การเปลี่ยนน้ำมันพืชใช้แล้วให้เป็นเชื้อเพลิงเหลวบนตัวเร่งปฏิกิริยา HZSM-5 และซัลเฟตเทตเซอร์โคเนีย

นายวิชชากร จารุศิริ

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

CATALYTIC CONVERSION OF USED VEGETABLE OIL TO LIQUID FUELS OVER HZSM-5 AND SULFATED ZIRCONIA

Mr.Witchakorn Charusiri

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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จุดประสงค์ของงานวิจัยนี้คือการแปรรูปน้ำมันพืชใช้แล้วซึ่งจัดว่าเป็นของเสียและมีศักยภาพศักยภาพในการเปลี่ยนให้เป็นเชื้อเพลิงเหลวโดยปฏิกิริยาการแตกตัวด้วยตัวเร่งปฏิกิริยาทำการทดลองในเครื่องปฏิกรณ์แบบแบตซ์ ช่วงอุณหภูมิที่ใช้ในการทดลอง 400 – 430 องศาเซลเซียส ความดันแก๊สไฮโดรเจนเริ่มต้นที่ 10 – 30 บาร์ เวลาที่ใช้ในการทำปฏิกิริยา 45 – 90 นาที โดยใช้ตัวเร่งปฏิกิริยา HZSM-5 ซัลเฟเทตเซอร์โคเนีย และตัวเร่งปฏิกิริยาแบบผสม HZSM-5 และซัลเฟเทตเซอร์โคเนียในสัดส่วนต่าง ๆ กัน เพื่อหาค่าร้อยละผลได้ของแก๊สโซลีน ผลิตภัณฑ์ที่ได้จากการแตกตัวประกอบด้วยของเหลว แก๊ส และของแข็งเล็กน้อย ผลิตภัณฑ์ของเหลวนำไปวิเคราะห์หาการแจกแจงผลิตภัณฑ์ตามคาบจุดเดือดด้วยเครื่องแก๊สโครมาโทกราฟพร้อมซอฟต์แวร์จำลองการกลั่น ผลการทดลองของการใช้ตัวเร่งปฏิกิริยาแบบผสมที่สัดส่วนของ HZSM-5 และซัลเฟเทตเซอร์โคเนีย 0.3 ต่อ 0.7 ให้ร้อยละผลได้ของแก๊สโซลีนสูงที่สุดที่ร้อยละ 26.57 โดยน้ำหนัก ที่ภาวะอุณหภูมิ 430 องศาเซลเซียส ความดันแก๊สไฮโดรเจนเริ่มต้น 10 บาร์ เวลาที่ใช้ทำปฏิกิริยา 90 นาที และมีองค์ประกอบเป็นคีโรซีน 10.65%, Light Gas Oil 23.02 % Gas Oil 6.05 % กากน้ำมัน 12.88 % โดยมีแก๊สไฮโดรคาร์บอน 20.20 % และของแข็ง 0.63 % โดยน้ำหนัก ซึ่งเป็นผลของการเติม HZSM-5 ปริมาณเล็กน้อยลงในซัลเฟเทตเซอร์โคเนียมีส่วนช่วยปรับปรุงประสิทธิภาพการแตกตัวของน้ำมันพืชใช้แล้วเป็นแก๊สโซลีนได้มากขึ้น แบบจำลองจลนพลศาสตร์ของการแตกตัวน้ำมันพืชใช้แล้วบนตัวเร่งปฏิกิริยาแบบผสม HZSM-5 และ ซัลเฟเทตเซอร์โคเนียเป็นปฏิกิริยาลำดับสองที่มีค่าพลังงานกระตุ้นเป็น 116.072 กิโลจูลต่อโมล และค่า pre-exponential เท่ากับ 2.67×10^{5} ต่อวินาที

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ภาควิชา....เคมีเทคนิค.......................................	ลายมือชื่อนิสิต…………………………………………..
สาขาวิชา…เคมีเทคนิค.......................................	ลายมือชื่ออาจารย์ที่ปรึกษา ……………………….…..
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KEY WORD : CATALYTIC CRACKING / USED VEGETABLE OIL/ ZEOLITE/
SULFATED ZIRCONIA/ HYBRID CATALYST

WITCHAKORN CHARUSIRI: CATALYTIC CONVERSION OF USED
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ZIRCONIA ADVISOR : ASSOC. PROF.THARAPONG VITIDSANT, Dr.de I'INPT.
CO ADVISOR : ASSOC.PROF. WITHAYA YONGCHAREON, Ph.D.
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The emphasis of this study was on catalytic cracking of used vegetable oil which classified as a waste which has potential for conversion into liquid fuels where performed in a batch microreactor at temperature of 400 – 430^{o}C, initial pressure of hydrogen gas at 10 - 30 bars, and reaction time of 45 - 90 minutes. The catalysts such as HZSM-5, Sulfated Zirconia and hybrid of HZSM-5 with Sulfated Zirconia were used to determine on the conversion and yield of Gasoline fraction. The major products obtained were liquid product, hydrocarbon gases and small amount of solid. Liquid products were analyzed by simulated distillation gas chromatograph and the product distribution was obtained. Hybrid catalyst obtained with physical mixing of HZSM-5 and Sulfated Zirconia at ratio of 0.3 : 0.7 showed the highest yield of gasoline with of 26.57 wt% at the temperature of 430^{o}C, hydrogen pressure at 10 bars, and reaction time of 90 minutes. Moreover, kerosene 10.65 wt%, light gas oil 23.02 wt%, gas oil 6.05 wt% and long residue 12.88 wt% whereas the light gaseous by product of 20.20 wt% and solids of 0.63 wt% were obtained. Hence, the addition of small amount of HZSM-5 to Sulfated Zirconia was a route to modify performance of catalytic cracking to increased gasoline fraction. The kinetic model of catalytic cracking used vegetable oil to liquid fuels over hybrid catalyst as the second order and shown the activation energy of 116.072 kJ mol^{-1} and pre-exponential factor (A) = 2.67 x 10^{5} s^{-1}

