	2-ethyl-2-ethoxy pentane
2,3-dimethyl-l-pentene	84.2	2,3-dimethyl-2-ethoxy pentane
2,3-dimethyl-2-pentene	97.4	2,3-dimethyl-2-ethoxy pentane
cis-3,4-dimethyl-2-pentene	89.2	2,3-dimethyl-3-ethoxy pentane
trans-3,4-dimethyl-2-pentene	91.5	2,3-dimethyl-3-ethoxy pentane
2-ethyl-3-methyl-l-butene	86.3	2,3-dimethyl-3-ethoxy pentane
2,4-dimethyl-l-pentene	81.6	2,4-dimethyl-2-ethoxy pentane
2,4-dimethyl-2-pentene	83.3	2,4-dimethyl-2-ethoxy pentane
3-ethyl-2-pentene	96.0	3-ethyl-3-ethoxy pentane
2,3,3-trimethyl-l-butene	77.6	2,3,3-trimethyl-2-ethoxy butane
l-ethylcyclopentene	106.3	l-ethyl-l-ethoxy cyclopentane

1,2-dimethylcyclopentene	106.8	1,2-dimethyl-l-ethoxy cyclopentane
1,5-dimethylcyclopentene	102.0	1,2-dimethyl-l-ethoxy cyclopentane
1,3-dimethylcyclopentene	92.0	1,3-dimethyl-l-ethoxy cyclopentane
1,4-dimethylcyclopentene	93.2	1,3-dimethyl-l-ethoxy cyclopentane
l-methylcyclohexene	110.0	l-methyl-l-ethoxy cyclohexane

CHAPTER III

LITERATURE REVIEWS

3.1 Etherification of Olefins with Alcohol

The oxygenate ethers can be produced from the etherification of olefin compounds or alkenes with alcohol such as methanol and ethanol. The liquid-phase synthesis of MTBE from methanol and isobutene (IB) over acidic zeolite catalysts, H-Beta and US-Y zeolites catalysts was studied to compare with Amberlyst 15, commercial catalyst (Collignon et al., 1999). 85-90% of MTBE yield can be obtained with both of zeolite H-Beta catalyst and Amberlyst 15. However, Amberlyst 15 gave higher selectivity in temperature range of 313-373 K. Likewise, Chu and Kuhl (1987) investigated the MTBE synthesized over zeolite catalysts in a stainless steel tube reactor at 200-300 psig catalyzed by ZSM-5, ZSM-11 and Amberlyst 15. They reported that ZSM-5 and ZSM-11 gave higher selectivity and thermal stability. In addition, they gave no acid effluent and less sensitive to the methanol-to-isobutene ratio. Parra et al. (1998) studied a comparative of 12 different styrene-divinylbenzene ion-exchange resins for MTBE synthesis such as; Bayer OC-1501, Amberlyst 35, and Purolite catalyst series. The experiment was carried out at 1.6 MPa and 323 K in a continuous packed-bed reactor. Bayer OC-1501 gave the highest reaction rate and methanol conversion. Pannemen and Beenackers (1995) studied the catalytic activity of various strong acid ion-exchange resins on the synthesis of MTBE in a packed bed reactor between 293-353 K. Comparing to Amberlyst 15, Kastel CS 381 and Amberlyst CSP had similar rate constants while Duolite ES 276 and Amberlyst XE 307 showed significantly higher. Although MTBE has been widely used in many countries, it can contaminate the underground water because of its high water solubility. Furthermore, it was found to be hardly degraded in both of aerobic (Stefan et al. 1997; Mo et al. 1997; Salanitro et al., 1994) and anaerobic condition (Yeh and Novak, 1994). Nowadays, the use of MTBE has already forbidden in 25 states of USA (ACE 2006; Szklo et al., 2007) and many countries because it may contaminate underground water. Japan has ceased to use MTBE though official specifications continue to allow a 7% volume limit (Japanese regulation values of automobile fuels). Therefore, other higher tertiary ether compounds, e.g. 2-methoxy-2-methylbutane (tert-amyl methyl ether, TAME) which showed lower water solubility have been of interest.

TAME can be synthesized by the etherification of isoamylenes (IA) with methanol. Rihko and Krause (1995) studied the kinetics of TAME synthesis using Amberlyst 16 as catalyst at temperatures between 324 and 354 K. The rates of reaction were determined experimentally in liquid phase continuous stirred tank reactor at a pressure of 0.8 MPa. Kinetic equations derived from three different mechanisms were compared. In the forward reaction the adsorbed methanol reacted with isoamylenes (2-methyl-1-butene or 2-methyl-2-butene) striking from the bulk liquid phase, and in the splitting reaction the adsorbed ether split to alcohol and isoamylenes. The kinetic equations were written in terms of activities, and the activity coefficients were calculated by the UNIQUAC method. The activation energy was determined to be 95 kJ/mol for the splitting reaction of TAME to 2-methyl-1-butene and methanol and 100 kJ/mol for the splitting reaction of TAME to 2-methyl-2-butene and methanol. Syed et al. (2000) studied the reaction equilibria for the synthesis of TAME by using Amberlyst 15 as a catalyst. The reaction were carried out in batch reactor at 1.03 MPa in range of temperature 298-348 K. As the temperature increases, the equilibrium composition of TAME decreases which was expected of exothermic

reactions. The composition of 2M2B relative to 2M1B also decreases with increasing temperature. A comparative study of TAME synthesis on ion-exchange resin beads (Amberlyst 16, Amberlyst 35 and XE586) and a fibrous ion-exchange catalyst (SMOPEX-101) in a continuous stirred tank reactor (CSTR) was investigated by Paakkonen and Krause (2003). They reported that the catalytic activity order was as Amberlyst 35>Amberlyst 16>SMOPEX-101>XE586 which are in the same trend of the ion exchange capacity. Although methanol can be also produced from biomass, the production is cost-intensive and also it currently made from natural gas which is more cost competitiveness. Therefore, methanol and methanol derivatives such as MTBE and TAME are not favorable in an environmental view point because they are mostly derived from natural gas whose production may contribute to global warning.
Ethanol, one of biofuels, is a renewable energy source for alleviate the oil crisis and global climate change. Carbon dioxide produced from ethanol combustion is not considered as a global warming contributor since it is carbon neutral.

Ethanol can be blended directly into gasoline (called “gasohol”); however, many recent researches reported disadvantages of the gasohol. One of good reviews on the effect of ethanol in gasoline is reported by Niven (2005). The overall air pollutant emissions from the use of gasohol are usually higher than those from the use of conventional gasoline because its high blending Reid vapor pressure (bRvp) leads to higher evaporative emissions. Ethanol-derived ethers can overcome the drawbacks of gasoline with direct ethanol blend. Ethers/gasoline fuel shows less volatility than gasohol. Therefore, ethers derived from ethanol still have drawn a number of research activities.

The most well-known ethanol derivatives ethers are ethyl tertiary butyl ether (ETBE) and tertiary amyl ethyl ether (TAEE). Commercially, ETBE and TAEE can be produced by etherification of ethanol with isobutene (IB) and isoamylenes (IA), olefinic compounds, respectively. The advantage of ETBE and TAEE is that they can be produced from a renewable resource, i.e., ethanol. They are good octane enhancer which RON of ETBE and TAEE are 118 and 105, respectively. Their blending Reid vapor pressure (bRvp) and water solubility are lower than that of ethanol and MTBE.

Several reports for the production of ETBE have been focused on the liquid-phase etherification of isobutene with ethanol on the ion-exchange resin. Fite et al. (1994) studied the ETBE synthesis in a continuous differential reactor operated at 1.6 MPa and 323-363 K catalyzed by Lewatit K2631. Rate data showed that the reaction was highly temperature sensitive, and isobutene had an enhancing effect on the rate whereas ethanol had an inhibitor one. In addition, Gomez et al. (1997) studied a simultaneous liquid-phase synthesis of MTBE and ETBE in batch reactor by using Bayer K2631 as the catalysts. The equilibria constants were determined experimentally in the temperature range 313-353 K at 1.6 MPa. They found that MTBE reached the equilibrium faster than ETBE.

TAEE can be synthesized via the liquid-phase etherification of isoamylenes (IA) with ethanol. This etherification can be catalyzed by a strongly acidic macro porous cation-exchange resin, e.g. Amberlyst 15 and Amberlyst 16. The kinetics and equilibrium of the heterogeneously liquid-phase formation of TAEE catalyzed by Amberlyst 16 were studied (Linnekoski et al., 1997). The experiments were carried out in a CSTR at 0.8 MPa and the operating temperature in range of 323-363 K. The measured reaction rates were fitted to three kinetic models; homogeneous, Eley-Rideal type, and Langmuir-Hinshelwood type. The Langmuir-Hinshelwood is the best fitted model to describe the experimental results. Verevkin (2004) studied the reaction equilibria of the liquid-phase synthesis of TAEE in the temperature range of 298-395

K by using Amberlyst 15 as a catalyst. The equilibrium constant decreased sharply as temperature increase. The reaction equilibria of the TAEE synthesis catalyzed by Amberlyst 15 was also studied by Kitchaiya and Datta (1995). They studied the etherification of two IA isomers (2M1B and 2M2B) to produce TAEE and their isomerization. Their experiment were occurred in a batch reactor in range of temperature as 293-343 K. The etherification equilibrium constant of 2M1B and 2M2B decreased monotonically with increasing temperature, less TAEE was produced at the higher temperatures from the both of isoamylenes. And the isomerization equilibrium constant also decreased with increasing temperature. Dowex M32 can also be used as catalyst for the TAEE synthesis (Rihko and Krause, 1993). These ion exchange resins are formed as assemble of gel like micro spheres having macro pores between these micro spheres diffusion resistances. Both in the macro pores and within the gel like micro gains may have significant influence on the observed rate (Oktar et al., 1999a and Dogu et al., 2003). Relative diffusion resistances among macro pores and micro pore are strongly dependent on the state (vapor or liquid) of the reactant. In the liquid phase major diffusion resistance was reported to be in the macro pore. However, in vapor phase macro pore and micro pore diffusion resistances are equally significant (Dogu et al., 2003). The activity of ion exchange resin which having different hydrogen exchange capacities ranging between 1.3 to 5.1 meq H^+/kg for TAEE synthesis from IA and EtOH was investigated in a fixed bed reactor (Boz et al., 2004). Several research groups have investigated the TAEE synthesis from IA and EtOH. Rihko and Krause (1993) reported for the reactivity of IA with EtOH. It was found that 2M1B was more reactive than 2M2B which also confirmed by other researches (Oktar et al., 1999b and Boz et al., 2004). The observed equilibrium constant corresponded with the thermodynamic value.

Alternative routes for synthesis of ethers were also currently explored. In our previous studies, ETBE and TAEE were produced from reactions between ethanol and tert-butyl alcohol (TBA), a major by-product of propylene oxide production, and tert-amyl alcohol (TAA), a major component of fusel oil which is a by-product obtained from biomass fermentation, respectively (Assabumrungrat et al., 2002, 2003; Kiatkittipong et al., 2003; Aiouache and Goto 2003a, b; Boonthamtirawuti et al., 2007).

However, unfortunately, the production of these olefinic compounds, i.e, IA, IB or alcohols, i.e., TBA, TAA are unlikely to meet demands for etherification feeds. Heavier reactive olefins should be considered as additional reactants for ether production.

Heavier reactive olefins should be considered as additional reactants for ether production. *tert*-Hexyl ethyl ethers, THEE can also be derived from ethanol by the liquid-phase etherification of C_6 olefins with ethanol. Zhang and Datta (1995 and 1996) published many reports for the liquid-phase synthesis of THEE which consisted of equilibrium conversion, selectivity limitation and including kinetic of reaction. The catalyst that they used in their experiment was Amberlyst 15. The equilibrium constant and the equilibrium conversion to THEE decreased with increasing temperature. 3-Methoxy-3-methylheptane was firstly investigated by etherified 2-Ethyl-1-hexene with methanol (Karinen and Krause, 2000). Consequently, etherification of C5- and C8- alkenes i.e., 2-methyl-1-butene and C8-2,4,4-trimethyl-1-pentene, respectively, with different C1- to C4-alcohols was studied (Karinen et al., 2001).

FCC light gasoline is a potential valuable feedstock of reactive olefins for production of oxygenated ethers. On the contrary, these olefinic compounds should also be diminished in order to meet the new mandatory of gasoline composition which allowed the olefin content not to exceed 18 vol% as regulated by Euro-4 standard.

3.2 FCC gasoline and olefin reduction

As mentioned above for the Euro-4 standard (2005), the maximum contents in gasoline are 1 vol. % for benzene, 50 ppm for sulfur, 35 vol. % for aromatic compounds, 18 vol. % for olefins, 2.7 wt. % for oxygen and Rvp in summer is not exceed 60 kPa. Owing to the enforcement of the new standard, many refineries would had to face the challenge. This regulation led to an increase in the proportion of isomerization and alkylation processes in oil refining (Zakumbaeva et al., 2007).

