การปรับปรุงคุณภาพน้ำมันเชื้อเพลิงที่ได้จากกระบวนการฟลูอิไดซ์คาตาไลติกแครกกิ้งด้วยเอทานอลโดยปฏิกิริยาอีเทอริฟิเคชัน

นางสาวปิยพร ทิพย์สุเนตร

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IMPROVEMENT OF FUEL OIL FROM FLUIDIZED CATALYTIC CRACKING UNIT WITH ETHANOL BY ETHERIFICATION REACTION

Miss Piyaporn Thipsunet

A Thesis Submitted in Partial Fulfillment of the Requirements
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ปิยพร ทิพย์สุเนตร: การปรับปรุงคุณภาพน้ำมันเชื้อเพลิงที่ได้จากกระบวนการฟลูอิไดซ์คาตาไลติกแครกกิ้งด้วยเอทานอลโดยปฏิกิริยาอีเทอริฟิเคชัน (IMPROVEMENT OF FUEL OIL FROM FLUIDIZED CATALYTIC CRACKING UNIT WITH ETHANOL BY ETHERIFICATION REACTION) อ. ที่ปรึกษา : รศ. ดร. สุทธิชัย อัสสะบำรุงรัตน์, อ. ที่ปรึกษาร่วม : ผศ. ดร. วรพล เกียรติกิตติพงษ์, 90 หน้า

งานวิจัยนี้เกี่ยวข้องกับการปรับปรุงคุณภาพของน้ำมันเชื้อเพลิงด้วยปฏิกิริยาอีเทอริฟิเคชันโดยตรงของน้ำมันที่ได้จากกระบวนการฟลูอิไดซ์คาตาไลติกแคร้กกิ้งด้วยเอทานอล ที่อุณหภูมิ 343 เคลวิน ในเครื่องปฏิกรณ์แบบอัดความดัน ภายใต้ความดัน 0.8 เมกะปลาสคาล โดยใช้เบต้า-ซีโอไลท์และแอมเบอร์ลิส 16 เป็นตัวเร่งปฏิกิริยา โดยทั่วไปสารโอเลฟินส์ที่ว่องไวในน้ำมันที่ได้จากกระบวนการฟลูอิไดซ์คาตาไลติกแคร้กกิ้งมีจำนวนคาร์บอนอยู่ในช่วง 5-7 อะตอมเป็นส่วนใหญ่ จากผลการทดลองแสดงให้เห็นว่า น้ำมันที่ผ่านการทำปฏิกิริยาอีเทอริฟิเคชันแล้ว จะมีค่าความดันไอของสารผสมน้อยกว่าแก๊สโซฮอล์ ซึ่งชี้ให้เห็นว่าน้ำมันที่ผ่านกระบวนการดังกล่าวมีความเหมาะสมสำหรับการใช้ในประเทศเขตร้อนหรือในช่วงฤดูร้อนมากกว่าแก๊สโซฮอล์ แต่น้ำมันดังกล่าวมีค่าออกเทนต่ำกว่าแก๊สโซฮอล์เล็กน้อย เมื่อพิจารณาถึงตัวเร่งปฏิกิริยา พบว่าเบต้า-ซีโอไลท์ เหมาะสมกับปฏิกิริยานี้มากกว่าแอมเบอร์ลิส 16 เนื่องจากให้ค่าออกเทนและค่าการเกิดของอีเทอร์ที่สูงกว่า รวมถึงให้ค่าความดันไอของสารผสมที่ต่ำกว่า ดังนั้นจึงนำตัวเร่งปฏิกิริยาเบต้า-ซีโอไลท์มาศึกษาถึงผลของอุณหภูมิดำเนินการที่มีต่อปฏิกิริยาอีเทอริฟิเคชันโดยตรงของน้ำมันที่ได้จากกระบวนการฟลูอิไดซ์คาตาไลติกแคร้กกิ้งด้วยเอทานอล โดยใช้เครื่องปฏิกรณ์เดิม ที่อุณหภูมิ 333, 343 และ 353 เคลวิน จากผลการศึกษาพบว่าเมื่ออุณหภูมิดำเนินการสูงขึ้น ค่าการเกิดและค่าผลได้จะมีค่าลดลงที่สมดุลย์ นอกจากนี้ได้นำเอทานอลที่อะซีโอโทรปทำปฏิกิริยากับน้ำมันที่ได้จากกระบวนการฟลูอิไดซ์คาตาไลติกแคร้กกิ้ง เพื่อศึกษาถึงปฏิกิริยาอีเทอริฟิเคชันและปฏิกิริยาไฮเดรชันที่เกิดขึ้น โดยใช้แอมเบอร์ลิส 16 เป็นตัวเร่งปฏิกิริยา ซึ่งพบว่าปริมาณน้ำที่ผสมอยู่ในสารป้อนส่งผลให้ค่าการเกิดและค่าผลได้สำหรับปฏิกิริยาอีเทอร์ริฟิเคชันลดลง

ภาควิชา.....วิศวกรรมเคมี.............
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ปีการศึกษา.......2549...................

ลายมือชื่อนิสิต.....ปิยพร ทิพย์สุเนตร.....
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ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....................

4870381421 : MAJOR CHEMICAL ENGINEERING
KEY WORD : FCC GASOLINE/ ETHANOL/ ETHERIFICATION/ HYDRATION/ OCTANE NUMBER/ BLENDING REID VAPOR PRESSURE

PIYAPORN THIPSUNET : IMPROVEMENT OF FUEL OIL FROM FLUIDIZED CATALYTIC CRACKING UNIT WITH ETHANOL BY ETHERIFICATION REACTION. THESIS ADVISOR: ASSOC. PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., THESIS COADVISOR: ASSIST. PROF. WORAPON KIATKITTIPONG, D.Eng., 90 pp.

This thesis concerns the fuel oil quality improvement by the direct etherification of FCC gasoline with ethanol. The reactions 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 experimental results showed that the bRvp of etherified FCC gasoline was lower than that of gasohol whereas the octane number is slightly 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. It was found that Beta-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 ethanol conversion with lower bRvp because some isomerization also occurred without aromatization to benzene. Therefore, Beta-zeolite was further investigated to determine the effect of operating temperature by using the same reactor at three temperature levels of 333, 343 and 353 K. It was observed that the etherification conversions and ether yields decreased with the increasing temperature. In addition, the azeotropic ethanol was used to study for the etherification and the hydration of FCC gasoline over Amberlyst 16. The presence of water in the ethanol azeotropic mixture caused a drop in the etherification conversion and ether yield.

Department ....Chemical Engineering......	Student's signature Piyaporn Thipsunet
Field of Study ..Chemical Engineering.....	Advisor's signature ....
Academic year ....2006...............	Co-advisor's signature........................

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NOMENCLATURE

N_{EtOH}	number of moles of ethanol	[mole]
$N_{\mathrm{EtOH,0}}$	number of initial moles of ethanol	[mole]
$N_{\mathrm{H_2O}}$	number of moles of water	[mole]
$N_{\mathrm{H_2O,0}}$	number of initial mole of water	[mole]
N_{IA}	number of moles of isoamylenes	[mole]
$N_{\mathrm{IA,0}}$	number of initial moles of isoamylenes	[mole]
N_{TAA}	number of moles of TAA	[mole]
N_{TAEE}	number of moles of TAEE	[mole]

Subscripts

approx	approximately

Abbreviations

2M1B	2-methyl-1-butene
2M2B	2-methyl-2-butene
bRvp	blending Reid vapor pressure
CO	carbon monoxide
CSTR	continuous stirred tank reactor
DI	Driveability Index
DVB	divinylbenzene
ETBE	ethyl tertiary butyl ether
EtOH	ethyl alcohol
FCC	Fluidized Catalytic Cracking
FBP	final boiling point
H_2O	water
IA	isoamylene
IB	isobutene

IBP	initial boiling point
MeOH	methanol
MON	motor octane number
MTBE	methyl tertiary butyl ether
RON	research octane number
Rvp	Reid vapor pressure
SBU’s	secondary building units
TAA	*tert*-amyl alcohol
TAEE	*tert*-amyl ethyl ether
TAME	*tert*-amyl methyl ether
TBA	*tert*-butyl alcohol
TEL	tretraethyl lead
THEE	*tert*-hexyl ethyl ether
VOCs	volatile organic compounds

CHAPTER I

INTRODUCTION

In 1990, due to the increasing of an awareness on environment problems, the Clean Air Act has set up the program to solve an air quality problem in the areas failed to attain the national ambient air quality standards (NAAQSs) for carbon monoxide (CO) and ozone (O_3). The restriction of the use of lead-containing engine knock suppressing additive and decreasing of benzene content below 1 vol% and total aromatics below 25 vol% make fuel octane number effectively drop off. The oxygenate fuel was introduced as octane enhancer to compensate the octane depletion and also to meet the demand of oxygen content in reformulated gasoline of at least 2 wt% for improving combustion efficiency, thereby reducing CO content and hydrocarbon emission from exhaust pipe. From this program, an approach on using oxygenated in the reformulated gasoline has been used on widespread scale rapidly.

Oxygenate compounds can be divided into two groups: alcohols, e.g. methanol (MeOH) and ethanol (EtOH), and their derivative ethers, e.g. methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME) and tertiary amyl ethyl ether (TAEE). MTBE was synthesized from methanol and isobutylene (IB) that it was introduced as gasoline additives in 1979 and are currently the most frequently used as a gasoline additive. However, MTBE is forbidden to use in USA, Japan and many countries because it can be contaminated in 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). As a substitute for MTBE, heavier tertiary ether, tert-amyl methyl ether (TAME) has already been used as octane enhancer. Both MTBE and TAME can be derived from the reaction of methanol with isobutene (IB) and isoamylenes (IA), respectively. In addition, 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 and TAME are not favorable in an environmental view point because their contribution on a global warning potential.

Ethanol is one of the most widely used as a renewable liquid fuel for solving the global climate change and oil crisis and may be the most potential utilization of existing infrastructure, i.e., road, gas station and vehicles. 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 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 Melone, 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). An ethanol-gasoline mixture also undergoes a phase separation on contact with water which increases the corrosion of steel underground storage tanks, increasing the risk of leakage to surrounding soil. Even though ethanol/gasoline (gasohol) can tolerate significantly higher water content than conventional gasoline before phase separation, the problem on the engine is more serious. Ethanol partitions preferentially into an aqueous phase and therefore leading the gasoline off spec. Combustion of this partition makes the lean burn effects (French and Melone, 2005). Refiners and auto-makers prefer to use ethers to meet the octane number and oxygenate requirement for technical reasons because ethers can overcome the drawback of gasoline with direct ethanol blend. The most well-known ethanol derivatives ethers are ETBE and TAEE. Commercially, ETBE and TAEE can be produced by etherification of ethanol with isobutene (IB) and isoamylene (IA), olefinic compounds, respectively.

Alternative routes for their 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; Kiatkittipong et al., 2003; Aiouache and Goto 2003a, b). 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 light 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 20 vol% as regulated by the International charter on clean fuels. Pescarollo et al. (1993) studied etherifying the entire light FCC gasoline with methanol. Simultaneous improvements in octane number and gasoline volume with reducing olefinicity, atmospheric reactivity and bRvp of gasoline were obtained.

However, very limited works focused on direct etherify FCC light gasoline with ethanol which is more environmental friendly process.

In this study, the process was investigated by etherifying the entire FCC gasoline with ethanol catalyzed by commercial catalysts. It was expected to gives a gasoline quality improvement with higher potential to use ethanol as fuel extender than direct blend for conventional engine which was limited with some ethanol content, i.e., 10 vol% (E10). The objectives of the study were to

1. screen the suitable catalyst for the etherification of FCC gasoline with ethanol.
2. compare the fuel characterizations such as octane number, blending Reid vapor pressure (bRvp) and distillation curve of FCC etherified gasoline and FCC direct ethanol blended with gasohol (E10) commercial fuel.

3. study the effect of operating conditions such as operating temperature and water content in the feed study on the reaction performance.