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Department…Chemical Technology………………. Student's signature…………………………...
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CHAPTER I

INTRODUCTION

As conventional energy sources are being depleted, currently some researchers are concentrating on developing alternative and renewable sources of liquid fuels, which are new energy resources to replace commercial petroleum products in proposed as alternatives to future energy resources which are also environmental friendly. Thailand manufacturing sectors use vegetable oil as cooking oil for food processing such as fried instant noodle, fried snacks about 47 million liters per year, excluding a large restaurant, fast food and households. Used vegetable oils were not collected to dispose of suitably and no reported concerning actually amount of used vegetable oils. Unscrupulous cooking trader will normally supply regenerated spent vegetable oil by bleaching the used vegetable oil and blended as new, they usually supply the reused vegetable oil in small and medium enterprise or general consumer. Street food venders are customer of this reused vegetable oil, because they are cheaper than fresh oil. The used vegetable oil is classified as waste while its potential as liquid fuels through physical and chemical remain highly interested. Used vegetable oil is attracting increasingly interest because they have great potential to be used as diesel substitutes known as bio-diesel. Direct synthesis via trans-esterification reaction of vegetable oils will yield of bio-diesel. Another interesting alternative route is the direct upgrade of vegetable oils to clean premium transportation fuels using catalytic cracking. These vegetable oils are long chain hydrocarbon molecules, which can be converted to light hydrocarbon over many types of catalysts. HZSM-5 was found to be most efficient in the oil cracking process of organic liquid fuels production giving mainly aromatic hydrocarbon from the properties of pore size and shape selectivity. In 1995 Adjaye et.al. also observed high conversion (greater than 75%) of canola oil over HZSM-5 at of the condition of temperature during 370 – 410 ^{o}C. The high conversions were probably due to the effectiveness of HZSM-5 catalyst to convert triglyceride such as oleic, linoleic, palmic and linoleic fatty acid belonging to the carboxylic groups which are the gasoline fraction. In an earlier work by Kantikaneni et.al. (2001) was observed that compounds with the carboxylic functional group were highly reactive over HZSM-5 with the conversions above 72.5% at the temperature of 400 ^{o}C and weight hourly space velocity 1.8 h^{-1}. Furthermore, Sulfated Zirconia has been termed as super acid catalyst which is a strong solid acid catalyst, effective for hydro-isomerization of n-butane at room temperature (Hino 1979) and more relative as cracking of long-chain paraffins and has found various uses as a commercial catalyst in many industrial processes. In 2001, Kantinekani and co-worker also observed the effectiveness of HZSM-5 produced more aromatic more than silica-alumina and highly selective of aromatic, was due to its shape selective property and pore structure while silica-alumina have acidity but no pore structure property. In order to add amount of HZSM-5 to silica-alumina was increased acidity and shape selective property of hybrid catalyst were due to the presence of HZSM-5 which imply increased deoxygenation by dehydration, it seems that the addition of HZSM-5 to silica-alumina was a route to modified performance of catalytic cracking to aromatic fuels and could be increased more than used only silica-alumina. The objective of this research is to study and investigate the effect of temperature, pressure, time and types of super acid catalysts such as HZSM-5, Sulfated Zirconia and their hybrid catalysts on the liquid yield conversion as transportation fuels, their were associated products distribution such as Gasoline, Kerosene, Gas Oil, and unwanted long chain hydrocarbon. Furthermore, Kinetic parameter such as Activation Energy (Ea) and pre-exponential (A) were obtained

The objectives of this study are:

1. To investigate the parameter which mainly affected to the selectivity of Gasoline and other chemicals such as effect of temperature, initial pressure of hydrogen gas, time of reaction and mass of catalyst over various type of catalysts. HZSM-5, Sulfated Zirconia and hybrid catalyst were obtained to investigated.
2. To determine and compare the selectivity of Gasoline fraction from catalytic cracking of used vegetable oil over various type of catalysts.
3. To investigate and develop kinetic model of the catalytic conversion of used vegetable oil to liquid fuels over various type of catalysts.

CHAPTER II

THEORY AND REVIEWS

2.1 Production of oil-yielding in Thailand (Office of Agricultural Economic, 2003)

Six types of oil-yielding plants are grown in Thailand such as soybean, palm oil, peanut, coconut, castor, and sesame. Of these, palm oil has the highest annual yield of 4.0 million tons, followed by coconut at 1.4 million tons.

Table 2.1 Production of vegetable oil in Thailand (unit : thousand tons)

Year	Oil palm	Coconut	Soybean	Peanut	Castor	Sesame
1995/96	2,255	1,413	386	147	6	34
1996/97	2,688	1,419	359	147	6	34
1997/98	2,681	1,386	338	126	6	35
1998/99	2,465	1,372	321	135	7	36
1999/00	3,514	1,381	319	138	7	37
2000/01	3,256	1,400	312	132	9	39
2001/02	4,089	1,396	261	107	9	39
2002/03	4,001	1,418	260	112	10	40

Source: (Office of Agricultural Economic, Ministry of Agricultural and Cooperation 2003)

Although the production of oil palm is highest among Thailand's oil yielding plants, Thailand contributes 630,000 tons or only 2.3% toward the world's production of oil palm, ranking as the fourth largest producer in 2003.

urthermore, used vegetable oil have not been studies as to their application in liquid fuels production. Roughly 42,000 tons of used vegetable oil are recycled and reused in the market each year.