Generally, the octane number of olefin is higher than that of alkane, but stability is lower. When olefenic compounds volatized into gas and mixed with NOx, they are lit by ultraviolet rays from the sun, then it forms poisonous photochemical smog, consequently, serious air pollution problem. The recent research works focus mainly on how to decrease the amount of olefins in FCC gasoline effectively. Converting olefins in FCC gasoline by hydroisomerization and aromatization were presently succeeded by many researchers (Fan et al., 2004, 2006; Cao et al., 2006). The loss of octane number from olefin reduction was compensated by the formation of iso-paraffins and aromatics. This process is also beneficial in the viewpoint of olefin reduction; however, aromatic compounds which have a greater tendency to emit unburned hydrocarbons (Perry and Gee, 1995) might be produced. In addition, the processes are still further required for oxygenate addition from the outside to meet the standard requirement.

Producing tertiary ethers from entire FCC gasoline are more interesting process. Reduction of olefins and consequently reduced in Rvp with an increase of the octane number of gasoline by oxygenated ether are simultaneously could be obtained in one step. The following sections are the literature reviews on the etherification of FCC gasoline with alcohol.

3.3 Etherification of FCC Gasoline with Alcohol

Pescarollo et al. (1993) firstly studied the etherification of the entire light FCC gasoline with methanol. FCC gasoline feed contained about 10% C_5 reactive olefins (2-methyl-2-butene (2M2B), 2-methyl-1- butene (2M1B)), 9-10% C_6 reactive olfins and 4-5% C_7 reactive olefins (Pescarolla et al., 1993). IA conversion was 68.8% which closely approaching thermodynamic equilibrium while conversions of C_6 and C_7 reactive olefins were 42.9% and 23.2%, respectively. Simultaneous improvements in octane number and gasoline volume with reducing olefinicity, atmospheric reactivity and bRvp of gasoline were obtained. Similar reaction was also studied by using Amberlyst 16, a cation-exchange resin, as a catalyst in a temperature range of 323-353 K (Rihko and Krause, 1996). They reported the initial etherification rates and thermodynamic limitations for the reaction of methanol with the C_5 and C_6 olefinic compounds. The equilibrium constants of C_6 olefins etherified with ethanol were lower than those of IA, C_5 olefins.

Zeolite catalyst showed promising properties on high thermal stability comparing with ion exchange resin catalyst (Oudshoorn et al., 1999). Recently, Hu et al. (2006) studied the catalytic activity of various zeolites on FCC light gasoline etherified by methanol. The activities were ordered as: Hβ > HMOR > HZSM-5. Hβ also showed higher catalytic stability than other catalysts.

CHAPTER IV
EXPERIMENT

4.1 Apparatus of Batch Reactor and Chemical

4.1.1 Batch Reactor Apparatus

A cylindrical shape autoclave type reactor with outside and inside diameter of 5 and 4 cm, respectively and 8 cm of height withstands operating pressure as high as 30 atm. The turbine for mixing and valve for liquid sampling including the thermocouple are installed at the top. The reactants were placed into the batch reactor with 10 g of catalyst at the room temperature. It should be noted that the reaction is not occurred without heating (Rihko et al., 1998). The mixture was stirred at the maximum speed of 1163 rpm in all the runs to minimize the external mass transfer resistance. Figure 4.1 shows the batch reactor apparatus. The experiments carried out at high pressure to ensure all reaction components were always in liquid phase.

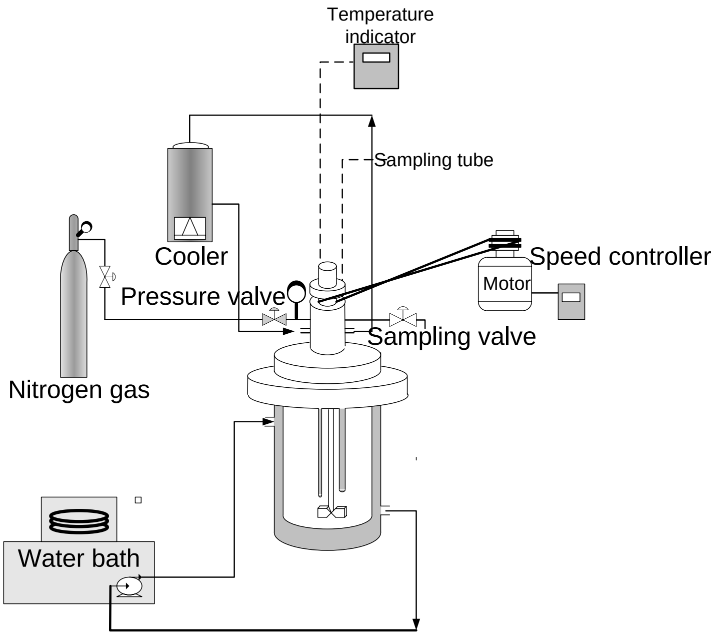

Figure 4.1 Batch Reactor Apparatus

4.1.2 Chemical

The chemicals used in this study consist of standard grade chemicals with purity higher than 99.5% for gas chromatograph calibration and reagent grade chemicals for major experiments. Table 4.1 provides the details of chemical purity and suppliers.

Table 4.1 Chemicals use in the study

Chemical materials	Purity (%)	Supplier
IA	> 99.5	Chemika Fluka
EtOH	> 99.5	SR lab
FCC gasoline	ND	Thaioil Public Company Limited
TAEE	90	Laboratory

4.2 Etherification of FCC Gasoline with Ethanol

4.2.1 Catalysts Selection

This study was the catalyst screening for the fuel oil quality improvement by the etherification of FCC gasoline with ethanol. Various commercial catalysts were chosen in the study as summarized in Table 4.2. It can be divided into 2 types; strong acid ion exchange resin and beta zeolite. Amberlyst 16 is the strong acid ion exchange resin that the pore size type is macrorecticular pore. Beta-zeolite which was used in the experiment has the Si/Al ratio of 40. The catalysts were dried overnight in an oven at 383 K before use.

Table 4.2 Physical properties of catalysts

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

4.2.1.1 Experimental procedure

1. The reaction system consisted of FCC gasoline and ethanol with a volume ratio of 80:20 and 70:30 with 10 g of catalyst.

2. The solution was pressurized by N_2 gas to 0.8 MPa to prevent vaporization of liquid solutions and heated to the desired reaction temperature (343 K) for 10 h and stirred at about 1163 rpm.

3. The samples of feed and product were collected at the initial and final of the experiment. It should be noted that for collecting the final product after run for 10 h, the reactor was cooled down to reach a room temperature before opening the reactor and collecting the sample in order to prevent the evaporation loss.

4.2.1.2 Analysis

1 Chemical compositions analysis

In gasoline investigations, the compounds called “PIANO” which consisted of paraffins, isoparaffins, aromatics, naphthenes and olefins were determined with the amount of the oxygenates. The samples of feed and product were investigated by following “PIANO” which was analyzed by the laboratory of Thai Oil Public Company Limited. This analysis, the liquid samples were tested by using a gas chromatograph with a SUPELCO capillary column.

2. Etherification conversion and TAEE production

Chemical compositions (Ethanol, Isoamylene and TAEE) of a liquid sample were analyzed by using a gas chromatograph (GC), Shimadzu GC 8A. The operating condition of the GC is shown in Table 4.3. The analysis was done by injecting 1 μl of sample in the column. It should be noted that a sample must be centrifuged before the injection in order to separate residue catalyst which can damage the GC column.

Table 4.3 Operating conditions of gas chromatography (Shimadzu GC8A)

Gas Chromatography Shimadzu GC8A					
Operating Conditions		**Intergration Parameter**			
Detector	TCD	Width (sec)	5	Slope (uV/min)	30
Carrier Gas	He (99.98 %)	Drift (uV.min)	0	T. DBL (min)	1000
Carrier Gas Flow rate (cm3/min)	30	Stop Time (min)	35	Atten (2^X mV)	5
Packed Column	Gaskuropack 54	Speed (mm/min)	2		
Length of Column (m)	2.5	**Quantitative Parameters**			
Mesh size of Packing	60/80	Method (0-8)	1	Curve (Calib. Fit Type)	0
Injection temperature (K)	443	Cal. Levl (0-15)	1	Min.Area (count)	100
Column temperature (K)	473	Win. Band (0:win 1: Band)	0	Window (%)	5
Detector temperature (K)	473	Spl. Wt	100	IS. Wt	0
Current (A)	80	Dilfact	1		

3. Fuel oil quality analysis

This analysis was contributed the standard analysis of Research Octane Number (RON), blending Reid vapor pressure (bRvp) and the distillation temperature which were carried out by following the standard methods of ASTM D-2699, ASTM D-5191 and ASTM D-86, respectively. All of analysis was tested by the laboratory of Thai Oil Public Company Limited. In addition, density and viscosity were analyzed by using the pycnometer and Oswalt viscometer, respectively.

CHAPTER V

RESULTS AND DISCUSSION

Etherification of FCC Gasoline with Ethanol

The suitable catalyst for the etherification of FCC gasoline with ethanol was studied in the batch reactor. Both of the etherification conversion and the fuel oil properties were considered for screening the appropriate catalyst.

5.1 Catalyst Screening

The catalyst screening experiments were carried out at the following condition; i.e. catalyst weight = 10 g, T = 343 K, P = 0.8 MPa and the ratio of FCC gasoline to ethanol = 80:20 and 70:30. The catalysts; Amberlyst 16 and Beta-zeolite (H^+ form) were screened. The compositions of FCC gasoline are shown in Table 5.1. Most olefins were in the range of C_5-C_7 hydrocarbons. The fraction of total olefins was about 25 vol%.

Table 5.1 Composition of FCC gasoline in volume percent

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

Table 5.2 provides the gasoline composition, olefins conversion and ethanol conversion of FCC gasolines directly blended and etherified with ethanol with a volume ratio of 80:20. Equations 5.1 presented the conversion calculation for ethanol.

$$\%\text{Conversion of ethanol} = \frac{N_{EtOH,0} - N_{EtOH}}{N_{EtOH,0}} \times 100 \qquad (5.1)$$

As shown in the table, since pure ethanol was supplemented into the FCC gasoline with 20 vol% (approx. 22.4 wt.%) the amount of final gasoline product was increased for both cases, i.e., direct blend and etherified gasoline. In the case of ethanol direct blend, the amount of each component is constant because the reaction cannot occur without the catalyst.

Table 5.2 Gasoline composition, olefins conversion and ethanol conversion of FCC gasoline direct blended and etherified with ethanol with a volume ratio of 80:20

Component	FCC Gasoline (g.)	Ethanol (g.)	20 vol% Ethanol		
			Direct Blend (g.)	Etherified Gasoline	
				Amberlyst 16 (g.)	Beta-Zeolite (g.)
Olefins					
- C4	1.76	-	1.76	0.92	0.86
- C5	8.85	-	8.85	6.15	5.1
- C6	5.69	-	5.69	4.42	3.54
- C7	4.54	-	4.54	3.56	2.73
- C8	1.09	-	1.09	0.29	0.28
- C9	0.44	-	0.44	0.29	0.29
- C10	0.35	-	0.35	0	0.15
Benzene	0.28	-	0.28	0.28	0.27
Other Hydrocarbon	55.49	-	55.49	52.21	52.39
Oxygenates					
- Ethanol	0	22.44	22.44	15.87	14.29
- Ether	0	-	-	16.01	19.56
Total	0	-	22.44	31.88	33.85
Grand total	78.49	22.44	100	100	100
C4 Olefins conversion (-)			0	0.48	0.51
C5 Olefins conversion (-)			0	0.31	0.42
C6 Olefins conversion (-)			0	0.22	0.38
C7 Olefins conversion (-)			0	0.22	0.40
Ethanol conversion (-)		-	0	0.29	0.36

Table 5.3 Gasoline composition, olefins conversion and ethanol conversion of FCC gasoline direct blended and etherified with ethanol with a volume ratio of 70:30

Component	FCC Gasoline (g.)	Ethanol (g.)	30 vol% Ethanol		
			Direct Blend (g.)	Etherified Gasoline	
				Amberlyst 16 (g.)	Beta-Zeolite (g.)
Olefins					
- C4	1.72	-	1.72	0.78	0.67
- C5	7.72	-	7.72	3.39	3.19
- C6	5.12	-	5.12	3.79	2.28
- C7	3.86	-	3.86	2.07	1.88
- C8	0.94	-	0.94	0.51	0.58
- C9	0.39	-	0.39	0.12	0.17
- C10	0.29	-	0.29	0.22	0.06
Benzene	0.28	-	0.28	0.24	0.22
Other Hydrocarbon	46.53	-	46.53	43.93	43.60
Oxygenates					
- Ethanol	-	33.15	33.15	18.69	16.06
- Ether	-	-	-	26.26	31.29
Total	-	-	33.15	44.95	47.35
Grand total	66.85	33.15	100	100	100
C4 Olefins conversion (-)			0	0.55	0.61
C5 Olefins conversion (-)			0	0.56	0.59
C6 Olefins conversion (-)			0	0.26	0.55
C7 Olefins conversion (-)			0	0.46	0.51
Ethanol conversion (-)		-	0	0.44	0.52

In the cases of etherified gasoline, Amberlyst 16 and Beta-zeolite were used as catalysts. Olefins and ethanol were mainly converted to ethers. Comparing between two catalysts, it was found that Beta-zeolite gives higher ethanol and olefins conversions, resulting in higher ether products. It is worthy to note that olefins conversions are lower with larger atomic number of olefins in both catalysts because large molecular of olefins hardly entries to pores of catalyst (Hu et al., 2006). The tendency of these results was similar to that of the etherified FCC gasoline with methanol experimented by Pescarollo et al. (1993). They reported that the conversions of C4, C5, C6 and C7 olefins were 0.84, 0.64, 0.43 and 0.23 respectively. Even though the FCC feed composition and the ratio of alcohol to FCC were different, a simple comparison between the performance of methanol (Pescarollo et al., 1993) and ethanol (as shown in Tables 5.2 and 5.3) for etherification could be noticed. Higher conversion of isobutene (C4) and isoamylene (C5) in FCC with methanol than with ethanol were observed. These results are similar to the individual study of C4 and C5 olefins with alcohol in the literature (Rihko and Krause, 1993; Rihko et al., 1994; Colombo et al., 1883; Izqulerdo et al., 1992; Vila et al., 1993). The activity of ethanol was less than that of methanol as a result of the decrease of dielectric constant or polarity. The value of dielectric constants decreased with increasing of molecular weights of alcohols which were 32.6 and 24.3 for methanol and ethanol, respectively. The more polar component could be preferably adsorbed over the actives sites than the less polar component (Karinen et al., 2001).