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. Some detail gasoline properties (octane number, bRvp and distillation temperature), oxygenates compound, FCC gasoline and catalysts (ion exchange resin and zeolite) 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. If an engine running on a particular gasoline makes such noises, they can be lessened or eliminated by using a gasoline with a higher octane number. 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. Under this system a regular grade gasoline has an octane number of about 87 and a premium grade of about 93. Most American-made cars that were built in the 1971 model year or later can use regular gasoline. To prevent knocking, premium grade gasoline must be used in many cars built before 1971 and in some new cars that have high-performance engines.

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. Its units are kilopascals, corrected to one atmosphere (101.3 kPa). For volatile petroleum products, vapor pressure is used as an indirect measure of evaporation rate. Vapor pressure can be measured by a variety of methods including Reid, dynamic, static, isoteniscopic, vapor pressure balance, and gas saturation. The most commonly used method for crude oils was the Rvp, as determined by ASTM method D 323 - Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method), (ASTM, 1996a). This test method determines 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). It is measured by saturating a known volume of oil in an air chamber of known volume and measuring the equilibrium pressure which is then corrected to one atmosphere (101.3 kPa).

2.1.3 Distillation Temperature

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 of around 170^{o}C from the initial boiling point (IBP) to the final boiling point (FBP). The temperature range over which the gasoline distills will depend on the composition of the gasoline and the efficiency of the distillation column. A very efficiency column may be able to separate individual compounds if they have moderate differences in boiling point and if each is present a reasonable amount. Gasolines usually contain many readily identifiable compounds (up to about 400) that the distillation curve is quite smooth, even when a high degree of fractionation is used. Figure 2.1 shows gasoline distillation curves obtained at two different levels of fractionation efficiency; curve A is the sort of curve that one might obtain with good fractionation, whereas curve B is the same gasoline but with very little fractionation using the standard ASTM D 86 test.

It will be seen that the temperature at which the mixture begins to distill is much lower with a high degree of fractionation, and the final temperature is much higher, showing that individual compounds or groups of similar boiling compounds are separated much more readily in this case. If one wanted an even better separation, then techniques such as gas/liquid chromatography could be used.

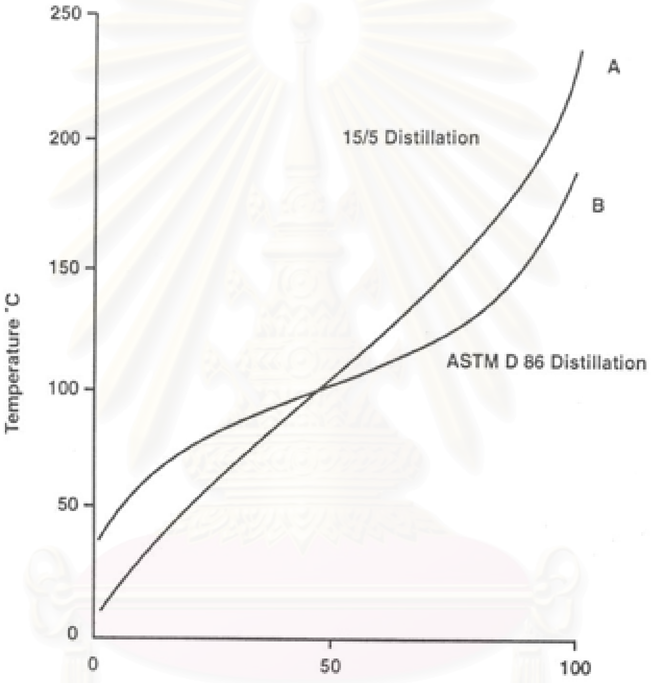


Figure 2.1 Gasoline distillation curve (Owen and Coley, 1995)

Figure 2.2 shows a gasoline distillation curve obtained using a low fractionation-efficiency and indicates the aspects of vehicle performance that difference part of it influence. It can be seen that if the distillation curve is displaced downwards the gasoline become more volatile, and vice versa. The front end, that is, the compounds in the gasoline having boiling points up to about 70^{o}C, is the first to be distilled over, and this controls ease of starting and the likelihood of hot weather problems such as vapor lock occurring. The mid-range largely controls the way that vehicle drives in cold weather, and particularly the time for the engine to warm up. It also influences to some extent the tendency for ice to form in the carburetor during cool, humid weather. The back and contains all the heavier, high boiling point compounds and these have a high heat content and so are important in improving fuel economy when the engine is fully warmed up. However, some of these heavier compounds may find their way past the pistons into the crankcase and dilute the crankcase oil. They are also not as readily combusted as the lighter components and give rise to combustion chamber deposits.

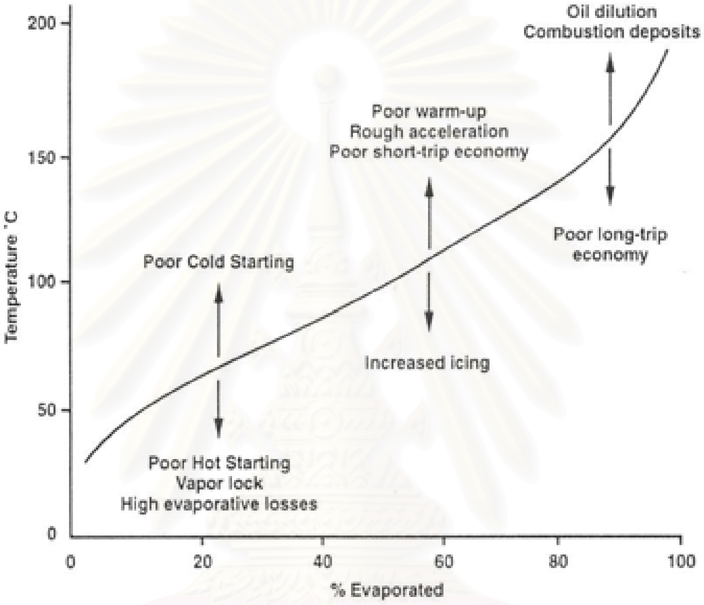


Figure 2.2 Compromising gasoline volatility (Owen and Coley, 1995)

It can be seen from Figure 2.2 that if one goes too far in the direction of making a gasoline more volatile, one set of problems can occur, and if one goes too far in the other direction, another set of difficulties is possible. Weather conditions, particularly ambient temperature, influence the choice of volatility required for satisfactory operation. Altitude also has a small effect because atmospheric pressure affects the rate of evaporation of gasoline. Vehicles themselves vary enormously in the way that they respond to gasoline volatility is not closely matched to the weather conditions prevailing. The vehicle design aspect which is the most important in this respect is the proximity of the fuel system to hot engine parts. It is necessary to avoid excessive vaporization during hot weather and yet to make sure that there is enough heat present during cold weather to adequately vaporize the gasoline.

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 using ASTM D 86. Similarly, they can also be represented by the percentage evaporated at a given temperature so that E70^{o}C (or E70^{o}C or E70) represents the percentage evaporated at 70^{o}C. It is considered preferable and more meaningful to use percentages evaporated rather than temperatures, particularly when carrying out blending calculations.

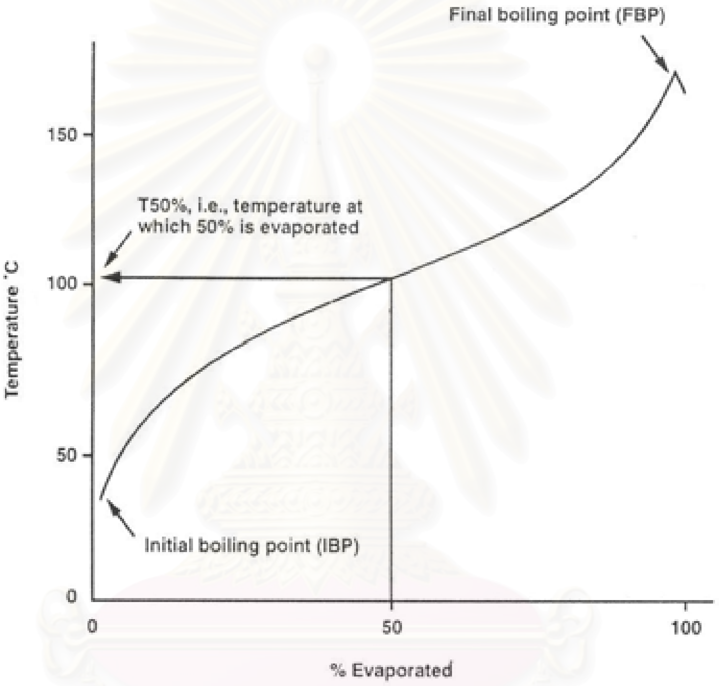


Figure 2.3 ASTM Distillation Curve (Owen and Coley, 1995)

Figure 2.3 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

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. Under these circumstances, too rich a mixture can also occur during the acceleration as the excess liquid “catches up” An uneven idle and “surging” during cruise in carbureted or single point injection cars may be caused by misdistribution of the fuel between cylinders, and this can be another reason for a stumble during an acceleration. Poor vaporization in cold weather is overcome to some extent by the provision of a choke giving over-rich mixtures during warm-up.

It is clear from the above that the ease with which a gasoline vaporizes in the engine determines the cold weather drivability of the fuel/vehicle combination. Fuel volatility and ambient temperature are obviously both important factors, but even more so is fuel system design. The use of multipoint fuel injectors rather than carburetors has a positive effect on drivability, as also do heating systems for the inlet manifold and good air-fuel ratio control during warm-up. Unfortunately, the need to meet emissions limits can sometimes mean that drivability performance is not always satisfactory under all conditions.

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:

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

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

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

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. Their structure provides a reasonable anti-knock value, thus 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 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 (2% oxygen can reduce CO by 16%) and HC (2% oxygen can reduce HC by 10%). 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. Oxygen in the fuel cannot contribute energy and consequently the fuel has less energy content. For the same efficiency and power output, more fuel has to be burnt, and the slight improvements in combustion efficiency that oxygenates provide on some engines usually do not completely compensate for the oxygen.

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

2.2.1.1 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.

2.2.1.2 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 ozone-forming potential. Furthermore, at low temperature the separation of the organic and water phases poses a risk. The infinite water solubility of ethanol could create a similar problem that created by MTBE if it were leak from underground gasoline storages.

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 biomass such as ETBE and TAEE.

2.2.2.1 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. The situation is better in Europe because double-walled storage tanks are common. 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. The US Environmental Protection Agency, EPA, has examined MTBE as a potential carcinogen, but recently it was decided that MTBE should not be classified as a human carcinogen. The health effects of MTBE continue to be somewhat obscure. 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.

2.2.2.2 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 still derived from methanol which currently still derived from natural gas as mention earlier.

2.2.2.3 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 (US and Europe), mainly in retrofit MTBE units, with similar yields and selectivity.

2.3 FCC and FCC Gasoline

Fluidized Catalytic Cracking (FCC) is the force for conservation that has been developed in the oil industry. It has the advantage that gasoline of high quality can be produced from almost any crude oil in equipment subject to careful control and operated at a low pressure, hence at comparatively lower cost. Catalytic gasolines also have the desirable characteristics of excellent response to tretraethyl lead (TEL), being low in gum formers and in corrosive sulfur compound, and have a uniform octane rating over boiling range of gasoline. This process employs a finely divided solid catalyst made by aerating the ground powder of an alumina-silica gel. This is maintained at all times as a simulated fluid by suspension in the reacting vapor or in the generating air. A high degree of turbulence is necessary throughout the system to ensure a uniform suspension. Under these conditions the solid catalyst similarly flows to a liquid exerts a like pressure. Because of the even distribution of the catalyst and because of its high specific heat in relation to the vapors reacting, the entire reaction can be maintained at a remarkably exact temperature. Separation of the catalyst from gases or vapors after the reaction and regeneration processes is done largely by means of means of cyclone separators. 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.

This process, more closely oriented towards refining than catalytic reforming, cannot be covered by a specific study here. However, some of its by-product represents significant effective or potential sources of olefins. Moreover, as shown by the typical analysis in Table 2.2, the yields of light cuts obtained on a fluid bed catalytic cracking installation, for instance, optimized for the maximum production of middle distillates, constitutes a large fraction of the feedstock (15 to 20 percent weight).

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

Finally, as shown by Table 2.3, these light cuts themselves contain significant concentrations olefinic hydrocarbons. Moreover, they are only effluents of catalytic cracking that the refiner may agree to make available for petrochemicals.