All type of vegetable oil generally compounds of the triglyceride fatty acid their structure consisting of C_3H_6 molecules connected to fatty acids containing 10 to 30 carbon atoms, accounting for 94 – 96 % of the molecular weight of the triglyceride, therefore, the chemical and physical properties of each type of vegetable oil depend on the properties of such fatty acid.

Table 2.2 Properties and composition of fatty acids in vegetable oil. (The Standing Committee on Energy, House of Representatives, 2002)

Oils	Iodine	Composition of Fatty Acids						
	Content	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3
Palm	14.1-21.0	ND-0.5	0.5-2.0	39.3-47.5	3.5-6.0	36.0-44.0	9.0-12.0	ND-0.5
Palm olein	> 56	0.1-0.5	0.5-1.5	38.0-43.5	3.5-5.0	398-46.0	10.0-13.5	ND-0.6
Palm sterine	< 48	0.1-0.5	1.0-2.0	48.0-74.0	3.9-6.0	15.5-36.0	3.0-10.0	0.5
Palm kernel	50.0-55.0	45.0-55.0	14.0-18.0	6.5-10.0	1.0-3.0	12.0-19.0	1.0-3.5	ND-0.2
Coconut	6.3-10.6	45.1-53.2	16.8-21.0	7.5-10.2	2.0-4.0	5.0-10.0	1.0-2.5	ND
Peanut	86-107	ND-0.1	ND-0.1	8.0-14.0	1.0-4.5	35.0-67.0	13.0-43.0	ND-0.3
Physical nut	101	ND	ND	14.9	6.0	41.2	37.4	ND
Rape seed	94-120	ND	ND-0.2	1.5-6.0	0.5-3.1	8.0-60.0	11.0-23.0	5.0-13.0
Soybean	124-139	ND-0.1	ND-0.2	8.0-13.5	2.0-5.4	17.7-28.0	49.8-59.0	5.0-11.0

* ND = Not detect

Most fatty acid in usually vegetable oil contain 12 to 18 carbon molecules, which account for the different level of saturated fatty acids in each type of oil. In addition, vegetable oil are unstable. Thus, they are easily oxidized when exposed to air and polymerize at high temperatures, resulting in a sticky substance.

Table 2.3 Representative the average composition of saturated and unsaturated fatty acid in vegetable oil (M. Mongkol, 2003)

Oils	Saturated fatty acid (%)	Unsaturated fatty acid (%)
Soybean oil	11.33	8867
Sunflower oil	10.71	89.29
Corn oil	13.00	87.00
Rice bran oil	21.60	78.40
Palm olein	44.91	55.09
Palm oil	56.98	43.02
Coconut oil	90.52	9.48

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2.2 Background of zeolites

Catalysts containing Y zeolites were introduced in 1962 by Mobil Co, and found widespread utilization displaced completely the natural and synthetic catalysts such as Activated clay and synthetic silica-alumina (Raseev, 2001). The properties and the performance of zeolites has been undergoes continuous improvements by mean to treatment of the produced catalysts and to the matrices used to the additive. The catalysts for catalytic cracking in basis of zeolite contain several components:

(1) The zeolite Y, usually together with rare earths oxide
(2) The matrix which be inert or catalytically active
(3) The promoters and additives that improve the performance of the catalyst and that may introduce during the actual synthesis of the zeolite or of the matrix.

Zeolites are highly crystalline, hydrated aluminosilicated that upon dehydration develop in crystal a uniform pore structure having minimum channel apertures of from about 0.3 to 1.0 nm. They are mainly responsible for the activity, selectivity, and stability for the catalyst, they are microporous materials widely used in industrials processes as multipurpose materials, are very good sorbents with a high internal surface area. Their channel-like structures make the intracrystal transport an easy process. Moreover, the high stability and numerous imperfection such as Si/Al substitutions compensated with acid protons or with extra-framework. Thus, zeolites perform well as heterogeneous catalysts.

2.3 Structure of zeolite

The basic structure of the zeolite consists of a three-dimensional framework of SiO_4 and AlO_4 tetrahedral, each of which contains a silicon or alumina atom in the center. The oxygen atom are shared between adjointing tetrahedral, which can be present in various ratios and arranged in a variety of ways

Zeolite X and Y is, as in the classic synthetic catalysts formed by groups of tetrahedral with the alumina and silicon atom occupying their centers and the oxygen atoms the vertexes. In case of the zeolites, the groups of tetrahedrons form in fact regular structures of octahedrons as namely by *sodalite cage* which has 8 hexagonal sides, constructed of 6 tetrahedrals and 6 square sides constructed of 4 tetrahedons, 24 vertexes and 36 edges.

Figure 2.1 solalite

A type molecular sieved have the basic element formed of the 4 sodalte structure, the square faces of which are joined by prisms.