However, the comparable or some higher conversions of C6 and C7 olefins with ethanol compared to those with methanol were unexpected. The higher conversion of C6 olefins with ethanol over that with methanol also has been previously observed by Rihko and Krause (1996). These contrasting results might be explained by the study of Cruz et al. (2005). They declared that ethanol can react with alkenes easier than methanol due to the higher acidity of ethanol. The complexity of the system might be related to the complicated mechanism of adsorption over active site. Many components; i.e., alcohol, ether and hydrocarbon having significantly different in polarity should play a role; therefore, the investigation of this issue should be further studied.

The ratio of FCC gasoline and ethanol was changed to 70:30 and the reaction was carried out at the same operating condition described earlier. The results are summarized in Table 5.3. Beta-zeolite still shows a better catalyst performance than Amberlyst 16. Comparing with Table 5.2, the ethanol conversion and all C4 to C7 olefins conversions increased with increasing ethanol fraction in feed. The remaining unreacted ethanol from the case with the feed ratio of 70:30 did not exceed the ethanol content of 15 vol% in the case of Beta-zeolite. Therefore it is not over the gasoline specification of i.e., E15 and E20. The effect of gasoline composition in both Tables 5.2 and 5.3 are further discussed with the gasoline properties shown in Table 5.4. As shown in Table 5.4, a research octane number (RON) of original FCC gasoline was 88 which was lower than that of the specification of regular gasolines (RON = 91). FCC with direct ethanol blend in 20 and 30 vol% showed RON up to 94.8 and 97.9, respectively. However, unfortunately their bRvp also increased dramatically. It should be noted that although the bRvp value does not exceed the specification of E10, lower bRvp can be more favorable for preventing evaporative loss and vapor lock especially in hot countries. As shown in Table 5, FCCs etherified with ethanol by using both Amberlyst 16 and Beta-zeolite catalysts can effectively decrease the values of bRvp because the reactive olefins in FCC gasoline and ethanol are converted to ethers which have lower bRvp. FCC etherified with 30 vol% ethanol both catalyzed by Beta-zeolite and Amberlyst 16 give lower bRvp than FCC directed blend with 20 vol%. These results also confirm the increase of the renewability of gasoline by adding renewable energy. Comparing with original FCC gasoline, the bRvp value of etherified gasoline catalyzed by Beta-zeolite is lower or similar in the cases of using 20 and 30 vol%, respectively. These results may strongly depend on the decrease of olefins content and the amount of unrected ethanol remaining in the solution.

Table 5.4 Comparison of gasoline properties

Properties	ASTM Standard	FCC Gasoline	Gasohol E10	20 vol% Ethanol			30 vol% Ethanol		
				Direct Blend	Etherified Gasoline		Direct Blend	Etherified Gasoline	
					Amberlyst 16	Beta-Zeolite		Amberlyst 16	Beta-Zeolite
RON	D-2699	88	95	94.8	93	94.1	97.9	96.9	98.2
bRvP (psi)	D-5191	6.5	< 9	7.441	7.05	5.657	8.0	7.24	6.58
Density (g/cm^3)		0.683	0.749	0.735	0.739	0.745	0.735	0.739	0.745
Viscosity x 10^6 (Pa s)		$6.09\text{x}10^{-4}$	$5.05\text{x}10^{-4}$	$6.20\text{x}10^{-4}$	$5.27\text{x}10^{-4}$	$6.18\text{x}10^{-4}$	$6.03\text{x}10^{-4}$	$5.92\text{x}10^{-4}$	$5.0\text{x}10^{-4}$
Distillation Temperature °C (°F)	D-86								
IBP		35.5(95.9)		41.9(107.4)	43.3(109.9)	47.7(117.9)	N.D.	N.D.	N.D.
T 10		57.1(134.8)	< 70(158)	55.2(131.4)	56.9(134.4)	59.7(139.5)			
T 50		99.0(210.2)	70-110 (158-338)	70.2(158.4)	75.0(167)	73.8(164.9)			
T 90		168.7(335.7)	< 170(338)	165.9(330.6)	167.1(332.8)	170.2(338.4)			
FBP		196.0(384.8)	< 200(392)	194.7(382.5)	193.1(379.6)	198.2(388.8)			
Driveability Index, DI °C (°F)		631(1168)	<677(1250)	617(1143)	635(1175)	638(1182)			

Comparing the RON between ethanol directly blended and etherified gasolines, the etherified gasoline by using Amberlyst 16 showed slightly lower octane number than FCC with direct ethanol blend because ethanol has higher value of octane number (RON = 118) than ethers, i.e., ETBE (RON = 118), TAEE (RON = 105), *tert*-hexyl-ethyl-ether (THEE) (RON = 110). However, etherified gasoline catalyzed by Beta-zeolite showed similar RON to that of ethanol directly blended gasoline and slightly higher than that of etherified gasoline catalyzed by Amberlyst 16. Fan et al., 2004 founded that Beta-zeolite was a reactive catalyst for upgrading FCC gasoline via isomerization and some aromatizations. However, as shown in Tables 5.3 and 5.4, fortunately, the amounts of benzene are not increased in the case of FCC gasoline etherified with Beta-zeolite. As the amounts of benzene are not increased, there is no greater tendency to emit unburned hydrocarbons. Therefore, the enhancement of octane number in the case of etherified by Beta-zeolite is not arisen from only etherification reaction but also isomerization. In addition, Corma et al. (1999) studied various zeolites as catalysts for the cracking of n-heptane, a model molecule of gasoline range. When using Beta-zeolite as a catalyst, the ratio of isobutene to n-butene and isopentene to n-pentene products were 1.27 and 2.0, respectively. Therefore, ether products may not be possibly limited by the amount of reactive olefins originally present in gasoline, the reactive olefins could be further obtained via cracking by Beta-zeolite.

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

Linnekoski et al. (1998) and Karinen et al. (2001) reported that only small amount of water resulted in significantly dropped in ethanol and olefins conversion. This is because the higher acidity of water compared to that of ethanol resulted in the increasing of basic solvated proton which lowers activity as previously mentioned in the literature (Ancilotti et al., 1977, 1978; Gicquel and Torck, 1983). In our experiments, although both catalysts were dried at 110 °C overnight, the water remaining adsorb in the pore of catalyst might be examined by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA).

TGA and DTGA of Amberlyst 16 were investigated as shown in Figs. 5.1 and 5.2, respectively. The weight loss of Amberlyst 16 at the temperature lower than 200 °C are almost 10 wt% which should be corresponding to the amount of water desorption (Balcerowiak, 1997; Zholobenko et al., 1997). The consecutive mass loss step of Amberlyst 16 might be the thermal desulfonation (Balcerowiak, 1997). The final peak at 470 °C of DTGA (Fig. 5.2) might be the thermooxidative decompositions of a polymers matrix (Balcerowiak, 1997) which corresponds well with high intensity exothermic as shown in Fig. 5.1.

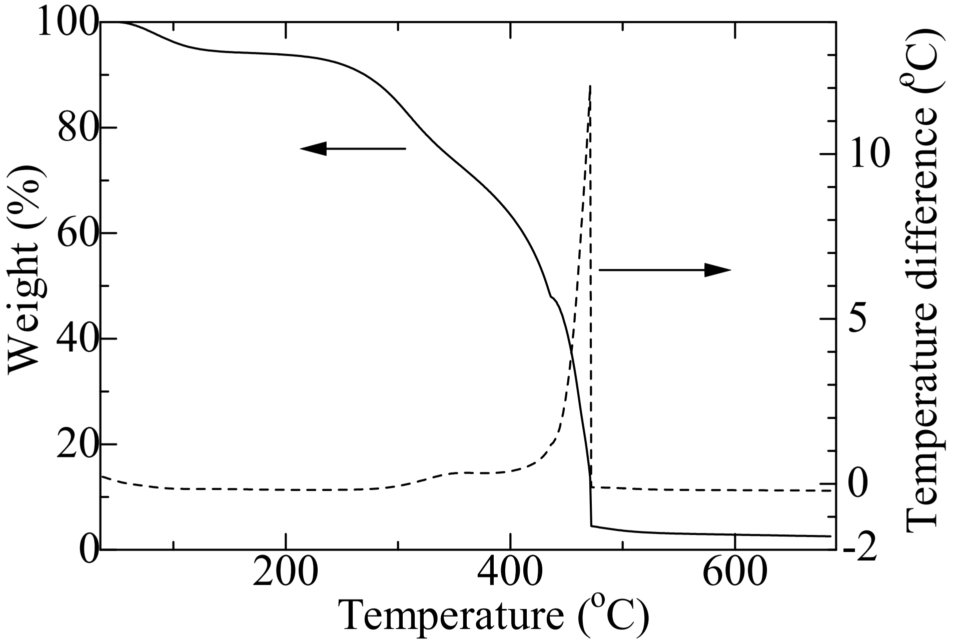

Figure 5.1 Thermogravimetric analysis (TGA) of Amberlyst 16.

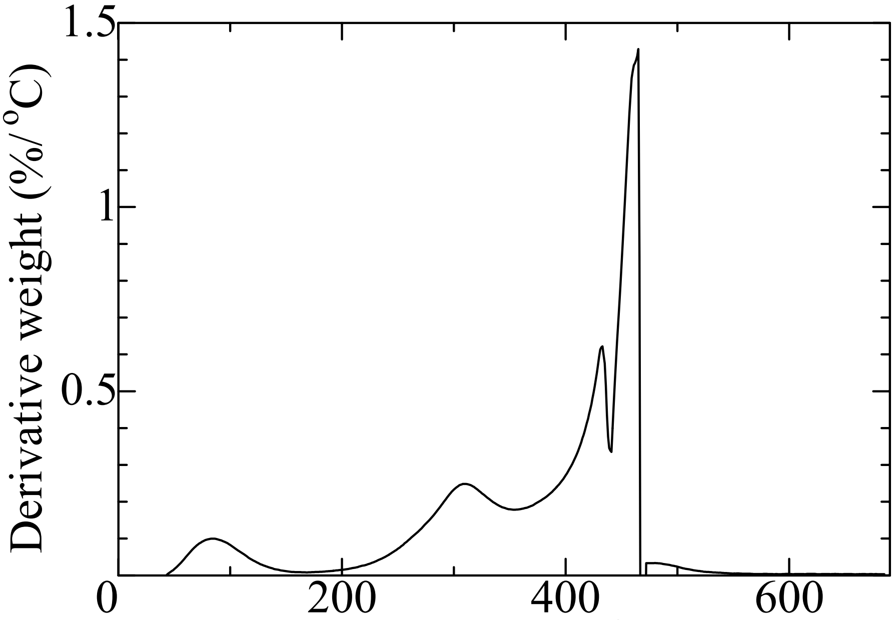

Figure 5.2 Differential thermogravimetric analysis (DTGA) of Amberlyst 16.

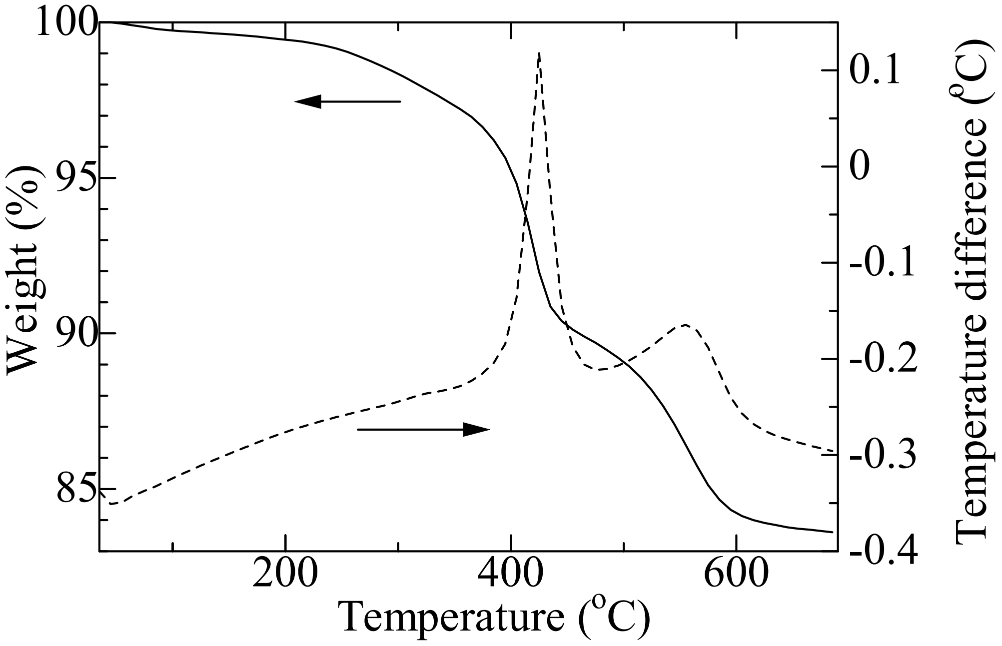

Figure 5.3 Thermogravimetric analysis (TGA) of Beta-zeolite.

