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นางสาวพิชชาภา คงเจริญ

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REDUCTION OF BENZENE IN REFORMATE BY ETHYLENE ALKYLATION WITH BENZENE

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พิชชาภา คงเจริญ: การลดปริมาณเบนซีนในรีฟอร์มเมตโดยเอทธิลีนอัลคิเลชันกับเบนซีน (REDUCTION OF BENZENE IN REFORMATE BY ETHYLENE ALKYLATION WITH BENZENE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร. สุทธิชัย อัสสะบำรุงรัตน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร. วรพล เกียรติกิตติพงษ์ 88 หน้า.

เบนซีนเป็นสารประกอบประเภทอะโรมาติกไฮโดรคาร์บอนที่เป็นองค์ประกอบในแก๊สโซลีนซึ่งมีเลขออกเทนสูง แต่เบนซีนเป็นสารก่อให้เกิดมะเร็งและมีค่าความดันไอสูงจึงระเหยได้ง่าย ในการผสมน้ำมันจากหลายส่วน ปริมาณเบนซีนส่วนมากมาจากส่วนรีฟอร์มเมต ดังนั้นจึงลดปริมาณเบนซีนในรีฟอร์มเมตก่อนที่จะผสมกับแก๊สโซลีนที่เป็นผลิตภัณฑ์จากหน่วยอื่น ๆ งานวิจัยนี้ศึกษาการลดปริมาณเบนซีนในรีฟอร์มเมตโดยการทำปฏิกิริยาอัลคิเลชันกับเอทธิลีน ในเครื่องปฏิกรณ์แบบอัดความดัน ที่อุณหภูมิ 225 องศาเซลเซียส ภายใต้ความดัน 45 บาร์ เป็นเวลา 20 ชั่วโมง โดยใช้เบต้า-ซีโอไลท์เป็นตัวเร่งปฏิกิริยา จากผลการทดลองเมื่อทำปฏิกิริยาอัลคิเลชันเบนซีนในรีฟอร์มเมตกับเอทธิลีนในปริมาณ ต่าง ๆ พบว่าผลิตภัณฑ์ที่ได้มีค่าออกเทนและอุณหภูมิการกลั่นสูงขึ้น และความดันไอลดลงได้ เพราะเอทิลเบนซีนถูกผลิตขึ้นมาแทนที่เบนซีน ดังนั้นการทำปฏิกิริยาอัลคิเลชันรีฟอร์มเมตสามารถปรับปรุงคุณภาพของแก๊สโซลีนได้ทั้งในด้านเทคนิคและสิ่งแวดล้อม ค่าร้อยละการเปลี่ยนแปลงของเบนซีนเพิ่มสูงขึ้นเมื่อปริมาณเอทธิลีนที่ป้อนเข้าทำปฏิกิริยาสูงขึ้น นอกจากนี้การเติมแกลเลียมในเบต้า-ซีโอไลต์สามารถพัฒนาค่าร้อยละการเปลี่ยนแปลงของเบนซีนและค่าออกเทนให้สูงขึ้นได้และมีค่าความดันไอลดลง อย่างไรก็ตามการพัฒนาคุณภาพน้ำมันที่ได้จากการเติมแกลเลียมนี้ไม่ได้เกิดจากการส่งเสริมของปฏิกิริยาอัลคิเลชันเบนซีนกับเอทธิลีนดังพิสูจน์ด้วยปฏิกิริยาระหว่างเบนซีนบริสุทธิ์กับเอทธิลีน

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PICHCHAPA KHONGJARERN : REDUCTION OF BENZENE IN REFORMATE BY ETHYLENE ALKYLATION WITH BENZENE. THESIS ADVISOR: PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., THESIS CO-ADVISOR: ASST. PROF. WORAPON KIATKITTIPONG, D.Eng., 88 pp.

Benzene is a key aromatic hydrocarbon which is an important high octane component of motor gasoline; however, benzene is known as a human carcinogen and also has high vapor pressure thus high evaporative emissions. Reformate is the largest portion of benzene in a gasoline pool and, therefore it was aimed to reduce benzene content prior to blending. Alkylation of reformate with ethylene was investigated in this research work. The reaction was performed in an autoclave reactor with a temperature of 225 °C and pressure of 45 bar for 20 h using β-zeolite as a catalyst. The alkylation products showed the increasing in research octane number (RON) and distillation temperature with decreasing in blending Reid vapor pressure (bRvp) because ethylbenzene is produced instead of benzene. Thus the process improves gasoline quality in both term of technical and environmental viewpoint. Benzene conversion is higher with higher ethylene in feed. Moreover, modified β-zeolite with Ga further improved benzene conversion and RON with decreasing bRvp. However, this improvement with Ga modification might not because of the enhancement of alkylation between benzene and ethylene as proven by the probe reaction of pure benzene with ethylene.

Department : Chemical Engineering	Student's Signature Pichchapa Khongjarern
Field of Study : Chemical Engineering	Advisor's Signature
Academic Year : 2009	Co-Advisor's Signature

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CHAPTER I

INTRODUCTION

1.1 Rationale

Currently, global awareness on environmental problem is increasing. The standards for vehicles will be further restricted in their emissions. The restriction not only applies to the vehicle manufacturers, but also refineries. Gasoline comprises of a mixture of numerous hydrocarbons including aromatics, olefins, naphthenes and paraffins. These compounds represent the exhaust of gasoline motor vehicles via both combustion and evaporation. Benzene is a key aromatic hydrocarbon with high octane number, but benzene is a known human carcinogen and also has high vapor pressure and poses a health risk due to evaporative emissions. Because of these reasons, the benzene content in motor gasoline was regulated to be less than 1 vol.% following Euro 5 standard (started on 2009). For Thailand, the current benzene content is limited at 3.5 vol.% and the enforcement for reducing to 1 vol.% will begin on January 2012 (Announcement of Department of Energy Business, 2007). Reformate is the largest blending stock for gasoline which constitutes up to 41.7 vol.% of the final product. Among the primary sources of benzene in gasoline pool i.e. reformate, isomerate, alkylated and FCC naphtha, reformate has the highest benzene content approx. 5 vol.% and therefore it contributes mostly of benzene presence in gasoline pool (Denis and Hiren, 2004). For this reason, many strategies for reducing benzene contents in gasoline have focused on removing a portion of benzene from reformate prior to blend.

The common strategies for reducing the benzene content in reformate include chemical processes and physical separation. Physical separations are the method which removes a portion of benzene. There are many techniques of physical separations which can be used to remove benzene such as distillation, solvent extraction, extractive distillation and adsorption. Distillation is not suitable because benzene has azeotropes with normal hexane and naphthenes (Kaul *et al.*, 1993). Solvent extraction process and extractive distillation process of benzene using sulfolane, n-methyl pyrolidone (NMP), n-formyl-morpholine (NFM) as solvent have been investigated. In spite of the advantages of high yield and selectivity, these methods have many drawbacks such as using of high boiling selective solvent (the boiling point of sulfolane is 285 °C) results in a high temperature in the extractive distillation tower and leads to decrease in the separation selectivity (Gaile et al., 2008). Moreover, the extraction processes use of special equipment to resist the corrosion of solvent which result in high manufacturing cost.

Adsorption processes have been used for removing all aromatics from nonaromatic fraction of mixed hydrocarbon stream. There are many adsorbent that use to separate aromatics such as alumino silicate zeolite, silica gel and molecular sieve etc. U.S.Pat. No. 5,294,334(1994) disclosed a process for reducing the benzene content by adsorption benzene using a zeolite layer and desorption of benzene is carried out using cyclohexane. It is worthy to note that separation of benzene from reformate via several methods of course decreases in octane and volume of gasoline; thus they are not satisfactory for reducing the benzene content.

For chemical processes, benzene is converted to other desirable and less restricted components for gasoline blending. U.S.Pat.No.5,284,984 (1994) disclosed a process for converting benzene in gasoline to aromatic nitrocompounds by directly nitrifying the benzene hydrogenating the aromatic nitrocompounds without separating them from gasoline and then transferring to a gasoline pool as an octane booster. However, the use of nitric acid in the nitrification step involves a large investment for a large scale plant. Moreover, the blending aromatic amines into gasoline possibly cause environmental problems that make it very difficult to apply this technology to a commercial plant (Dessau *et al*., 1994).

Hydrogenation reaction for converting benzene to cyclohexane has drawn many researches’ attention to improve gasoline properties. However, cyclohexane has lower octane rating than benzene. In order to partially recover the octane number loss, Lee *et al*. (1998) disclosed a process which uses a dual functional catalyst to hydrogenate benzene to cyclohexane and further isomerize the cyclohexane to methylcyclopentane which has an octane rating between cyclohexane and benzene. Nevertheless, this method increases the refining cost and reduces the grade of gasoline blending stock (Lin et al., 2007).

To overcome these drawbacks, it has been found that benzene may be alkylated with olefins that improve both octane and volume of gasoline (Hsieh *et al*., 1993). For example, Bellussi et al. (1995) investigated the alkylation of benzene with light olefins to produce alkylbenzene which is less toxic and desirable high octane blending compounds such as ethylbenzene, isopropylbenzene. One commercial process of this type is the Mobil Benzene Reduction (MBR) process which used a fluidized zeolite catalyst to convert benzene to alkylaromatics using olefins from sources such as fluidized catalytic cracking (FCC), excess LPG. The yield-octane uplift of MBR process makes processes become economically beneficial in petroleum refining (Umansky *et al*., 2009).

This study focuses on alkylating of reformate with ethylene. Beta-zeolite with and without modification will be employed as a catalyst. The gasoline properties i.e. paraffins, iso-paraffins, aromatics, naphthenes and olefins (PIANO) analysis, benzene content, blending Reid vapor pressure (bRvp), research octane number (RON) will be determined.

1.2 Objective

To reduce the benzene content in reformate by ethylene alkylation with suitable catalyst and operating conditions.

1.3 Scope

1. Study the catalytic activity of Hβ-zeolite and Ga-modified Hβ-zeolite catalysts in benzene alkylation with ethylene by using pure benzene and reformate as a feed.
2. Study the characterization of the prepared catalysts by the following methods.
    - Analysis structure and crystallinity of catalyst by X-ray diffraction (XRD)
    - Analysis pore volume and surface areas of catalysts by Brunauer-Emmett-Teller (BET) surface area measurement.
    - Analysis the acidity of catalysts by temperature programmed desorption of ammonia (NH_3-TPD).
3. Investigate the effect of ethylene content in feed and operating temperature i.e. 225, 205 and 185 °C on the reaction performance.

4. Analysis properties of reformate alkylation product i.e. PIANO analysis, benzene and ethylbenzene content, RON, bRvp and distillation temperature were carried out by follows the standard methods.

CHAPTER II

THEORY

This chapter contributes some background information necessary for the fuel oil quality improvement by reduction of benzene in reformate with olefin alkylation. Some detail of reforming process, gasoline properties (octane number, bRvp and distillation temperature) and catalysts were provided.

2.1 Reforming Process

In early 1930s, the requirement for higher-octane gasoline had been developed. Distilled gasoline had very low octane numbers, and any process would aid in meeting the demand for higher octane number gasoline. Such thermal reforming was developed and used widely, but lesser extent than thermal cracking processes; cracking converts heavier oils into gasoline whereas reforming converts gasoline into higher octane gasoline. The equipment for thermal reforming is essentially the same as for thermal craking, but higher temperatures are used.

2.1.1 Thermal Reforming

In the thermal reforming process a feedstock such as naphtha or a straight-run gasoline is heated to 510-595 °C in a furnace with pressures from 27 to 68 atm. As the heated naphtha leaves the furnace, it is cooled or quenched by the addition of cold naphtha. The material then enters a fractional distillation tower where any heavy products are separated. The remainder of the reformed material leaves the top of the tower to be separated into gases and reformate. The higher octane number of reformate is due primarily to the cracking of longer chain paraffins into higher octane olefins.

The products of thermal reforming are gases, gasoline, and residual oil or tar. The amount and quality of the gasoline, known as reformate, is very dependent on the temperature. A general rule is the higher of reforming temperature and octane number, but the lower of reformate yield. Thermal reforming is less effective and less economic than catalytic processes and has been largely displaced. The improvement of octane number degree depended on the extent of conversion but was not directly proportional to the extent of crack per pass. At very high conversions, the product of coke and gas became prohibitively high. The gases produced were generally olefinic and the process required either a separate gas polymerization operation or one in which C3 to C4 gases were added back to the reforming system. (Synthetic fuels handbook: properties, process, and performance, 2008)

2.1.2 Catalytic Reforming

Like thermal reforming, catalytic reforming converts low octane gasoline into high-octane gasoline (reformate). When thermal reforming could produce reformate with research octane numbers of 65 to 80 depending on the yield, catalytic reforming produces reformate with octane numbers on the order of 90 to 95. Catalytic reforming is conducted in the presence of hydrogen over hydrogenation-dehydrogenation catalysts, which may be supported on alumina or silica-alumina. Depending on the catalyst, a definite sequence of reactions takes place, involving structural changes in the feed stock. This more modern concept actually rendered thermal reforming somewhat archaic.

In the re-arranges or re-structures of process, the hydrocarbon molecules in the naphtha feedstocks were broken into smaller molecules. The overall effect is that the product of reformate contains hydrocarbons with more complex molecular shapes have had higher octane values than the hydrocarbons in the naphtha feedstock. So, hydrogen atoms was separated the hydrocarbon molecules of process and the process produces very significant amounts of byproduct hydrogen gas for use in a number of the other processes involved in a modern petroleum refinery. Other byproducts are small amounts of methane, ethane, propane and butanes. Dehydrogenation is a main chemical reaction in catalytic reforming and hydrogen gas is consequently produced in large quantities. The hydrogen recycled though the reactors where the reforming takes place to provide the atmosphere necessary for the chemical reactions and also prevents the carbon from being deposited on the catalyst, thus extending its operating life. An excess of hydrogen above whatever is consumed in the process is produced as a result, catalytic reforming processes are unique in that they are the only petroleum refinery processes to produce hydrogen as a by-product.

2.1.3 Reformate composition

Table 2.1 shows a typical reformate composition. For motor fuel applications, the octane number is the main parameter of product quality. A higher octane number reflects a lower tendency of the hydrocarbon to undergo a rapid, inefficient detonation in an internal combustion engine. This rapid ignition is heard as a knocking sound in the engine, so octane is often referred to as the antiknock quality of a gasoline. Other property specifications of the reformate include volatility or vapor pressure, often given in terms of the Reid vapor pressure or RVP, end point, color, etc. High end point reformates, for example, may not combust well in an internal combustion engine.

Reformulated gasolines, a requirement of the 1990 Clean Air Act, are the subject of much legislation. Specifications require a lower benzene content, lower volatility, and lower end point. Other specifications may pertain to the oxygenate content and other factors that affect the burning characteristics. The gasolines available to the consumer consist of a mixture of gasoline fractions from many refinery sources, including: straight run (unprocessed fraction), isomerate, alkylate, reformate, and FCC fractions.

Table 2.1 Reformate composition (Handbook of Petroleum Processing, 2006.)

Component	Mass %	Liq vol %
Aromatics		
Benzene	3.72	3.39
Toluene	13.97	12.93
Ethylbenzene	3.13	2.90
o-xylene	4.83	4.47
m-xylene	7.47	6.91
p-xylene	3.39	3.14
C9+ Aromatics	36.05	33.30

Table 2.1 Reformate composition (Cont.)

Component	**Mass %**	**Liq vol %**
Total aromatics	72.56	67.04
Total olefins	0.82	1.02
Paraffins		
Propane	0.00	0.00
Isobutane	0.14	0.20
n-butane	0.94	1.32
Isopentane	2.52	3.29
n-pentane	1.74	2.29
C6 Isoparaffins	3.91	4.77
n-Hexane	1.74	2.12
C7 Isoparaffins	7.70	9.02
n-Heptane	2.22	2.60
C8 Isoparaffins	2.86	3.24
n-Octane	0.62	0.70
C9 Paraffins	0.90	0.99
C10 Paraffins	0.24	0.26
C11 Paraffins	0.03	0.04
Total Paraffins	25.56	30.84
Naphthenes		
Cyclopentane	0.10	0.10
Methylcyclopentane	0.28	0.30
Cyclohexane	0.03	0.03
C7 Cyclopentanes	0.33	0.35
Methylcyclohexane	0.04	0.04
C8 Cyclopentanes	0.14	0.14
C8 Cyclohexanes	0.06	0.06
C9 Naphthenes	0.04	0.04
C10 Naphthenes	0.04	0.04
C11 Naphthenes	0.00	0.00
Poly Naphthenes	0.00	0.00

2.2 Fuel oil properties

The worldwide has aware of the limitations of energy supplies. Alternative energy sources must meet certain criteria to be competitive with conventional fuels. Some of the special requirements these energy supplies will have to meet are as follows;

1. Fuels must be capable of being stored over extend time periods.
2. Storage, transportation and distribution of fuels used should be economical.
3. Handling of alternate fuels should not involve additional hazards such as fire, explosion, etc., in comparison to conventional fuels.
4. Alternate fuels should not impose major engineer changes to process and/or system using them.

Other traditional requirements were brief as follows.

2.2.1 Octane Number

Octane number, figure of merit represent the resistance of gasoline to premature detonation when exposed to heat and pressure in the combustion chamber of an internal-combustion engine. Such detonation is wasteful of the energy in the fuel and potentially damaging to the 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., of 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 (RON) and motor octane numbers (MON), are determined by burning the gasoline in an engine under different, but specified, conditions. Usually the motor octane number is lower than the research octane. 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.

A high tendency to autoignite, or low octane rating, is undesirable in a gasoline engine but desirable in a diesel engine. The standard for the combustion quality of diesel fuel is the cetane number. A diesel fuel with a high cetane number has a high tendency to autoignite, as is preferred.

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.