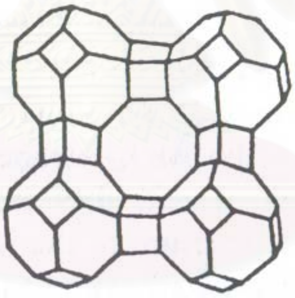

Figure 2.2 molecular sieve zeolite A

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In order to the X-zeolite and Y-Zeolites, the basic element is form by 6 sodalites structures, the hexagonal faces of which are joined by the prisms

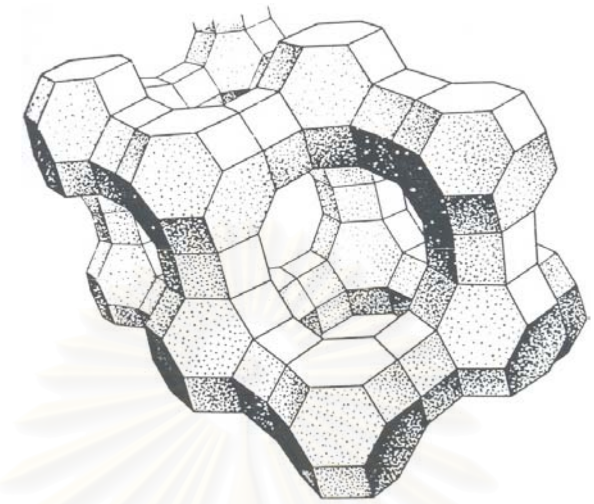

Figure 2.3 Faujasite (Raseev, 2004)

Zeolites may be represented by the empirical formula

$$M_{2/n}\ Al_2O_3\ xSiO_2\ yH_2O$$

or by a structural formula

$$M_{x'/n}[(Al_2O_3)_{x'}(SiO_2)_{y'}].wH_2O$$

wherein $(Al_2O_3)_{x'}(SiO_2)_{y'}$ is the crystallographic unit cell. The metal cation (of valence n) is present to produce electron neutrality sine for each aluminum tetrahedron in the lattice there is an overall charge of -1. Moreover, the pore size of zeolite is determined by the number of oxygen atom that form the pore aperture and by the possible obstruction of the pore by cations, the pore in HZSM-5 consist of 10 rings of oxygen atom. Some structural information on other zeolites of particular interest in catalysis is represent in Table 2.4

Table 2.4 Selected Well-Characterized Zeolite of Interest in Catalysis

Number of O atom in the larger aperture ring	Channel geometry, nm	Secondary building unit, sbu	Structure type
12			
A. Modernite	One-dimensional tube 0.65 x 0.70 interconnecting with an 8 ring pore structure 0.29 x 0.57, one-dimensional	5-1	MOR
B. Faujasite (Zeolite X,Y, LZ-210)	Three dimensional, with 0.74 aperture, leading to 1.2 diameter cavities	D6R	FAU
C. Offretite (zeolite O, LZ-217)	0.64 One-dimensional with cavities, connecting with a 2-dimensional 8-ring system consisting of 0.36 x 0.49 channels. Overall, 3-dimensional system	S6R	OFF
D. Linde type L (in K Form)	One-dimensional, 0.71 aperture, leading to cavities of about 0.48 x 1.24 x 1.07	S6R	LTL
E. Mazzite (ZSM-4, Ω, LZ-2002)	One-dimensional, nearly cylindrical channel 0.74 diameter, separated from one-dimensional 8 –ring channels, 0.34 x 0.56	5-1	MAZ
F. Zeolite β (Nu-2)	Three dimension network		
10			
A. Zeolite ZSM-5	Two-dimensional, 0.51 x 0.55 tube interconnecting with zigzag 0.53 x 0.56 tube	5-1	MFI
B. ZSM-11	Two-dimensional, interconnecting tubes, 0.53 x 0.54	5-1	MEL
C. Ferrierite (ZSM-35)	Two-dimensional interconnection network of 10- and 8-ring pores, 0.54 x 0.42 and 0.48 x 0.35	5-1	FER
8			
A. Erionite	0.36 x 0.51 (tortuous), three-dimensional	S6R	ERI
B. Linde A.	Three-dimensional, 0.41		

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Zeolites have long been used for water softening, utilizing their ion-exchange capabilities, drying and catalysis. From the catalytic point of view, zeolites are special interest in that exhibit unusually high activity for various acid-catalyzed reaction such as cracking, the ability to combine a molecular-sieving property with catalysis, and unusual selectivity behavior.

2.4 Pore Structure

The structures of zeolite are described in terms of the pore channel such as a one-dimensional, two-dimensional, and three-dimensional structure. In each type of dimensional may be the same size and shape, difference, or more commonly. The channels may be circular, tubular, elliptical, may be straight or zig-zags. In two-dimensional structure have a secondary array, right angels of pores some extend smaller than the one-dimensional structure. Thus, the molecules can be submitted only in the larger pores in a one-dimensional structure. In order to ZSM-5 and ZSM-11 which are a two-dimensional pores structure, is permitted complete access from any one pore to all others in the structure.

ZSM-5 have 10 oxygen atoms in the aperture ring which the pores are shown as arrays of tubular channels in the two-dimensional pore structures. In addition ZSM-11 is similar in structure and pore size to ZSM-5, but both sets of pores are straight whereas ZSM-5 is one pore type has straight and slightly elliptical opening zig-zags and circular opening

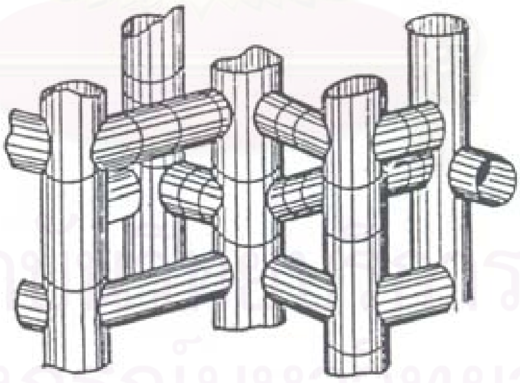

Figure 2.4 Structure of zeolite HZSM-5 (Raseev, 2004)