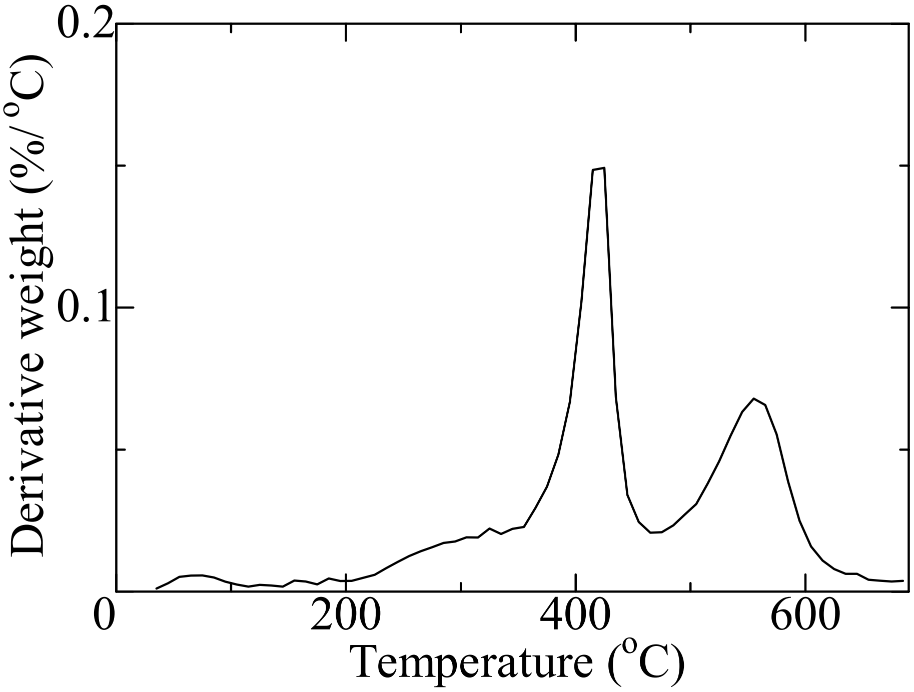

Figure 5.4 Differential thermogravimetric analysis (DTGA) of Beta-zeolite.

On the contrary, insignificantly of weight loss at the temperature lower than 200 °C can be observed in the case of Beta-zeolite as shown in Fig. 5.3, therefore trace amount of water desorption. Thermal analysis also revealed desorption of precursor component such as organic template (Zholobenko et al., 1997) i.e. at the temperature of 420 and 560 °C. The DTGA in Fig. 5.4 showed corresponding well of intense exothermic heat. However, it should be noted that weight loss and exothermic heat were much more pronounced in the case of Amberlyst 16. This TGA results also confirm the higher thermal stability of Beta-zeolite than that of Amberlyst 16.

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

Apart from bRvp which represents the volatility property of gasoline, T10, T50 and T90 (D-86 temperature at 10, 50 and 90 vol%, respectively) and drivability index which are key motor gasoline specifications are also provided in Table 5.4. Initial boiling point (IBP) increased with the presence of ethanol both in gasoline with direct ethanol blend and etherified gasoline with some unreacted ethanol. Comparing with unmodified FCC gasoline, the distillation temperatures of in all vol% and final distillation temperatures decrease in the case of gasoline with direct ethanol blend and etherified with Amberlyst 16. While in the case of etherfied with Beta-zeolite, the distillation temperature decreased only for T10 and T50. These may imply that distillation temperatures of ethanol existing fuels are dependent on the evaporation of ethanol and their amount. These results can also be confirmed with the decrease of the bRvp as shown in the Table 5.4, i.e. with higher ethanol converted, the distillation temperatures in the case of Beta-zeolite seem to be higher than those of Amberlyst 16 and ethanol directly blended, respectively. It is worthy to note that T50 of FCC with direct ethanol blend was marginal with the specification value of gasohol E10, it is possibly that blending with higher amount of ethanol, i.e. 30 vol% may make the T50 off specs therefore the distillation temperature of ethanol 30 vol% were not determined and the available results are enough for discussion. The drivability index, DI was defined as follow (French and Malone, 2005; Magyar et al., 2005).

$$\text{Drivability index (DI)} = (1.5 \times T10) + (3 \times T50) + T90 \qquad (5.2)$$

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

$$DI = (1.5 \times T10) + (3 \times T50) + T90 + 20 \times \text{wt\% oxygen} \qquad (5.3)$$

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

For other gasoline properties as shown in Table 5.4, the density and the viscosity of the etherified gasoline were close to those of the commercial gasohol. The full ranges of distillation temperature were presented as a distillation curve as shown in Figure 5.5 and further discussed in some details.

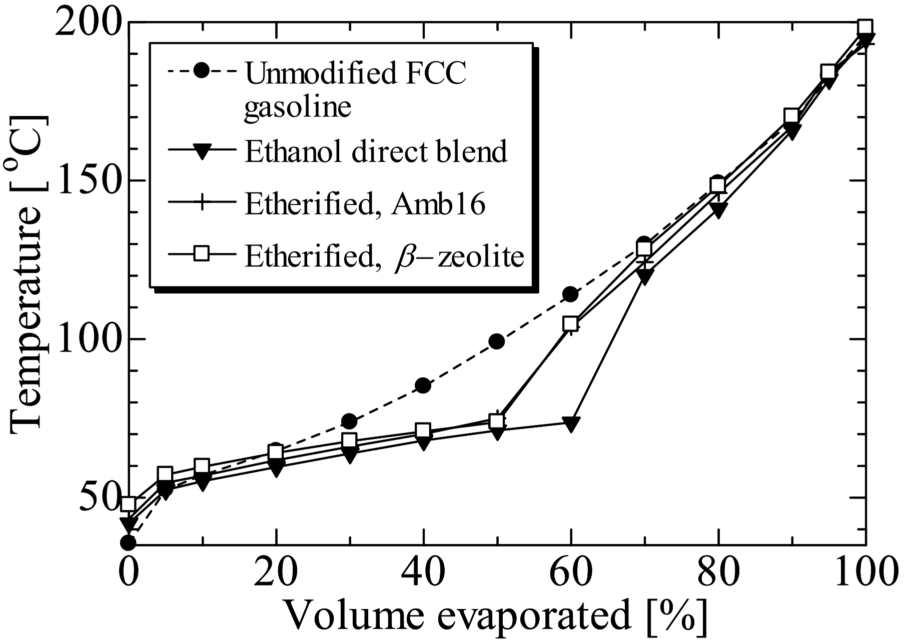

Figure 5.5 Distillation curves from ASTM D-86 tests.

Although the change in bRvp affected the distillation temperature through the whole temperature range, the most effect appeared at the front end of the curve. Therefore the different between etherified gasoline catalyzed by β-zeolite and Amberlyst 16 which are two most similar compositions could be observed only at the front end of distillation curve. It is worthy to note that the distillation temperature of FCC with direct ethanol blend at 60 vol% evaporated is much lower than the others. It may be explained by the differences in boiling point values (ethanol; about 78 °C and gasoline; about 35-200 °C). The results agreed well with those from the study by Hsieh et al. (2002) who tested ethanol–gasoline blended fuels in a spark-ignition (SI) engine. Their results showed significantly decrease of the 50% distillation temperature when ethanol was blended with more than 10 vol% into gasoline whose boiling temperature is in a range of 25-230 °C.

Therefore, the process could be satisfied to decrease gasoline volatility which affects not only a vehicle's drivability but also its VOCs emissions in both evaporative and end pipe exhaust emissions and it should be noted that this method allows the use of ethanol in gasoline at higher content than does the conventional method with direct blending.

CHAPTER VI

CONCLUSION

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

REFERENCES

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

Agarwal, A.K. “Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines,” *Prog. Energ. Combust. Sci.* 33 (2007): 233–271

Aiouache, F. and Goto, S. “Sorption effect on kinetics of etherification of *tert*-amyl alcohol and ethanol,” *Chem. Eng. Sci.* 58 (2003a): 2056-2077.

Aiouache, F. and Goto, S. “Reactive distillation-pervaporation hybrid column for *tert*-amyl alcohol etherification with ethanol,” *Chem. Eng. Sci.* 58 (2003b): 2456-2477.

Ancilotti, F., F. Mauri, E. Pescarollo. “Ion exchange resin catalyzed addition of alcohols to olefins,” *J. Catal.* 46 (1977):49-57

Ancilotti, F., F. Mauri, E. Pescarollo, L. Romagnoni. “Mechanisms in the reaction between olefins and alcohols catalyzed by ion exchange resins,” *J. Mol. Catal.* 4, 1 (1978): 37-48

Assabumrungrat, S., Kiatkittipong, W., Srivitoon, N., Praserthdam, P. and Goto, S. “Kinetics of Liquid Phase Synthesis of Ethyl *tert*-Butyl Ether from *tert*-Butyl Alcohol and Ethanol Catalyzed by Supported β-Zeolite,” *Int. J. Chem. Kinet.* 34 (2002): 292-299.

Assabumrungrat, S., Kiatkittipong, W., Praserthdam, P. and Goto, S. “Simulation of Pervaporation Membrane Reactors for Liquid Phase Synthesis of Ethyl *tert*-Butyl Ether from *tert*-Butyl Alcohol and Ethanol,” *Catal. Today* 79-80 (2003): 249-257.

Assabumrungrat, S., Wongwattanasate, D., Pavarajarn, V., Praserthdam, P., Arpornwichanop, A. and Goto, S. “Production of Ethyl tert-Butyl Ether from tert-Butyl Alcohol and Ethanol Catalyzed by β-zeolite in Reactive Distillation”, *Korean J. Chem. Eng.* 21 (6) (2004) 1139-1146.

Balcerowiak, W. “Speciation analysis of sulfonic groups of cation exchanger using thermogravimetry,” *React. Funct. Polym.* 33 (1997): 323-327

Boz, N., Dogu, T., Murtezaoglu, K., and Dogu, G. “Effect of hydrogen ion-exchange capacity on activity of resin catalysts in *tert*-amyl ethyl ether (TAEE) synthesis," *Appl. Catal. A-Gen.* 268 (2004): 175-182.

Boz, N., Dogu, T., Murtezaoglu, K., and Dogu, G. "Mechanism of TAME and TAEE Synthesis From Diffuse Reflectance FTIR Analysis," *Catal. Today* 100 (2005): 419-424.

Cao, Z., Liu, J. and Li, D. "FCC Gasoline Hydroisomerization Over Pt/HZSM-5 Catalysts," *Petrol. Sci. Technol.* 24 (2006):1027–1042.

Chauvel, A. and Lefebvre, G.; "Petrochemical Process Technical and Economic Characteristics," *Gulf Publishing Co*, (1989).

Chu, P. and Kuhl, G.H. "Preparation of Methyl *tert* -Butyl Ether (MTBE) over Zeolite Catalysts," *Ind. Eng. Chem. Res.* 26 (1987): 365-369.

Collignon, F., Loenders, R., Martens, J.A., Jacobs, P.A. and Poncelet, G. "Liquid Phase Synthesis of MTBE from Methanol and Isobutene Over Acid Zeolites and Amberlyst-15," *J. Catal.* 182 (1999): 302-312.

Colombo, F., L. Cori, L. Dallora, P. Delogu. "Equilibrium Constant for the Methyl tert-Butyl Ether Liquid-Phase Synthesis by use of UNIFAC," *Ind. Eng. Chem. Fund.*, 22, 219 (1983).

Corma, A., V. González-Alfaro and A.V. Orchillés. "The role of pore topology on the behaviour of FCC zeolite additives," *Appl. Catal. A-Gen.* 187 (1999):245-254

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

Cunill, F., Vila, M., Izquierdo, J.F., Iborra, M., and Tejero, J. "Effect of Water Presence on Methyl *tert*- Butyl Ether and Ethyl *tert*-Butyl Ether Liquid-Phase Synthesis," *Ind. Eng.Chem. Res.* 32 (1993): 564-569.

Delion, B., Torck, B., and Hellin, M. "Hydration of Isopentenes in an Acetone Environment over Ion-Exchange Resin: Thermodynamic and Kinetic Analysis," *J. Catal. 103* (1987): 177-187.