Table 2.2 Octane number of pure hydrocarbons (Modern Petroleum Technology,1984)

Hydrocarbon	Actual		Blending	
	RON	MON	RON	MON
Paraffins				
n-butane	93		113	114
n-pentane	62	62	62	67
2-methylbutane	92	90	99	104
2,2-dimethylpropane	85	80	100	90
n-hexane	25	26	19	22
2,2-dimethylbutane	92	93	89	97
n-heptane	0	0	0	0
2,2-dimethylpentane	93	96	89	93
2,2,3-trimethylbutane	>100	>100	113	113
2,2,3-trimethylpentane	100	100	105	112
2,2,4-trimethylpentane	100	100	100	100
Olefins				
1-pentane	91	77	152	135
2-methyl-2-buten	97	85	176	141
3-methyl-2-pentene	97	81	130	118
4-methyl-2-pentene	99	84	130	128

Table 2.2 Octane number of pure hydrocarbons (Cont.)

Hydrocarbon	Actual		Blending	
	RON	MON	RON	MON
2,2,4-trimethyl-1-pentene	>100	86	164	153
2,2,4-trimethyl-2-pentene	>100	86	148	139
<u>Aromatics</u>				
Benzene	>100	>100	99	91
Toluene	>100	>100	124	112
o-xylene	>100	>100	120	103
m-xylene	>100	>100	145	124
p-xylene	>100	>100	146	127
Ethylbenzene	>100	98	124	107
1,2-diethylbenzene[a]	183	-	-	-
1,3-diethylbenzene[a]	154	-	-	-
1,4-diethylbenzene[a]	209	-	-	-
1,3,5-trimethylbenzene	>100	>100	171	137
Propylbenzene	>100	98	127	129
Isopropylbenzene (cumene)	>100	99	132	124
<u>Naphthenes</u>				
Cyclopentane	101		141	141
Methylcyclopentane	91		107	99
Cyclohexane	83		110	97
Methylcyclohexane	75		104	84
0-dimethylcyclohexane	81		85	83
m-dimethylcyclohexane	67		67	65
p-dimethylcyclohexane	68		66	63

2.2.2 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 anindirect 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 °C (100 °F) of petroleum products and crude oils with initial boiling point above 0 °C (32 °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).

Table 2.3 Properties of some components of gasoline (Source : Spiro, 1996)

Component	Vapor pressure (psi @ 100 °F	Component	Vapor pressure (psi @ 100 °F
Butane	51	Cyclohexane	3.3
n-pentane	15.5	Methylcyclohexane	1.6
n-hexane	5.0	Benzene	3.3
Methyl propane	82	Toluene	1.04
2-methylbutane	20	*meta*-xylene	0.33
2-methylpentane	6.6	Ethanol	17
2-methylhexane	2.2	Methanol	60
iso-octane	1.65	Methyl tert-butyl ether (MTBE)	8
1-butene	50		
1-methylpropene	62	Ethyl tert-butyl ether (ETBE)	4
1-pentene	19		

2.2.3 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 170oC 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.

The distillation curve can be observed that 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 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 represents the percentage evaporated at 70oC. It is considered preferable and more meaningful to use percentages evaporated rather than temperatures, particularly when carrying out blending calculations.

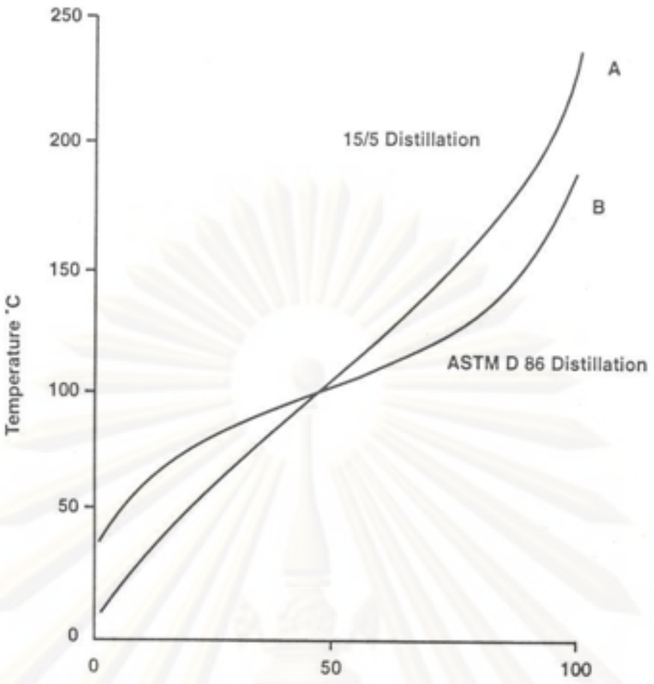


Figure 2.1 Gasoline distillation curve (Owen and Coley et al., 1995)

2.3 Benzene

Benzene or benzol, is an organic compound with the molecular formula C_6H_6. Benzene is a colorless and highly flammable liquid with a sweet smell and a relatively high melting point. Because it is a known carcinogen, its use as an additive in gasoline is now limited, but it is an important industrial solvent and precursor in the production of drugs, plastics, synthetic rubber, and dyes. Benzene is a natural constituent of crude oil, and may be synthesized from other compounds present in petroleum. Benzene is a cyclic hydrocarbon with a continuous pi bond.

Benzene is a naturally clear, colorless, noncorrosive, highly flammable liquid and has an aromatic odour. The principle physical and chemical properties of benzene are shown in Table 2.4.

Table 2.4 Some physical and chemical properties of benzene (IPCS, 1993)

Properties	
Physical form (20 °C)	Clear colorless liquid
Relative molecular mass	78.11
Flash point	-11.1 °C
Flammable limits	1.3 – 7.1 %
Melting/Freezing point	5.5 °C
Boiling point	80.1 °C
Density	0.878
Relative vapor density (air =1)	2.7
Vapor pressure (26 °C)	13.3 kPa
Solubilities:	
Water	1800 mg/litre at 25 °C
Non-aqueous solvents	Miscible with most
Odour threshold	4.8 – 15.0 mg/m^3
Taste threshold (water)	0.5 – 4.5 mg/litre
Log n-octane/water partition coefficient	1.56 – 2.15
Sorption coefficient (logKoc- distribution coefficient between benzene adsorbed to soil organic carbon and benzene in solution)	1.8 – 1.9

2.3.1 Health Hazard Information

Benzene is found in the air from emissions, burning coal and oil, gasoline service stations, and motor vehicle exhaust. Benzene exposure has serious health effects. Outdoor air may contain low levels of benzene from tobacco smoke, wood smoke, automobile service stations, the transfer of gasoline, exhaust from motor vehicles, and industrial emissions. Vapors from products that contain benzene, such as glues, paints, furniture wax, and detergents, can also be a source of exposure, although many of these have been modified or reformulated since the late 1970s to eliminate or reduce the benzene content. Thus, the emissions of benzene at these sources need to be sticky controlled with a proper technology.

- ***Acute Effects:***
  - Coexposure to benzene with ethanol (e.g., alcoholic beverages) can increase benzene toxicity in humans.
  - Neurological symptoms of inhalation exposure to benzene include sleepiness, dizziness, headaches, and unconsciousness in humans.
  - Exposure to liquid and vapor may irritate the skin, eyes, and upper respiratory tract in humans. Redness and blisters may result from dermal exposure to benzene. (http://www.epa.gov/ttn/atw/hlthef/benzene.html)
  - Tests involving acute exposure of rats, mice, rabbits, and guinea pigs have demonstrated benzene to have low acute toxicity from inhalation, moderate acute toxicity from ingestion, and low or moderate acute toxicity from dermal exposure.
- ***Chronic Effects (Noncancer):***
  - Chronic inhalation of certain levels of benzene causes disorders in the blood in humans. Benzene affects bone marrow (the tissues that produce blood cells). Aplastic anemia, excessive bleeding, and changes antibodies in blood levels and loss of white blood cells) may develop.
  - Benzene causes both structural and numerical chromosomal aberrations in humans.
- ***Cancer Risk:***
  - Increased incidence of leukemia has been observed in humans occupationally exposed to benzene.
  - EPA has classified benzene as a Group A, known human carcinogen.

2.4 Ethylene

Ethylene (ethene) is the chemical compound with the formula C_2H_4. It is the simplest alkene. Ethylene is called an unsaturated hydrocarbon or an olefin because it contains a carbon-carbon double bond. It is extremely important in industry and also has a role in biology as a hormone. To meet the increasing demand for ethylene, quick increases in production facilities have been added globally.

2.5 Ethylbenzene

Ethylbenzene is an organic compound with the formula $C_6H_5CH_2CH_3$. This aromatic hydrocarbon is important in the petrochemical industry as an intermediate in the production of styrene, a commonly used plastic material. Although often present in small amounts in crude oil, ethylbenzene is produced in bulk quantities by combining benzene and ethylene in an acid-catalyzed chemical reaction:

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5CH_2CH_3$$

Table 2.5 Some physical and chemical properties of ethylbenzene (HSDB, 1994)

Properties	
Physical form (20 °C)	Colorless liquid
Relative molecular mass	106.16 g/mol
Flash point	15-20 °C
Auto-ignition temperature	460 °C
Melting/Freezing point	-95 °C
Boiling point	136.2 °C
Density	0.8665 g/mL, liquid
Relative vapor density (air =1)	3.7
Vapor pressure (20 °C)	0.9 kPa
Solubilities:	
Water	0.015 g/100 ml at 20 °C
Ethanol and ether	Soluble
Viscosity	0.669 cP at 20 °C
Explosive limits, vol% in air	1.0-6.7

2.5.1 Local environmental effects

Because of its physical and chemical properties, more than 96% of ethylbenzene in the environment can be expected to be present in air, where it will undergo photochemical degradation reactions with hydroxyl radicals (half-life 0.5 to 2 days) and partially return to earth in rain. The photo-oxidation reaction of ethylbenzene in the atmosphere may contribute to photochemical smog formation. Ethylbenzene levels in air at urban areas have been found in range from 0.74 to 100 mg/m^3 and less than 2 mg/m^3 in rural sites. Photochemical oxidants may be harmful to crops and natural vegetation. Releases into water will be reduced through evaporation to air and via biodegradation processes, although the rate of loss will be dependent upon local environmental conditions. Representative half-lives are several days to 2 weeks. Some ethylbenzene may be adsorbed by sediment but based upon its octanol/water partition coefficient, significant bioconcentration in fish is not expected to occur. In surveys of representative US municipal water supplies, ethylbenzene has been detected in a number of cases at low concentrations. Much higher levels have been reported for groundwater contaminated via waste disposal, fuel spillage and industrial facilities. The log octanol-water partition coefficient of ethylbenzene is 3.13, indicating a potential for bioaccumulation. However, the limited evidence available shows that ethylbenzene bioconcentration factors are low for fish and molluscs. Elimination from aquatic organisms appears to be rapid. Biomagnification through the food chain is unlikely. On the basis of available data, it is concluded that ethylbenzene is unlikely to be found at levels in the environment that will cause adverse effects on aquatic and terrestrial ecosystems, except in cases of spills or point-source emissions. When released onto soil, it will be only moderately absorbed, with the soil acting only as a reservoir. The concentration in the soil will be controlled almost entirely by the rate at which it can evaporate. While there are no direct data concerning its biodegradability in soil, it is likely that it may biodegrade slowly after acclimation of ambient microorganisms.

2.6 Alkylation of benzene

Alkylation reactions are reactions where an alkyl group is introduced into a molecule. Many different types of alkylation reactions are known. For example, alkyl groups can be introduced into aliphatic hydrocarbons or aromatic hydrocarbons by alkylation reactions. Alkylation reactions can also be used to prepare ethers from alkyl alcohols or aromatic alcohols. Alkylated amines can be prepared by alkylation;

however, special methods are normally required to control the number of alkyl groups introduced onto nitrogen. Important synthetic methodology also exists for the alkylation of enolate ions. Alkylation is often promoted through the use of heat or of an appropriate catalyst such as an acid catalyst.

Many alkyl halides, alcohols, or alkenes can be reacted with benzene in the presence of certain catalysts to give an alkylbenzene. Other aromatic hydrocarbons give similarly substituted alkyl aromatic products. A Lewis acid, such as aluminum chloride, is often the catalyst used for this reaction. This reaction is used industrially for the synthesis of hydrocarbons. If the reaction is carried out at high temperatures, rearrangement of the alkyl group may occur. For example reaction of n-propyl halides with benzene at low temperatures affords mainly n-propyl benzene but at higher temperatures the major product is isopropyl benzene. Alkylation is used industrially to produce basic building blocks for the synthesis of more elaborate materials. One commonly used application is in the production of anti-knock gasoline.

Alkylation in the petroleum industry refers to a process for the production of high-octane motor fuel components by the combination of olefins. The reaction of iso-butane with olefins, using an aluminum chloride catalyst, is a typical alkylation reaction.

In acid-catalyzed alkylation reactions, only paraffins with tertiary carbon atoms, such as iso-butane and iso-pentane react with the olefin. Ethylene is slower to react than the higher olefins. Olefins higher than propene may complicate the products by engaging in hydrogen exchange reactions.

Cycloparaffins. Especially those containing tertiary carbon atoms, are alkylated with olefins in a manner similar to the iso-paraffins; the reaction is not as clean, and the yields are low because of the several side reactions that take place.

Aromatic hydrocarbons are more easily alkylated than the iso-paraffin by olefins. Cumene (iso-propylbenzene) is prepared by alkylating benzene with propene over an acid catalyst. The alkylating agent is usually an olefin, although cyclopropane, alkyl halides, aliphatic alcohols, ethers, and esters may also be used. The alkylation of aromatic hydrocarbons is presumed to occur through the agency of the carbonium ion (Figure 2.2).

Thermal alkylation is also used in some plants, but like thermal cracking, it is presumed to involve the transient formation of neutral free radicals and therefore tends to be less specific in production distribution.

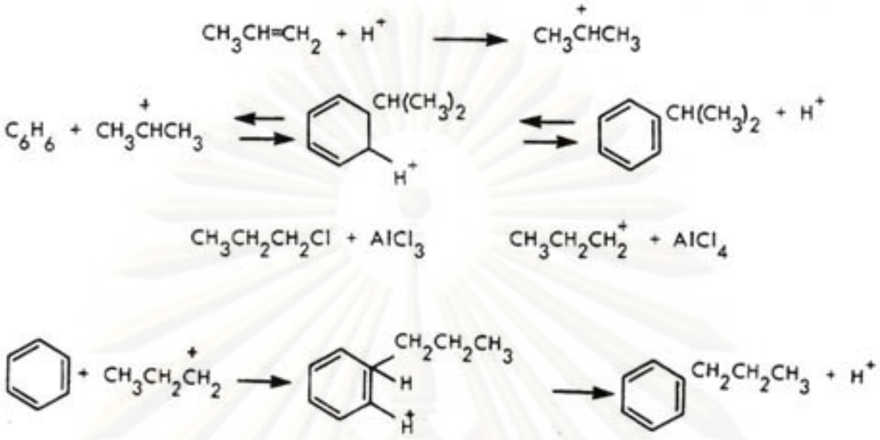


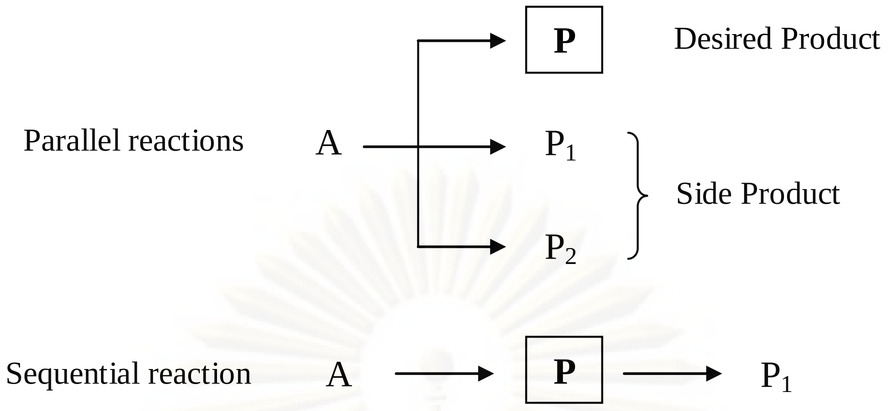
Figure 2.2 Alkylation of benzene with propene (Speight, 2007)

2.7 Catalyst

2.7.1 Properties and characteristics of industrial catalysts

The suitability of a catalyst for an industrial process depends mainly on the following three properties (Hagen, 1999).

- **Activity** is a measure of how fast one or more reactions proceed in the presence of the catalyst. Activity can be defined in terms of kinetics or from a more practically oriented viewpoint. In formal kinetic treatment, it is appropriate to measure reaction rate in the temperature and concentration ranges that will be present in the reactor.
- **Selectivity** of a reaction is the fraction of the starting material that is converted to the desired product. It is expressed by the ratio of the amount of desired product to the reacted quantity of reaction partner A and therefore gives information about the course of the reaction. In addition to the desired reaction, parallel and sequential reactions can also occur (Scheme 2.1)



Scheme 2.1 Parallel and sequential reactions

- **Stability** (chemical, thermal and mechanical) of a catalyst determines its lifetime in industrial reactors. Catalyst stability is influenced by numerous factors, including decomposition, coking and poisoning. Catalyst deactivation can be followed by measuring activity or selectivity as a function of time. Catalysts that lose activity during a process can often be regenerated before they ultimately have to be replaced. The total catalyst lifetime is of crucial importance for the economics of process.

Today the efficient use of raw materials and energy is of major importance, and it is preferable to optimize existing processes than to develop new ones. For various reasons, the target quantities should be given the following order of priority (Hagen J., 1999):

Selectivity > Stability > Activity

2.7.2 Type of catalysts

Catalysts can be divided into two main types: heterogeneous and homogenous.

- *Heterogeneous reaction*: the catalyst is in a different phase from the reactants. Phase boundaries are always present between the catalyst and the reactants. Heterogeneous catalysts are either automatically removed in the process (e.g. gas-phase reactions in fixed-bed reactions) or they can be separated by simple methods such as filtration or centrifugation.

- *Homogeneous reaction*: the catalyst is in the same phase as the reactants, starting materials, and products. Homogeneous catalysts have a higher degree of dispersion than heterogeneous catalysts only the surface atoms are active [Hagen, 1999]. The major disadvantage of homogeneous catalysts is the difficulty of separating the catalyst from product.