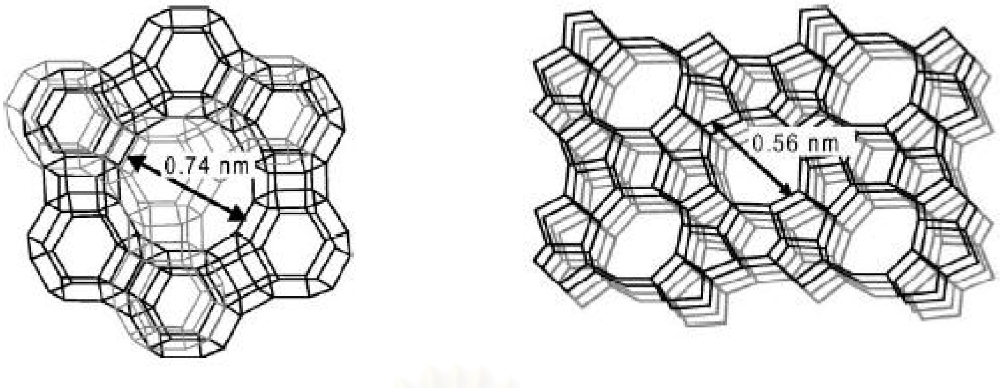

Figure 2.5 comparison between pore size in X-zeolite (left) and HZSM-5 (right)

In order to the difference in their structures, the cavities inside the X- and Y-zeolites have a mean diameter of 13 ^{o}A that communicate with the outside through 7.4 ^{o}A openings, whereas the type A molecular sieve have the inlet opening of 3 ^{o}A for the potassium form and 4 ^{o}A for the sodium form. Thereby the properties of inlet orifites in the X and Y-zeolites allowed the access of suitable molecules such as naphthalene or simply hydrocarbon molecules. The type A-molecular sieve allow exclusively the access of n-alkane whereas the structure of HZSM-5 consists of 2 types of pores such as straight channel with pore sizes of 0.53 nm x 0.56 nm and cross-linked sinusoidal channels of 0.51 nm x 0.55 nm. Due to the small porous property, only linear and mono-branched hydrocarbons can easy enter the pores of HZSM-5

2.5 Zeolite acid sites

Classical Bronsted and Lewis acid models of acidity are sued to classify the active site on the zeolites. Bronsted acidity is proton donor activity, a tridiaganally coordinated alumina atom is an electron deficient and can accept an electron pare therefore as a Lewis acid

In general, the increased in Si/Al will increased acidity strength and thermal stability of zeolite ratio (Raphael, 1997; Liu, 2004) Since the number of acidity –OH groups depend on the number of aluminium zeolite’s framework, while decreased in all content is expect to reduce catalytic activity. If the effect of increase in the acidic center, increase Al content, shall the results in enhancement of catalytic activity.

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Base on electrostatitc consideration, the change density at a cation site increased with increased Si/Al ratio. It was conceived that the phenomena are related to reduction of electrostatic interaction between framework sites, and possibility to deference in the order of aluminium in zeolite crystalline location of Al in crystalline.

In the earlier works (Barthoment, 1984) reported the mean charge on proton was shifted regularly toward higher values as the Al content decreased. Simulaneously the total number of acidic hydroxyls governed by the Al atom were decreased. This evidence emphasized that the entire acid strength distribution was shifted toward stronger value (such as weak was shift toward medium) That is the weaker acid site become stronger with the decrease in Al content. An important in thermal and hydrothermal stability has been described to the low density of hydroxyls groups which is parallel to the Al content. A longer distance between hydroxyl groups decreases the probability of dehydrogenation that generates detects on structure of zeolite.

2.6 Generation of acid centers (Szostak R., 1989; Tanabe, 1997)

Protonic acid centers of zeolite are generated in varies way. Figure 2.6 shows the thermal decomposition of ammonium exchange zeolite yield the hydrogen form.

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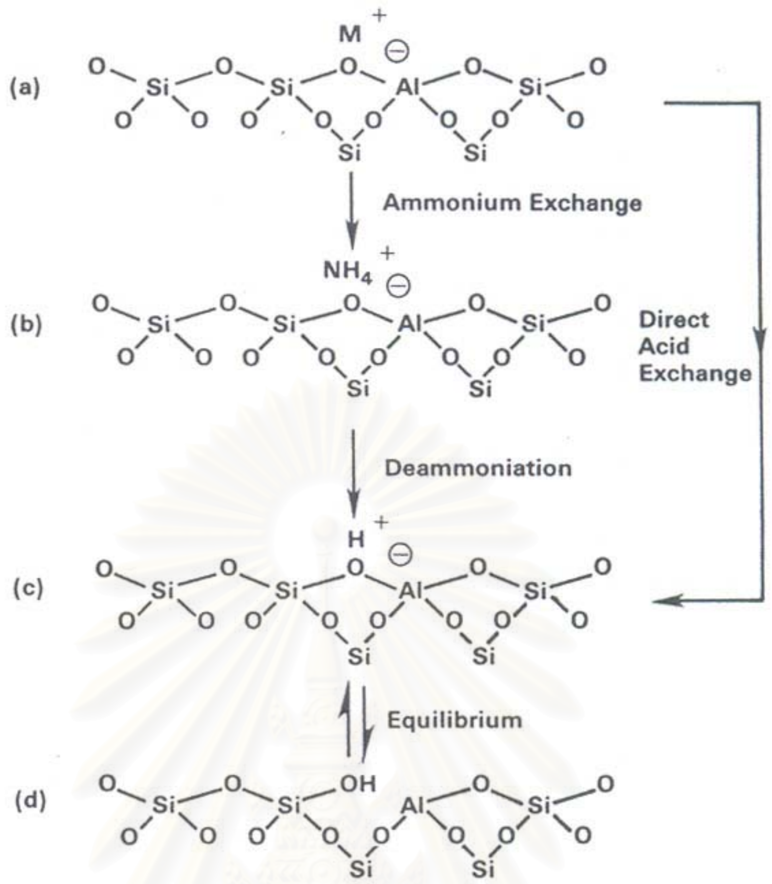