Table 2.3 Typical analyses of light cuts from catalytic cracking. (Chauvel and Lefebvre , 1989)

C_2 cut		**C_3 cut**		**C_4 cut**		**C_5 cut**	
Hydrocarbon	**%Wt**	**Hydrocarbon**	**%Wt**	**Hydrocarbon**	**%Wt**	**Hydrocarbon**	**%Wt**
Hydrogen	1.3	C_{2-}	0.4	C_{3-}	0.5	C_{4-}	2.0
Methane	29.5	Propane	26.9	n-butane	11.0	Isopentane	31.5
Ethane	25.4	Propylene	72.0	Isobutane	33.0	n-pentene	5.5
Ethylene	20.9	C_{4+}	0.7	1-butene	12.0	1-pentene	2.5
Propane	3.5			Cis 2-butene	11.0	Cis 2-pentene	8.0
Propylene	11.8			trans 2-butene	14.0	Trans 2-pentene	12.0
Inerts	7.6			Isobutene	18.0	2-methyl 1-butene	12.5
				Butadiene		3-methyl 1-butene	3.5
				Acetylenics		2-methyl 2-butene	21.5
				C_{5+}	0.5	C_{6+}	1.0
total	100.0	Total	100.0	total	100.0	total	100.0

On the whole, process performance, namely the product distribution, varies according to the operating conditions (space velocity, pressure, temperature, catalyst circulation rate), the feedstock and catalyst, and the inherent design of the unit (moving or fluidized beds, reactor and regenerator design). Hence the values given in Table 2.2 and 2.3 provide only one illustration.

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

2.4 Catalysts

2.4.1 Ion exchange resin

An ion exchange resin is an insoluble polymeric matrix or support structure, usually supplied as white or yellowish bead (shown in Figure 2.4) and with electrically charged sites at which one ion may replace another in a process called ion exchanging.

Figure 2.4 Ion exchange resin beads

2.4.1.1 Physical Structure of Resin

Generally, ion exchange resin can be manufactured from a material which has basic requirements of ion exchange bead. It must be insoluble under normal operating condition, and must be uniform dimension form of sphere. The swelling and contraction of resin bead during exhaustion and regeneration must not cause the bead to burst. In addition, the active site must be permanently attached to the bead. Usually, there are two physical structures of resin; i.e. micro porous and macro porous resin.

Micro porous resin (also called gel resin) is generally a translucent and homogenous crosslink polymer. It does not have permanent pore structure. Therefore, it has no measurable porosity, generally considered to be quite small, usually less than 30 ^{o}A and referred as gellular pore or molecular pores. The pore structure is determined by the distance between the polymer chains and crosslinks which depends on the % crosslinkage of the polymer, the polarity of the solvent, and the operating condition. Normally, it has higher operating efficiencies and lower cost than macro porous resin.

Macro porous resin (also called macroreticular resin) is a large multichannel porous structure and it can be made of two continuous phases; a continuous pore phase and a continuous gel polymeric phase which is structurally composed of small spherical micro gel particles agglomerated together to form cluster, which are fastened together at the interfaces and form inter-connecting pore. It not only has high effective surface area to facilitate ion exchange process and to give access to the exchange site for large ion but also give better physical stability, primarily because of its sponge like structure which gives more stress relief, and better oxidation resistance. Unfortunately, the multi-channel porous structure like sponge allows the active portion of the bead to contain a high level of DVB crosslinking without affecting the exchange kinetics; it means that it has a lower capacity because the beads contain less exchange sites. The “pore” can take up to 10 to 30 % of the polymer which is the reason to reduce the ion exchange capacity proportionately.

Usually, synthetic ion exchange resins are cast as porous beads with considerable external and pore surface where ions can attach. Whenever there is a great surface area, adsorption plays a role. If a substance is adsorbed to an ion exchange resin, no ion is liberated. While there are numerous functional groups that have charge, only a few are commonly used for principle ion exchange resins. These are:

1. Strongly acidic; sulfonic acid groups $-SO_3H$ which is strongly ionized to $-SO_3$
2. Strongly basic; $-NR_3^+$ that has a strong, permanent charge. (R stands for some organic group)
3. Weakly acidic; carboxylic acid groups $-COOH$ which is weakly ionized to $-COO^-$
4. Weakly basic; $-NH_2$ that weakly attracts protons to form NH_3^+, -secondary and tertiary amines that also attract protons weakly

These groups are sufficient to allow selection of a resin with either weak or strong positive or negative charges.

2.4.1.2 Chemical Structure of Resin

Commonly, there are two basic types of chemical structures; styrene and acrylic matrix material while divinylbenzene (DVB) is still used as a crosslinker in these matrixes.

The acrylic based material is straight chained hydrocarbons based on polyacrylate and polymethacrylate. The active exchange site of acrylic differing from the styrene is part of the physical structure. The acrylic based material is advantageous in application where organics are presented because it does not foul nearly as much as a styrene based material. However, when an acrylic resin chemically degrades, which is the weak link beyond the physical structure. Furthermore, when an acrylic resin oxidizes, it will swell and become mushy, therefore is usually limited to industrial application. Presently, most ion exchange resins are manufactured by using styrene as the matrix material.

Ion exchange resin based on the copolymerization of styrene and DVB the most commonly used in the world today has been developed since 1944 by an American scientist, D' Alelio and is referred to as being gellular in structure. DVB is the cross linking agent, link together the back bone of styrene polymer contributed to three dimension of the network, fashion it insoluble and determines to what extent the resin is free to swell and shrink. The term "Cross linkage" in a styrene - DVB resin refers to the fraction of DVB. For example, 8 percent crosslinkage means that it contain 92 percent of styrene and 8 percent of DVB. Resins are available today with a DVB content of from 2 to 20% or higher. Higher DVB content gives the bead additional strength but the additional crosslinking can hinder kinetic by making the bead too resistant to the shrinking when in contact with non polar solvent and to swelling when charging from one ionic form to another form, during normal operating.

2.4.1.3 Physical and Chemical Properties of Ion Exchange Resins

Since ion exchange resin is the copolymer of styrene and DVB, it has most of ideal network properties consisting of a structure resistant to breakage, mechanical wear, oxidation or reduction, uniform of shape in small spheres with good hydraulic properties and insoluble in solvents. The properties of resin depend on the crosslinkage of styrene and DVB and the particle size of resin. These factors are important parameters to describe several properties; that is, moisture content, capacity, equilibration rate, selectivity for various ions, porosity, and flow rate of solution and physical stability.

1) Crosslinkage

The amount of crosslinking depends on the proportions of different monomers used in the polymerization step. Practical ranges are 4 % to 16 %. Resins with very low crosslinking tend to be watery and change dimensions markedly depending on which ions are bound. Properties that are interrelated with crosslinking are:

- Moisture Content

A physical property of the ion exchange resins that varies with changes in crosslinkage is the moisture content of the resin. For example, sulfonic acid groups attract water, and this water is tenaciously held inside each resin particle. The quaternary ammonium groups of the anion resins behave in a similar manner.

- Capacity

The total capacity of an ion exchange resin is defined as the total number of chemical equivalents available for exchange per some unit weight or unit volume of resin. The capacity may be expressed in terms of mole-equivalents per unit mass of dry resin or in terms of mole-equivalents per unit volume of wet resin.

Generally, the resins have the higher crosslinked, the more difficult to introduce additional functional groups. Sulfonation is carried out after the crosslinking has been completed and the sulfonic acid groups are introduced inside the resin particle as well as over its surface. Likewise, the quaternary ammonium groups are introduced after the polymerization has been completed and they also are introduced both inside the particle as well as on its surface. Fewer functional groups can be introduced inside the particles when they are highly crosslinked and hence the total capacity on a dry basis drops slightly.

This situation is reversed when a wet volume basis is used to measure the capacity on a resin. Although fewer functional groups are introduced into a highly crosslinked resin, these groups are spaced closer together on a volume basis because the volume of water is reduced by the additional crosslinking. Thus the capacity on a wet volume basis increases as cross-linking increases.

- Equilibrium Rate

Ion exchange reactions are reversible reactions with equilibrium conditions being different for different ions. Crosslinkage has a definite influence on the time required for an ion to reach equilibrium. An ion exchange resin that is highly crosslinked is quite resistant to the diffusion of various ions through it and hence, the time required for reaching equilibrium is much longer. In general, the larger ion or molecule diffusing into an ion exchange particle, or the more highly crosslinked the polymer, the longer the time is required to reach equilibrium conditions.

Copolymers of styrene containing low amounts of divinylbenzene (1- 4%) are characterized as having high degree of permeability, large amount of moisture, and high rate to reach equilibrium, but poor physical stability, and selectivity. However, ability to accommodate larger ions is increased. Copolymers of styrene containing high amounts of divinylbenzene (12-16%) exhibit characteristics in the opposite direction.

2) Particle Size

The physical size of the resin particles is controlled during the polymerization step. Screens are used to sieve resins to get a fairly uniform range of sizes. Mesh sizes in Table 2.4 refer to U.S. standard screens. A higher mesh number means more and finer wires per unit area and thus a smaller opening.

Table 2.4 Diameter of particles related to mesh range

Mesh Range	Diameter of particles (Inches)	Diameter of particles (Micrometers)
20 - 50	0.0331-0.0117	840-297
50 - 100	0.0117-0.0059	297-149
100 - 200	0.0059-0.0029	149-74
200 - 400	0.0029-0.0015	74-38
minus 400	< 0.0015	< 38

For the equilibration rate, the particle size of an ion exchange resin influences the time required to establish equilibrium conditions. There are two types of diffusion that must be considered in an ion exchange equilibrium. The first is called film diffusion or the movement of ions from a surrounding solution to the surface of an ion exchange particle. The second is called internal diffusion which is the movement of ions from the surface to the interior of an ion exchange particle. Film diffusion is usually the controlling reaction in dilute solutions whereas internal diffusion is controlling in more concentrated solutions. The particle size of an ion exchange resin affects both film diffusion and internal diffusion. A fine mesh particle presents more surface area for film diffusion and also contains less internal volume through which an ion must diffuse. A decrease in particle size thus shortens the time required for equilibrium condition.

2.4.2 Zeolite

Zeolites are crystalline aluminosilicates with fully cross-linked open framework structures made up of corner-sharing SiO_4 and AlO_4 tetrahedral. The first zeolite, stibnite, was discovered by Cronstedt in 1756, who found that the mineral loses water rapidly on heating and thus seems to boil. The name “Zeolite” comes from the Greek words zeo (to boil) and lithos (stone). A representative empirical formula of zeolite is $M_{2/n}.Al_2O_3.xSiO_2.yH_2O$, where M represents the exchangeable cation of valence n. M is generally a group I or II ion, although other metal, non-metal and organic cations may also balance the negative charge created by the presence of Al in the structure. The framework may contain cages and channels of discrete size, which are normally occupied by water. In addition to Si^{4+} and Al^{3+}, other elements can also be present in the zeolitic framework. They do not need to be isoelectronic with Si^{4+} and Al^{3+}, but must be able to occupy framework sites. Aluminosilicate zeolites display a net negative framework charge.

2.4.2.1 Structure of Zeolite

The framework of a zeolite is based on an extensive three-dimensional network in which the polyhedral sites, usually tetrahedral, are linked by oxygen atoms. The crystalline framework contains cages and channels of discrete size and 3-30^{o}A in diameter. The primary building unit of a zeolite is the individual tetrahedral unit. The T atom (T = Si or Al) belonging to a TO_4 tetrahedron is located at each corner, but the oxygen is located near the mid-points of the lines joining each pair of T atoms. The topology of all known zeolite framework types can be described in terms of a finite number of specific combinations of tetrahedral called “secondary building units”(SBU’s). A zeolite framework is made up of one type of SBU only.

Description of the framework topology of a zeolite involves “tertiary” building units corresponding to different arrangements of the SBU’s in space. Various alternative ways have been proposed. The framework may be considered in terms of large polyhedral building blocks forming characteristic cages. For example, sodalite, zeolite A and zeolite Y can all be generated by the truncated octahedron known as the beta-cage. An alternative method of describing extended structures uses two-dimensional sheet building units. Sometimes various kinds of chains can be used as the basis for constructing a zeolite framework.