Due to their high degree of dispersion, homogeneous catalysts exhibit a higher activity per unit mass of metal than heterogeneous catalysts. The high mobility of the molecules in the reaction mixture results in more collision with substrate molecules. The reactant can approach the catalytically active center from any direction, and a reaction at an active center does not block the neighboring centers. This allows the use of lower catalyst concentrations and milder reaction conditions. Table 2.6 summarizes the advantages and disadvantages of the two classes of catalyst.

Table 2.6 Comparison of homogeneous and heterogeneous catalyst (Hagenl J., 1999)

	Homogeneous	**Heterogeneous**
Effective		
- Active centers	All metal atoms	Only surface atoms
- Concentration	Low	High
- Selectivity	High	Low
Catalyst properties		
- Diffusion problems	Practically absent	Present (mass-transfer-controlled reaction
- Reaction conditions	Mild (50-200 °C)	Severe (often > 250 °C)
- Applicability	Limited	Wide
- Activity loss	Irreversible reaction with product (cluster formation); poisoning	Sintering of the metal crystallites; poisoning

Table 2.6 Comparison of homogeneous and heterogeneous catalyst (Cont.)

	Homogeneous	**Heterogeneous**
- Structure/Stoichiometry	Defined	Undefined
- Modification possibility	High	Low
- Thermal stability	Low	High
Catalyst separation	Sometimes laborious (chemical decomposition, distillation, extraction)	Fixed-bed: unnecessary Suspension: filtration
Catalyst recycling	Possible	Unnecessary (fixed-bed) or easy (suspension)
Cost of catalyst losses	High	Low

2.8 Zeolite molecular sieves

Molecular sieves are porous materials that exhibit selective adsorption properties which can be classified on the IUPAC definitions into three types depending on their pore size that are microporous materials, mesoporous materials, and macroporous materials. Properties and examples of these materials are shown in Table 2.7.

Table 2.7 IUPAC classification of porous materials

Type of material	Pore size (Å)	Examples
Micropores	< 20	Zeolites, activated carbon
Mesopores	20 - 500	M41s, SBA-15, pillared clays
Macropores	> 500	glasses

2.8.1 Zeolite structures (Breck, 1997)

Zeolites, a type of molecular sieves, are crystalline aluminosilicates of alkali and alkaline earth metals (such as sodium, potassium, magnesium, calcium, strontium, and barium). A zeolite has a three dimensional network structure of tetrahedral primary building units (PBU) which made of four oxygen anions with either silicon $[SiO_4]$ or aluminum cation $[AlO_4]^-$ in the center as shown in Figure 2.3

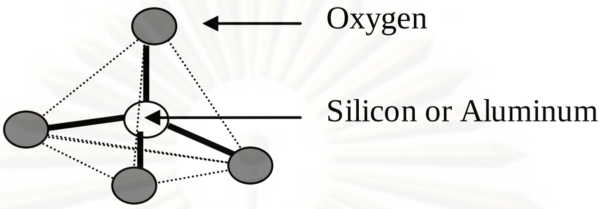


Figure 2.3 Primary Building Unit (PBU) of zeolites.

A secondary building unit (SBU) consists of selected geometric groupings of those tetrahedral. There are nine such building units, which can be described all of the known zeolite structures. The secondary building unit (SBU's) consist of 4,6 and 8-member single rings, 4-4, 6-6 and 8-8-member double rings, and 4-1, 5-1 and 4-4-1 branched rings as illustrated in Figure 2.4.

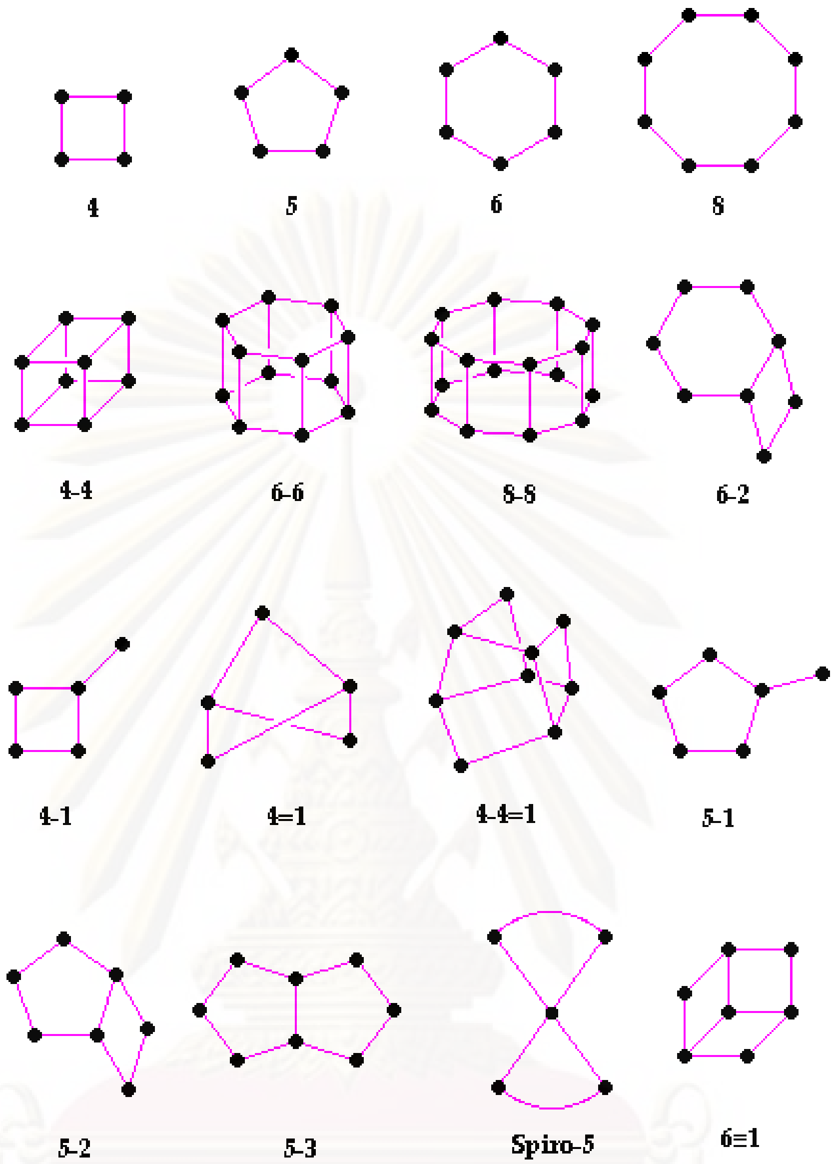


Figure 2.4 Secondary Building Units (SBU's) in zeolites.

The tetrahedrons are mutually connected by sharing oxygen atom as shown in Figure 2.5 which produces the framework of zeolite. The negative charge of the lattice is neutralized by the positive charge of the metal cations. In the basic zeolites these are usually cation of univalent and bivalent metals or their combination. The general formula for the composition of zeolites is

$$M_{x/n}[(AlO_2)_x(SiO_2)_y].wH_2O$$

Where M is the cation of valence n, generally from the group I or II ions, although other metals, nonmetals, and organic cations are also possible, w is the number of water molecules. Water molecules presented are located in the channels and cavities, as the cations that neutralize the negative charge created by the presence of the AlO_2^- tetrahedral unit in the structure.

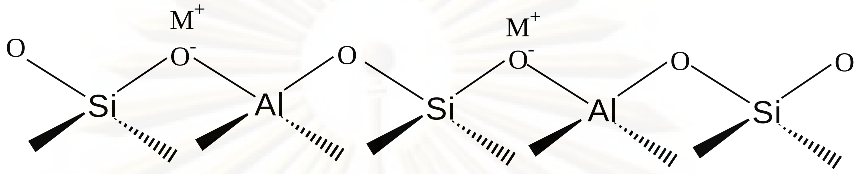


Figure 2.5 The structure of zeolites (Breck, 1997)

2.8.2 Properties of zeolites

- Acid sites of zeolites

Most industrial application of zeolites are based upon technology adapted from the acid silica/alumina catalysts originally developed for the cracking reaction [16, 44, 45]. This means that the activity required is based upon the production of Br∅nsted acid sites arising from the creating hydroxyls within the zeolites pore structure. These hydroxyls are formed by ammonium exchange followed by a calcination step. Zeolites as normally synthesized usually have Na^+ balancing the framework charges, but these can be readily exchanged for protons by direct reaction with an acid, giving hydroxyl groups, the Br∅nsted acid sites. Alternatively, if the zeolite is not stable in acid solution, it is common to use the ammonium, NH_4^+, salt, and then heat it so that ammonia is driven off, leaving a proton. Further heating removes water from Br∅nsted sites, exposing a tricoordinated Al ion, which has electron-pair acceptor properties; this is identified as a Lewis acid site. A scheme for the formation of these sites is shown in Figure 2.6. The surfaces of zeolites can thus display either Br∅nsted or Lewis acid sites, or both, depending on how the zeolite is prepared. Br∅nsted sites are converted into Lewis sites as the temperature is increased above 500 °C, and water is driven off.

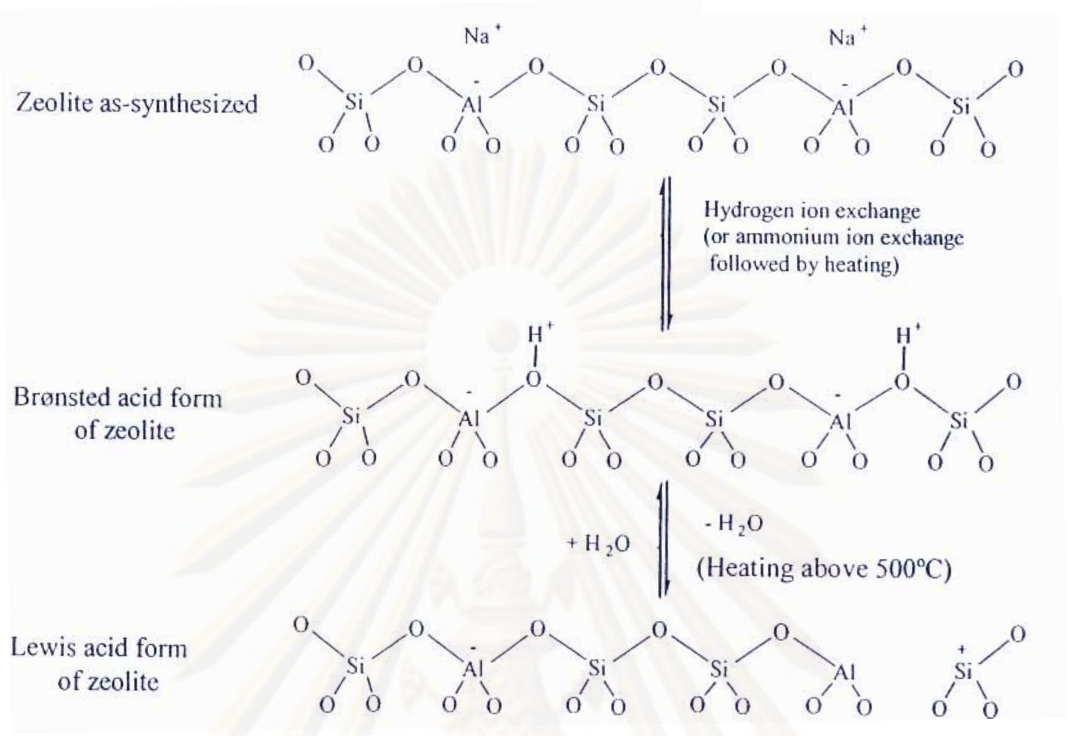


Figure 2.6 The generation of Br∅nsted and Lewis acid sites in zeolite (Derouane, 1980)

Hydrothermal syntheses of silica-rich zeolites generally consist of water as the solvent, a silicon source, an aluminum source, and a structure-directing agent. Better understanding of the effect of the structure-directing agent has long been aimed at. This will entail better control of the resulting structure, and even prediction of the specific structure could be possible. Some progress in the field has been made some general rules of correlation between the structure-directing agent and the structure of zeolite with high silica content:

1. Hydrothermal silicate syntheses result in dense crystalline and layered materials when no structure-directing agent is present.
2. Linear structure-directing agents usually result in one-dimensional molecular sieves with 10-ring channels.
3. Br∅nsted structure-directing agents tend to form multi-dimensional zeolites with pore diameters of 4-7 Å.

4. One-dimensional, large pore zeolites often result from large polycyclic structure-directing agents.

- Shape selectivity

Shape selectivity plays a very important role in catalysis. Highly crystalline and regular channel structures are among the principal features that zeolite used as catalysts offer over other materials. Shape selectivity is divided into 3 types: reactant shape selectivity, product shape selectivity and transition-state shape selectivity effectively enter and diffuse inside the zeolites. These types of selectivity are shown in Figure 2.7. Reactant selectivity means that only starting materials of a certain size and shape can penetrate into the interior of the zeolite pores and undergo reaction at the catalytically active sites. Starting material molecules that are larger than the pore apertures cannot react. Product selectivity arises when, corresponding to the cavity size of a zeolite, only products of a certain size and shape that can exit from the pore system are formed. Restricted transition-state 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 transition state is too bulky to form readily.

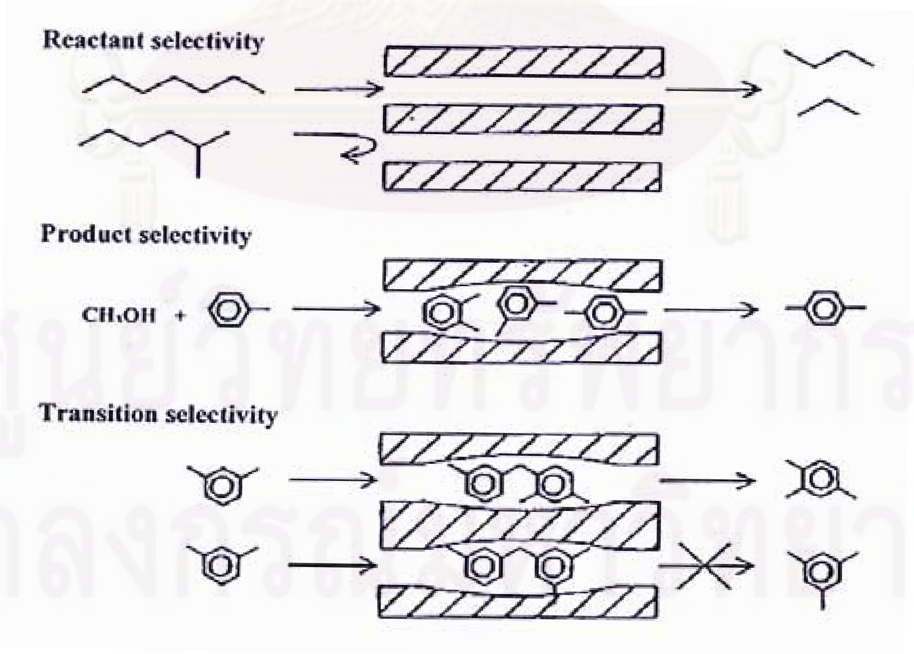


Figure 2.7 Three types of selectivity in zeolites: reactant, product and transition-state shape selectivity (Szostak, 1988).

Heterogeneous catalysis is important in fine-chemical and pharmaceutical and pharmaceutical manufacture and in petroleum refining. Many of the catalysts used by these industries are based on aluminosilicates, which combine high stability with excellent activity in acidmediated reactions. Within this class of material, zeolites microporous crystalline aluminosilicates with three-dimensional framework structures have attracted particular attention: they are significantly more active than the layered structures (clays) and mesoporous structures.

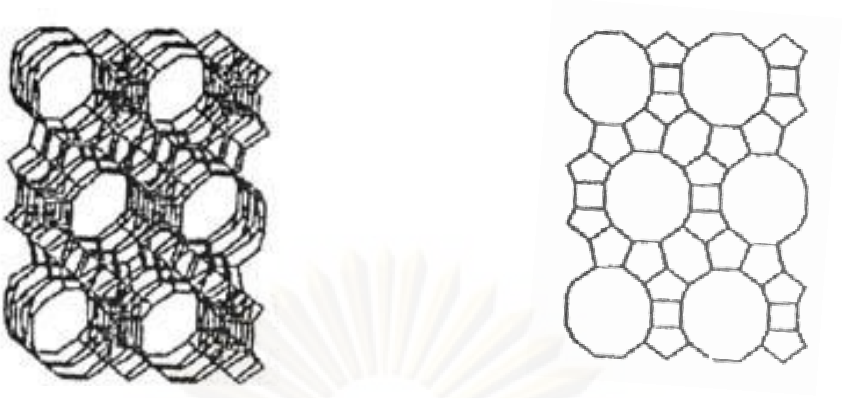
2.9 Beta zeolite

Beta zeolite is an old zeolite discovered before Mobil began the “ZSM” naming sequence. As the name implies, it was the second in an earlier sequence. 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, 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 °A x 7.5 °A. The tortuous channel system consists of the interactions of two linear channels of approximate dimensions of 5.6 °A x 6.5 °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 2.8.



(a) framework structure

(b) framework projection

(c) tortous channel

(d) straight channel

Figure 2.8 Structure of beta zeolite

CHAPTER III

LITERATURE REVIEWS

This chapter contains the research reviews of strategies for reducing the benzene content in reformate and alkylation of benzene. The researches review for a useful knowledge such as operating condition, catalyst selection, advantages and drawbacks of their strategies.

3.1 Strategies of benzene reduction

Benzene is a key aromatic hydrocarbon which is a known human carcinogen and has high vapor pressure. So, the benzene content is limited. Kaul *et al.*, 1993 reported that the distillation process is not suitable primarily to reduce the benzene content because benzene which has a normal boiling point of about 176 °F, form low boiling azeotropes with normal hexane and naphthenes such as cyclohexane. Furthermore, the distillation process for reducing the benzene has the undesirable effect of decreasing both the octane rating and the volume of gasoline (Hsieh *et al.*, 1993).