Demirbas, A. "Progress and recent trends in biofuels," *Prog. Energ. Combust. Sci.* 33 (2007): 1–18.

Dogu, T., Aydin, E., Boz, N., Murtezaoglu, K., and Dogu, G. "Diffusion Resistances and Contribution of Surface Diffusion in TAME and TAEE Production Using Amberlyst-15," *Int. J. Chem. React. Eng.* 1 (2003): ArticleA6.

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

Fite, C., Iborra, M., Tejero, J., Izquierdo, J.F. and Cunill, F. "Kinetics of the Liquid-Phase Synthesis of Ethyl tert-Butyl Ether (ETBE)," *Ind. Eng. Chem. Res.* 33 (1994): 581-591.

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

Gomez, C., Cunill, F., Iborra, M., Izquierdo, F. and Tejero, J. "Experimental Study of the Simultaneous Synthesis of Methyl *tert*-Butyl Ether and Ethyl *tert*-Butyl Ether in Liquid Phase," *Ind. Eng. Chem. Res.* 36 (1997): 4756-4762.

Gonzalez, J. C., and Fair, J.R. "Preparation of Tertiary Amyl Alcohol in a Reactive Distillation Column. 1. Reaction Kinetics, Chemical Equilibrium, and Mass-Transfer Issues.," *Ind. Eng. Chem. Res.* 36 (1997): 3833-3844 .

Habenicht, C., Kam, L.C., Wilschut, M.J. and Antal, M. J.Jr. "Homogeneous Catalysis of Ethyl *tert*-Butyl Ether Formation from *tert*-Butyl Alcohol in Hot, Compressed Liquid Ethanol," *Ind. Eng. Chem. Res.* 34 (1995): 3784-3792.

Halim, M.A.A. "The Handbook of MTBE and Other Gasoline Oxygenates," *Marcer Dekker Inc* (2004).

Harmer, M.A. and Q. Sun. "Solid acid catalysis using ion-exchange resins," *Appl. Catal. A-Gen.* 221 (2001):45-62

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

Iborra, M., Izquierdo, J.F., Cunill, F. and Tejero, J. "Application of the Response Surface Methodology to the Kinetic Study of the Gas-Phase Addition of Ethanol to Isobutene on a Sulfonated Styrene-Divinylbenzene Resin," *Ind. Eng. Chem. Res.* 31 (1992): 1840-1848.

Izqulerdo, J., Cunlil, F., Vila, M., Tejero, J. and Iborra, M. "Equilibrium Constants for Methyl *tert*-Butyl Ether Liquid-Phase Synthesis," *J. Chem. Eng. Data* 37 (1992): 339-343.

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

Jensen, K.L. and R. Datta. "Ethers from ethanol.1.Equilibrium thermodynamic analysis of the liquid-phase ethyl *tert*-butyl ether reaction," *Ind. Eng. Chem. Res.* 34(1995): 392-399.

Karinen, R.S., J.A. Linnekoski and A.O.I. Krause, "Etherification of some C_8 – alkenes to fuel ethers," *Catal. Lett.* 76 (2001): 81-87

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

Kitchaiya, P. and Datta, R. "Ethers from Ethanol. 2. Reaction Equilibria of Simultaneous *tert*-Amyl Ethyl Ether Synthesis and Isoamylene Isomerization," *Ind. Eng. Chem. Res.* 34 (1995): 1092-1101.

Linnekoshi, J.A., Rihko ,L.K. and Krause, A.O.I. "Kinetics of the Heterogeneously Catalyzed Formation of *tert*-Amyl Ethyl Ether," *Ind. Eng. Chem. Res.* 36 (1997): 310-316.

Linnekoshi, J.A., Rihko ,L.K. and Krause, A.O.I. "Etherification and Hydration of Isoamylenes with Ion Exchange Resin," *Appl. Catal. A-Gen.* 170 (1998): 117-126.

Linnekoski, J.A., Kiviranta-Paakkonen, P. and Krause, O.A. "Simultaneous Isomerization and Etherification of Isoamylenes," *Ind. Eng. Chem. Res* 38 (1999): 4563-4570.

Lippa, A.J. (2006). Software fuel volatility measurement - US Patent 7,059,313

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

Mo, K., Lora, C.O., Wanken, A.E., Javanmardian, M., Yang, N. and Kulpa, C.F.

"Biodegradation of Ethyl *tert*-Butyl Ether by Pure Bacterial Cultures," *Appl. Microbiol. Biotechnol.* 47 (1997): 69-72.

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

Oktar, N., Murtezaoglu, K.,Dogu, T., and Dogu, G. "Dynamic Analysis of Adsorption for ETBE, and TAME Production," *Can. J. Chem. Eng.* 77 (1999a):406-412.

Oktar N, Murtezaoglu K, Dogu G, Gonderten I, and Dogu T "Etherification Rates of 2-Methyl-2-Butene and 2-Methyl-1-Butene with Ethanol for Environmentally Clean Gasoline Production," *J. Chem. Technol. Biot.* 74 (2) (1999b): 155-161.

Oudshoorn, O.L., M. Janissen, W.E.J. van Kooten, J.C. Jansen, H. van Bekkum, C.M. van den Bleek, H.P.A. Calis. "A novel structured catalyst packing for catalytic distillation of ETBE," *Chem. Eng. Sci.* 54(1999): 1413-1418.

Owen, K. and Coley, T. "Automotive fuels reference book," *Society of Automotive Engineers* (1995).

Paakkonen, P.K., Struckmann L.K., Linnekoski, J.A., and Krause A.I.O. "Dehydration of the Alcohol in the Etherification of Isoamylenes with Methanol and Ethanol," *Ind. Eng. Chem.Res.* 37 (1998): 18-24.

Panneman, H.J. and Beenackers, A.A., C. M. "Synthesis of Methyl *tert*-Butyl Ether Catalyzed by Acidic Ion-Exchange Resins. Influence of the Proton Activity," *Ind. Eng. Chem. Res.* 34 (1995): 4318-4325.

Parra, D., Izquierdo, J. F., Cunill, F., Tejero, J., Fite, C., Iborra, M. and Vila M. "Catalytic Activity and Deactivation of Acidic Ion-Exchange Resins in Methyl *tert*-Butyl Ether Liquid-Phase Synthesis," *Ind. Eng. Chem. Res.* 37 (1998): 3575-3581.

Perry, R and Gee, I.L. "Vehicle emissions in relation to fuel composition," *Sci. Total Environ.* 169 (1995): 149-156.

Pescarollo, E., Trotta, .R. and Sarathy, P.R. "Etherify light gasolines," *Hydrocarbon Processing* 73 (1993): 53-60.

Rihko, L.K. and Krause, A.O.I. "Reactivity of Isoamylene with Ethanol," *Appl. Catal. A-Gen.* 101 (1993): 283-295.

Rihko, L.K. and Krause, A.O.I. "Kinetics of Heterogeneously Catalyzed *tert*-Amyl

Methyl Ether Reactions in the Liquid Phase," *Ind. Eng.* Chem. Res. 34 (1995): 1172-1180.

Rihko, L.K. and Krause, A.O.I. "Etherification of FCC Light Gasoline with Methanol," *Ind. Eng. Chem.Res.* 35 (1996): 2500-2507.

Rihko, L.K., Linnekoshi, J.A. and Krause, A.O.I. "Reaction Equilibria in the Synthesis of 2- Methoxy-2-methylbutane and 2-Ethoxy-2-methylbutane in the Liquid Phase," *J. Chem. Eng. Data* 39 (1994): 700-704.

Sahapatsombud, U., Arpornwichanop, A., Assabumrungrat, S., Praserthdam, P. and Goto, S. "Simulation of Reactive Distillation for Synthesis of tert-Amyl Ethyl Ether" *Korean J. Chem. Eng.*, 22 (2005) 387-392.

Salanitro, J.P., Diaz, L.A., Williams, M.P. and Wisniewski, H.L. "Isolation of a Bacterial Culture that Degrades MTBE," *Appl. Environ. Microbiol.* 60 (1994): 2593-2596.

Sheehan, J., Cambreco, V., Duffield, J., Garboski, M., Shapouri, H. "An overview of biodiesel and petroleum diesel life cycles," A report by US Department of Agriculture and Energy, (1998) :1–35.

Slomkiewicz, P.M. "Isomerization of C-4 alkenes catalysed by macroporous ion exchange resin." Reactive & Functional Polymers, 33 (1997): 299-304

Sola, L., Perkas, M.A., Cunill, F. and Tejero, J. "Thermodynamic and Kinetic Studies of the Liquid Phase Synthesis of *tert*-Butyl Ethyl Ether Using a Reaction Calorimeter," *Ind. Eng. Chem. Res.* 34 (1996): 3718-3725.

Stefan, R.J., McClay, K., Vaiberg, S., Condee, C.W. and Zhang, D. "Biodegradation of the Gasoline Oxygenates Methyl *tert*-Butyl Ether, Ethyl *tert*-Butyl Ether, *tert*-Amyl Ethyl Ether by Propane-Oxidizing Bacteria," *Appl. Environ. Microbiol.* 63 (1997): 4216-4222.

Syed, F.H., Egleston, C. and Datta, R. "*tert*-Amyl Methyl Ether (TAME). Thermodynamic Analysis of Reaction Equilibria in the Liquid Phase," *J. Chem. Eng. Data* 45 (2000): 319-323.

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

Ture, S., Uzun, D., Ture, I.E. “The potential use of sweet sorghum as a non-polluting source of energy” *Energy* 22 (1997):17–19.

Velo, E., Puigjaner, L. and Recasens, F. “Inhibition by Product in the Liquid-Phase Hydration of Isobutene to *tert*-Butyl Alcohol: Kinetics and Equilibrium Studies,” *Ind. Eng. Chem.Res.* 27 (1988): 2224-2231.

Vila, M. , F. Cunill, J. F. Izquierdo., J. Tejero, M. Iborra. “ Equilibrium Constants For Ethyl tert-Butyl Ether Liquid-Phase Synthesis,” Chem. Eng. Commun., 124, 223 (1993).

Yeh, C.K. and Novak, J.T. “Anaerobic Biodegradation of Gasoline Oxygenates in Soils” *Water Environ. Res.* 66 (1994): 744-752.

Zakumbaeva, G. D., A. D. Gazizova, A. V. Danilov, R. I. Egizbaeva and D. V. Sokol’skii. “Hydrorefining of catalytic naphtha cuts” Chem. Technol. Fuels Oils 43 (2007) 408-410.

Zhang, T. and Datta, R. “Ether from Ethanol. 3. Equilibrium Conversion and Selectivity Limitations in the Liquid-Phase Synthesis of Two *tert*-Hexyl Ethyl Ethers,” *Ind. Eng. Chem. Res.* 34 (1995): 2237-2246.

Zhang, T. and Datta, R. “Ether from Ethanol.5. Equilibrium and Kinetics of the Coupled Reaction Network of Liquid-Phase 3-Methyl-3-Ethoxy-Pentane Synthesis,” *Chem. Eng. Sci.* 51 (1996): 649-661.

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

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1) **Worapon Kiatkittipong**, Piyaporn Thipsunet, Shigeo Goto, Piyasan Praserthdam and Suttichai Assabumrungrat "Simultaneous enhancement of ethanol supplement in gasoline and its quality improvement" ได้รับการตอบรับเพื่อตีพิมพ์ในวารสาร Fuel Processing Technology (impact factor 2007 = 1.883)

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1) **Worapon Kiatkittipong**, Piyaporn Thipsunet, Suttichai Assabumrungrat, Shigeo Goto and Piyasan Praserthdam "Fuel oil quality improvement by etherifying FCC light gasoline with ethanol" 4th Asia Pacific Congress on Catalysis (APCAT 4), Singapore, 6-8 December, 2006 (oral presentation)

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อยู่ระหว่างการพิจารณาเพื่อตีพิมพ์

Worapon Kiatkittipong, Khamron Yoothongkham, Piyasan Praserthdam, Shigeo Goto, Choowong Chaisuk and Suttichai Assabumrungrat, "Fuel oil quality improvement and olefin reduction of FCC gasoline by etherification with ethanol" อยู่ระหว่างการพิจารณาเพื่อตีพิมพ์ในวารสาร Catalysis Letter (impact factor 2007 = 1.883)