2.4.2.2 Properties of Zeolite

The most important application of zeolite is used a catalyst. Zeolites combine high acidity with shape selectivity, high surface area, and high thermal stability and have been used to catalyze a variety of hydrocarbon reactions, such as cracking, hydrocracking, alkylation and isomerisation. The reactivity and selectivity of zeolites as catalysts are determined by the active sites brought about by a charge imbalance between the silicon and aluminium atoms in the framework. Each framework aluminium atom induces a potential active acid site. In addition, purely siliceous and $AlPO_4$ molecular sieves have Brønsted acid sites whose weak acidity seems to be caused by the presence of terminal OH bonds on the external surface of crystal. Shape selectivity, including reactant shape selectivity, product shape selectivity or intermedia shape selectivity plays a very important role in zeolite catalysis. The channels and cages in a zeolite are similar in size to medium-sized molecules. Different sizes of channels and cages may therefore promote the diffusion of different reactants, products or intermedia species. High crystallinity and the regular channel structure are the principal features of zeolite catalysts. Reactant shape selectivity results from the limited diffusivity of some of the reactants, which cannot effectively enter and diffuse inside the crystal. Product shape selectivity occurs when slowly diffusing product molecules cannot rapidly escape from the crystal, and undergo secondary reactions. Restricted intermedia shape selectivity is a kinetic effect arising from the local environment around the active site: the rate constant for a certain reaction mechanism is reduced if the necessary intermedia are too bulky to form readily.

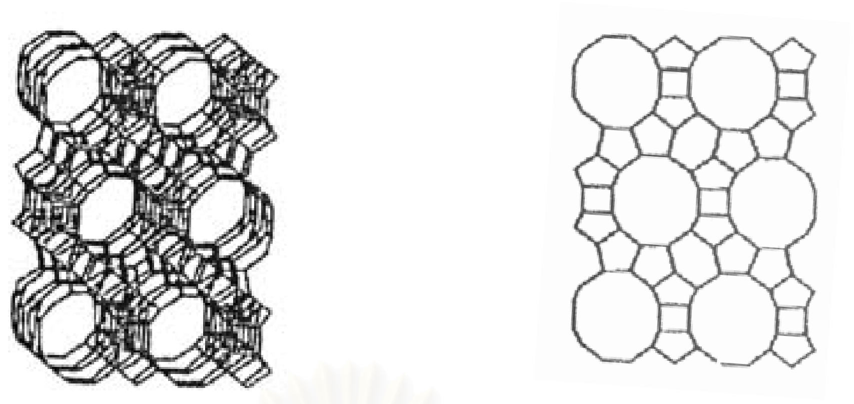
Zeolites are selective, high-capacity adsorbents because of their high intracrystalline surface area and strong interactions with adsorbates. Molecules of different size generally have different diffusion properties in the same molecular sieve. Molecules are separated on the basis of size and structure relative to the size and geometry of the apertures of zeolite. Zeolites adsorb molecules, in particular those with a permanent dipole moments, and exhibit other interactions not found in other adsorbents. Different polar molecules have a different interaction with the zeolite framework, and may thus be separated by a particular zeolite. This is one of the major uses of zeolites. An example is the separation of N_2 and O_2 in the air on zeolite A, by exploiting different polarities of the two molecules.

Zeolites with low Si/Al ratios have strongly polar anionic frameworks. The exchangeable cation creates strong local electrostatic fields and interacts with highly polar molecules such as water. The cation-exchange behaviour of zeolites depends on (1) the nature of the cation species - the cation size (both anhydrous and hydrated) and cation charge, (2) the temperature, (3) the concentration of the cationic species in the solution, (4) the anion associated with the cation in solution, (5) the solvent (most exchange has been carried out in aqueous solutions, although some works have been done in organics) and (6) the structural characteristics of the particular zeolite.

2.4.2.3 Solid Heterogeneous Catalyst: Beta Zeolite

Beta zeolite was initially synthesized by Wadlinger *et al*. (1995) using tetraethylammonium hydroxide as an organic template. The chemical composition of beta zeolite is $(TAE,Na)_2O.Al_2O_3.5\text{-}100SiO_2.4H_2O$

Beta zeolite is a large pore, high silica and crystalline aluminosilicate. The framework and the pore structure of the zeolite have several unique features. It is the only large pore zeolite to have chiral pore interactios. The high silica zeolites are attractive catalytic materials because of their thermal and hydrothermal stabilities, acid strength, good resistance for deactivation and hydrophobicity. The pore structure of beta zeolite consists of 12 membered rings interconnected by cages formed by the interaction of channels. The dimension of pore opening in the linear channel is 5.7 ^{o}A x 7.5 ^{o}A. The tortuous channel system consists of the interactions of two linear channels of approximate dimensions of 5.6 ^{o}A x 6.5 ^{o}A. Beta zeolite has a total pore volume around 0.2 ml/g. The above characteristics make beta zeolite a potential candidate for a variety of hydrocarbon conversion reactions. The framework structures of beta zeolite are shown in Figure 2.5.



(a) framework structure (b) framework projection

c) tortous channel (d) straight channel

Figure 2.5 Structure of beta zeolite

CHAPTER III

LITERATURE REVIEWS

Due to the restriction of the use of lead containing engine knock suppressing additives with decreasing of benzene and aromatic content lower than 1 and 25 vol%, respectively and increasing of oxygen content to at least 2 wt% in the reformulated gasoline (Oktar et al., 1999). Following the restriction of reformulated gasoline properties, the blending of oxygenates into gasoline has been widely used for the clean gasoline production.

Oxygenate compounds such as alcohols and ethers were blended into gasoline to reduce air pollution and enhance octane number. Furthermore, good burning characteristics and low atmospheric reactivity of oxygenates have interested to use for the fuel quality improvement. Typically, ethers are lower bRVP than alcohols and also much less photochemically reactive than alcohol. Therefore, ethers are more suitable oxygenate for gasoline than alcohol. Ethers can be derived from the etherification of alcohol with olefins. The researches of their production also review for a useful knowledge such as operating condition and catalyst selection.

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.

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. Although MTBE was already phase out and others methanol derivative i.e., TAME might not attractive enough as mentioned.

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 is one of the ethanol derivatives ethers which 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 catalyzed liquid-phase formation of TAEE were studied by Linnekoski et al. (1997) that the catalyst used was Amberlyst 16. 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.

Furthermore, *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.

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.

Thus, the alternative sources of tertiary alkenes were explored to solve this crisis. FCC gasoline was one of the alkene sources, not only isobutene or isoamylenes but also heavier tertiary alkenes. Therefore, tertiary ethers can be produced from the etherification of FCC gasoline with alcohol such as methanol and ethanol. Producing tertiary ethers from entire FCC gasoline was an economic alternative to reduce olefins and consequently Rvp together with an increase of the octane number of gasoline (Oktar et al., 1999). The following sections are the literature reviews on the etherification of FCC gasoline with alcohol.

3.2 Etherification of FCC Gasoline with Alcohol

Due to the supply of isobutene and isoamylenes may become limited while the high demand for tertiary ethers (MTBE, TAME, ETBE and TAEE) as oxygenate to blend with gasoline has greatly expanded. Therefore, it is important to explore alternative sources of tertiary alkenes. FCC light gasoline is a potential valuable feedstock of reactive olefins for production of oxygenates ethers because significant quantities of reactive olefins C_5, C_6 and C_7 were present in the FCC gasoline. As was reported by Pescarolla et al (1993) about 10% C_5 reactive olefins (2-methyl-2-butene (2M2B), 2-methyl-1- butene (2M1B)), 9-10% C_6 reactive olfins and about 4-5% C_7 reactive olefins were obtainable in the FCC gasoline. Furthermore, the etherifications of these olefins with ethanol decrease the bRvp of the gasoline product while RON increased (Oktar et al., 1999). 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 20 vol% as regulated by the International charter on clean fuels. Pescarollo et al. (1993) studied etherifying the entire light FCC gasoline with methanol. 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.

Converting olefins in FCC gasoline by hydroisomerization and aromatization were presently succeeded by Fan et al. (2004, 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.

3.3 Hydration of Olefin Compounds with Water

To reduce the production cost, water/ethanol azeotropic mixture were used as a substitute for pure ethanol to etherify with FCC gasoline. Therefore, the hydration can be carried out from the water presence in ethanol with olefin compounds in FCC gasoline such as isobutene and isoamylenes to produce tertiary alcohols such as *tert*-butyl alcohol (TBA) and tert-amyl alcohol (TAA) as shown in following equation.

Hydration of IB: $$H_2O + IB \rightleftharpoons TBA \qquad (3.1)$$

Hydration of IA: $$H_2O + IA \rightleftharpoons TAA \qquad (3.2)$$

Tertiary alcohols from the hydration can be used as octane booster and can further reacted with ethanol to form tertiary ethers as follow;

$$TBA + EtOH \rightleftharpoons ETBE + H_2O \qquad (3.3)$$

$$TAA + EtOH \rightleftharpoons TAEE + H_2O \qquad (3.4)$$

However, it was found that only a few works have been studied for the hydration of IB and IA. Velo et al. (1988) studied the liquid-phase hydration of IB to TBA on Amberlyst 15 in a solvent-free. They reported that although inhibition by water may be present, the effect of TBA is much more significant. Thus, the alcohol is found to inhibit the rate more than expected from the values of the equilibrium constant for the hydration reaction. Linnekoski et al. (1998) studied the etherification and hydration of IA catalyzed by Amberlyst 16 in a CSTR. They found that the effect of water on the reaction rate of the TAEE formation was studied by adding 6 wt% water in the ethanol that resulted in 50% drop of the overall olefins conversion and 80% drop of the etherification yield and an 85% increase in the *tert*-amyl alcohol yield. The measured reaction rates were fitted to a model of Langmuir-Hinshelwood type. The rate determining step in the model was the surface reaction between adsorbed alcohol and isoamylenes or between adsorbed water and isoamylene. Likewise, Gonzalez and Fair (1997) reported the hydration of isoamylenes using Amberlyst-15 as catalyst and acetone as a solvent. They chose acetone as a reaction medium to enable single liquid phase and to enhance the reaction rate. In their study found that at temperatures below 343 K the intraparticle diffusion is negligible and proposed a kinetic expression based on Langmuir-Hinshelwood formalism. The reaction rate was of first order in isoamylenes and *tert*-amyl alcohol in both forward and reverse reactions, whereas, water acted as an inhibitor in both reactions. Cunill et al. (1993) investigated the effect of water presence on the liquid-phase syntheses of MTBE and ETBE by using Bayer K2631 as a catalyst in batch reactor. They reported that the presence of water in amounts equal to or lower than that in azeotropic ethanol does not affect the equilibrium constants of ETBE or MTBE synthesis reactions and even is able to increase the isobutene conversion. Even in small amounts, water shows a hard inhibitor effect and ETBE and MTBE production rates are strongly lowered, particularly at the beginning of a batch operation. TBA equilibrium is reached quicker than that for the ethers, especially for ETBE. However, a longer time is needed to reach equilibrium for ether syntheses. ETBE or MTBE and TBA could be simultaneously produced from azeotropic ethanol or methanol impurified with water, respectively, in existing MTBE units whenever the reactor length is long enough to get a high isobutene conversion. In addition, Zhang et al. (2003) studied the TBA synthesis via IB hydration over Amberlyst 15 by using pure water and aqueous TBA solution. They found that the kinetics in the chemical reaction-controlled regime had shown that the reaction was pseudo first-order in IB concentration and that product TBA inhibited the rate of the overall reaction due to the significant reverse reaction resulting from an equilibrium constant of 26 at 343 K.

For the reaction of TBA and TAA with ethanol have been published only a few reports. Habenicht et al. (1995) studied the reaction of TBA in water/ethanol mixtute (10% by volume of water) at 3 MPa and 170 ^{o}C over sulfuric acid catalyst. They found that TBA was reacted quickly to form ETBE and IB and the presence of water in the reactant mixture significantly reduces the conversion of TBA, but has a lesser effect on the yield of product ETBE. Furthermore, Aiouache and Goto (2003a and 2003b) studied the kinetic model of etherification of TAEE from TAA and EtOH catalyzed by Amberlyst 15 with the focus on a sorption effect. Their experiment were carried out in batch reactor at 0.8 MPa in temperature range of 323-353 K. Not only the etherification of TAA to produce TAEE, but the dehydration of TAA to IA and the etherification of IA to TAEE can also occur. Since the dehydration of TAA to IA takes place, TAA is more rapidly consumed than EtOH. At a higher temperature, IA is produced more and TAEE produced less, because of the dehydration of TAA as the endothermic reaction and the etherification of IA as the exothermic reaction.