Gaile et al., 2004 studied separation of benzene, toluene and xylene from reformate by combined extraction fractionation-extraction using n-methylpyrolidone and sulfolane (70:30) as solvent. C_6-C_8 aromatic hydrocarbons are separated with a yield of 99.8 wt%. After benzene separation, the distillate contains less than 1 vol % of benzene and can be used as component of automobile gasoline. However, extraction methods that use sulfolane as solvent have many drawbacks such as using of high boiling selective solvent (the boiling point of sulfolane is 285 °C) results in a high temperature in the extractive distillation tower and leads to decrease in the separation selectivity (Gaile et al., 2008). Moreover, extraction process with sulfolane use of special equipment to resist the corrosion of solvent and appearance of sulfur impurities in the gasoline product (Kaul et al., 1993). Hsieh *et al*. (1993) reported that physical separating benzene from gasoline by distillation or extraction has the undesirable effect of decreasing both the octane rating and the volume of gasoline.

The octane loss can be compensated by addition of oxygenates resulting in increase the investment cost (Jain and Chopra, Engineering India Ltd.).

Adsorption processes have been used for removing all aromatics from nonaromatic fraction of mixed hydrocarbon stream. For example, Olsen *et al*. (1995) disclosed the use of silica gel for separating all aromatics from gasoline or kerosene fractions. The silica gel containing adsorbed aromatics can then be desorbed with a suitable desorbent such as toluene containing process stream which is passed over the adsorbent. Masuda *et al*. (1993) reported that various techniques can be used to selectively remove benzene from gasoline boiling range stream using solid adsorbents. The use of solid adsorbents such as molecular sieves present advantage over distillation and solvent extraction technique. However, desorption of aromatic from solid adsorbents is particularly difficult as aromatic molecules tend to be very strongly adsorbed relative to paraffinic, naphthenic and olefinic molecules. Thus adsorbed aromatics such as benzene are usually desorbed using a large excess of desorbent such as toluene or xylene which do not readily displace benzene leading to long desorption times. The adsorption – desorption operation in the adsorbent layer cannot be operated continuously resulting in high investment cost (Toshio S., 1998). Moreover, adsorption of benzene loses octane and volume of gasoline (Kaul et al., 1994).

Hydrogenation reaction that converts benzene to cyclohexane draws many researches's attention to improve gasoline properties. For example, Hsieh *et al*. (1993) reported reduction of benzene in gasoline may be hydrogenated to a non-aromatic compound. This approach is also undesirable, because it requires a relatively high pressure operation and consumes hydrogen which is usually expensive in a refinery. Hydrogenation of benzene also reduces the octane rating of gasoline. Shimizu (1998) disclosed a process for selective hydrogenation benzene in hydrocarbon oils. The benzene in hydrocarbon oils can be selectively converted into cyclohexane by using metal in Group VIII of the periodic table catalyst such as noble metal, Ni, Ru, Rh, Pd and Pt. Nevertheless the cyclohexane reduces in the grade of gasoline because the octane rating of cyclohexane is much lower than benzene (Lin *et al*., 2007). In order to partially recover the octane number loss, Lee *et al*. (1998) disclosed a process for reducing benzene in gasoline blending stock which used a dual functional catalyst to hydrogenate benzene into cyclohexane and isomerize the cyclohexane into methylcyclopentane which has an octane rating between cyclohexane and benzene. However, the process requires the use of highly active catalyst (Jain and Chopra, Engineering India Ltd.). Goundani *et al*., 2004 studied the benzene elimination from reformate by high pressure hydrogenation in fixed-bed reactor using Pt/TiO_2 catalyst. It was found that toluene content in feed inhibit the benzene hydrogenation because toluene adsorbed more strongly and had higher activity than benzene.

One effective to reduce benzene content while maintaining the octane of gasoline is alkylation the benzene. Hsieh *et al*. (1993) studied process to remove benzene from refinery streams. At least about 30% of the benzene initially present in the stream is catalytically alkylated with C_2-C_4 olefins to form alkylated products. The alkylation zone is present in the distillation column at temperature within range from 350 °F to 450 °F, pressure within a range from 150 psig to 300 psig and LHSV from 1 to 3. The remaining non-alkylated benzene is hydrogenated to cyclohexane and isomerized to boost the octane of C_5-C_7 paraffins in a single reactor. This process produced the product without deleterious effect on octane numbers and with increased volume as compared to the original refinery. In 1996, Chin *et al*. studied reduction of benzene-rich gasoline stream by alkylation with higher olefins in contact with a fluid bed of ZSM-5 zeolite catalyst. Besides enhancing the octane value of the feed stream, the process results in a lower Reid vapor pressure. Furthermore, the alkylated product such as toluene and ethylbenzene are less toxic than benzene (Umansky *et al*., 2009).

3.2 Reduction of benzene by alkylation

In the commercial processes, the reactions have conventionally been catalysed by mineral acids (e.g., solid phosphoric acid) and Friedel–Crafts systems e.g., $AlCl_3$ (Bentham *et al*., 1997). The using of both catalysts gives rise to many problems concerning handling, safety, corrosion, and waste disposal. Much effort has been put into developing alternative catalyst such as zeolite-based catalysts, are used to catalyse the direct alkylation of benzene with propene or ethylene (Corma, 1995). In this way, several commercial processes have been developed for the production of cumene and ethylbenzene based on zeolite catalysts (Corma, 2000; Bellussi et al., 1995; Buelna et al., 2006).

According to the ExxonMobil MBR^{TM} process (Hydrocarbon Processing. Refining Handbook, 1992), benzene rich cut from either full range reformate or naphtha is vaporized, mixed with FCC off-gas and charged to a dense fluid bed of a specially developed ZSM-5 catalyst to alkylate benzene. They claimed that about 50–60% of benzene becomes C_7–C_{10} alkylbenzenes. Additionally, increments 10 units in octane number were obtained. ExxonMobil process, Benzout^{TM} (Hydrocarbon Processing Refining Handbook, 1992; Umansky *et al*., 2007) claimed a benzene reduction giving as a final product a gasoline pool complying with the new benzene regulations, octane number increments of 2–5 and increased flexibility in reformer feed for increased hydrogen production. A similar process recently by UOP, Alkymax (Coldwel, 2008; UOP Inc., 1990) declared that benzene content was reduced from 2.4 to 0.6 vol%, with a gasoline production 3% higher and an increment of 0.5 in octane number. The procedure, they said, employed a highly selective Beta catalyst.

Umansky *et al*., US.Patent No. 7,498,474 B2 (2009) studied a process for the production of high octane number gasoline from light refinery olefins (ethylene and propylene) and benzene containing aromatic streams such as reformate. The alkylation reaction is carried out in the liquid phase with a catalyst which preferably comprises a member of the MWW family of zeolites such as MCM-22 using a fixed catalyst bed. In further studied of Umansky, the process operates in the vapor phase with high temperatures about 350 °C which does impose some economic , compared to a process capable of operating at lower temperatures. In addition, the larger volume associated with vapor phase operation may make limit unit capacity with smaller volume existing units are converted to this process. Therefore it would be desirable to offer a process operating at lower temperature in the denser liquid phase (Umansky *et al*., US.Patent No. 7,476,774 B2, 2009).

Hsieh *et al*. (1993) disclosed the use of LZY-82 and Beta zeolite as catalyst for alkylation benzene with off-gas (mixture C_1-C_3) to reduce the benzene from reformate. The Beta zeolite activity for benzene conversion is higher than LZY-82 (24.6% and 28.6% benzene conversion for LZY-82 and beta zeolite catalyst, respectively). Chin *et al*. (1996) disclosed the use of ZSM-5 for benzene reduction in gasoline by alkylation mix 50/50 v/v of light FCC Naphtha and Refornate cut blend with C_2-C_9 olefins at 800 °F, 75 psig and Benzene/C_2-C_9 olefins mole ratio = 0.94. Benzene conversion 32.3 % of this process were obtained. Yeh et al. (1994) compared activity of catalyst between Beta, Y and ZSM-5 zeolite by means of a synthetic feedstock (benzene/toluene/hexane/heptane) to simulate benzene rich reformate and mixed propylene/propane feed at 180-220 °C and 2.8-4.5 MPa in a batch reactor. The order of activity for benzene conversion was Beta > Y > ZSM-5.

Several medium to large pore zeolite (i.e., MCM-22 and beta) are highly effective catalysts for the reaction of alkylation of benzene to produce cumene, as they do not produce significant amounts of linear n-propylbenzene, unlike medium-pore zeolites. Several catalytic studies reported that reactions using large-pore Beta zeolite with high acidities at medium temperatures (close to 200 °C) resulted in high cumene yield and selectivity (Halgeri and Das, 1999; Siffert *et al*., 2000). Nevertheless, the main drawback in the use of the highly reactive zeolites is that they suffer from rapid deactivation (Ma et al., 1995; Siffert and Su, 1999). As one of the most active catalysts, MCM-22 zeolite with a MWW frame structure shows higher monoalkylate selectivity than large pore zeolites including Beta and Y for benzene alkylation with propylene (Degnan *et al*., 2001). Corma *et al*. (2000) investigated the benzene alkylation with ethylene and propylene which has been carried under liquid phase reaction over zeolites MCM-22, Beta, ZSM-5. MCM-22 zeolite is a good catalyst to carry out benzene alkylation with short olefins comparing with a commercial Beta zeolite. MCM-22 shows similar activity and selectivity but better stability. ZSM-5 zeolite appears to be a poor catalyst for alkylation of benzene with ethylene in liquid phase and deactivate fast owing to formation of oligomers.

One of the difficulties encountered in alkylation reaction is forming polyalkylated product. To limit these polyalkylation reactions, Hendriksen *et al*. (1999) use a large excess of benzene with respect to the ethylene at the entry of the alkylation reactors catalyzed by beta zeolite. Innes *et al*. (1990) discloses a process for the alkylation of an aromatic hydrocarbon with C_2 to C_4 olefin under liquid phase conditions and Beta zeolite catalyst. The aromatic hydrocarbon feed should be present in stoichiometric excess. It is preferred that the molar ratio of aromatics to olefins about 4:1 to prevent rapid catalyst fouling.

3.3 Benzene Alkylation with Ethylene

The alkylation of benzene with ethylene to produce ethylbenzene (EB) is widely used in the petrochemical industry. EB is the intermediate for styrene production. Most of the benzene alkylation with ethylene is catalyzed by Friedel-Crafts such as $AlCl_3$, BF_3 and mineral acids such as solid phosphoric acid (Bentham *et al*., 1997). However, these corrosive catalysts cause a number of problems concerning equipment corrosion, environmental disposal issues and cost arising from utilizing these conventional catalysts (Bellussi *et al*., 1995; Wichterlova *et al*.,1996). Various process and catalyst had been developed of new technologies in which solid acids such as zeolite-based catalyst. Since 1976 the Mobil-Badger process used the medium pore zeolite ZSM-5 for vapor phase alkylation of benzene with ethylene (Chen et al., 1986). Moreover, ZSM-5 shows a higher resistance to coking compared to cage type like faujasite. Various kinds of crystalline aluminosilicates, zeolites, known as the solid acid catalysts were put to practice to catalyze the alkylation benzene with olefins. Because of their strong acid strength and their molecular sieve property, their activity and selectivity were appreciable. Good performances of β-zeolite were also reported for the benzene alkylation in liquid phase with both ethylene and propylene (Cavani *et al*., 1991). Bellussi *et al*. (1995) studied the catalytic performance of β-zeolite in the liquid phase alkylation of benzene and compared with other solid catalyst. β-zeolite is more active and more selective than zeolite Y in the alkylation with propylene and ethylene. The catalytic activity is affected by the composition and the particle size of β-zeolite. Decreasing the Al content produces a decrease in both conversion and selectivity in EB synthesis.

Corma *et al*. (2000) studied catalytic behavior of benzene alkylation with ethylene and propylene under liquid phase condition over zeolite MCM-22, Beta and ZSM-5. The reaction was performed in fixed bed stainless steel tubular microreactor. They reported that ethylene is less reactive and much lower oligomerization than propylene. For reaction time 400 minutes, deactivation of catalyst is not observed under Beta and MCM-22. ZSM-5 zeolite is a poor catalyst for the alkylation of benzene with ethylene in liquid phase because catalyst deactivates fast form formation of oligomer. They concluded that Beta is more active than MCM-22 for ethylbenzene production. Beta zeolite present high ethylbenzene selectivity (~ 90% referred ethylene and > 95% referred to benzene).

Genoveva *et al*. (2006) investigated alkylation of pure benzene with propylene using batch and continuous fixed-bed reactors in gas phase. For the batch reactor, β-zeolite produced the highest cumene yield and selectivity of 72% and 92%, respectively, at 225°C. Ga modification of the H-β zeolite significantly enhanced cumene yield in the continuous fixed-bed reactor at 225°C, from 27% of the unmodified β-zeolite to 36% for the Ga-modified one. Alkylation of benzene with propylene on β-zeolite under gaseous, liquid, vapor-liquid coexistence and supercritical condition has been investigated by Xiangyan *et al*. (2002). The highest yield of cumene and stability of the catalysts were observed when the reaction was carried out on Ga-modified H-βzeolite under supercritical conditions near the critical point, which may be ascribed to the effective dissolution and diffusion of the coke precursors deposited on the zeolites.

CHAPTER IV

EXPERIMENTAL

This chapter describes the experimental procedures for the improvements of the fuel oil quality by the alkylation of benzene in reformate. It is divided into four parts; Chemical and apparatus of batch reactor, catalyst preparation, the alkylation of benzene in reformate with ethylene and alkylation of pure benzene with ethylene.

4.1 Chemical and apparatus of batch reactor

4.1.1 Chemical

The chemicals that used in this study are shown the details of chemical purity and suppliers in Table 4.1.

Table 4.1 Details of chemicals use in the study

Chemical materials	Purity (%)	Supplier
Hβ zeolite preparation		
NH_4NO_3	> 99.5%	Fluka
Na^+β zeolite		Tosoh
Ga-Hβ zeolite preparation		
$Ga(NO_3)_3.6H_2O$		Sigma-Aldrich
Na^+β zeolite		Tosoh
Alkylation reaction		
Reformate (Benzene 9.84 vol%)		Bangchak Petroleum Public Company Limited.
Benzene	99%	Merk
Ethylene	> 99%	TIG

4.1.2 Batch reactor apparatus

Figure 4.1 shows the batch reactor apparatus. An autoclave reactor with 300 ml consisted of a vessel and a lid that contained an electric stirrer, a thermocouple, a pressure gauge, and a pressure release valve. A heating mantle maintained the reactor at the desired temperature. The thermocouple was placed in the headspace of the reactor, close to the bottom of the reactor to monitor temperature.

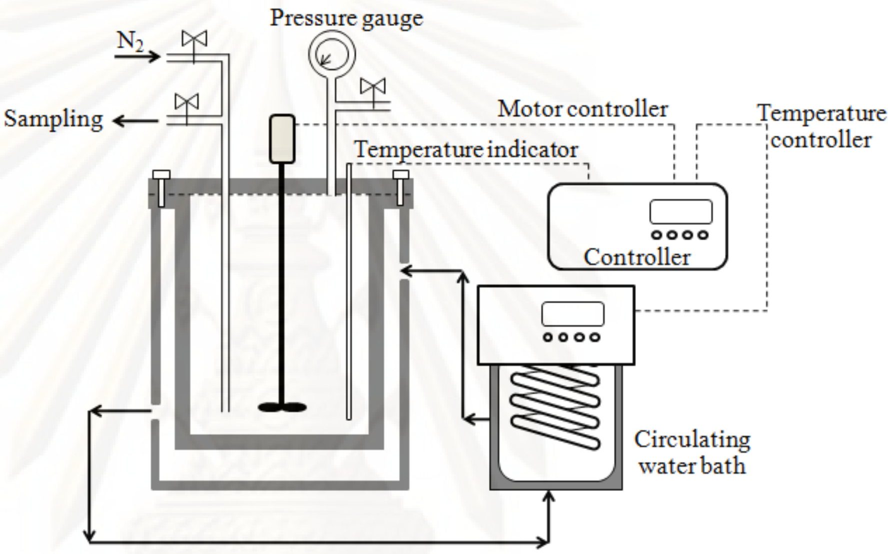


Figure 4.1 Schematic diagram of the autoclave reactor.

4.2 Catalyst preparation

4.2.1 Preparation of Hβ-zeolite powder

Na^+β-zeolite commercial catalyst was converted into H-form by following procedure: Na^+β-zeolite and 2 M NH_4NO_3 solution (20 mg/g) were place in a flask. The mixture was stirred at 70 °C for 5.5 h to give NH_4-Beta. Then the material was filtered under suction and washed with distilled water. The filtered material was dried at 80 °C overnight. The exchange sample was further calcined in air at 550 °C for 4 h, the obtained crystals were Hβ-zeolite. (Siffert *et al.*,2000)

4.2.2 Preparation of Ga modified Hβ-zeolite

1 %wt Ga modified Hβ-zeolite were prepared by impregnating the fine particles of Hβ-zeolite with the gallium nitrates ($Ga(NO_3)_2.6H_2O$ obtained from Aldrich) from their aqueous solution by incipient wetness technique, evaporating the water in oven at 120 °C for 5 h and then calcining in air at 450 °C for 4.5 h (Vasant *et al.*, 2003).

4.2.3 Characterization of the catalysts

- X-ray diffraction (XRD)

XRD patterns of the catalysts were performed with D/MAX-2200 Ultima+ X-ray diffractometer (XRD) equipped with Cu target X-ray tube at 2 theta angle between 2 to 40 degree.

- Surface area analysis

The surface area of solid, average pore size diameters and pore size distribution are determined by physisorption of nitrogen (N_2) using Micromeritics ASAP 2020 (surface area and porosity analyzer)

- Temperature-programmed desorption (TPD) of ammonia

Temperature programmed desorption (TPD) study of NH_3 was performed in a Micromeritic ChemiSorb 2750 automated system attached with ChemiSoft TPx software. The amount of NH_3 adsorbed on the surface was determined by temperature programmed desorption. The thermal conductivity detector was used to measure the amount of NH_3.

- Scanning Electron Microscope (SEM) and Energy Dispersive X-ray spectroscopy (EDX)

SEM observation with a scanning electron microscope JEOL JSM-6400 and energy dispersion Microspec WDX at Scientific Technological Research Equipment Center, Chulalongkorn University was employed to investigate the Ga content on Hβ-zeolite.