Figure 2.6 Diagram of the surface of zeolite framework (Szostak R., 1989)

The Bronsted acidity due to water ionization on polyvalent cations, describes below, is depicted in Figure 2.7

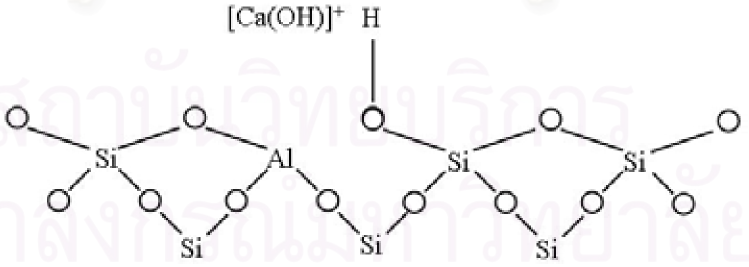

Figure 2.7 Water molecules coordinated to polyvalent cation are dissociated by heat treatment yield Bronsted acidity

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$$M^{n+} \quad + \quad xH_2O \longrightarrow M(OH)x^{(n-x)+} + xH^+$$

The exchange of monovalent ions by polyvalent cations could improve the catalytic property. Those highly charged cations create very acidic centers by hydrolysis phenomena

The Bronsted acid sites are also generated by the reductions of transition metal cations. The concentration of OH groups of zeolite containing transition metals was noted to increase by reduction with hydrogen at 250 – 450 °C to increase with the rise of the reduction temperature.

$$Cu^{2+} \quad + \quad H_2 \longrightarrow Cu^0 \quad + \quad 2H^+$$

$$Ag^+ \quad + \quad 1/2H_2 \longrightarrow Ag^0 \quad + \quad H^+$$

The formation of Lewis acidity from Bronsted sites represented in figure 2.8 The dehydration reaction decreases the number of protons and increases that of Lewis sites.

Bronsted (OH) and Lewis (Al) sites represented simultaneously in the structure of zeolite at high temperature. Dyhydroxylation is though to occur in ZSM-5 above 500 °C and calcinations at 800 – 900 °C produced irreversible dehydroxylation which causes defection in crystal structure of zeolite. Furthermore, Dealumination is believed to occur during dehydroxylation which may result from the steam generation within the sample. The dealumination is indicated by an increased in the surface concentration of aluminum on the crystal. The extent of dealumination monotonously increases with the partial pressure of steam.

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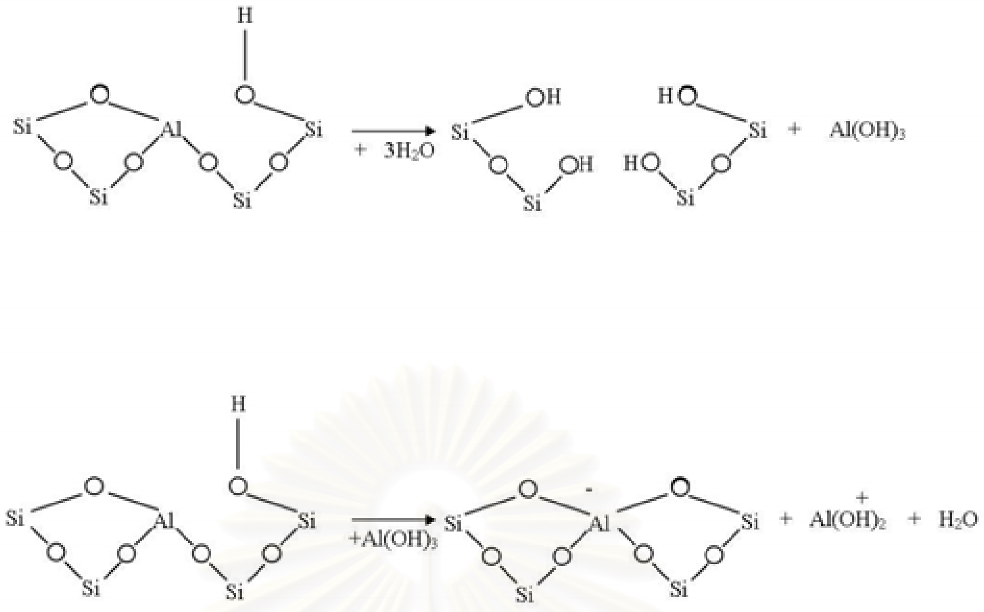

Figure 2.8 Steam dealumination process in zeolite

The enhancement of the acid strength of OH groups recently proposed to be pertinent to their interaction with those aluminium species site tentatively represented in figure 2.9 Partial dealumination might therefore yield a catalyst of higher activity while severe stream reduces the catalytic activity.