CHAPTER IV

EXPERIMENT

This chapter describes the experimental procedure for the improvement of the fuel oil quality by the etherification of FCC gasoline with ethanol in the batch reactor. It is divided into four parts; Apparatus of batch reactor and chemical materials, the etherification of FCC gasoline with pure ethanol and the etherification and hydration of FCC gasoline with water/ethanol azeotropic mixture.

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.

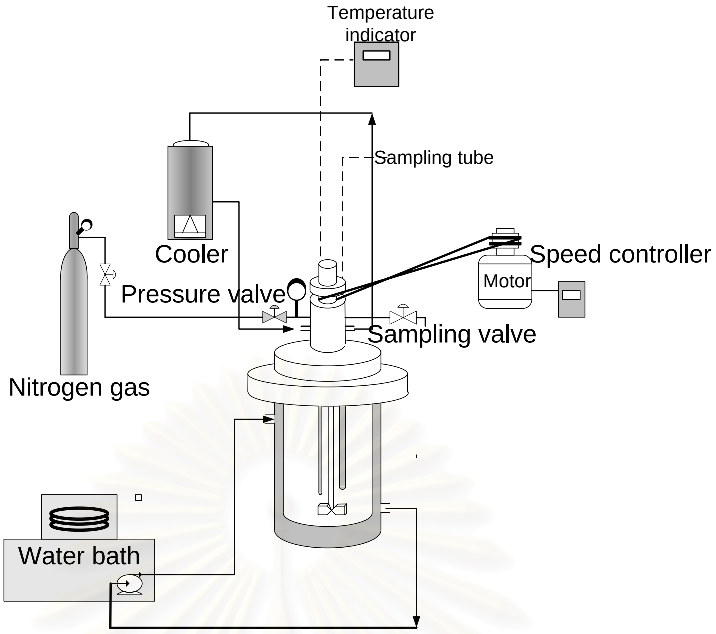


Figure 4.1 Batch Reactor Apparatus

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 Details of chemicals use in the study

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

4.2 Etherification of FCC Gasoline with Pure Ethanol

4.2.1 Catalysts Screening

This study was the catalyst screening for the fuel oil quality improvement by the etherification of FCC gasoline with pure 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	Ion Exchange Capacity (meqH$^+$/kg Catalyst)	Surface Area (m^2/g)	Pore Diameter (nm)	Pore Volume (cm^3/g)
Amberlyst 16	Chemika Fluka	5.0	900	1000	1.82
β-zeolite	Tosoh (Japan)	ND	425	250	0.129

ND = Not Determined

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 that the separation column was 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.

4.2.2 Effect of Operating Temperature

This part was a studying of the influence of operating temperature on the ethanol conversion and the TAEE yield.

4.2.2.1 Experimental Procedure

1. 80 cm^3 of FCC gasoline , 20 cm^3 of EtOH and 10 g of Beta-Zeolite catalyst were added into the reactor together.

2. The experiments were varied the operating temperature (333, 343 and 353 K). Each of experiment was carried out in the batch reactor under pressure 0.8 MPa and then stirred at about 1163 rpm for 12 hours.

3. Liquid samples (1.5 cm^3) were taken for analysis at 0, 0.25, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9, 10 hours

4.2.2.2 Analysis

Chemical compositions (Ethanol, Isoamylenes and TAEE) of a liquid sample were analyzed by using a gas chromatograph (GC), Shimadzu GC 8A. The operating condition of the GC used as same as the previous part.

4.3 Etherification and Hydration of FCC Gasoline with Water/Ethanol Azeotropic Mixture

This section, 95% purity of ethanol was used as one reactant. So, the reaction system consisted of FCC gasoline, ethanol and H_2O. The reactions involving in this study were etherification and hydration reaction. Reactive olefins in FCC gasoline were etherified with ethanol to formed tertiary ether and were hydrated carried with H_2O to produced tertiary alcohol.

4.3.1 Experimental Procedure

1. 80 cm^3 of FCC gasoline, 20 cm^3 of 95% purity EtOH and 10 g of catalysts (Amberlyst 16 and Beta-zeolite) were added into the reactor.

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 (333, 343 and 353 K) and stirred at about 1163 rpm for 10 hours.

3. Liquid samples (0.5 cm^3) were taken for analysis at 0, 0.25, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9, 10 hours.

4.3.2 Analysis

Chemical compositions (Ethanol, H_2O, IA, TAA and TAEE) of a liquid sample were analyzed by using a gas chromatograph (GC), Shimadzu GC 8A. The operating condition of the GC used as same as the previous part.

CHAPTER V

RESULTS AND DISCUSSION

This chapter describes the results and discussion for the fuel oil quality improvement by the etherification of entire FCC gasoline with ethanol in batch reactor. It can be divided into two sections; the etherification of FCC gasoline with pure ethanol and the etherification and hydration of FCC gasoline with water/ethanol azeotropic mixture.

5.1 Etherification of FCC Gasoline with Pure Ethanol

In first stage of this part, 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. In the second stage, the effect of temperature on the etherification conversion and the ether productivity was investigated.

5.1.1 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 and 5.2 presented the conversion calculation for ethanol and IA. 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. 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, Beta-zeolite gives higher ethanol and olefins conversions which give more ethers production. It is worthy to note that olefins conversions are lower with larger atomic number of olefins in both catalysts. These results were similar to etherified FCC gasoline with methanol reported by Pescarollo et al. (1993).

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

$$\%\text{Conversion of IA} = \frac{N_{IA,0} - N_{IA}}{N_{IA,0}} \times 100 \quad (5.2)$$

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 (at 343 K)

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	0.39	0.25
- C5	8.85	-	8.85	6.15	5.10
- 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	55.48	57.05
Oxygenates					
- Ethanol	0	22.44	22.44	15.87	14.29
- Ether	0	-	-	13.27	15.05
Total	0	-	22.44	29.14	31.14
Grand total	78.49	22.44	100	100	100
C4 Olefins conversion (%)			0	77.8	85.8
C5 Olefins conversion (%)			0	30.5	42.4
C6 Olefins conversion (%)			0	22.3	37.8
C7 Olefins conversion (%)			0	21.6	23.3
Ethanol conversion (%)		-	0	29.3	36.32

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 most of olefins conversion increased with increasing ethanol fraction in feed. In the case of FCC gasoline and ethanol ratio 70:30 catalyzed by Beta-zeolite, the unreacted ethanol remaining was less than 15 vol%, therefore it is not over the gasoline specification such as of E15 or 15 vol% of ethanol. This is an example to indicate an increased in the possibility of renewable with ethanol by approx. two times.

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 (at 343 K)

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	0.23	0.07
- C5	7.72	-	7.72	3.26	2.77
- 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	47.61	49.62
Oxygenates					
- Ethanol	-	33.15	33.15	18.69	16.06
- Ether	-	-	-	23.26	26.29
Total	-	-	33.15	41.95	42.35
Grand total	66.85	33.15	100	100	100
C4 Olefins conversion (%)			0	86.6	69.6
C5 Olefins conversion (%)			0	57.7	64.1
C6 Olefins conversion (%)			0	26.0	55.5
C7 Olefins conversion (%)			0	46.4	51.3
Ethanol conversion (%)		-	0	43.6	51.5

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 5.4, 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. Note that FCC etherified with 30 vol% ethanol catalyzed by both Beta-zeolite and Amberlyst 16 give lower bRvp than FCC directly blended with 20 vol% ethanol. 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 (gf-s/cm^2)		6.213		6.325	5.374	6.310	6.152	6.035	5.160
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)			
Drivability Index, DI °C (°F)		631(1168)	<677(1250)	542(1008)	557(1035)	561(1042)			

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 were not increased in the case of FCC gasoline etherified by using Beta-zeolite. As the amounts of benzene were not increased, there is no greater tendency to emit unburned hydrocarbons. Therefore, the enhancement of octane number in the case of etherified FCC gasoline using Beta-zeolite is not arisen from only etherification reaction but also from isomerization. Furthermore, the liquid phase exothermic reaction was catalyzed by sulfonic acid resin as Amberlyst 16 can be released sulfonic groups and sulfuric acid from the catalyst, causing a loss of activity and giving rise to corrosion problems. Whereas, Beta-zeolite which was a large pore crystalline aluminosilicate catalyst was more thermal stability than Amberlyst 16. As a result of functional groups of catalyst, Beta-zeolite had more activity than Amberlyst 16 for the etherification of FCC gasoline with ethanol and no acid effluent. It can be concluded that Beta-zeolite is a more suitable catalyst for upgrading FCC gasoline with ethanol compared to Amberlyst 16.

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 in the US. 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.

$$\text{Drivability index (DI)} = (1.5 \times T10) + (3 \times T50) + T90 \qquad (5.3)$$

Drivability index provides the relationship between drivability and distillation properties. T10 represents the gasoline ability to vaporize quickly 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 once good drivability is achieved, there is no benefit to further lowering the value of DI. Since the olefins generally have higher boiling points than those of paraffins and ethanol, respectively. Therefore, the DI of original FCC was higher than those of etherified gasoline with ethanol and gasoline with directly blend ethanol, respectively.

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 5.1 and further discussed in some details.

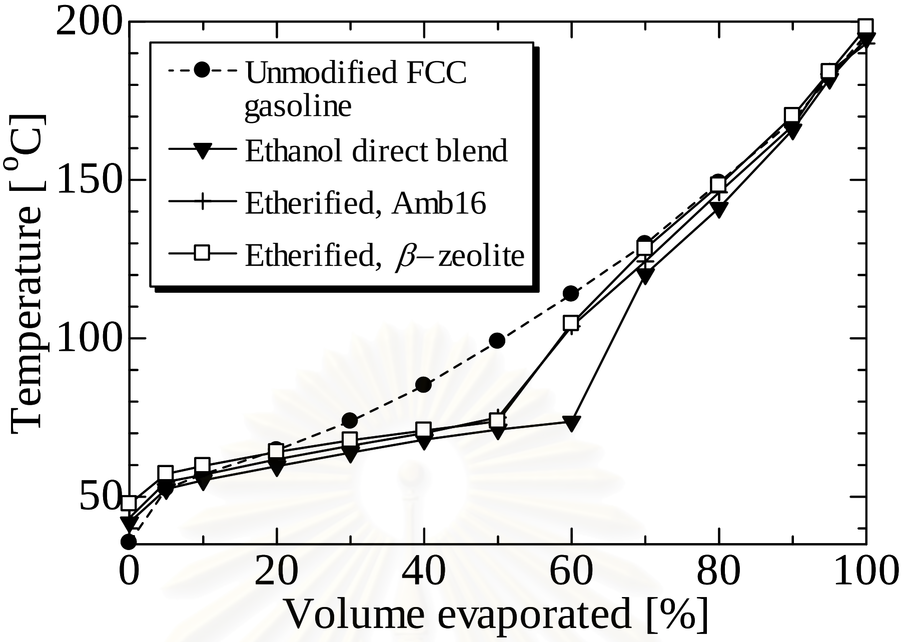


Figure 5.1 Distillation Curve following ASTM D 86 of FCC Gasoline, Ethanol Directly Blending Gasoline, Etherified Gasoline Catalyzed by Amberlyst 16 and Beta-Zeolite

It is worthy to note that the distillation temperature of FCC with direct ethanol blend at 60 vol% was much lower than the others. It could be since the boiling point of ethanol is about 78 °C while the boiling temperature of gasoline is about 35-200 °C. The results were agreed well with the study of using ethanol–gasoline blended fuels for SI engine by Hsieh et al. (2002). Their results showed significant decrease of the 50% distillation temperature when ethanol was blended with more than 10 vol% into gasoline which the boiling temperature in 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.