4.3 Alkylation of benzene in reformate with ethylene

4.3.1 Operating conditions

Table 4.2 Operating condition

Variable	**Condition**
Temperature	225, 205, 185 °C
Pressure	45 bar
Ethylene pressure	3.03, 5.57, 8.95 bar
Catalyst type	Hβ zeolite, Ga-Hβ zeolite
Amount of catalyst	0.5 g
Reaction time	20 h

4.3.2 Experimental procedure

Initially, 0.5 g of catalyst and 150 ml of reformate were added to 300 ml reactor vessel. Next, the reactor was assembled and ethylene was filled to desired B:E molar ratio. Then N_2 was quickly charged to a pressure of 45 bar and stirred at 500 rpm. Temperature was raised to the desired reaction temperature and held 20 h for all run. At the end of reaction time, the reactor was left to room temperature before collecting the sample.

4.3.3 Analysis

- Chemical compositions analysis

The samples of feed and product were analyzed in benzene and ethylbenzene content and the compounds called “PIANO” which consisted of paraffins, isoparaffins, aromatics, naphthenes and olefins.

- Fuel oil quality analysis

The standard analysis of Research Octane Number (RON), blending Reid vapor pressure (bRvp) and distillation temperature were carried out by follows the standard methods of following the standard methods of ASTM D -2699, ASTM D 5191-99 and ASTM D 86-05, respectively. All of analyses were tested by the laboratory of Bangchak Petroleum Public Company Limited.

4.4 Alkylation of pure benzene with ethylene and ethanol

4.4.1 Experimental procedure

The experiment with pure benzene feedstocks were carried out following a similar procedure and operating condition of alkylation benzene in reformate.

4.4.2 Analysis

- Chemical compositions analysis

Chemical compositions (benzene, ethylbenzene and ethanol) of liquid sample were analyzed by using a gas chromatograph (GC), Shimadzu GC 14B. The product compositions of pure benzene alkylation with ethylene were analyzed with Gs-Alumina column. The alkylation benzene with ethanol products were analyzed by DB-1 column. The operating condition of the GC is shown in Table 4.3. The analysis was done by injecting 0.2 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 GC14B

Gas Chromatography Shimadzu GC14B			
Operating Conditions for Gs- Alumina column			
Detector	FID	Length of Column (m)	50
Carrier Gas	He (99.98 %)	Injection temperature (°C)	250
Carrier Gas Flow rate (cm3/min)	60	Column temperature (°C)	200
Capillary Column	Gs-Alumina	Detector temperature (°C)	280
Operating Conditions for DB-1 column			
Detector	FID	Length of Column (m)	30
Carrier Gas	He (99.98 %)	Injection temperature (°C)	250
Carrier Gas Flow rate (cm3/min)	45	Column temperature (°C)	50-240 (5°C/min)
Capillary Column	DB-1	Detector temperature (°C)	200

CHAPTER V

RESULTS AND DISCUSSION

This chapter can be divided into three sections; characterization of β-zeolites, the alkylation of benzene in reformate with ethylene and the alkylation of pure benzene with ethylene as a probe reaction. Details are as follows.

5.1 Characterization of catalyst

Various techniques were employed to characterize β-zeolites catalysts, i.e. X-Ray Diffraction (XRD), BET surface area and Temperature Programmed Desorption (TPD). The details of catalyst characterization were provided as follows.

5.1.1 Chemical analysis

The chemical composition of Ga modified H-β-zeolite are shown in Table 5.1. The Ga content on the surface of Ga modified Hβ-zeolite catalyst observed by SEM-EDX is 0.93 wt %.

Table 5.1 Chemical composition of Ga-Hβ-zeolite by SEM-EDX

Element	% Atomic	% Weight
Si	43.99	56.68
Al	2.92	3.62
O	52.81	38.77
Ga	0.29	0.93

5.1.2 X-Ray Diffraction (XRD)

The XRD pattern of the Hβ-zeolites and Ga-Hβ-zeolites catalyst are shown in Figure 5.1. The pattern was corresponding well with those reported by Occelli *et al.*

(1999) as shown in Figure 5.2. However, no obvious peak of Ga metal was observed which might be due to small loading. As shown in Figure 5.1, calcination of Hβ-zeolite or modification with Ga does not affect their crystallinity of β-zeolite.

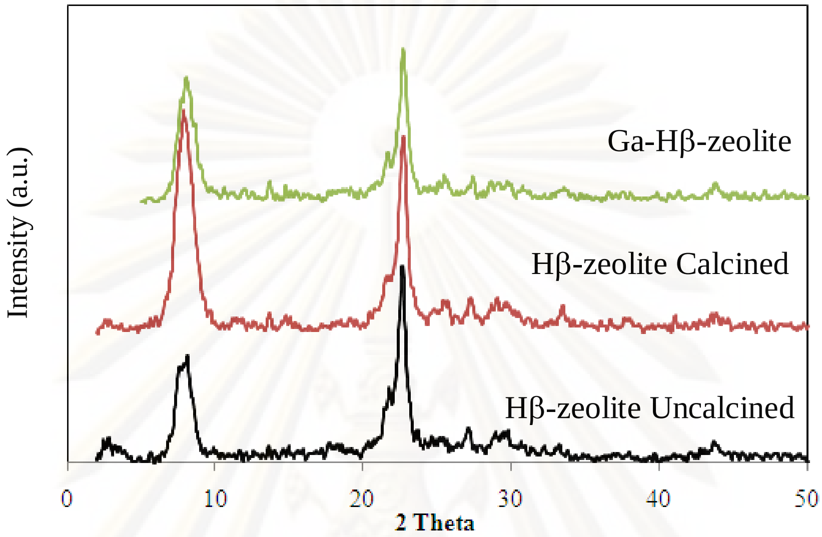


Figure 5.1 XRD patterns of Hβ-zeolite and Ga-Hβ-zeolite

5.1.3 BET surface area

Table 5.2 shows the surface area and pore volume of Hβ-zeolites and Ga-Hβ-zeolites. It was observed that the introduction of Ga results in decreasing of the BET surface area and pore volume.

Table 5.2 Surface area and pore volume of Hβ-zeolites and Ga-Hβ-zeolites

β-zeolite	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Hβ-zeolite	667.39	0.38	4.57
Ga-Hβ-zeolite	573.25	0.35	4.76

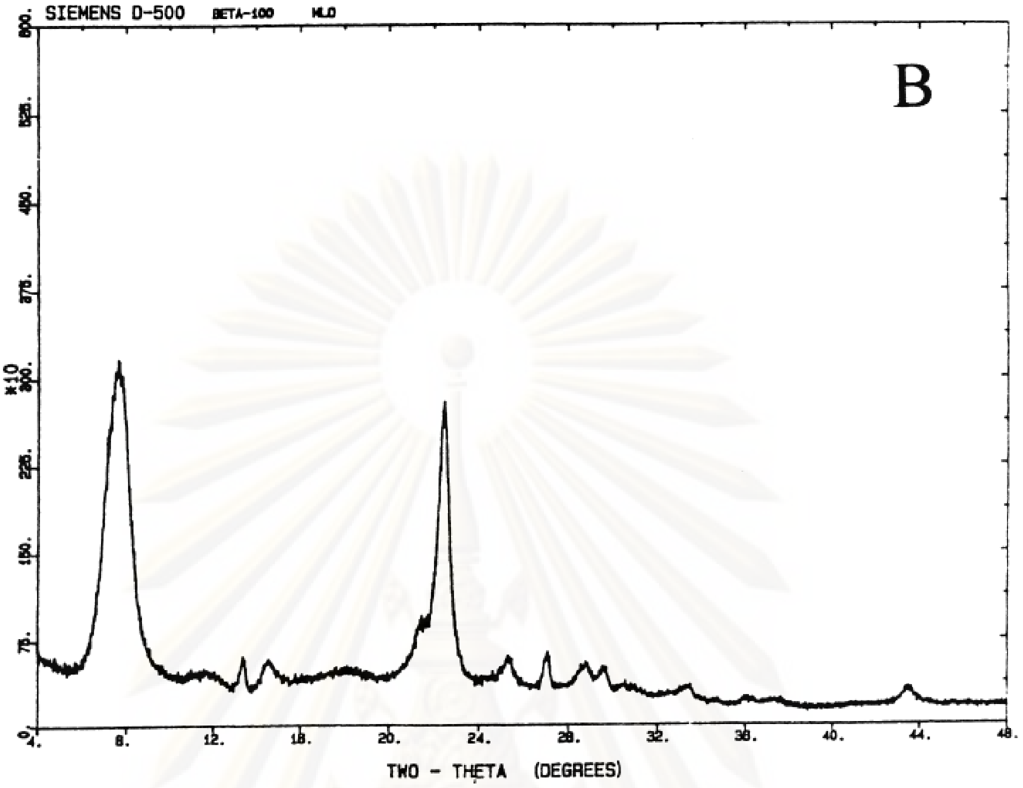


Figure 5.2 X-ray diffraction pattern of β-zeolite (Occelli *et al.*, 1999).

5.1.4 Temperature-programmed desorption of ammonia (NH_3-TPD)

Temperature-programmed desorption of ammonia is a useful method to determine the surface acid sites of solid acids. The amount of desorbed ammonia can be considered as the amount of the acid sites on the sample. The strength of the acid sites can be determined by desorption temperature. The higher ammonia desorption temperature is the stronger acid sites. NH_3-TPD profiles of Hβ-zeolite and Ga-Hβ-zeolite are shown in Figure 5.3. There are two ammonia TPD peaks in the profiles, which mean there are weak acid sites and strong acid sites on the zeolites. The Ga-Hβ-zeolite showed higher acidity than that of Hβ-zeolite.

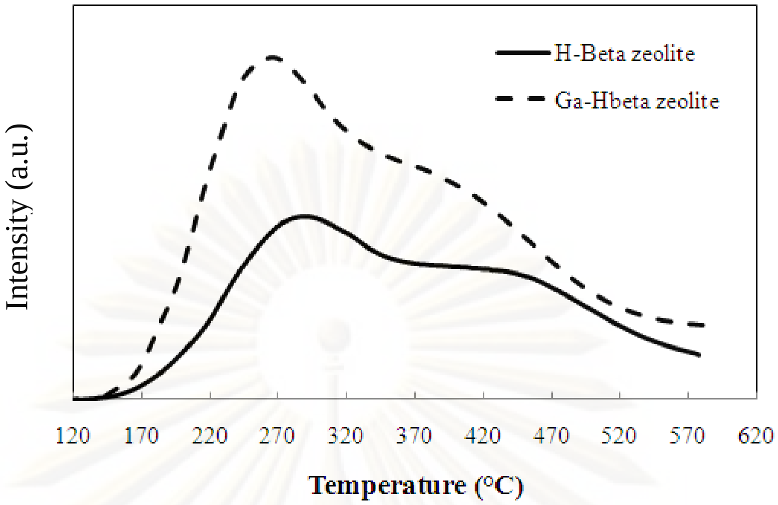


Figure 5.3 NH_3-TPD results of Hβ-zeolite and Ga-Hβ-zeolite

5.2 Alkylation of pure benzene with ethylene and ethanol

The catalytic performance of benzene alkylation in difference reactants (i.e. ethylene and ethanol) was studied at the following condition, i.e. Hβ-zeolite catalyst weight = 0.5 g, temperature = 225 °C, pressure = 45 bar, and reaction time = 20 h with approximately similar ratio of benzene to ethylene (3.64:1) and benzene to ethanol (3.80:1).

Table 5.3 Comparison the catalytic performance of benzene alkylation in difference reactant

Catalyst	Reactant	Benzene Reacted (mol x 10^7)	EB (mol x 10^7)	% Benzene conversion	% EB selectivity
Hβ-zeolite	Ethylene	9.73	4.76	43.35	48.99
	Ethanol	1.22	0.91	10.89	74.45

A comparison of catalytic performance between ethylene and ethanol for benzene alkylation is shown in Table 5.3. Ethylene gives significant higher benzene conversion and EB yield however lower selectivity than that of ethanol. When ethanol reacted with benzene, three reactions are possibly occurred including alkylation of benzene (Eq. 5.1), dehydration of alcohol (Eq. 5.2), and C-C cleavage (Eq. 5.3) (Raimondo *et al.*, 1997). It is worthy to note that Hβ-zeolite catalyst in this study shows the opposed catalytic performance comparing to others catalysts i.e. HZSM-5 and mordenite which ethanol give higher EB yield than that of ethylene (Raimondo et al., 1997). Consequently, we use ethylene as alkylating agent for further experiment.

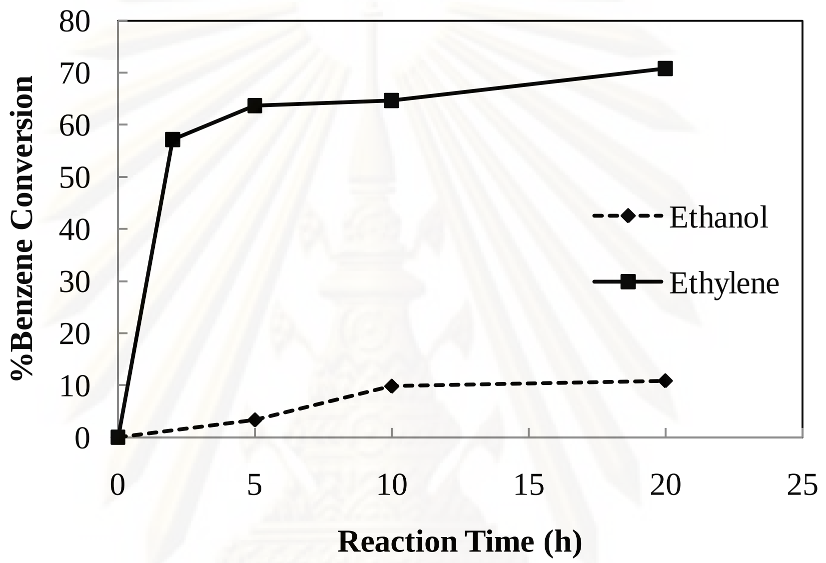
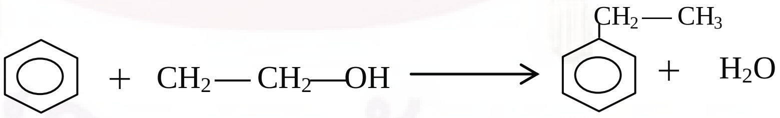


Figure 5. 4 Benzene conversion at 225 °C at Hβ-zeolite catalyst in different alkylating agent

Alkylation:



$$C_6H_6 + CH_2-CH_2-OH \longrightarrow C_6H_5CH_2-CH_3 + H_2O \qquad \text{Eq. (5.1)}$$

Dehydration: $CH_2-CH_2-OH \xrightarrow{-OH} CH_2{=}CH_2 + H_2O$ Eq. (5.2)

C-C cleavage: $CH_2{=}CH_2 \longrightarrow CH_3 + CH_3$ Eq. (5.3)

5.3 Alkylation of benzene in reformate with ethylene

5.3.1 Effect of ethylene content in feed

The compositions of original reformate and alkylation products analyzed by PIANO analysis were declared in Table 5.4-5.8. The gasoline properties of reformate and alkylation products with different ethylene content can be summarized in Table 5.9. The effect of ethylene content was studied by varying the pressure of ethylene. The benzene conversion increased with higher ethylene feed content. At higher ethylene content increases the polyalkylation such as diethylbenzene and triethylbenzene (Perego *et al*., 2002).

As expected, benzene conversion increased with higher ethylene in feed according to Le Chatelier's principle. The alkylated products i.e. ethylbenzene, di- and tri-ethylbenzene increased accompany with decreased of benzene content. The RON of benzene and ethylbenzene are 99 and 167 while that of o-, m-, p-diethyl benzene were estimated as 183, 154 and 209 (Ramadhan *et al*., 1999). Therefore, the RON of alkylated products is higher than that of original reformate. The improvement of RON could be observed in all ethylene content of Hβ-zeolite and Ga-Hβ-zeolite. However, the tendency of increasing RON with lower ethylene content are in contrast with the lowering of benzene converting to EB, DEB and TEB as shown in the table. Therefore, the alkylation of benzene to EB, DEB and TEB could not be a sole reason of RON improvement. It is difficult to explain this contrast of the tendency because there are many reactions that could be occurred and effect on RON. One observable trend of increasing of C7 and C8 aromatics with decreasing of ethylene content and in the case of Ga- Hβ-zeolite could be one of the reasons of increasing RON (Figure 5.5). C7 aromatic (toluene) has RON of 120 while C8 aromatic (apart from ethylbenzene) consist of *o*-, *m*-, *p*-xylene which has the RON of 120, 117 and 146, respectively. Moreover, Rvp of alkylated reformate decreased (Table 5.9) and distillation temperature increased in all range of % evaporated (Fig 5.6). This is due to the relative volatilities of benzene to ethylbenzene, toluene, p- and m-xylene are 7.0, 3.5, 7.4 and 7.6, respectively (Berg *et al*., 2004; Kesselman *et al*., 1968). The beneficial of decreasing Rvp and increasing distillation temperature is less evaporative emission and hence decreased the chance of a vapor lock problem. The obtained products pose desired gasoline properties especially in tropical country or in summer.

Table 5.4 Composition of reformate in volume percent

	Carbon number	n-paraffins	i-paraffins	Olefins	Naphtenes	Aromatics	Total
Reformate	C4	1.38	0.24	0.00	0.00	0.00	1.62
	C5	2.57	4.03	0.06	0.07	0.00	6.73
	C6	3.89	9.01	0.09	0.58	8.80	22.37
	C7	2.73	10.08	0.07	0.55	19.30	32.73
	C8	0.49	1.73	0.49	0.13	16.86	19.70
	C9	0.06	0.00	0.00	0.00	7.78	7.84
	C10	0.00	1.32	0.00	0.00	0.61	1.93
	C11	0.00	0.41	0.00	0.00	0.11	0.52
	C12	0.00	0.00	0.00	0.00	0.04	0.04
	C13	0.00	0.00	0.00	0.00	0.00	0.00
	C14+	0.00	0.00	0.00	0.00	0.00	6.51
	Total	11.12	26.82	0.71	1.33	53.50	99.99

Table 5.5 Product composition of reformate alkylation with ethylene on Hβ-zeolite catalyst at ethylene pressure = 3.03 bar in volume percent

	Carbon number	n-paraffins	i-paraffins	Olefins	Naphtenes	Aromatics	Total
B:E =9:1	C4	0.39	0.05	0.00	0.00	0.00	0.44
	C5	1.93	2.60	0.00	0.06	0.00	4.59
	C6	3.95	8.64	0.00	0.56	8.21	21.36
	C7	3.05	10.98	0.00	0.60	19.41	34.04
	C8	0.56	1.97	0.55	0.15	19.08	22.31
	C9	0.06	0.07	0.00	0.00	10.91	11.04
	C10	0.00	1.54	0.00	0.00	2.26	3.80
	C11	0.00	1.40	0.00	0.05	0.20	1.65

Table 5.5 Product composition of reformate alkylation with ethylene on Hβ-zeolite catalyst at ethylene pressure = 3.03 bar in volume percent (cont.)