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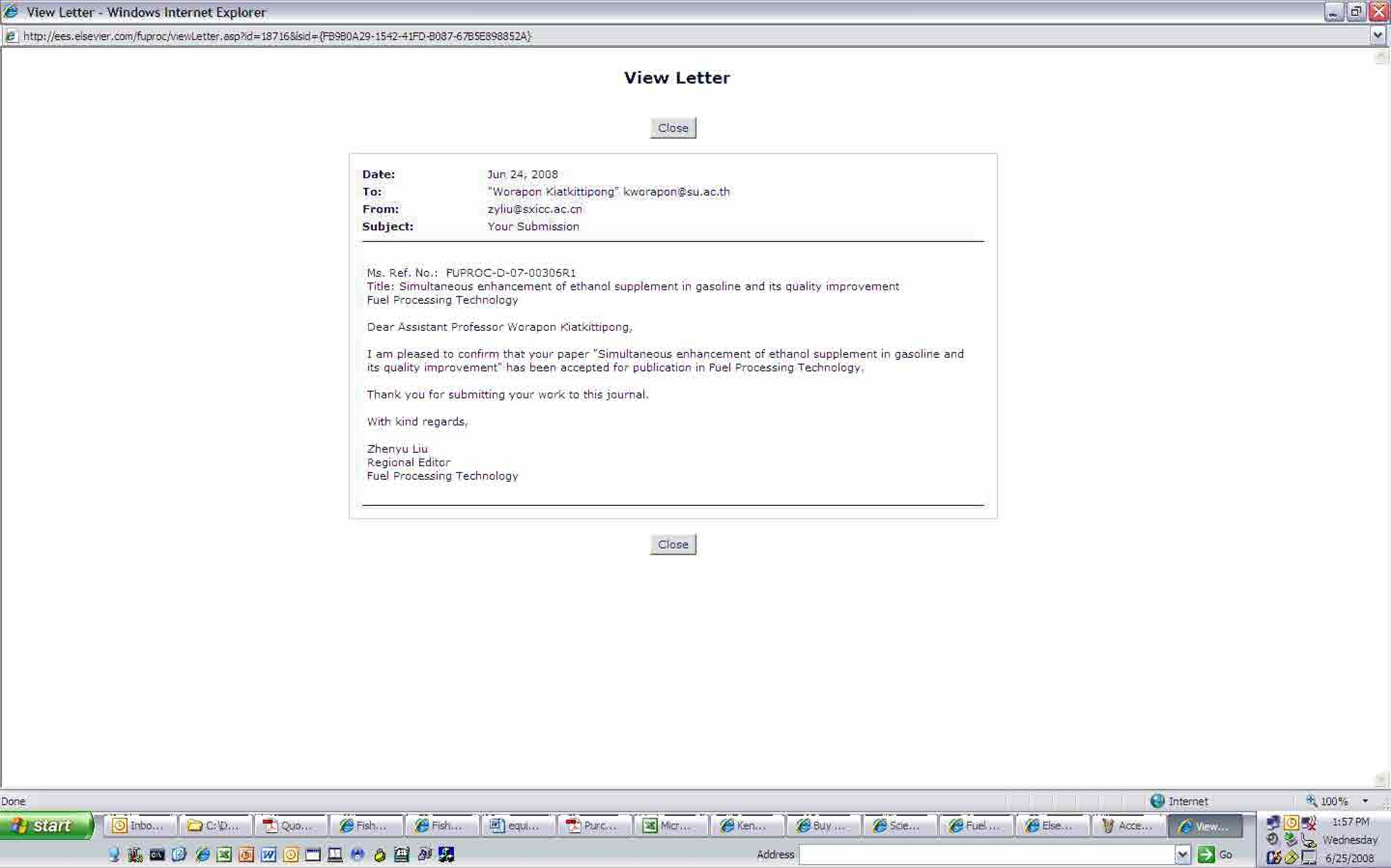

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Dear Assistant Professor Worapon Kiatkittipong,

I am pleased to confirm that your paper "Simultaneous enhancement of ethanol supplement in gasoline and its quality improvement" has been accepted for publication in Fuel Processing Technology.

Thank you for submitting your work to this journal.

With kind regards,

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Article title:	Simultaneous enhancement of ethanol supplement in gasoline and its quality improvement
Reference:	FUPROC2384
Journal title:	Fuel Processing Technology
Corresponding author:	Dr. Worapon Kiatkittipong
First author:	Dr. Worapon Kiatkittipong
Received at Editorial Office:	19 Nov 2007
Article revised:	8 Jun 2008
Article accepted for publication:	24 Jun 2008
Received at Elsevier:	24 Jun 2008
Journal publishing agreement sent to author:	26 Jun 2008
Offprint form sent to author:	26 Jun 2008
Free paper offprints supplied with this article:	25
Expected dispatch of proofs:	17 Jul 2008
Journal publishing agreement returned:	26 Jun 2008
Offprint order form returned:	26 Jun 2008
DOI information:	10.1016/j.fuproc.2008.06.007
Status comment:	At this moment it is not yet possible to give you information about the publication date. This depends on the number of articles lined up for publication in the journal. Citation information will be shown when available.

Submitted to Fuel Processing Technology

Type of Contribution: Short Communication

Simultaneous enhancement of ethanol supplement in gasoline and its quality improvement

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Abstract

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

Keywords: Fuel; FCC gasoline; ethanol; etherification; octane number; blending Reid vapor pressure

1. Introduction

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

Oxygenated compounds can be divided into two groups: 1) alcohols, e.g. methanol and ethanol, and 2) alcohol derivatives like ethers, e.g. methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME) and *tert*-amyl ethyl ether (TAEE). The etherification of methanol and C_4-C_5 alkenes has been studied relatively widely. The kinetic expression and thermodynamic equilibrium were reported for MTBE [1] and TAME [2] production. The mechanisms generally proposed for the reactions are of Langmuir-Hinshelwood type [2,3] and of Eley-Rideal type[4,5]. However, the use of MTBE has already forbidden in 25 states of USA [6,7] and many countries because it may contaminate underground water. Japan has ceased to use MTBE though official specifications continue to allow a 7% volume limit [8]. Moreover, methanol and methanol derivatives such as MTBE and TAME are not favorable in an environmental view point because they are mostly derived from natural gas whose production may contribute to global warming.

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

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

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

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

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

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

2. Experimental

2.1 Chemicals

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

2.2 Catalysts

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

2.3 Apparatus

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

2.4 Analysis

Chemical compositions of a liquid sample were analyzed by using a gas chromatograph, Shimadzu GC 14B with hydrogen flame ionization detector. The separation column was a DB-1 capillary column and He was used as a carrier gas with a flow rate of 1 cm^3 min^{-1}. The analysis was done by injecting 1 μl of sample in the column. The injector temperature and the detector temperature were set at 250 and 300

^{o}C, respectively. One ramp of the column temperature was programmed from 40 ^{o}C (isotherm during 5 min) to 260 ^{o}C with a temperature ramp rate of 10 ^{o}C min^{-1} and kept at the final temperature of 260 ^{o}C for 5 min. The standard analysis of Research Octane Number (RON), blending Reid vapor pressure (bRvp) and the distillation temperature were carried out by following the standard methods of ASTM D-2699, ASTM D-5191 and ASTM D-86, respectively.

2.5 Operation procedure

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

3. Results and Discussion

3.1 Etherification of FCC gasoline with ethanol

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

As shown in Table 5, a research octane number (RON) of original FCC gasoline was 88 which was lower than that of the specification of regular gasolines (RON = 91). FCC with direct ethanol blend in 20 and 30 vol% showed RON up to 94.8 and 97.9, respectively. However, unfortunately their bRvp also increased dramatically. It should be noted that although the bRvp value does not exceed the specification of E10, lower bRvp can be more favorable for preventing evaporative loss and vapor lock especially in hot countries. As shown in Table 5, FCCs etherified with ethanol by using both Amberlyst 16 and Beta-zeolite catalysts can effectively decrease the values of bRvp because the reactive olefins in FCC gasoline and ethanol are converted to ethers which have lower bRvp. FCC etherified with 30 vol% ethanol both catalyzed by Beta-zeolite and Amberlyst 16 give lower bRvp than FCC directed blend with 20 vol%. These results also confirm the increase of the renewability of gasoline by adding renewable energy. Comparing with original FCC gasoline, the bRvp value of etherified gasoline catalyzed by Beta-zeolite is lower or similar in the cases of using 20 and 30 vol%, respectively. These results may strongly depend on the decrease of olefins content and the amount of unrected ethanol remaining in the solution.

Comparing the RON between ethanol direct blended and etherified gasolines, the gasoline etherified by Amberlyst 16 shows slightly lower octane number than FCC with direct ethanol blend because ethanol has higher value of octane number (RON = 118) than ethers, i.e., ETBE (RON = 118), TAEE (RON = 105), *tert*-hexyl-ethyl-ether (THEE) (RON = 110). However, etherified gasoline catalyzed by Beta-zeolite shows similar RON to that of ethanol direct blended gasoline and slightly higher than that of etherified gasoline catalyzed by Amberlyst 16. It should be noted that β-zeolite gave higher value of octane number, probably due to the possible isomerization and some aromatizations. The percentages of the olefins reduction were 33.6 and 45.7% in the cases of Amberlyst 16 and β-zeolite, respectively. The remaining olefins were lower than that of the Euro III standard limitation of 18 vol%. It can be concluded that β-zeolite is a more suitable catalyst for the etherification of FCC gasoline with ethanol compared to Amberlyst 16.

For other gasoline properties, the density and the viscosity of the etherified gasoline are close to those of the commercial gasohol. The distillation curves from

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

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

4. Conclusion

The simultaneous operation for FCC gasoline quality improvement and supplement by ethanol was investigated in the heterogeneous catalytic system. Although direct ethanol blend could improve RON of gasoline, bRvp of blending gasoline increased significantly. Etherified FCC gasolines with ethanol increased RON comparably or slightly lower than FCC with direct ethanol blend while bRvp was effectively lower. Therefore, FCC etherification with ethanol gave a higher potential for utilization of ethanol as a fuel extender than direct blending for conventional engine which was limited at some ethanol contents, i.e., 10 vol% (E10). Comparing between two catalysts, it was reported that β-zeolite was a more suitable catalyst for the etherification of FCC gasoline with ethanol because it offered products with higher RON and ethanol conversion with lower bRvp.

Acknowledgement

Financial supports from the Thailand Research Fund and Commission on Higher Education are gratefully acknowledged. The authors also gratefully acknowledged the technical supports from Thai Oil Public Company Limited.

References

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

[31] O. Boonthamtirawuti, W. Kiatkittipong, S. Assabumrungrat, A. Arpornwichanop, P. Praserthdam, Kinetics of liquid phase synthesis of tert-amyl ethyl ether from tert-amyl alcohol and ethanol over Amberlyst 16. J. Ind. Eng. Chem. (2008) Article in press.

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

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

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

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

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

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

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

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

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

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

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

Figure Captions

Figure 1. Schematic diagram of the experimental apparatus.

Figure 2. Distillation curves from ASTM D-86 tests.

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Table 1. Compositions of FCC gasoline in volume percent.

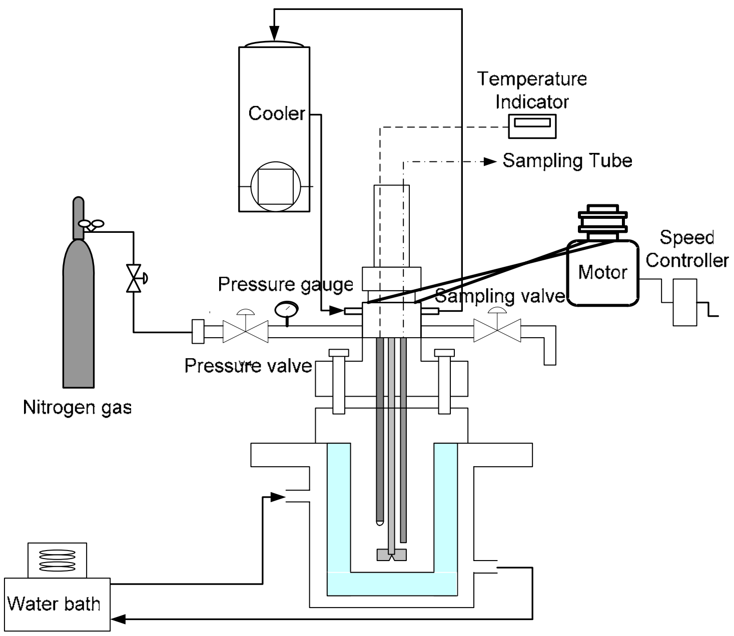
Carbon number	*n*-paraffins	*i*-paraffins	olefins	naphtenes	aromatics	Total
C4	0.435	0.268	1.976	0	0	2.679
C5	1.054	8.109	8.739	0.112	0	18.014
C6	0.816	7.759	6.856	1.821	0.333	17.584
C7	0.766	0.18	6.097	3.023	2.373	18.439
C8	0.932	4.805	1.129	3.737	4.979	15.582
C9	0.28	3.991	0.655	2.522	4.944	12.391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

Table 2. Physical properties of catalysts.

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

Table 3. Comparison of gasoline properties.