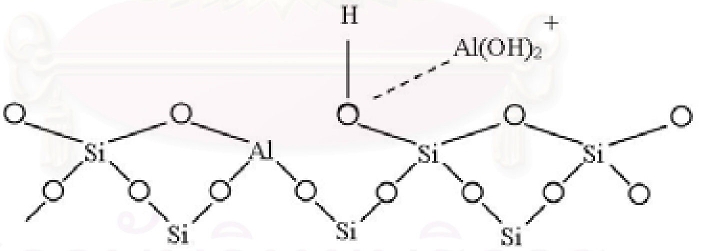

Figure 2.9 The enhancement of acid strength of OH group by their interaction with dislodge aluminum species

2.7 Basic site

In certain instances reactions have been shown to be catalyzed at basic sites in zeolites without any influence from acid sites. The best characterized example of this is that of K-Y which splits n-hexane isomers at 500 ^{o}C. The potassium cations have

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been shown the control the unimolecular cracking (β-scission). Free radical mechanisms also contribute to surface catalytic reaction

2.8 Shape selectivity

The pore and shape in zeolite may affect the selectivity of a reaction in three ways :

a) Reactant selectivity

The selectivity occurs when the aperture size of the zeolite is such that it admits only certain smaller molecules and excludes larger molecules.

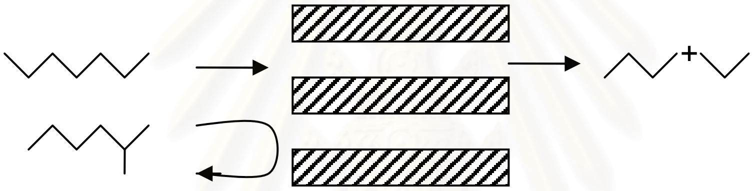

Figure 2.10 Reactant selectivity (Szostak, 1989)

b) Product selectivity

This reaction occurs when bulkier product molecules cannot diffuse out, and if formed, they are converted to smaller molecules or to carbonaceous deposits within the pore. These eventually may cause pore blockage.

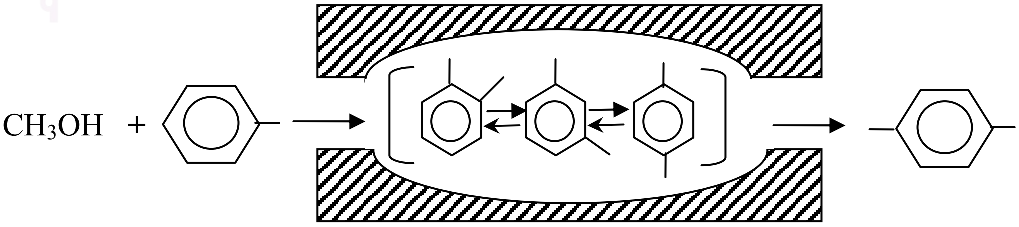

Figure 2.11 Product selectivity (Szostak, 1989)

c) Transient state selectivity

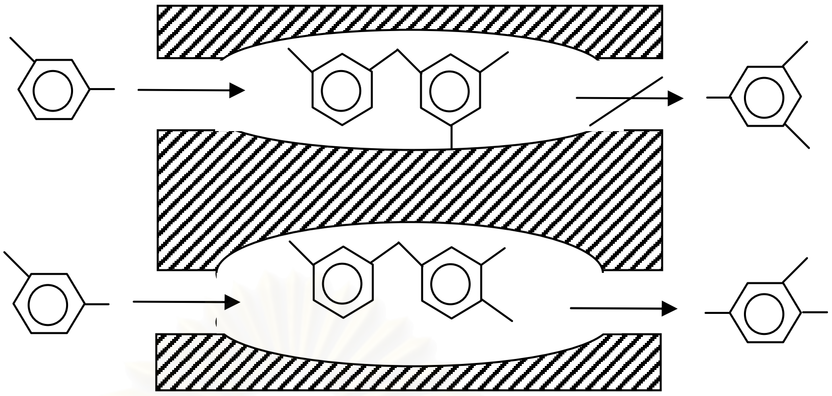

Figure 2.12 Transient state selectivity (Szostak, 1989)

Reactant of change selectivity results form the limited diffusibility of some of the reactants, which can not effectively enter and diffuse inside crystallinity pore structure of the zeolite. Therefore, product shape selective occurs as slowly diffusing molecule, can not access through the crystal pore and undergo secondary reaction. The study of zeolite by X-ray diffraction and by nuclear magnetic resonance allowed the determination of the location of the cations that compensate the negative change of AlO_4- tetrahedrals.

In Figure 2.13 shows the sizes of the cavities and of the access opening of various types of zeolites, together with the necessary size for access through the pores of different types of hydrocarbons. Figure 2.14 represents the correlation between pore size of HZSM-5 and Y- zeolite and kinetic diameter of some molecules which can pass through openings which are smaller than their critical diameters or pore size.

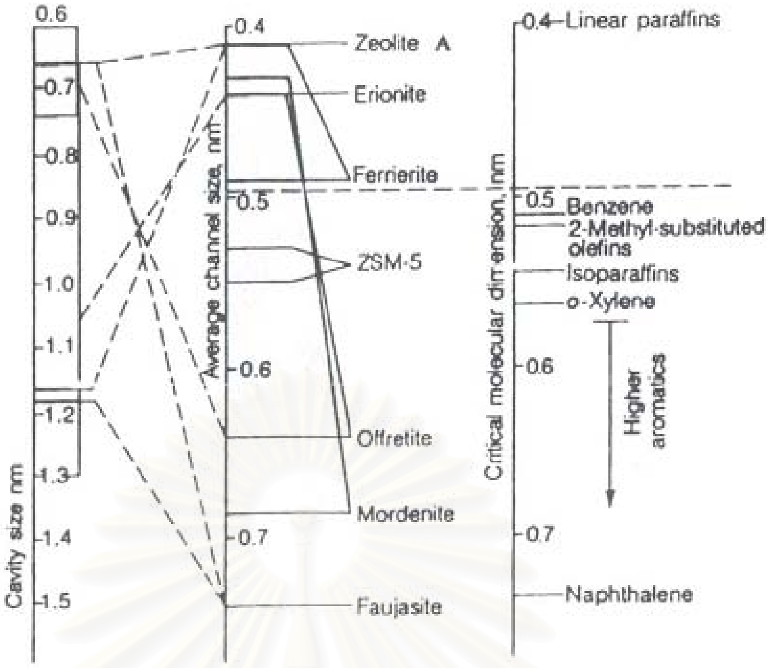

Figure 2.13 Cavities and pore size, compared to molecule size (Raseev, 2004)