	Carbon number	n-paraffins	i-paraffins	Olefins	Naphtenes	Aromatics	Total
B:E =9:1	C12	0.00	0.00	0.00	0.00	0.64	0.64
	C13	0.00	0.00	0.00	0.00	0.00	0.00
	C14+	0.00	0.00	0.00	0.00	0.00	0.13
	Total	9.93	27.26	0.55	1.43	60.7	100

Table 5.6 Product composition of reformate alkylation with ethylene Hβ-zeolite catalyst at ethylene pressure = 5.57 bar in volume percent

	Carbon number	n-paraffins	i-paraffins	Olefins	Naphtenes	Aromatics	Total
B:E = 5:1	C4	0.94	0.17	0.00	0.00	0.00	1.11
	C5	2.34	3.50	0.00	0.07	0.00	5.91
	C6	3.96	8.95	0.00	0.56	7.38	20.85
	C7	2.95	10.68	0.00	0.58	17.11	31.32
	C8	0.54	1.90	0.53	0.14	17.50	20.61
	C9	0.06	0.07	0.00	0.00	11.14	11.27
	C10	0.00	1.36	0.00	0.00	2.68	4.04
	C11	0.07	1.93	0.00	0.09	0.44	2.53
	C12	0.00	0.04	0.00	0.00	1.12	1.16
	C13	0.00	0.03	0.00	0.00	0.00	0.03
	C14+	0.00	0.00	0.00	0.00	0.00	1.01
	Unknown	0.00	0.00	0.00	0.00	0.00	0.05
	Total	10.86	28.63	0.53	1.44	57.37	99.89

Table 5.7 Product composition of reformate alkylation with ethylene on Hβ-zeolite catalyst at ethylene pressure = 8.95 bar in volume percent

	Carbon number	n-paraffins	i-paraffins	Olefins	Naphtenes	Aromatics	Total
B:E = 3:1	C4	0.87	0.17	0.00	0.00	0.00	1.04
	C5	2.24	3.35	0.00	0.06	0.00	5.65
	C6	3.85	8.71	0.00	0.54	6.79	19.89
	C7	2.87	10.38	0.00	0.53	15.87	29.65
	C8	0.53	1.84	0.51	0.14	17.22	20.24
	C9	0.06	0.00	0.00	0.00	11.92	11.98
	C10	0.00	1.37	0.00	0.00	3.55	4.92
	C11	0.04	2.23	0.00	0.00	0.49	2.76
	C12	0.00	0.04	0.00	0.00	1.32	1.36
	C13	0.00	0.04	0.00	0.00	0.00	0.04
	C14+	0.00	0.00	0.00	0.00	0.00	2.22
	Unknown	0.00	0.00	0.00	0.00	0.00	0.15
	Total	10.46	28.14	0.51	1.35	57.16	99.9

Table 5.8 Product composition of reformate alkylation with ethylene on Ga-Hβ-zeolite catalyst at ethylene pressure = 3.03 bar in volume percent

	Carbon number	n-paraffins	i-paraffins	Olefins	Naphtenes	Aromatics	Total
B:E = 9:1	C4	0.00	0.00	0.00	0.00	0.00	0.00
	C5	0.80	0.77	0.00	0.04	0.00	1.61
	C6	3.35	6.75	0.00	0.49	7.38	17.97
	C7	3.13	10.95	0.00	0.59	20.15	34.82
	C8	0.62	2.12	0.57	0.17	21.34	24.82
	C9	0.07	0.09	0.00	0.11	12.50	12.77
	C10	0.00	1.91	0.00	0.00	2.91	4.82
	C11	0.00	1.72	0.00	0.00	0.25	1.97

Table 5.8 Product composition of reformate alkylation with ethylene on Ga-Hβ-zeolite catalyst at ethylene pressure = 3.03 bar in volume percent (cont.)

	Carbon number	n-paraffins	i-paraffins	Olefins	Naphtenes	Aromatics	Total
B:E = 9:1	C12	0.00	0.00	0.00	0.00	0.71	0.71
	C13	0.00	0.00	0.00	0.00	0.00	0.00
	C14+	0.00	0.00	0.00	0.00	0.00	0.33
	Unknown	0.00	0.00	0.00	0.00	0.00	0.18
	Total	7.97	24.31	0.57	1.40	65.24	100.0

Table 5.9 Gasoline properties of reformate and alkylation products

Properties	Reformate	Hβ-zeolite			Ga-Hβ-zeolite
		E = 3.03 bar	E = 5.57 bar	E = 8.95 bar	E = 3.03 bar
Benzene (vol%)	8.81	8.21	7.38	6.79	7.38
EB (vol%)	2.06	3.53	3.80	4.15	4.12
DEB (vol%)	0.12	0.49	0.41	0.74	0.58
TEB (vol%)	0.00	0.03	0.07	0.08	0.04
RON	92.8	98.2	95.8	94.4	99.4
RvP (psi)	5.94	5.5	5.4	5.5	4.9
Distillation Temperature °C					
IBP	44	44	45	44	45
10 %	66	67	68	68	72
50 %	115	122	122	122	130
90 %	141	149	150	153	150
FBP	164	175	174	180	171

E = Ethylene

EB = Ethylbenzene

DEB = *d* i-Ethylbenzene

TEB = *tri*-Ethylbenzene

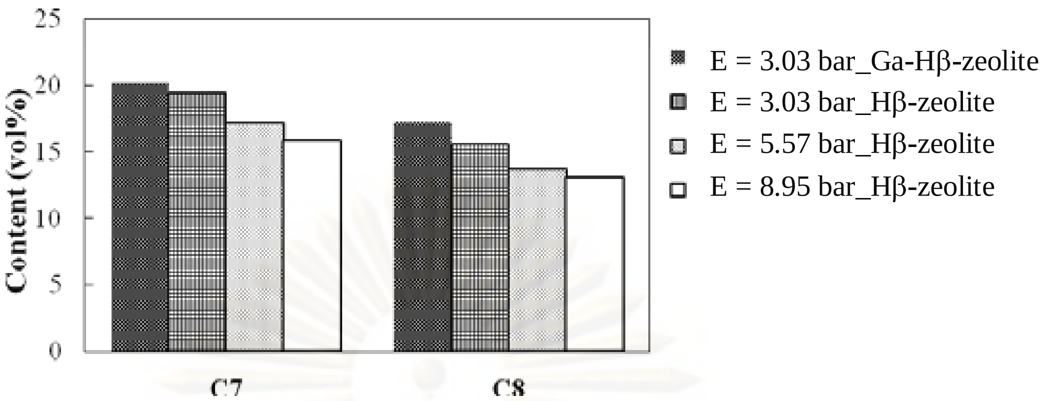


Figure 5.5 Content of C7 and C8 aromatic (excluded di-ethylbenzene) in alkylated reformate in different ethylene feed content and catalyst

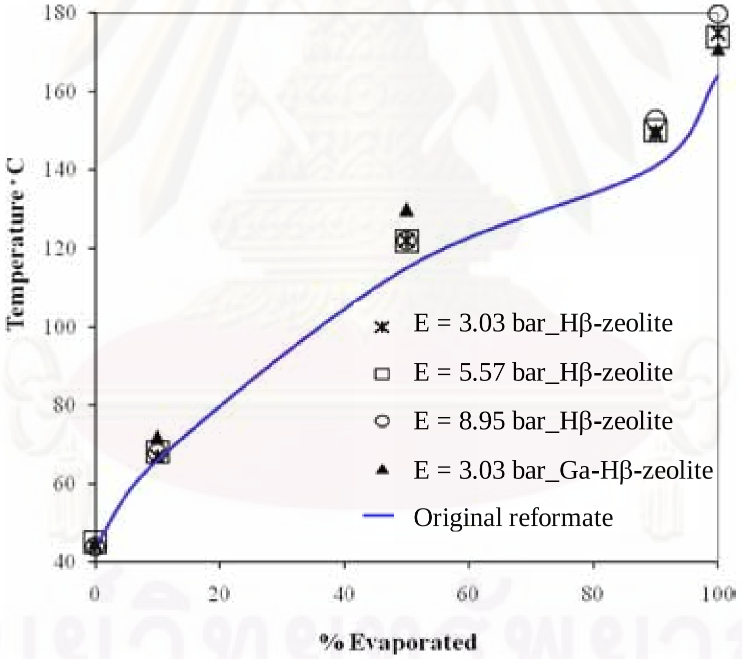


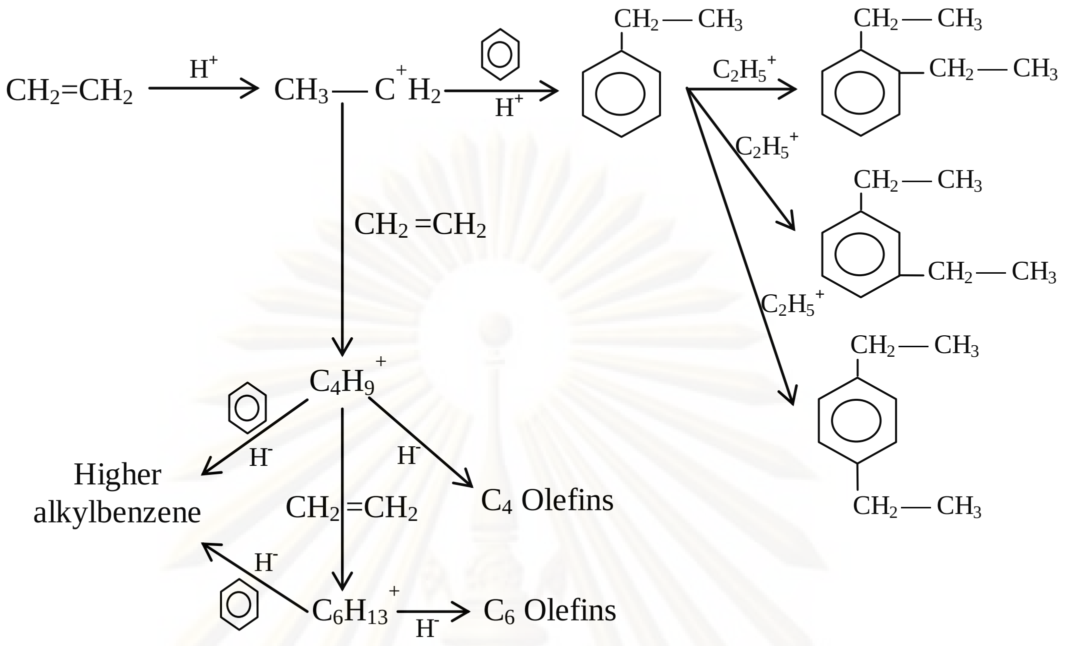
Figure 5.6 Distillation curve of original reformate and product of reformate alkylation with ethylene in different ethylene feed content catalyzed by Hβ-Zeolite

5.4 The alkylation of pure benzene with ethylene as probe reaction

As shown in previous section although RON could be increased with decreasing of Rvp in all ethylene pressure of Hβ-zeolite and Ga-Hβ-zeolite, the tendency of benzene reduction and EB, DEB formation among the samples are not follows. Therefore, alkylation of pure benzene with ethylene was investigated as a probe reaction.

It is worthy to note that when ethylene was charged to the autoclaved reactor, ethylene was presence in both liquid and gas phase. The amount of ethylene in the reactor could be calculated by the summation of dissolved ethylene in benzene and ethylene gas in head space of the reactor. With ethylene pressure reported in this part as 15.70, 28.26 and 37.00 bar are equivalent to the amount of ethylene of 0.31, 0.68 and 1.11 mole, respectively (see the calculation in Appendix B).

The effect of reaction time on conversion of pure benzene with different ethylene content was shown in Figure 5.7. Benzene conversion increased dramatically within 2 hrs of reaction time and then increased with lower rate of reaction. The benzene conversions at 20 hrs were summarized in Table 5.10. Benzene conversion increased with increasing ethylene feed content; however selectivity of EB was slightly decreased. This tendency is similar to the case of alkylation of reformate with ethylene. The slight decreased of EB selectivity might be due to ethylene molecule can react with other ethylene through alkenyl carbonium ion to from an oligomer (Yingchum *et al.*, 2002) and undergo polyalkylation to *di* and other polyethylbenzenes (Perego *et al.*, 2002) according to the reactions depicted in Scheme 5.1.



Scheme 5.1 Reaction pathways of benzene alkylation with ethylene

Generally, the alkylation of benzene with ethylene to produce ethylbenzene (EB) is an electrophilic substitution on aromatic ring. Alkylation reactions catalyzed by acidic zeolites are considered as proceeding through carbonium ion type mechanism (Bellussi *et al*., 1995; Corma *et al*., 2000). Ethylene is protonated by the acid sites of catalyst to form the active species (carbonium ion). Then, this ion is weakly adsorbed on benzene or EB to produce EB or diethylbenzene (DEB), respectively.

Therefore, the higher ethylene content could induce the higher ethylene oligomer and polyalkylation formation and thus lower selectivity.

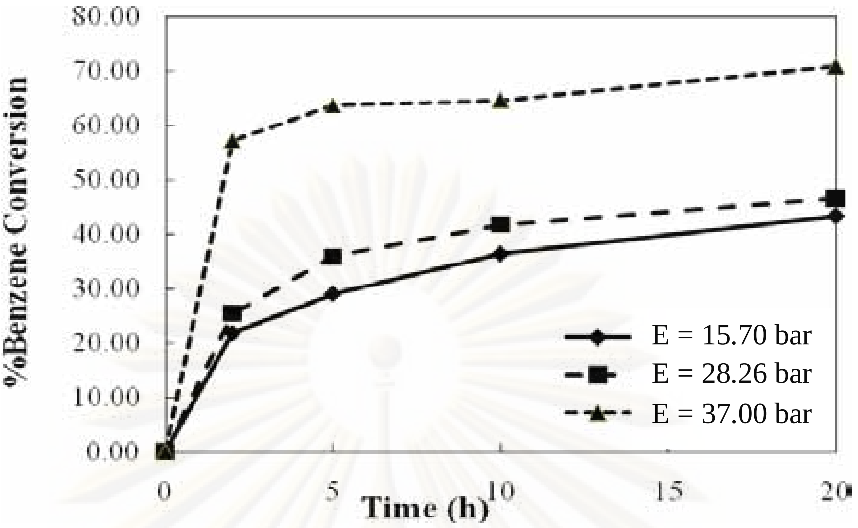


Figure 5.7 Benzene conversions at 225 °C with Hβ-zeolite catalyst in different ethylene feed content

Table 5.10 Pure benzene alkylation with ethylene at 225 °C in difference ethylene feed content and catalyst

Catalyst	Ethylene Pressure (bar)	Benzene Reacted molx10^7	EB molx10^7	DEB molx10^7	TEB molx10^7	TetEB molx10^7	MPB molx10^7	% Benzene conversion	% EB selectivity
Hβ-zeolite	15.70	9.73	4.76	4.60	0.32	0.00	0.05	43.35	48.99
	28.26	10.46	4.80	5.15	0.48	0.01	0.02	46.63	45.91
	37.00	15.90	7.00	N.D.	N.D.	N.D.	N.D.	70.84	44.04
Ga-Hβ-zeolite	15.70	5.61	5.51	N.D.	N.D.	N.D.	N.D.	25.00	98.28

EB = Ethylbenzene DEB = *di*-Ethylbenzene
TEB = *tri*-Ethylbenzene TetEB = *Tetra*-Ethylbenzene
MPB = Methylpropylbenzene

Ga-Hβ-zeolite showed much lower benzene conversion that that of Hβ-zeolite but much higher EB selectivity. The results in the case of pure benzene were not in the similar manner to the case of reformate. Therefore, it could be implying that higher benzene conversion in reformate with Ga-Hβ-zeolite is not came from the enhancement of alkylation of benzene with ethylene. Genovena *et al.*, (2006) modified Ga on Hβ-zeolite for alkylation of pure benzene with propylene in gas phase reaction. Impregnation with Ga can extend the catalyst life time while catalytic activity are insignificantly improved and the selectivity was slightly higher than Hβ-zeolite (Genovena *et al*., 2006). As shown in our results, the roles of Ga on alkylation of benzene are different depending on the catalytic reaction system. Acidic amount of Ga-Hβ-zeolite is larger than Hβ-zeolite (as shown in Fig. 5.2), however Occelli *et a*l., 1999 reported that modification of Hβ-zeolite with Ga decrease Br∅nsted acid sites strength. The catalytic alkylation reaction is supposed to be catalyzed by Br∅nsted acid sites on the catalyst (Wang and Xin, 2001).

5.4.1 Effect of temperature on reformate alkylation with ethylene

The effect of reaction temperature was investigated at the following condition, i.e. Hβ-zeolite catalyst weight = 0.5 g, temperature = 225, 205 and 185 °C, Total pressure = 45 bar, pressure of ethylene = 3.03 bar and reaction time = 20 h. The influence of reaction temperature on the conversion is shown in Table 5.11. Benzene conversion decreases at higher temperatures, due to the alkylation reaction is exothermic.

Table 5.11 Reformate alkylation with ethylene at ethylene pressure of 3.03 bar on H-βzeolite catalyst in difference reaction temperature

	Benzene (vol%)	EB (vol%)	DEB (vol%)	TEB (vol%)	% Benzene Conversion
Reformate	8.80	2.06	0.12	0.00	0.00
T = 225 °C	8.21	3.53	0.49	0.03	6.74
T = 205 °C	8.12	3.16	0.28	0.01	7.76
T = 185 °C	7.58	2.93	0.21	0.006	13.89

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The process of reformate gasoline quality improvement by reducing the benzene content were studied by the alkylation of reformate with ethylene in batch reactor. The following conclusions can be drawn from the investigation.