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



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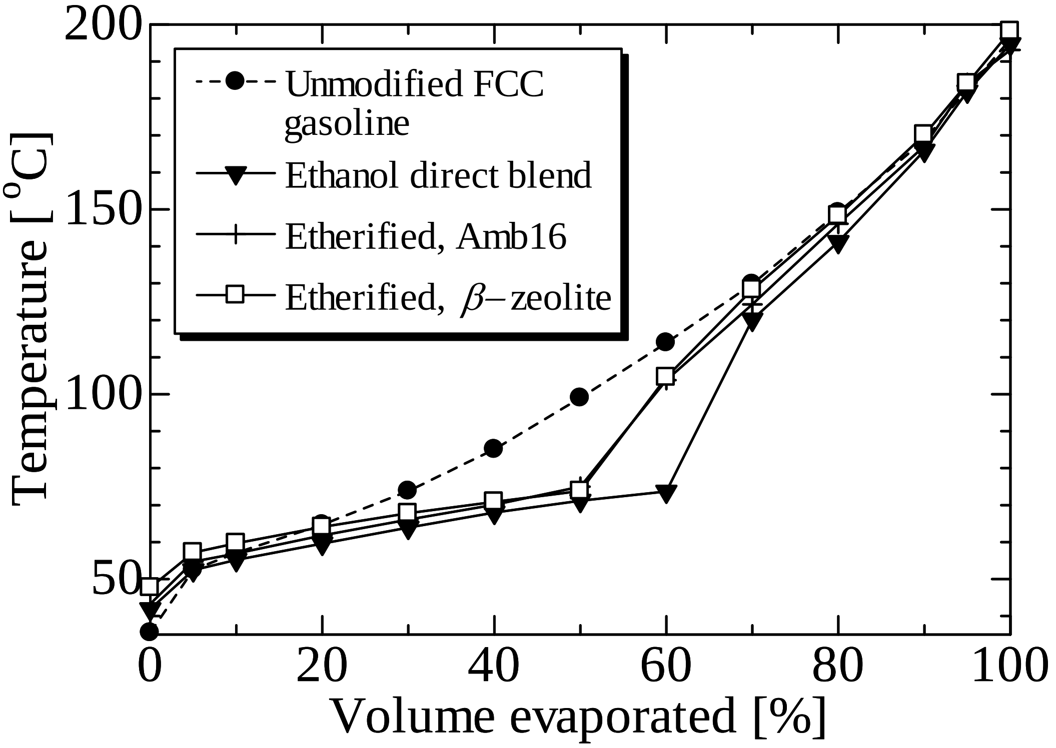

Figure 2. Distillation curves from ASTM D-86 tests.

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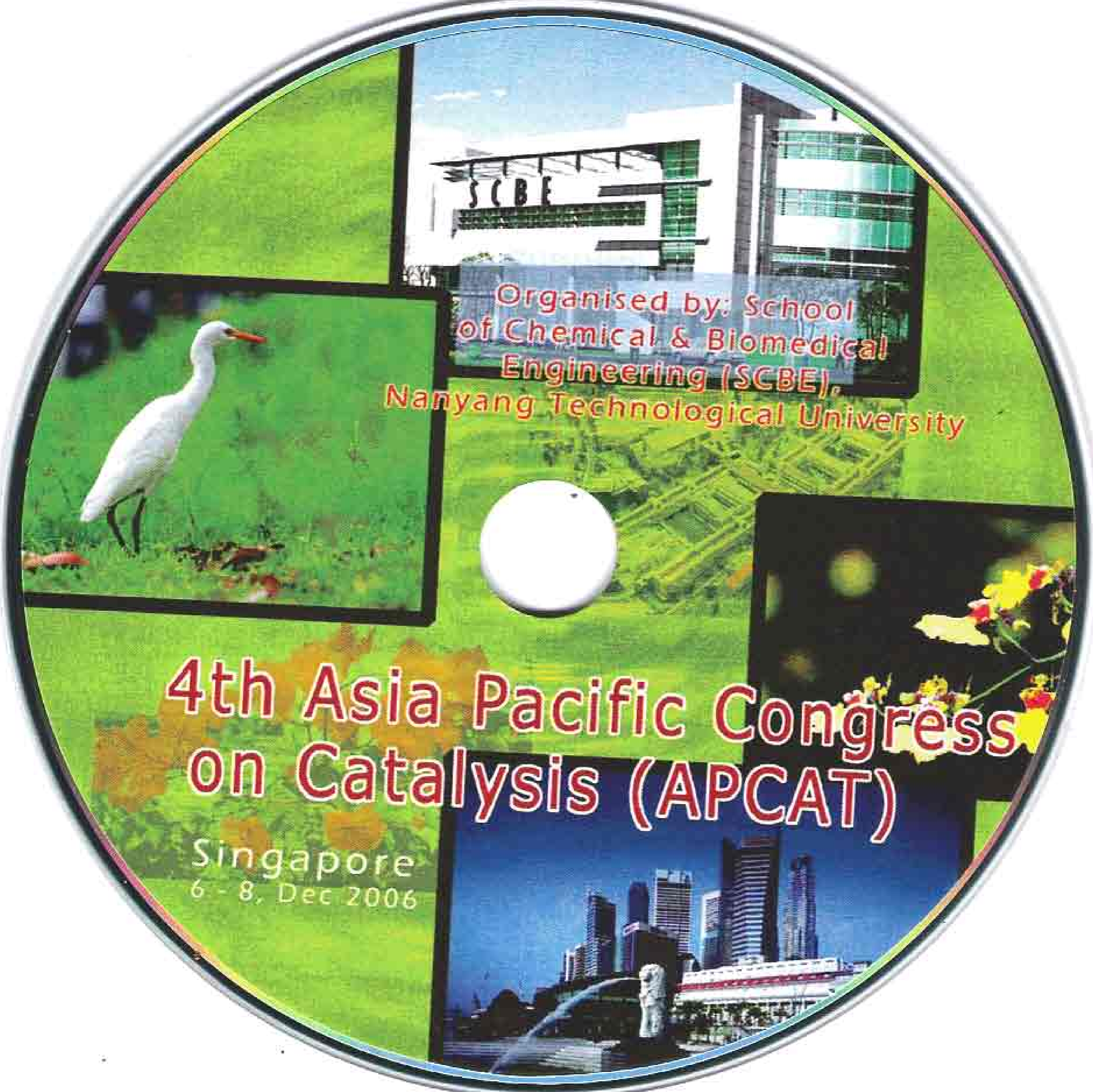

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4th Asia Pacific Congress on Catalysis (APCAT)

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Fuel oil quality improvement by etherifying FCC light gasoline with ethanol

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ABSTRACT

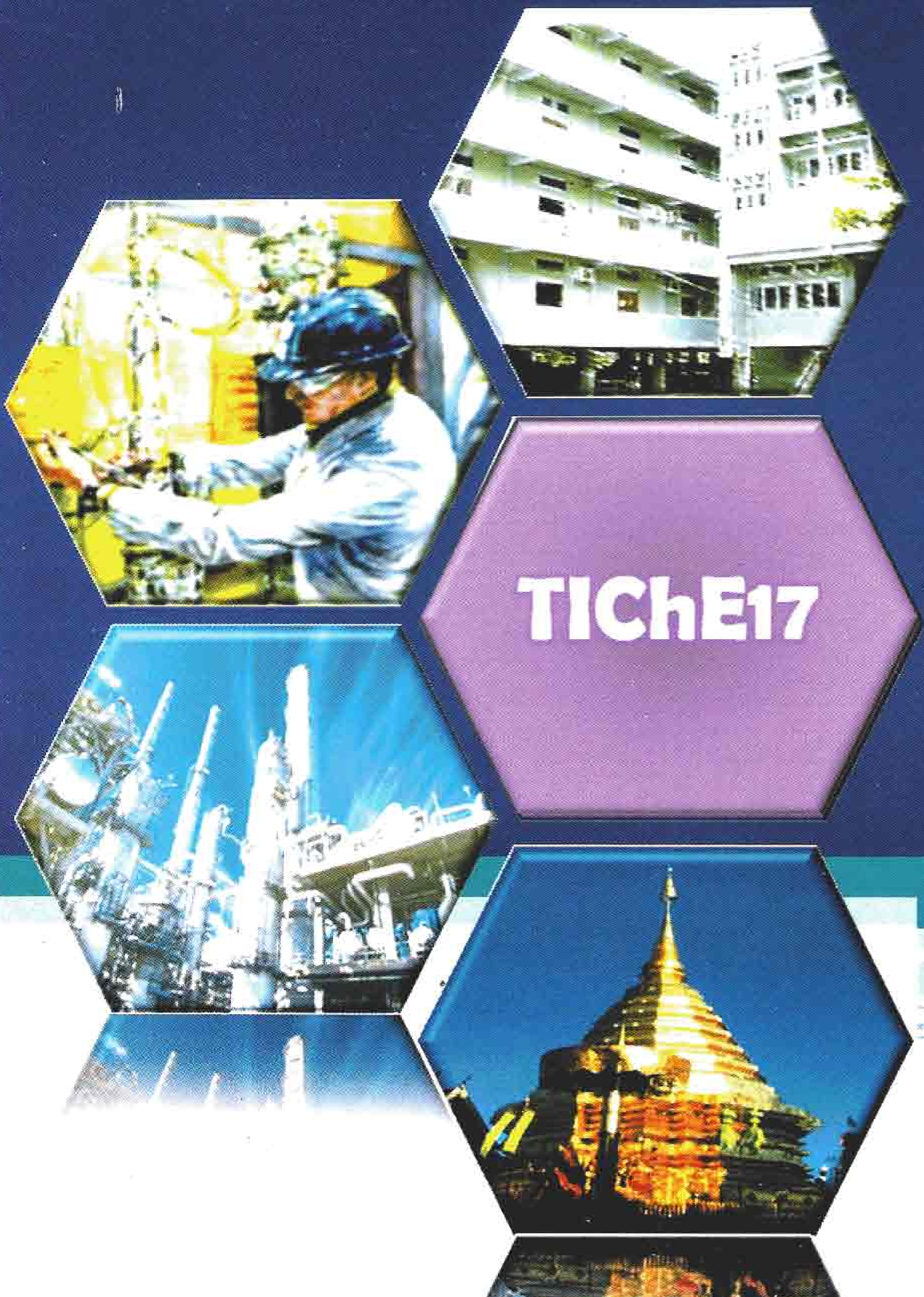
Ethanol and ethanol derivatives are the main renewable resources and nowadays are very interesting. Even though, ethanol can be blended direct into gasoline (called "gasohol") and is mostly fashionable, the overall air pollutant emissions from using gasohol are higher than those from using conventional gasoline because of its high blending Reid vapor pressure (bRvp). Ethanol-gasoline also undergoes a phase separation on contact with water which increases the corrosion of steel underground storage tanks, increasing the risk of leakage to surrounding soils. It increases the solubility of the more hazardous, monoaromatic constituents of gasoline such as BTEX and also inhibits their biodegradation. Ethers derived from ethanol may overcome these drawbacks. Direct etherification of FCC light gasoline with ethanol was investigated. The reactions were carried out in a pressurized liquid phase reactor at 8 bar with various commercial catalysts i.e., Beta-zeolite, Amberlyst 15 and Amberlyst 16. Typically, the reactive olefins available in FCC light gasoline are mainly in range of C_5 to C_7 compounds. *tert*-Amyl-ethyl-ether (TAEE) produced from isoamylene (IA), C_5 reactive olefins, and ethanol are the main reaction. The bRvp of etherified FCC gasoline was lower than gasohol when adding with the same amount of ethanol, therefore, the gasoline from this process is more suitable than gasohol especially for the tropical zone or in summer. The water solubility is also lower,

reducing the possibility for polluting underground water. However, the octane number of etherified FCC gasoline was slightly lower than that of the gasohol. It should be noted that this method gives a higher potential to use ethanol than direct blend for conventional engine which was limited with some ethanol content. The relatively small amount of unreacted ethanol could be left in gasoline as octane enhancer without the problems.

Acknowledgements

The authors gratefully acknowledged the supports from the Comission on Higher Education, The Thailand Research Fund (TRF) and Thai Oil Public Company Limited.

การประชุมวิชาการวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย ครั้งที่ 17



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การปรับปรุงคุณภาพน้ำมันเชื้อเพลิงที่ได้จากกระบวนการฟูอิไดซ์คะตาไลติกแครกกิ้งและการเพิ่มความสามารถในการใช้พลังงานทดแทนด้วยเอทานอล

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คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย กรุงเทพมหานคร 10330

1. บทนำ

น้ำมันเชื้อเพลิงที่ได้จากกระบวนการฟูอิไดซ์คะตาไลติกแครกกิ้ง (FCC แก๊สโซลีน) จะมีโอเลฟินส์อยู่ในปริมาณมาก ซึ่งจะส่งผลเสียต่อสิ่งแวดล้อม งานวิจัยในปัจจุบันโดย Fan และคณะ [1,2] มุ่งเน้นการลดปริมาณโอเลฟินส์ใน FCC แก๊สโซลีนด้วยปฏิกิริยาเกิดไอโซเมอร์ (isomerization) และการเกิดสารอะโรมาติกส์ (aromatization) โดยทั้งสองปฏิกิริยาสามารถชดเชยค่าออกเทนที่สูญเสียไปจากปริมาณโอเลฟินส์ที่ลดลงได้ อย่างไรก็ตามปริมาณ NOx เบนซีน และความว่องไวของก๊าซไอเสียจะเพิ่มขึ้นเมื่อมีปริมาณสารอะโรมาติกส์ในน้ำมันเพิ่มขึ้น และในปัจจุบันก็มีความพยายามที่จะลดปริมาณสารอะโรมาติกส์ในน้ำมันลง อีกทั้งการพัฒนาคุณภาพด้วยวิธีที่กล่าวมายังไม่เกิดการชดเชยการใช้เชื้อเพลิงประเภทฟอสซิลด้วยพลังงานทดแทนแต่อย่างใด งานวิจัยนี้เป็นการศึกษาการใช้พลังงานทดแทนเพื่อปรับปรุงคุณภาพน้ำมันเชื้อเพลิงโดยใช้เอทานอลทำปฏิกิริยาการผลิตอีเทอร์ (Etherification) กับ FCC gasoline และเปรียบเทียบคุณภาพเชื้อเพลิงที่ได้กับการผสมเอทานอลโดยตรงในน้ำมันเชื้อเพลิง (น้ำมันแก๊สโซฮอล์) ที่ใช้อยู่ในปัจจุบัน

2. อุปกรณ์และวิธีการทดลอง

2.1. สารเคมี

FCC gasoline, เอทานอล, ตัวเร่งปฏิกิริยาAmberlyst 16 และ β-zeolite (Si/Al = 40)

2.2 วิธีการทดลอง

ขั้นตอนแรกศึกษาหาตัวเร่งปฏิกิริยาที่เหมาะสมโดยใช้ Amberlyst 16 และ β-zeolite ในปริมาณ 10 กรัม ทำการทดลองที่อุณหภูมิ 343 K ความดัน 0.8 MPa อัตราส่วน FCC gasoline ต่อ เอทานอล 80:20 โดยปริมาตร ต่อมาศึกษาผลของอุณหภูมิต่อปฏิกิริยา 333, 343, 353 K ความดัน 0.8 MPa ใช้เวลาในการทำปฏิกิริยาทั้งหมด 12 ชั่วโมง ใช้ถังปฏิกรณ์แบบแบชน์ขนาด 100 มิลลิลิตร

2.3 การวิเคราะห์ผล

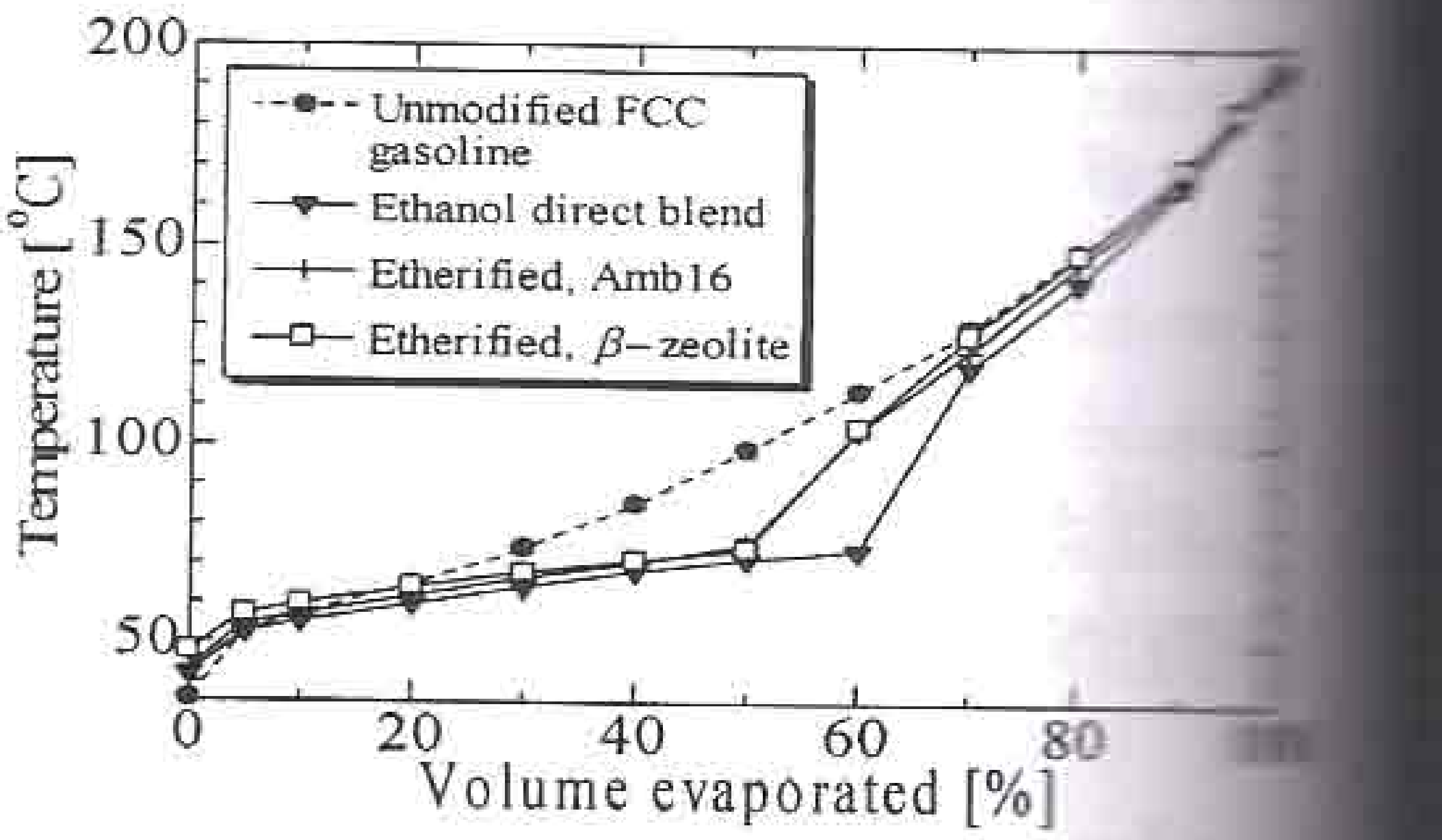
ในการวิเคราะห์จะใช้ syringe ดึงตัวอย่าง ปริมาณ 1 ไมโครลิตร แล้วฉีดวิเคราะห์ด้วยแก๊สโครมาโทกราฟฟี (shimadzu GC 8A)

3. ผลการทดลองและวิจารณ์ผล

ผลการทดลองเมื่อนำเอทานอลบริสุทธิ์มาทำปฏิกิริยาอีเทอริ กับ FCC gasoline ได้ว่าอัตราส่วนโดยปริมาตรของเอทานอลต่อ gasoline ที่เหมาะสมเป็น 20:80 อุณหภูมิ 343 K ความดัน 0.8 ตัวเร่งปฏิกิริยาที่ใช้ คือ Amberlyst 16 และ β-zeolite ซึ่งได้ ทดลองแสดงดังตารางที่ 1

ตารางที่ 1 คุณสมบัติของน้ำมันเชื้อเพลิงที่ได้จากกระบวนการต่าง

ประเภท / คุณสมบัติ	FCC gasoline	Commercial gasohol (E 10)	FCC with ethanol direct blend	Etherified
				Amberlyst 16
RON	88	95	94.8	93
bRvp (psia)	6.5	<9	7.44	7.05
Density (g/cm3)	0.6828	0.7485	0.7346	0.7388
Viscosity (x 10^{6} gf-s/cm^{2})	6.2125	5.1532	6.3253	5.3743
Ethanol conversion (%)	-	-	-	29.26



รูปที่ 1 distillation curve โดยมาตราฐาน ASTM 86 ของ การผสมลงไปโดยตรง, และการนำมาทำปฏิกิริยากับตัวเร่ง Amberlyst 16 และ β-zeolite

จากตารางที่ 1 จะพบว่าค่าออกเทนของ FCC gasoline ทำการปรับปรุงคุณภาพโดยการผสมลงไปโดยตรง หรือ ปฏิกิริยา ให้ค่า ออกเทนที่สูงขึ้นและมีค่าใกล้เคียงกับเชื้อ อยู่ในปัจจุบัน แต่พบว่าค่าความดันไอของน้ำมันที่มาจากกา

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*Corresponding author: one1_neung1@hotmail.com, [illegible]ความดันไอที่ต่ำกว่า และเมื่อพิจารณาจากค่าความ[illegible]แน่นของน้ำมันเชื้อเพลิงที่ได้ก็มีค่าใกล้เคียงกับ[illegible]ในท้องตลาด โดยสำหรับตัวเร่งปฏิกิริยาที่เป็น β-[illegible]การเปลี่ยนของปฏิกิริยาที่ดีกว่า Amberlyst 16 [illegible]ถึงผลของอุณหภูมิต่อการทำปฏิกิริยานั้นพบว่า ที่[illegible] 343, 353 K นั้นมีค่าการเปลี่ยนของเอทานอลเป็น [illegible] 46.77% ซึ่งสอดคล้องกันกับปฏิกิริยานี้ที่เป็นปฏิกิริยา[illegible] สำหรับรูปที่ 1 นั้นแสดงกราฟอุณหภูมิการกลั่น[illegible]เอทานอลเพิ่มขึ้นนั้นจะทำให้จุดเดือดของน้ำมัน[illegible]เพิ่มขึ้น โดยตัวเร่งปฏิกิริยาทั้งสองนั้นให้ค่าจุดเดือดที่[illegible]านอลลงไปโดยตรงซึ่งบอกได้ว่ามีเอทานอลเหลืออยู่[illegible]พิจารณาที่ตัวเร่งปฏิกิริยา β-zeolite ที่จุด T10 และ[illegible]จุดเดือดที่ต่ำกว่าซึ่งสอดคล้องกับค่าการเปลี่ยนของเอทา[illegible] นั้นมีค่าสูงกว่า Amberlyst 16 โดยค่า T10, T50 และ[illegible]นำไปใช้ ในการคำนวณหา ดัชนีความสามารถในการติด[illegible]ability Index) ดังนั้นการนำเอทานอลมาทำปฏิกิริยานั้น[illegible]ที่เป็นมิตรกับสิ่งแวดล้อมและเพิ่มประสิทธิภาพใน[illegible]มาใช้ในน้ำมันเชื้อเพลิง ซึ่งได้น้ำมันเชื้อเพลิงที่มี[illegible]ต้องกับท้องตลาดและมีผลดี

[illegible]ทดลอง

[illegible]ทดลองพบว่าการนำ FCC gasoline มาทำปฏิกิริยากับเอทา[illegible] จะทำให้ได้คุณภาพของน้ำมันเชื้อเพลิงดีขึ้นและเป็นการ[illegible]ใช้ได้มากขึ้น สำหรับในการทดลองหาตัวเร่งปฏิกิริยาที่[illegible]ปฏิกิริยานี้ คือ β-zeolite ซึ่งให้ค่าการเปลี่ยนและคุณสมบัติ[illegible]ว่า Amberlyst 16 อุณหภูมิ 343 K ความดัน 0.8 MPa.

[illegible]ประกาศ

[illegible]คุณสำนักงานกองทุนสนับสนุนการวิจัย (สกว.) และ[illegible]กรรมการการอุดมศึกษา (สกอ.) สำหรับทุนวิจัย รวมทั้ง[illegible] เกียรติกิตติพงศ์ รศ.ดร. สุทธิชัย อัสสะบำรุงรัตน์ สำหรับ[illegible]ยิ่ง และบริษัทไทยออยล์ จำกัด(มหาชน) ที่ได้[illegible]ตัวอย่าง FCC gasoline ในการศึกษาวิจัยครั้งนี้

[illegible]อ้างอิง

[illegible] Bao X., Shi G., Wei W. and Xu J "Olefin reduction of [illegible] gasoline via hydroisomerization aromatization over modified [illegible]HZSM-5/Hβ composite carriers," *Appl. Catal. A*. 275, [illegible] (2004)

[illegible] Bao X., Lei D., Shi G. Wei W and Xu J "A Novel [illegible] System Based on Quadruple Silicoaluminophosphate and [illegible]silicate Zeolites for FCC Gasoline Upgrading," *Fuel*, 84, [illegible] (2005)

[3] Andrezej Wyczesany(1995), *Chemical Equilibria in the process of Etherification of Light FCC Gasoline with Methanol*, Ind. Eng. Chem Res. 34, 1320-1326.

[4] Hosokawa; Katsumi Kaneko, all of Japan, Patent Number, US 4,499,313

[5] Dow Chemical; "Dowex - Ion Exchanger," Dow Chemical (1958). Guibet J. and Faure-Birchem E.; "Fuels and engines," Paris: Editions Technip (1999).

[6] Halim, M.A.A.; "The Handbook of MTBE and Other Gasoline Oxygenates," Marcer Dekker, Inc, (2004).

[7] Kitchaiya, P. and Datta, R.; "Ethers from Ethanol. 2. Reaction Equilibria of Simultaneous tert-Amyl Ethyl Ether Synthesis and Isoamylene Isomerization,"Ind. Eng. Chem. Res., 34, 1092-1101 (1996).

[8] Linnekoski, J.A., Kiviranta-Paakkonen, P. and Krause, O.A.; "Simultaneous Isomerization and Etherification of Isoamylenes," Ind. Eng. Chem. Res, 38, 4563-4570 (1999).

[9] Mizrahi, S., Tabak S.A., Sorensen C.M. "Etherification of gasoline," European patent EP 0451989, 1991

[10] Kiviranta-Paakkinen, P., Struckmann L.K., Linnekoski, J.A., and Krause A.I.O.; "Dehydration of the Alcohol in the Etherification of Isoamylenes with Methanol and Ethanol," Ind. Eng. Chem.Res., 37, 18-24 (1998).

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

[12] Pescarollo, Trotta R. and Sarathy P.R. "Etherify light gasolines," Hydrocarbon Process., 73, 53-60 (1993).