5.1.2 Effect of Operating Temperature

The results were summarized in Table 5.5 which consisted of the equilibrium conversion and yield of ethanol, IA and TAEE which calculated by equation 5.4, 5.5 and 5.6, respectively.

$$\%\text{Equilibrium Conversion of ethanol} = \frac{N_{EtOH,0} - N_{EtOH,eq}}{N_{EtOH,0}} \times 100 \qquad (5.4)$$

$$\%\text{ Equilibrium Conversion of IA} = \frac{N_{IA,0} - N_{IA.eq}}{N_{IA,0}} \times 100 \qquad (5.5)$$

$$\%\text{Yield of TAEE} = \frac{N_{TAEE}}{N_{IA}} \times 100 \qquad (5.6)$$

Table 5.5 Effect of temperature on ethanol conversion, IA conversion and TAEE production at the volume ratio of FCC gasoline to ethanol = 80:20

Operating Temperature (K)	% Equilibrium Conversion		%Yield of TAEE
	EtOH	IA	
333	52.47	42.52	38.37
343	48.68	37.64	35.38
353	46.77	27.80	25.03

As shown in Table 5.5, the conversion of ethanol was more than the conversion of IA because not only C_5 olefins but ethanol can also be etherified with the higher C_5 olefins presented in FCC gasoline to formed ether. For example, tertiary hexyl ethyl ether, THEE, can be produced from the etherification of C_6 olefin with ethanol (Zhang and Datta, 1996). The decrease in etherification conversions with increasing temperature was anticipated because the equilibrium constant of the etherification of olefins to ether decreased with increasing temperature, owning to the exothermicity of all of the etherification reaction (Kitchaiya and Datta, 1995, Aiouache and Goto, 2003).

5.2 Etherification and Hydration of FCC Gasoline with Water/Ethanol Azeotropic Mixture

The effect of water presence in the azeotropic mixture ethanol on the hydration and its inhibition effect on etherification was preliminarily investigated in this experiment. FCC gasoline was placed in a batch reactor with an azeotropic mixture of ethanol and water in the temperature of 333 K. Beta-zeolite and Amberlyst 16 are used as a catalyst for this study with the volume ratio of FCC gasoline to ethanol azeotropic of 80:20. In the experiment, it found that the water presence in the azeotropic ethanol affected on Beta-zeolite which was transformed from powder to gel like substrate when it contacted with water. Furthermore, the formed gel would clog the valve and tube of reactor. Therefore, it can be implied that Beta-zeolite was not suitable for the hydration of FCC gasoline since it cannot tolerate water.

Table 5.6 The conversion of water, ethanol and IA and TAA and TAEE yield for the etherification and hydration of FCC gasoline with pure ethanol and azeotropic ethanol over Amberlyst 16 at 333 K

	%Conversion			%Yield	
	H2O	EtOH	IA	TAA	TAEE
Pure ethanol	0	49.87	40.54	0	36.08
Azeotropic ethanol	37.85	34.58	26.05	3.76	18.97
%Conversion Drop	-	30.66	35.74	-	47.42
%Conversion Drop by Linnekoski et al.(1998)	-	-	50.00		78.43

Table 5.6 showed the conversion and yield for the etherification and hydration of FCC gasoline catalyzed by Amberlyst 16. It provides the conversion of ethanol, IA and water (in the case of filling with ethanol azeotropic) and the yields of TAEE and TAA from the etherification and hydration, respectively which was catalyzed by Amberlyst 16. The conversion and yield calculated by equations 5.1, 5.2, 5.6, 5.7 and 5.8.

$$\%\text{Conversion of water} = \frac{N_{H_2O,0} - N_{H_2O}}{N_{H_2O,0}} \times 100 \qquad (5.7)$$

$$\%\text{Yield of TAA} = \frac{N_{TAA}}{N_{IA}} \times 100 \qquad (5.8)$$

The ethanol and IA conversion decrease to 30.66% and 35.74%, respectively with the presence of water in the ethanol azeotropic mixture. Similar result was obtained by Linnekoski et al. (1998) who studied the etherification and hydration of pure IA and azeotropic ethanol catalyzed by Amberlyst 15 with ethanol/olefin molar ratios of 0.3, 1 and 3. Therefore, it can be implied that Amberlyst 16 exhibit less water inhibition effect than that of Amberlyst 15. It is possible that the Amberlyst 16 catalyst may tolerate water in hydration reaction. Therefore the possible of FCC upgrading by the hydration with water was further preliminary studied. The reaction system consisted of 90 and 10 cm^3 of FCC gasoline and water, respectively with 10 g of Amberlyst 16 catalyst. The amount of water in feed solution was determined by Coulometric Karl-Ficsher titration which was corresponding to 13.9 wt%. After reacted for 10 h and centrifuged for catalyst separation, the reaction mixture was analyzed by Coulometric Karl-Ficsher titration again. The water content was dramatically decreased to 0.012 wt%. This trace amount of water was significantly less than the water content limitation in gasoline, i.e., 0.7 wt% for Thailand gasoline specification. Therefore, in conclusion, FCC hydration also exhibited as an alternative process for FCC gasoline improvement. The olefinic content could be eliminated by converting to *tert*-alcohols which were octane enhancer.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The simultaneous process of FCC gasoline quality improvement and supplement by ethanol were studied by the etherification of entire FCC gasoline with ethanol in the heterogeneous catalytic system. The following conclusions can be drawn from the investigation.

6.1.1 Etherification of FCC Gasoline with Pure Ethanol

6.1.1.1 Catalyst screening

6.1.1.1.1 Etherified FCC gasolines with ethanol increase RON comparably or slightly lower than FCC with direct ethanol blend while bRvp is effectively lower. Therefore, FCC etherification with ethanol gives a higher potential for using ethanol as a fuel extender than direct blending for a conventional engine fuel which is limited with some ethanol contents, i.e., 10 vol% (E10).

6.1.1.1.2 Comparing between Amberlyst 16 and Beta-zeolite catalysts, Beta-zeolite is a more suitable catalyst for the etherification of FCC gasoline with ethanol because it offers products with higher RON and ethanol conversion with lower bRvp because some isomerizations also occur without aromatization to benzene.

6.1.1.1.3 The physical properties of the etherified gasoline such as density and viscosity are close to the commercial gasohol, therefore it is possible to develop the etherified gasoline.

6.1.1.2 Effect of operating temperature

Beta-zeolite was chosen to study the effect of operating temperature in the batch reactor at 0.8 MPa and three temperatures (333, 343 and 353 K). The results demonstrate that the etherification conversion and their obtained yield of ether decrease with the increase of operating temperature. Therefore, the suitable operating temperature of this process is about 333 K.

6.1.2 Etherification and hydration of FCC gasoline with water/ethanol azeotropic mixture

6.1.2.1 Etherification of FCC gasoline with azeotropic mixture of ethanol is not a promising process because the presence of water in the ethanol azeotropic mixture causes the decreasing of ethanol and IA conversion. Comparing between two catalysts, Amberlyst 16 catalyst showed higher water tolerance in hydration reaction than Beta-zeolite.

6.1.2.2 The FCC upgrading by the hydration with water is possible an alternative process because almost water could be consumed to produce *tert*-alcohols which are octane enhancer. A trace amount of unreacted water was significantly less than the water content limitation in gasoline, i.e., 0.7 wt% for Thailand gasoline specification.

6.2 Recommendations

Because the FCC compositions are various, therefore the suitable amount of ethanol added into gasoline could be varied. It is recommended that simulation to find the equilibrium conversion should be investigated to predict the unreacted ethanol which remains in the final gasoline product. The ethanol content should not be over the ethanol limitation which depends on engine specification. Furthermore, for the hydration with water, the amount of water can be added in the FCC gasoline should be also simulated. The water content in the gasoline product should not over the restriction to prevent the engine knock.

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APPENDICES

APPENDIX A

CALIBRATION CURVES

The calibration curves of all components involving in the reaction system were prepared. The gas chromatography (Shimadzu model 8A) equipped with gaskuropack 54 column and thermal conductivity detector was used to analyze the composions of all components. The calibration curves of H_2O, Ethanol, IA, TAA and TAEE in relationship between volume and area are obtained as below.