6.1.1 Characterization of catalyst

The Ga content on the surface of Ga modified Hβ-zeolite catalyst observed by SEM-EDX is 0.93 wt %. The Ga-Hβ-zeolites does not affect their crystallinity and decrease the BET surface area and pore volume. The Hβ-zeolite shows lower the acidity than Ga-Hβ-zeolite.

6.1.2 Alkylation of pure benzene with ethylene and ethanol

Ethylene gives significant higher benzene conversion and EB yield however lower selectivity than that of ethanol. So, we use ethylene as alkylating agent in further experiment.

6.1.3 Alkylation of benzene in reformate with ethylene

6.1.3.1 Effect of ethylene feed content

The effect of ethylene feed content was studied by varying the mole of ethylene. The benzene conversion increased with increasing ethylene feed content. At higher ethylene content increases the polyalkylation such as diethylbenzene and triethylbenzene. The RON of alkylated products is higher than that of original reformate. The improvement of RON could be observed in all ethylene feed content of Hβ-zeolite and Ga-Hβ-zeolite. The tendency of increasing RON with lower ethylene feed content is in contrast with the lowering of benzene converting to EB, DEB and TEB. One observable trend of increasing of C7 and C8 aromatics with decreasing of ethylene feed content and in the case of Ga- Hβ-zeolite could be one of the reasons of increasing RON. Moreover, Rvp of alkylated reformate decreased and distillation temperature increased in all range of % evaporated. So, the obtained products pose desired gasoline properties especially in tropical country or in summer.

6.1.4 The alkylation of pure benzene with ethylene as probe reaction

Alkylation of pure benzene with ethylene was investigated as a probe reaction. The effect of reaction time on benzene conversion with different ethylene feed content shows the benzene conversion increased dramatically within 2 hrs of reaction time and then increased with lower rate of reaction. Benzene conversion increased with higher ethylene feed content and selectivity of EB was slightly decreased. This tendency is similar to the case of alkylation of reformate with ethylene.

Ga-Hβ-zeolite showed much lower benzene conversion that that of Hβ-zeolite but much higher EB selectivity. The results were not in the same tendency with alkylation of reformate and ethylene.

6.1.4.1 Effect of temperature on reformate alkylation with ethylene

Benzene conversion decreases at higher temperatures, due to the alkylation reaction is exothermic.

6.2 Recommendations

6.2.1 The effect of Si/Al mole ratio and Br∅nsted acid in β-zeolite on catalytic activity in reformate alkylation should be further investigated.

6.2.2 The side reaction in reformate alkylation on β-zeolite and Ga modified β-zeolite should be further investigated.

REFERENCES

Announcement of Department of Energy Business, 2007

Bellussi, G., Pazzuconi, G., Perego, C., Girotti, G., ang Terzoni, G. Liquid phase Alkylation of Benzene with Light olefins Catalyzed by β-Zeolite. *J. Catal.*, 157 (1995): 227-234.

Bentham, M. F., Gajda, G. J., Jensen, R. H., and Zinnen, H. A. *Erdöl Erdgas Kohle.* 113, 84 (1997): 123-127.

Breck, D.W. *Zeolite Molecular sieves: Structure and Use*, New York: John Wiley & sons, 1997.

Cavani, F., Arrigoni, V., and Bellussi, G. Process for alkylating benzene. *European Patent 0432814 B1*, 1991.

Chen, N.Y., and Garwood, W.E. Industrial application of shape-selective catalysis. *Catal.Rev.Sci.Eng.* 28 (1986): 185-264.

Chin, A.A., Collins, N.A., Harandi, M.N., Thomson, R.T., and Ware, R.A. Benzene reduction in gasoline by alkylation with higher olefins. *U.S. Patent 5,491,270* to Mobil Oil Corporation, Patent and Trademark Office, 1996.

Coldwell, R.F. *Benzene in gasoline Regulation & remedies*, Process Engineering Associates LLC [Online] , 2008, Available from http://www.processengr.com/ppt_presentations/msat_ regulation_options.pdf. [2009,November]

Corma, A., Mart´ınez-Soria, V., and Schnoeveld, E. Alkylation of Benzene with Short Chain Olefins over MCM-22 Zeolite: Catalytic Behaviour and Kinetic Mechanism. *Journal of Catalysis* 192 (2000):163–173.

Das, J., Bhat, Y.S. and Halgeri, A. B. Transalkylation and disproportionation of toluene and C9 aromatics over zeolite beta. *Catal. Lett.*, 23 (1994): 161-168.

David, S. J. and Pujad, P. R. *Handbook of Petroleum Processing*, Netherlands : Springer, 2006.

Derouane, E.G. New aspects of molecular shape-selectivity:Catalytic by zeolite ZSM-5. *Studies Surface Science Catal*. 5(1980):5.

Dessau, R.M., Q.N. Le, A. Tabaki, and R.T. Thomson. Gasoline upgrading by aromatics amination. *US patent 5,284,984*, to Mobil Oil Corp., Patent and Trademark Office, 1994.

Gaile, A.A., Zalishchevskii, G.D., Erzhenkov, A.S., and Koldobskaya, L.L. Benzene Separation from the Benzene Fraction of Reformer Naphtha by Extractive Rectification with N-Methylpyrrolidone–Sulfolane Mixtures. *Russian Journal of Applied Chemistry*, 81(2008): 1375–1381.

Gaile, A.A., Zalishchevskii, G.D., Gafur, N.N., Semenov, L.V., Varshavskii, O.M., Fedyanin, N.P., and Kaifadzhyan, E.A. Separation of Aromatic Hydrocarbons from Reformate. Combined Extraction Fractionation–Eextraction, *Chemistry and Technology of Fuels and Oils*, 40(2004) : 131-136.

Gildert, G.R., Hearn, D., Putman, H.M. Hydrogenation of unsaturated cyclic compounds. *U.S. Patent 5,773,670*, Patent and Trademark Office, 1998.

Girotti, G., Rivetti, F., Ramello, S., Carnelli, L. Alkylation of benzene with isopropanol on β-zeolite: influence of physical state and water concentration on catalyst performances. *J. Mol. Catal. A: Chem.* 204–205 (2003): 571–579.

Goundani, K., Papadopoulou, C., and Kordulis, C. Benzene elimination from reformate gasoline by high pressure hydrogenation in a fixed-bed reactor, *React.Kinet.Catal.Lett.*, 82(2004)

Hagen, J. *Industrial catalysis*, New York: Weinheim Wiley, 1999.

Halgeri, A. B. and Das, Novel catalytic aspects of beta zeolite for alkyl aromatics transformation. *J. Appl. Catal. A Gen.*, 181(1999): 347–354.

Hendriksen, D.E., Lattner, J.R., Johannes, M., and Janssen, G. Alkylation process using zeolite beta, *U.S. patent 6,002,057* to Exxon Chemical Patents Inc., 1999.

Hobson, G.D. *Modern Petroleum Technology*, 5th Edition Part II, Wiley, 1984.

Hseieh, C.R., and Robinson, R.C. Process to remove benzene from refinery stream. *US patent 5,210,348*, to Chevron Research and Technology Company, Patent and Trademark Office, 1993.

ICPS, *Environmental health criteria 150: Benzene*. The international program on chemical safety. Genewa: World Health Organization, 1993.

Intaragamjon, N., Shiono, T., Jongsomjit, B., Elucidation of solvent effects on the catalytic behaviors for [t-BuNSiMe2Flu]TiMe2 complex during ethylene/1-hexene copolymerization. *Catalysis Communications*, 7 (2006): 721–727

Kaul, B.K., Bara, J.T., Savage, D.W., Dennis, J.P., and Kantner E., Benzene removal from gasoline boiling range streams. *US patent 5,186,819*, to Exxon Research and Engineering Company, Patent and Trademark Office, 1993.

Kaul, B.K., Runaldue, D.C., Bara, J.T., Sabottke, C.Y., and Niessen, E., Benzene removal and conversion from gasoline boiling range streams. *US patent 5,294,334*, to Exxon Research and Engineering Company, Patent and Trademark Office, 1994.

Kostrab, G., Lovic, M., Janotka, I., Bajus, M., and Mravec, D. tert-Butylation of toluene with isobutylene over zeolite catalysts: Influence of water. *Appl. Catal. A Gen*., 323 (2007): 210–218.

Lee, C.H., Tsai, C.H., and Fung ,J. Process of producing a debenzenated and isomerized gasoline blending stock by using a dual functional catalyst. *US patent 5,830,345*, to Chinese Petroleum Corp., Patent and Trademark Office, 1998.

Lin, T.B., Hwang, J.H., Shen, H.C., and Wu, K.Y. Integrated process for removing benzene from gasoline and producing cyclohexane. *US patent 2007/0299294 A1,* to AMT International Inc.; Chinese Petroleum Corp., 2007.

Lloyd Berg, P. J. KoberThe separation of ethylbenzene from *p*- and *m*-xylene by extractive distillation using mixtures of polychloro compounds, *AIChe*. 26 (2004):862-865.

Masuda, T., Sonobe, T., and Horie, M., Process for fraction separation of multi-component fluid mixture, *U.S. Patent 5,198,120* to Japan Organo Co., Ltd., Patent and Trademark Office, 1993.

Meng, X., Qin, Z., Zhang, Y., Dong, M., and Wang, J. Alkylation of benzene with propene on Beta zeolites under supercritical conditions. *Catal. Lett.,* 83 (2002) : 265-269.

National Library of Medicine, *Hazardous Substances Data Bank*: *Ethylbenzene*. [Online]. 1994. Available from: http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~eOJ8Rz:1 [2009, November 9]

Occelli, M.L., Eckert, H., WÖlker, A., Auroux, A. Crystalline galliosilicate molecular sieves with the beta structure. *Microporous Mesoporous Mater.*30 (1999) : 219–232.

Olsen, J.L., Separation of aromatic from gasoline or kerosene fractions, *US patent 2,717,144* to Sun Oil Company, Patent and Trademark Office, 1995.

Owen, K., Coley, T. *Automotive Fuels Reference Book*, 2nd Edition. Society of Automotive Engineers, Inc., Warrendale, PA, 1995.

Puppe, L., Weisser, J. Synthesis conditions and catalytic properties oh highly acidic zeolite. UTM-1.*U.S. Patent 4,439,409*, 1990.

Raimondo, M., Perez G., Stefanis A. De, Tomllnson, A.A.G., Ursini, O. PLS vs. zeolites as sorbents and catalysts 4. Effects of acidity and porosity on alkylation of benzene by primary alcohols. . *Appl. Catal. A Gen.*, 164 (1997): 119-126.

Scott J., *Zeolite Technology and Applications*. New Jercy: Noyes Date Corporation, 1980.

Shimizu, T. Process for hydrogenating benzene in hydrocarbon oils,*US patent 5,777,186*, to Cosmo Research Inst.; Cosmo Oil co., Ltd. Patent and Trademark Office, 1998.

Speight, J.G. *Synthetic fuels handbook : properties, process, and performance*, 2008.

Speight, J. G. *The Chemistry and technology of petroleum*. 4th ed. CRC Press, 2007

Spiro, G.T. and Stingliani, W.M., *Chemistry of the environment*, New Jersey: Prentice-Hall, 1996.

Siffert, S., Gaillard, L., and Su, B. L., Alkylation of benzene by propene on a series of Beta zeolites: Toward a better understanding of the mechanisms. *J. Molec. Catal. A Chem.*, 153(2000): 267–279.

Siffert, S. and Su, B. L. Pure propane as alkylating agent in the formation of cumene from benzene on gallium-modified h-mfi and h-beta zeolites. *React. Kinet. Catal. Lett.*, 68(1999): 191–195.

Szostak, R. *Molecular Seive Principles of Synthesis and Identification*, New Van Nostrand Reinhold, New York, 1998.

Thipsunet P., *Improvement of fuel oil from fluidize catalytic cracking unit with ethanol by etherification reaction.* Master’s Thesis, Department of Chemical Engineering Faculty of Engineering Chulalongkorn University, 2006.

Umansky, B.S., Clark, M.C., Dandekar, A.B., and Elia C.N. Vapor phase aromatics alkylation process., *US patent 7,498,474B2*, to Exxon Research and Engineering Company, Patent and Trademark Office, 2009.

Umansky, B., Clark, M.C., Zhao, X. Banish the benzene, boost the octane, *Hydrocarbon Eng.* 12 (2007) 61–62.

UOP Inc. A low-cost way to remove benzene from gasoline. *Chem. Eng*. 97 (1990): 23.

Wang, H. and Xin, W. Surface acidity of H-beta and its catalytic activity for alkylation of benzene with propylene. *Catal. Lett.*, 76 (2001): 225-229.

Westphalen, D., and Shethna, H. Refinery wide simulation. *Hydrocarbon engineering*. (2004):53-55.

Wichterlova, B., Cejka, J., and Zilkova, N. Selective synthesis of cumene and p-cymene over Al and Fe silicates with large and medium pore structures. *Microporous Matter.*6 (1996) : 405-414.

Yeh, C.Y., Barner, H.E., Suciu, G.D., Zeolite Catalysis for Upgrading Gasoline. *Stud. Surf. Sci. Catal*. 84 (1994) : 2311–2318.

Zhuze, T. P. and Zhurba, A. S., solubilities of ethylene in hexane, cyclohexane, and Benzene under pressure. *Izvestiya Akademii Nauk SSSK.* 2(1960):364-366.

Zones, S.I., Holtermann, D.I., Innes, R.A., Pecoraro, T.A., Santilli, D.S., and Ziemer, J.N. Textural and catalytic properties of MCM-22 zeolite crystallized by the vapor phase transport method. *U.S. Patent 4,826,667*, 1989.

APPENDICES

APPENDIX A

CALIBRATION CURVES

The calibration curves of all components involving in the reaction system were prepared. The gas chromatography (Shimadzu model 14B) equipped with GS Alumina column and frame ionization detector (FID) was used to analyze the composions of all components. The calibration curves of benzene and ethylbenzene in relationship between mole and area are obtained as below.

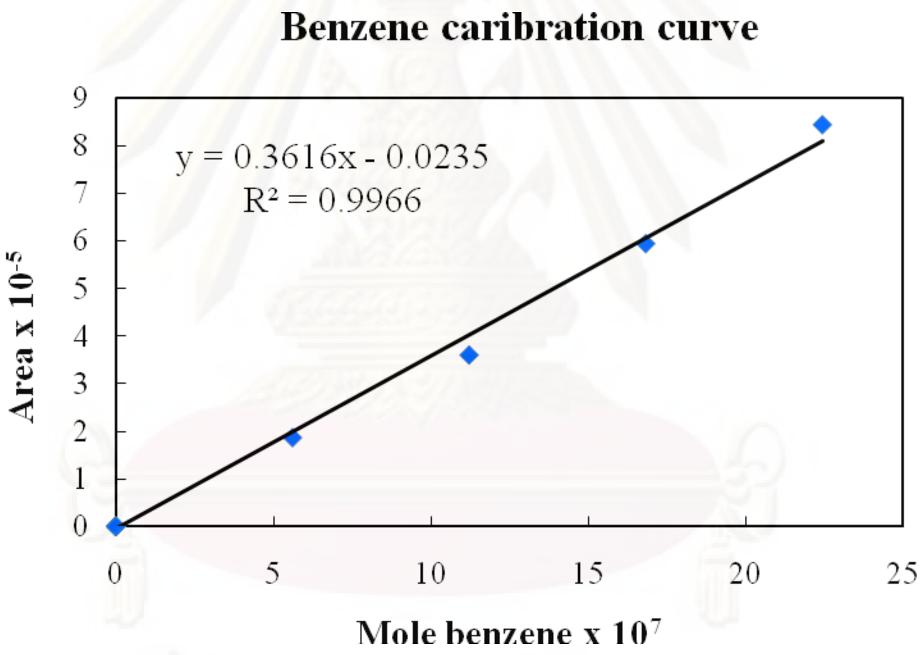


Figure A.1 The calibration Curve of Benzene with GS alumina column

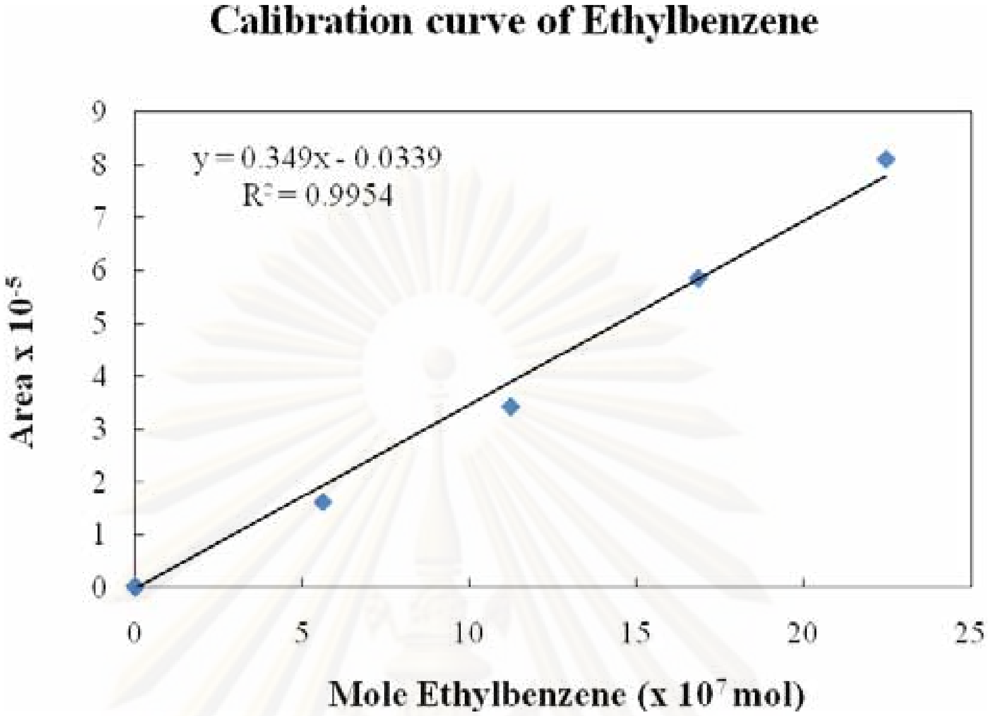


Figure A.2 The calibration Curve of Ethylbenzene with GS alumina column

The calibration curves of all components involving in the reaction system were prepared. The gas chromatography (Shimadzu model 14B) equipped with DB-1 column and frame ionization detector (FID) was used to analyze the composions of ethanol, benzene ethylbenzene. The calibration curves of ethanol, benzene and ethylbenzene in relationship between mole and area are obtained as below.