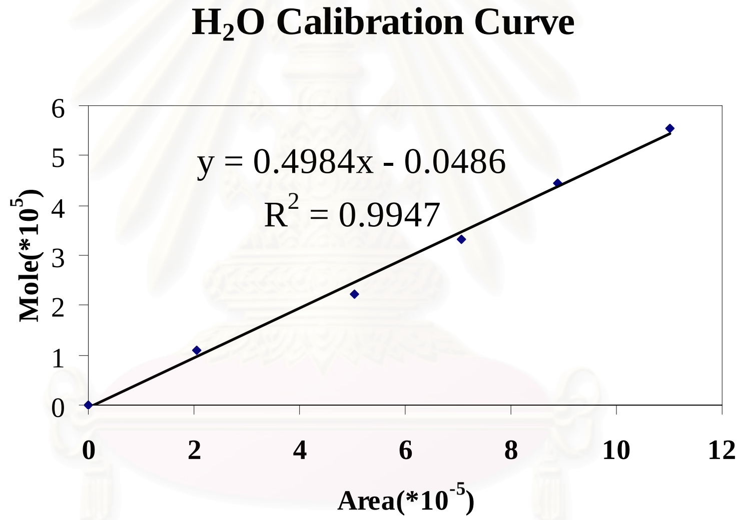

Figure A.1 The calibration Curve of Water

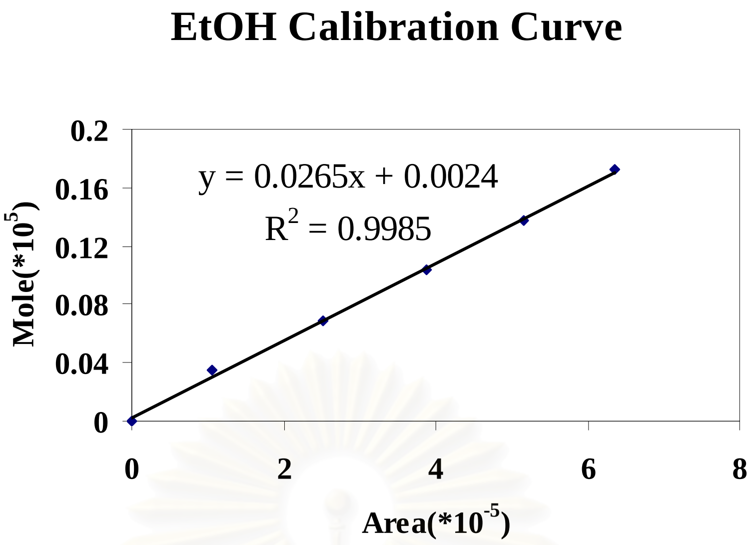

Figure A.2 The calibration Curve of Ethanol

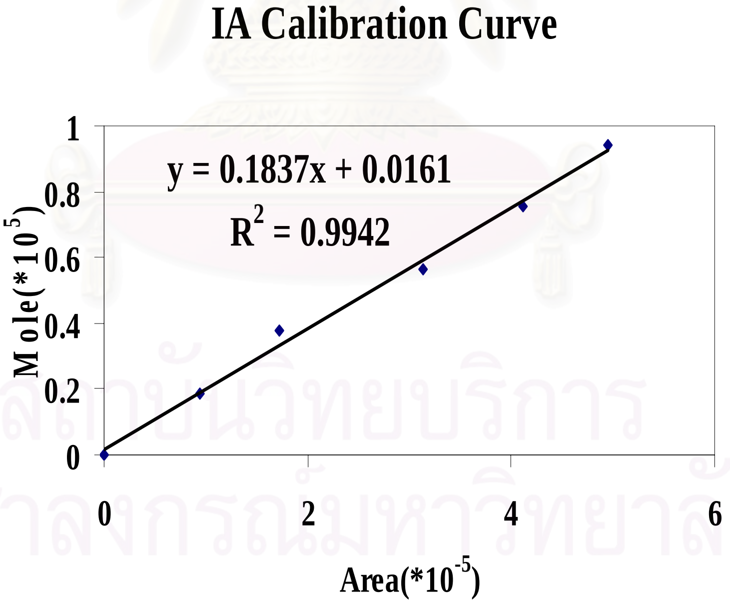

Figure A.3 The calibration Curve of Isoamylenes

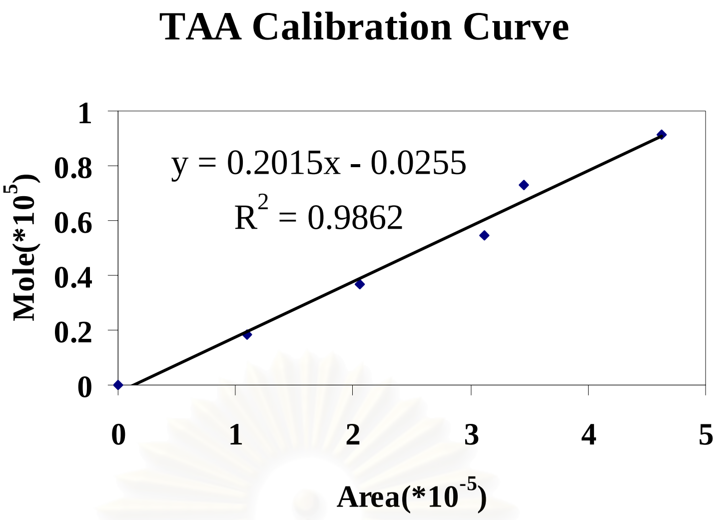

Figure A.4 The calibration Curve of TAA

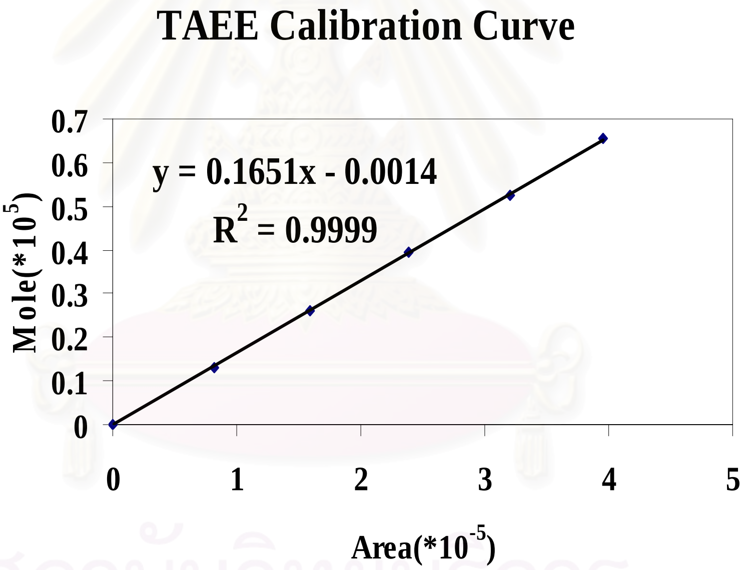

Figure A.5 The calibration Curve of TAEE

APPENDIX B

ASTM D 86

STANDARD TEST METHOD FOR DISTILLATION OF PETROLEUM PRODUCT AT ATMOSPHERIC PRESSURE

1. Scope

1.1 This test method covers the atmospheric distillation of petroleum products using a laboratory batch distillation unit to determine quantitatively the boiling range characteristics of such products as natural gasolines, light and middle distillates, automotive spark-ignition engine fuels, aviation gasolines, aviation turbine fuels, 1-D and 2-D regular and low sulfur diesel fuels, special petroleum spirits, naphthas, white spirits, kerosines, and Grades 1 and 2 burner fuels.

1.2 The test method is designed for the analysis of distillate fuels; it is not applicable to products containing appreciable quantities of residual material.

1.3 This test method covers both manual and automated instruments.

1.4 Unless otherwise noted, the values stated in SI units are to be regarded as the standard. The values given in parentheses are provided for information only.

1.5 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Summary of Test Method

2.1 Based on its composition, vapor pressure, expected IBP or expected EP, or combination thereof, the sample is placed in one of five groups. Apparatus arrangement, condenser temperature, and other operational variables are defined by the group in which the sample falls.

2.2 A 100 mL specimen of the sample is distilled under prescribed conditions for the group in which the sample falls. The distillation is performed in a laboratory batch distillation unit at ambient pressure under conditions that are designed to provide approximately one theoretical plate fractionation. Systematic observations of temperature readings and volumes of condensate are made, depending on the needs of the user of the data. The volume of the residue and the losses are also recorded.

2.3 At the conclusion of the distillation, the observed vapor temperatures can be corrected for barometric pressure and the data are examined for conformance to procedural requirements, such as distillation rates. The test is repeated if any specified condition has not been met.

2.4 Test results are commonly expressed as percent evaporated or percent recovered versus corresponding temperature, either in a table or graphically, as a plot of the distillation curve.

3. Significance and Use

3.1 The basic test method of determining the boiling range of a petroleum product by performing a simple batch distillation has been in use as long as the petroleum industry has existed. It is one of the oldest test methods under the jurisdiction of ASTM Committee D02, dating from the time when it was still referred to as the Engler distillation. Since the test method has been in use for such an extended period, a tremendous number of historical data bases exist for estimating end-use sensitivity on products and processes.

3.2 The distillation (volatility) characteristics of hydrocarbons have an important effect on their safety and performance, especially in the case of fuels and solvents. The boiling range gives information on the composition, the properties, and the behavior of the fuel during storage and use. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially explosive vapors.

3.3 The distillation characteristics are critically important for both automotive and aviation gasolines, affecting starting, warm-up, and tendency to vapor lock at high operating temperature or at high altitude, or both. The presence of high boiling point components in these and other fuels can significantly affect the degree of formation of solid combustion deposits.

3.4 Volatility, as it affects rate of evaporation, is an important factor in the application of many solvents, particularly those used in paints.

3.5 Distillation limits are often included in petroleum product specifications, in commercial contract agreements, process refinery/control applications, and for compliance to regulatory rules.

APPENDIX C

ASTM D 2699
STANDARD TEST METHOD FOR RESEARCH OCTANE NUMBER OF SPARK-IGNITION ENGINE FUEL

1. Scope

1.1 This laboratory test method covers the quantitative determination of the knock rating of liquid spark-ignition engine fuel in terms of Research O.N., except that this test method may not be applicable to fuel and fuel components that are primarily oxygenates.2 The sample fuel is tested using a standardized single cylinder, four-stroke cycle, variable compression ratio, carbureted, CFR engine run in accordance with a defined set of operating conditions. The O.N. scale is defined by the volumetric composition of PRF blends. The sample fuel knock intensity is compared to that of one or more PRF blends. The O.N. of the PRF blend that matches the K.I. of the sample fuel establishes the Research O.N.

1.2 The O.N. scale covers the range from 0 to 120 octane number but this test method has a working range from 40 to 120 Research O.N. Typical commercial fuels produced for spark-ignition engines rate in the 88 to 101 Research O.N. range. Testing of gasoline blend stocks or other process stream materials can produce ratings at various levels throughout the Research O.N. range.

1.3 The values of operating conditions are stated in SI units and are considered standard. The values in parentheses are the historical inch-pound units. The standardized CFR engine measurements continue to be in inch-pound units only because of the extensive and expensive tooling that has been created for this equipment.

1.4 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use

2. Summary of Test Method

2.1 The Research O.N. of a spark-ignition engine fuel is determined using a standard test engine and operating conditions to compare its knock characteristic with those of PRF blends of known O.N. Compression ratio and fuel-air ratio are adjusted to produce standard K.I. for the sample fuel, as measured by a specific electronic detonation meter instrument system. A standard K.I. guide table relates engine C.R. to O.N. level for this specific method. The fuel-air ratio for the sample fuel and each of the primary reference fuel blends is adjusted to maximize K.I. for each fuel. The fuel-air ratio for maximum K.I. may be obtained

2.1.1 By making incremental step changes in mixture strength, observing the equilibrium K.I. value for each step, and then selecting the condition that maximizes the reading.

2.1.2 By picking the maximum K.I. as the mixture strength is changed from either rich-to-lean or lean-to-rich at a constant rate.

2.2 Bracketing Procedures

The engine is calibrated to operate at standard K.I. in accordance with the guide table. The fuel-air ratio of the sample fuel is adjusted to maximize the K.I., and then the cylinder height is adjusted so that standard K.I. is achieved. Without changing cylinder height, two PRF blends are selected such that, at their fuel-air ratio for maximum K.I., one knocks harder (higher K.I.) and the other softer (lower K.I.) than the sample fuel. A second set of K.I. measurements for sample fuel and PRF blends is required, and the sample fuel octane number is calculated by interpolation in proportion to the differences in average K.I. readings. A final condition requires that the cylinder height used shall be within prescribed limits around the guide table value for the calculated O.N. Bracketing procedure ratings may be determined using either the equilibrium fuel level or dynamic fuel level fuel-air ratio approach.

2.3 C.R. Procedure

A calibration is performed to establish standard K.I. using the cylinder height specified by the guide table for the O.N. of the selected PRF. The fuel-air ratio of the sample fuel is adjusted to maximize the K.I. under equilibrium conditions; the cylinder height is adjusted so that standard K.I. is achieved. The calibration is reconfirmed and the sample fuel rating is repeated to establish the proper conditions a second time. The average cylinder height reading for the sample fuel, compensated for barometric pressure, is converted directly to O.N., using the guide table. A final condition for the rating requires that the sample fuel O.N. be within prescribed limits around that of the O.N. of the single PRF blend used to calibrate the engine to the guide table standard K.I. condition.

3. Significance and Use

3.1 Research O.N. correlates with commercial automotive spark-ignition engine antiknock performance under mild conditions of operation.

3.2 Research O.N. is used by engine manufacturers, petroleum refiners and marketers, and in commerce as a primary specification measurement related to the matching of fuels and engines.

3.2.1 Empirical correlations that permit calculation of automotive antiknock performance are based on the general equation:

$$\text{Road O.N.} = (k_1 * \text{Research O.N.}) + (k_2 * \text{Motor O.N.}) + k_3 \qquad \text{(C-1)}$$

Values of k_1, k_2, and k_3 vary with vehicles and vehicle populations and are based on road-O.N. determinations.

3.2.2 Research O.N., in conjunction with Motor O.N., defines the antiknock index of automotive spark-ignition engine fuels, in accordance with ASTM D 4814. The antiknock index of a fuel approximates the Road octane ratings for many vehicles, is posted on retail dispensing pumps in the U.S., and is referred to in vehicle manuals.

$$\text{Antiknock index} = 0.5\ \text{Research O.N.} + 0.5\ \text{Motor O.N.} + 0 \qquad \text{(C-2)}$$

This is more commonly presented as:

$$\text{Antiknock Index} = \frac{RON + MON}{2} \qquad \text{(C-3)}$$

3.2.3 Research O.N. is also used either alone or in conjunction with other factors to define the Road O.N. capabilities of spark-ignition engine fuels for vehicles operating in areas of the world other than the United States.

3.3 Research O.N. is used for measuring the antiknock performance of spark-ignition engine fuels that contain oxygenates.

3.4 Research O.N. is important in relation to the specifications for spark-ignition engine fuels used in stationary and other nonautomotive engine applications.

APPENDIX D

ASTM D 5191

STANDARD TEST METHOD FOR VAPOR PRESSURE OF PETROLEUM PRODUCTS

1. Scope

1.1 This test method covers the use of automated vapor pressure instruments to determine the total vapor pressure exerted in vacuum by air-containing, volatile, liquid petroleum products. This test method is suitable for testing samples with boiling points above 0°C (32°F) that exert a vapor pressure between 7 and 130 kPa (1.0 and 18.6 psi) at 37.8°C (100°F) at a vapor-to-liquid ratio of 4:1. Measurements are made on liquid sample sizes in the range from 1 to 10 mL. No account is made for dissolved water in the sample.

(NOTE 1-Samples can also be tested at other vapor-to-liquid ratios, temperatures, and pressures, but the precision and bias statements need not apply.

NOTE 2-The interlaboratory studies conducted in 1988, 1991, and 2003 to determine the precision statements in Test Method D 5191 did not include any crude oil in the sample sets. Test Method D 6377, as well as IP 481, have been shown to be suitable for vapor pressure measurements of crude oils.)

1.1.1 Some gasoline-oxygenate blends may show a haze when cooled to 0 to 1°C. It shall be indicated in the reporting of results. The precision and bias statements for hazy samples have not been determined.

1.2 This test method is suitable for calculation of the dry vapor pressure equivalent (DVPE) of gasoline and gasoline oxygenate blends by means of a correlation equation. The calculated DVPE very closely approximates the dry vapor pressure that would be obtained on the same material when tested by Test Method D 4953.

1.3 The values stated in SI units are regarded as standard. The inch-pound units given in parentheses are provided for information only.

1.4 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Summary of Test Method

2.1 A known volume of chilled, air-saturated sample is introduced into a thermostatically controlled, evacuated test chamber, or a test chamber with a moveable piston that expands the volume after sample introduction, the internal volume of which is five times that of the total test specimen introduced into the chamber. After introduction into the test chamber, the test specimen is allowed to reach thermal equilibrium at the test temperature, 37.8°C (100°F). The resulting rise in pressure in the chamber is measured using a pressure transducer sensor and indicator. Only total pressure measurements (sum of the partial pressure of the sample and the partial pressure of the dissolved air) are used in this test method, although some instruments can measure the absolute pressure of the sample as well.

2.2 The measured total vapor pressure is converted to a dry vapor pressure equivalent (DVPE) by use of a correlation equation .

3. Significance and Use

3.1 Vapor pressure is a very important physical property of volatile liquids.

3.2 The vapor pressure of gasoline and gasoline-oxygenate blends is regulated by various government agencies.

3.3 Specifications for volatile petroleum products generally include vapor pressure limits to ensure products of suitable volatility performance.

3.4 This test method uses a small sample size (1 to 10 mL), and requires about 7 min to complete the test.

APPENDIX E

CONDITION OF PIANO ANALYZER

E.1 Column Information

Column Information	
Detector	FID
Carrier Gas	He (99.98 %)
Carrier Gas Flow rate (psig)	50
Capillary Column	SUPELCO
Length of Column (m)	100
Diameter of Column (mm)	0.25
Maximum Temperature (K)	523

E.2 Operating Condition

Conditions			
Experiment Time (min)	111.83		
Injection Volume (μL)	0.5		
Injection Temperature (K)	523		
Detector Temperature (K)	523		
Column Temperature	Program Rate (^{o}C/min)	Temperature (K)	Holding Time (min)
Initial	0.0	5	11.0
Ramp 1	6.0	65	45.0
Ramp 2	3.0	180	5.0
Ramp 3	10.0	200	0.5

E.3 Chromatogram of SUPELCO column

Time	Component
8.882	Isobutene
9.499	1-butene, isobutene
9.529	Isobutene
9.802	n-butane
10.164	trans-2-butene
10.708	cis-2-butene
12.203	3-methyl-1-butene
13.197	Isopentane
14.119	1-pentene
14.571	2-methyl-1-butene
14.854	n-pentane
15.153	Isoprene
15.415	trans-2-pentene
15.774	3,3-dimethyl-1-butene
15.931	cis-2-pentene
16.266	2-methyl-2-butene
16.44	trans-1,3-pentadiene
17.096	3-methyl-1,2-butadiene
17.302	2,2-dimethylbutane
18.514	Cyclopentene
18.906	4-methyl-1-pentene
18.973	3-methyl-1-pentene
19.306	Cyclopentane
19.526	2,3-dimethylbutane
19.655	4-methyl-cis-2-pentene
19.922	2-methylpentane
20.048	4-methyl-trans-2-pentene
21.015	3-methylpentane
21.446	2-methyl-1-pentene

Time	Component
21.536	1-hexene
22.41	2-ethyl-1-butene
22.475	n-hexane
22.688	trans-3-hexene
22.753	cis-3-hexene
22.909	trans-2-hexene
23.106	2-methyl-2-pentene
23.337	3-methyl-cis-2-pentene
23.426	3-methylcyclopentene
23.691	cis-2-hexene
24.245	3,3-Dimethyl-1-pentene
24.348	3-methyl-trans-2-pentene
24.58	2,2-dimethylpentane
24.719	Methylcyclopentane
25.186	2,4-dimethylpentane
25.342	2,2,3-trimethyl-1-butene
25.476	Cyclodiolefin or triolefin
25.599	2,2,3-trimethylbutane
25.853	cyclodiolefin or triolefin
26.362	3,4-dimethyl-1-pentene
26.75	4,4-dimethyl-cis-2-pentene
26.819	2,4-dimethyl-1-pentene
26.944	1-methylcyclopentene
27.021	Benzene
27.194	3-methyl-1-hexene
27.371	2-methyl-cis-3-hexene
27.533	3,3-dimethylpentane
27.851	5-methylhexene-1
27.954	Cyclohexane
28.275	2-methyl-trans-3-hexene
28.377	diolefin (hexadiene)

Time	Component
28.457	2-ethyl-3-methyl-1-butene
28.604	4-methyl-1-hexene
28.872	4-methyl-cis-2-hexene
29.063	2-methylhexane
29.209	2,3-dimethylpentane
29.474	1,1-dimethylcyclopentane
29.713	Cyclohexene
30.04	3-methylhexane
30.437	3,4-dimethyl-cis-2-pentene
30.735	cis-1,3-dimethylcyclopentane
31.069	trans-1,3-dimethylcyclopentane
31.256	3-ethylpentane
31.409	trans-1,2-dimethylcyclopentane
31.607	1-heptene
31.698	2-ethyl-1-pentene
32.38	3-methyl-cis-3-hexene
32.865	trans-3-heptene
33.106	n-heptane
33.385	2-methyl-2-hexene
33.521	3-methyl-cis-2-hexene
33.777	trans-2-heptene
33.977	3-ethyl-2-pentene
34.42	cis-2-heptene
34.938	2,3-dimethyl-2-pentene
35.102	3-ethylcyclopentene
35.774	cis-1,2-dimethylcyclopentane
35.903	methylcyclohexane
36.383	1,1,3-trimethylcyclopentane
37.757	ethylcyclopentane
37.976	2,5-dimethylhexane
38.145	2,2,3-trimethylpentane

Time	Component
38.292	2,4-dimethylhexane
39.255	cis-1,2-cis&trans-4-trimethylCyC5
40.578	trans-1-,cis-2,3-trimethylcyclopentane
41.199	2,3,4-trimethylpentane
41.908	Toluene
43.266	2,3-dimethylhexane
43.517	2-methyl-3-ethylpentane
43.714	1,1,2-trimethylcyclopentane
44.597	2-methylheptane
44.901	4-methylheptane
45.104	3-methyl-3-ethylpentane
45.237	3,4-dimethylhexane
45.811	cis-1,3-dimethylcyclohexane
46.256	3-methylheptane
46.502	cis-1,2-trans-3-trimethylcyclopentane
46.696	3-ethylhexane
46.972	trans-1,4-dimethylcyclohexane
47.407	1,3-octadiene
48.851	2,2,5-trimethylhexane
49.141	cis-3-methylethylcyclopentane
49.384	2,6-dimethyl-1-heptene
49.664	trans-3-methylethylcyclopentane
49.96	trans-2-ethylmethylcyclopentane
50.143	1-octene
50.635	2,2,4-trimethylhexane
51.144	trans-1,2-dimethylcyclohexane
51.532	trans-4-octene
52.293	cis-1-,cis-2,3-trimethylcyclopentane
52.705	trans-1,3-dimethylcyclohexane
53.052	n-octane
54.119	trans-2-octene

Time	Component
56.489	cis-2-octene
57.806	2,2,3,4-tetramethylpentane
58.284	2,3,4-trimethylhexane
60.144	2,3,3-trimethyl-1-hexene
60.385	cis-1,2-dimethylcyclohexane
62.304	1,1,4-trimethylcyclohexane
63.151	2,2,3-trimethylhexane
63.548	2,4-dimethylheptane
64.664	4,4-dimethylheptane
65.046	ethylcyclohexane
65.379	n-propylcyclopentane
65.779	2,6-dimethylheptane
66.179	3,3-dimethylheptane
66.737	2,5-dimethylheptane
67.484	1,1,3-trimethylcyclohexane
67.847	trans-1,2-Dimethyl-cis-4-ethylCyC5
69.065	ethylbenzene
70.744	2-methyloctene-1
71.323	1,3-dimethylbenzene
71.625	1,4-dimethylbenzene
72.006	2,3-dimethylheptane
72.576	3,4-dimethylheptan
73.211	3,4-dimethylheptane
74.574	4-ethylheptane
74.924	4-methyloctane
75.329	2-methyloctane
75.845	cis-1-,trans-2,3-trimethylCyC6
76.417	3-ethylheptane
76.87	3-methyloctane
77.431	3,3-diethylpentane
77.943	1,2-dimethylbenzene

Time	Component
78.266	trans-1,2-cis-4-trimethylcyclohexane
81.275	1-nonene
81.588	isobutylcyclopentane
83.003	trans-7-methyl-3-octene
83.558	cis-2-nonene
84.282	trans-3-nonene
84.745	n-nonane
85.058	1,1-methylethylcyclohexane
85.784	trans-2,2,5,5-tetramethyl-3-hexene
85.982	cis-1-cis-2,3-trimethylCyC6
86.99	isopropylbenzene
88.927	2,2-dimethyloctane
90.9	2,6-dimethyloctane
91.306	2,5-dimethyloctane
92.02	n-butylcyclopentane
93.388	3,3-dimethyloctane
94.121	n-propylbenzene
94.535	3,6-dimethyloctane
94.918	3-methyl-5-ethylheptane
95.964	1,3-methylethylbenzene
96.371	1,4-methylethylbenzene
97.702	2,3-dimethyloctane
99.22	5-methylnonane
99.605	1,2-methylethylbenzene
100.155	2-methylnonane
100.444	3-ethyloctane
101.48	3-methylnonane
102.061	3-ethyl-2-methyl-2-heptene
102.898	1,2,4-trimethylbenzene
103.162	*tert*-butylbenzene
103.891	isobutylcyclohexane

Time	Component
104.945	1-decene
105.764	2,3-dimethyl-2-octene
105.979	isobutylbenzene
106.488	*sec*-butylbenzene
107.244	n-decane
108.44	1,2,3-trimethylbenzene
108.639	1,3-methyl-isopropylbenzene
109.281	1,4-methyl-isopropylbenzene
110.865	*sec*-butylcyclohexane
111.784	1,2-methyl-isopropylbenzene
113.889	1,3-diethylbenzene
114.126	1,3-methyl-n-propylbenzene
114.783	1,4-diethylbenzene
114.948	1,4-methyl-n-propylbenzene
115.375	n-butylbenzene
115.636	1,3-dimethyl-5-ethylbenzene
116.024	1,2-diethylbenzene
116.511	trans-decahydronaphthalene
117.824	1,2-methyl-n-propylbenzene
118.574	1,4,dimethyl-2-ethylbenzene
119.632	1,3-dimethyl-4-ethylbenzene
121.688	1,2-dimethyl-4-ethylbenzene
122.545	1,3-dimethyl-2-ethylbenzene
123.116	1,4-methyl-t-butylbenzene
124.32	1,2-ethyl-i-propylbenzene
124.73	n-undecane
125.162	1,4-ethyl-isopropylbenzene
125.7	1,2-methyl-n-butylbenzene
125.871	1,2,3,5-tetramethylbenzene
128.275	5-methylindan
129.289	4-methylindan

Time	Component
129.788	1,2-ethyl-n-propylbenzene
130.204	2-methylindan
130.51	1,3-methyl-n-butylbenzene
130.852	1,3-diisopropylbenzene
131.364	s-pentylbenzene
131.563	n-pentylbenzene
132.138	trans-1-M-2-(4-MP)cyclopentane
132.521	1,2-diisopropylbenzene
133.359	1,4-diisopropylbenzene
133.921	tetrahydronaphthalene
134.556	naphthalene
135.501	1,4-ethyl-trans-butylbenzene
137.506	1,3-di-n-propylbenzene
139.592	n-dodecane
142.284	1,3,5-triethylbenzene
146.359	n-hexylbenzene
149.901	2-methylnaphthalene
151.934	n-tridecane

VITAE

Miss Piyaporn Thipsunet was born on August 8, 1982 in Songkhla, Thailand. She obtained the bachelor’s degree in Chemical Engineering from Prince of Songkla University (PSU), Songkhla, in March, 2005. Then she continued her master degree in Chemical Engineering at Chulalongkorn University and graduated in March, 2007.