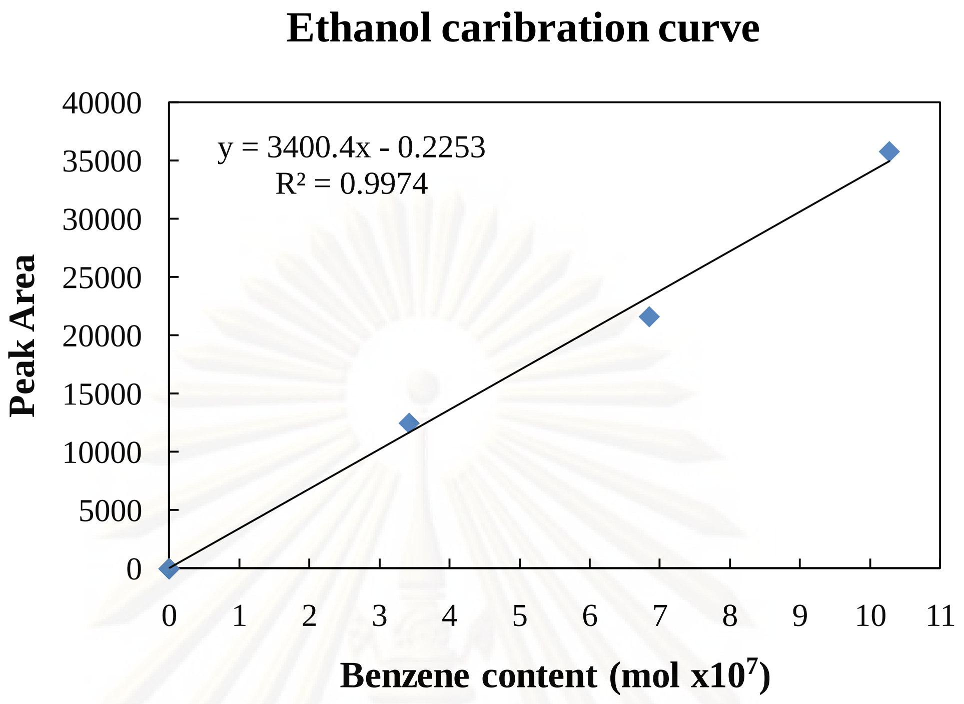


Figure A.3 The calibration Curve of Ethanol with DB-1 column

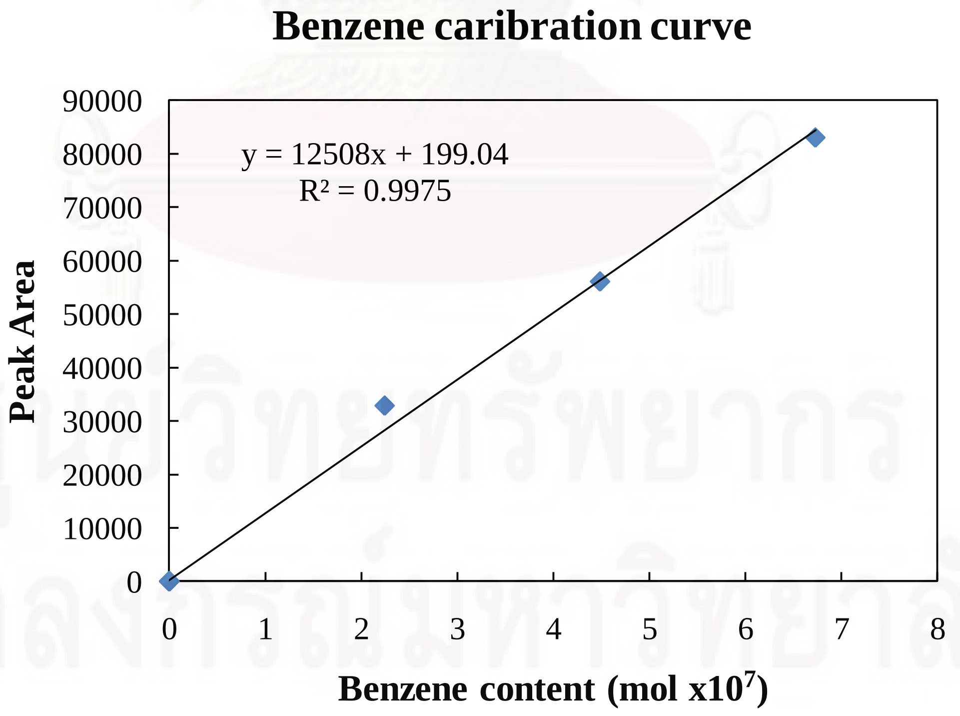


Figure A.4 The calibration Curve of Benzene with DB-1 column

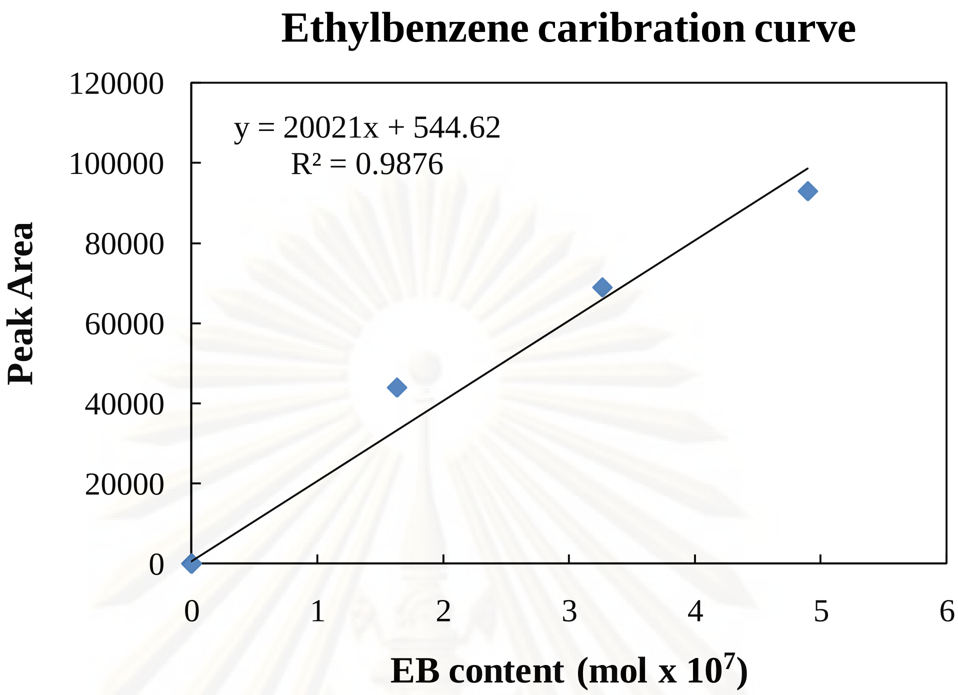


Figure A.5 The calibration Curve of Ethylbenzene with DB-1 column

APPENDIX B

DATA OF EXPERIMENT

- **Calculation of benzene conversion**

$$\%\ \text{Benzene Conversion} = \frac{N_{Benzene,0} - N_{Benzene}}{N_{Benzene,0}} \times 100$$

Where $N_{Benzene,0}$ = Mole of Benzene at time 0 h

$N_{Benzene}$ = Mole of Benzene at time 20 h

- **Calculation of selectivity to ethylbenzene**

$$\%\ \text{Ethylbenzene Selectivity} = \frac{N_{EB}}{N_{Benzene,reacted}} \times 100$$

Where N_{EB} = Mole of Ethylbenzene produced

$N_{Benzene,reacted}$ = Mole of Benzene reacted

- **Calculation of B:E molar ratio for pure benzene alkylation**

Ethylene content in the reactor consist of ethylene which dissolve in benzene and ethylene in head space of the reactor.

<u>Mole of benzene</u>

100 ml of benzene in feed = 100 ml x 0.875 g/mol x 1/(106.167 g/mol)

= 1.1221 mol

Mole of ethylene

- ***Mole of dissolved ethylene in liquid benzene***

1. At Pressure = 15.7 bar

Temperature = 30 °C

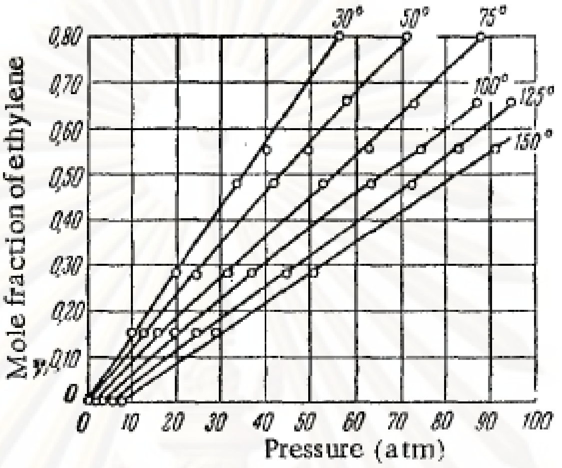


Figure B.1 Solubility isotherm for ethylene in benzene (Zhuze *et al.*, 1960)

From Figure B.1, mole fraction of ethylene in liquid phase is 0.14

Hence, Solute ethylene in 100 ml of liquid benzene

$$0.14 = \frac{N_{Ethylene}}{N_{Ethylene} + N_{Benzene}}$$

$$N_{Ethylene} = \frac{0.14 \times N_{Benzene}}{(1 - 0.14)}$$

$$= \frac{0.14 \times 1.1221}{(1 - 0.14)}$$

$$= 0.1827$$

2. At Pressure = 28.26 bar

Temperature = 30 °C

From Figure B.1, mole fraction of ethylene in liquid phase is 0.29

Hence, Solute ethylene in 100 ml of liquid benzene

$$0.29 = \frac{N_{Ethylene}}{N_{Ethylene} + N_{Benzene}}$$

$$N_{Ethylene} = \frac{0.29 \times N_{Benzene}}{(1-0.29)}$$

$$= \frac{0.29 \times 1.1221}{(1-0.29)}$$

$$= 0.4583$$

3. At Pressure = 37 bar

Temperature = 30 °C

From Figure B.1, mole fraction of ethylene in liquid phase is 0.42

Hence, Solute ethylene in 100 ml of liquid benzene

$$0.42 = \frac{N_{Ethylene}}{N_{Ethylene} + N_{Benzene}}$$

$$N_{Ethylene} = \frac{0.42 \times N_{Benzene}}{(1-0.42)}$$

$$= \frac{0.42 \times 1.1221}{(1-0.42)}$$

$$= 0.8126$$

- ***Mole of gas ethylene in head space of reactor***

From PV = znRT

Where

V = Volume of gas ethylene 200 ml

T = Temperature 30 °C

z = Compressibility factor 0.9945

(for ethylene at 30°C, 1 bar)

n = Mole of ethylene

R = Gas constant 8.314 $\frac{m^3.Pa}{mol.K}$

P = Ethylene pressure

1. At Pressure of ethylene of 15.7 bar

$$n = \frac{PV}{zRT}$$

$$= \frac{15.7\ \text{bar} \times 200\ \text{cm}^3}{0.9945 \times 8.314 \frac{m^3.Pa}{mol.K} \times 303K}$$

$$= 0.1253\ \text{mol}$$

So, mole of ethylene in gas phase is 0.1253 moles

2. At Pressure of ethylene of 28.26 bar

$$n = \frac{PV}{zRT}$$

$$= \frac{28.26\ \text{bar} \times 200\ \text{cm}^3}{0.9945 \times 8.314 \frac{m^3.Pa}{mol.K} \times 303K}$$

$$= 0.2256\ \text{mol}$$

So, mole of ethylene in gas phase is 0.2256 moles

3. At Pressure of ethylene of 37.0 bar

$$n = \frac{PV}{zRT}$$

$$= \frac{37.0\ \text{bar} \times 200\ \text{cm}^3}{0.9945 \times 8.314 \frac{m^3.Pa}{mol.K} \times 303K}$$

$$= 0.2954\ \text{mol}$$

So, mole of ethylene in gas phase is 0.2954 moles

B:E molar ratio

For ethylene pressure of 15.70 bar

$$\frac{B}{E} = \frac{\text{Mole of benzene 100 ml}}{\text{Total mole of ethylene in liquid and gas phase}}$$

$$= \frac{1.1221}{0.1827 + 0.1253}$$

$$= \frac{1.1221}{0.308}$$

$$= 3.64$$

For ethylene pressure of 15.70 bar

$$\frac{B}{E} = \frac{1.1221}{0.4583 + 0.2256}$$

$$= \frac{1.1221}{0.6839}$$

$$= 1.64$$

For ethylene pressure of 15.70 bar

$$\frac{B}{E} = \frac{1.1221}{0.8126 + 0.2954}$$

$$= \frac{1.1221}{1.108}$$

$$= 1.01$$

- **Calculation of ethylene content for reformate alkylation**

Ethylene content in the reactor consist of ethylene which dissolve in reformate and ethylene in head space of the reactor.

Mole of dissolved ethylene in reformate

Content of dissolved ethylene in reformate calculate from solubility of ethylene in reformate which consist of many component such as aromatic, paraffin, olefin and naphthenes.

Table B.1 Solubility of ethylene in heptanes and toluene at ethylene pressure 50 psi

Solvent	Solubility	
	@ 70 °C (mol/l)	@ 0 °C (mol/l)
Heptane	0.811	1.086
Toluene	0.826	1.115

<u>Mole of ethylene in head space of reactor</u>

Ethylene content in head space of reactor calculate as same method which shows above.

APPENDIX C

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 D

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 E

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.

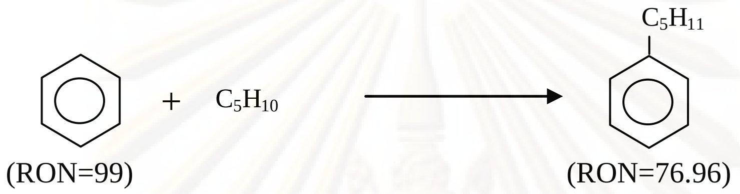
3.3 Specifications for volatile petroleum products generally include vapor pressure limits to ensure products of suitable volatility performance.

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

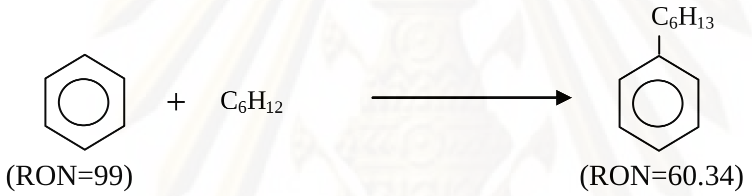
APPENDIX F

SIDE REACTION IN REFORMATE

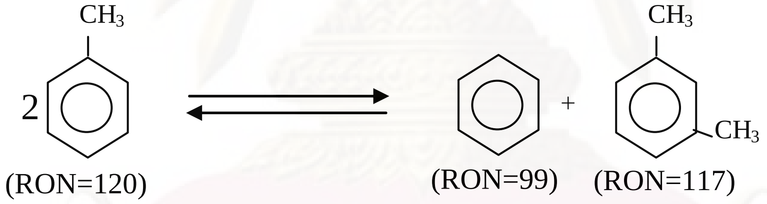
Eq. (F.1)



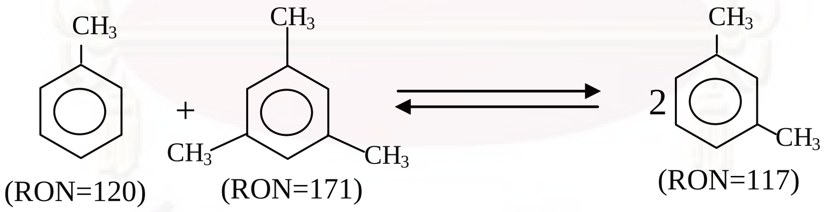
Eq. (F.2)



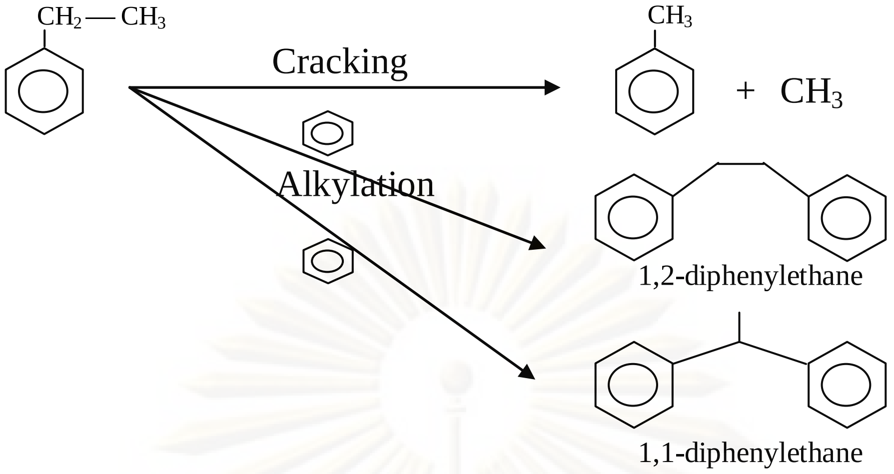
Eq. (F.3)



Eq. (F.4)



Eq. (F.5)



Scheme F.1 Reaction scheme for EB cracking and alkylation

VITAE

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Worapon Kiatkittipong, Pichchapa Khongjarern and Suttichai Assabumrungrat, “Reduction of benzene in reformate by olefin alkylation” Pure and Applied Chemistry International Conference 2010, Ubon Ratchathani,Thailand, January, 2010.