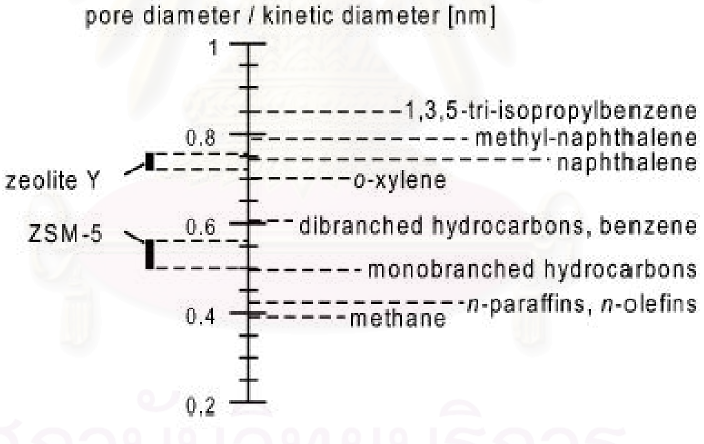

Figure 2.14 Correlation between pore size of HZSM-5 and Zeolite Y and kinetic diameters of some molecules (Hollander, 2002)

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2.9 Sulfated Zirconia (Yadav, 1999; Ganapati D, 1999; Prescott, 2004)

Zirconium oxide, or Zirconia, when modified with anions such as sulfate ions forms a highly acidic or superacidic catalyst depending on the treatment conditions,was first reported in 1979 by Makoto Hino et al as a solid super acid catalyst for isomerization of n-butane at the ambient room temperature (M. Hino, 1979). It has also been shown to be active for a number of other reactions including cracking, alkylation, and esterification (K.Arata, 1990). At present, commercial application was mainly due to the short life and narrow surface area of the catalyst. Sulfated Zirconia is found to be well suited for catalyzing reactions of industrial processes such as hydrocarbon isomerization, methanol conversion to hydrocarbons, alkylation, acylation, esterification, etherification, condensation, nitration, cyclization, hydration–dehydration, carbonylation, oligomerization, Fischer–Tropsch reaction, cracking and hydrocracking reactions, methane oxidative coupling, thioacetalization, adamantylation, manufacture of hydrogen peroxide, etc. The surface properties of these catalysts can be further modified in conjunction with noble or transition metals as promoters as well as with carbon molecular sieves.

In general, metal oxides have been used extensively either as such or as supports in conjunction with other active components for many industrial oxidation, reduction and acid–base-catalyzed reactions. The surface of zirconium oxide is known to possess all these catalytic activities. Zirconium oxide, or Zirconia, when modified with anions, such as sulfate ions, forms a highly acidic or superacidic catalyst that exhibits superior catalytic activity to catalyze many reactions.

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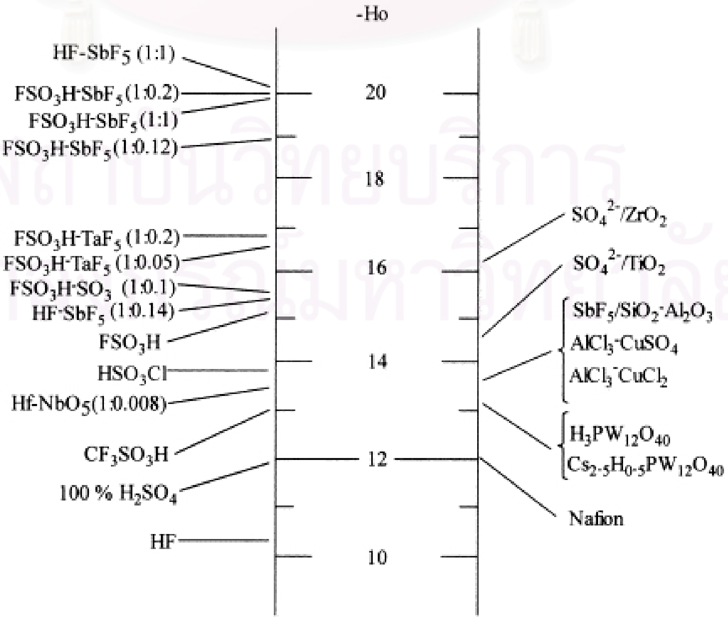

Figure 2.15 Acid strengths of liquid and solid superacids. (Yadav,1999)

Sulfated Zirconia has been widely used to catalyze reactions such as hydrocarbon isomerization, methanol conversion to hydrocarbons, alkylation, acylation, esterification, etherification, condensation, nitration, cyclization, etc. Thus, Sulfated Zirconia and modified Sulfaed Zirconia form an important class of catalysts**,** Inaddition Sulfated Zirconia behaves as a solid superacid, depending on its method of preparation and activation**.** The exact structure of the active sites, (Lewis or Bronsted type), is a subject of debate. Attempts have, however, been made to unearth these features of the catalysts. Kumbhar had speculated the structure of Sulfated Zirconia

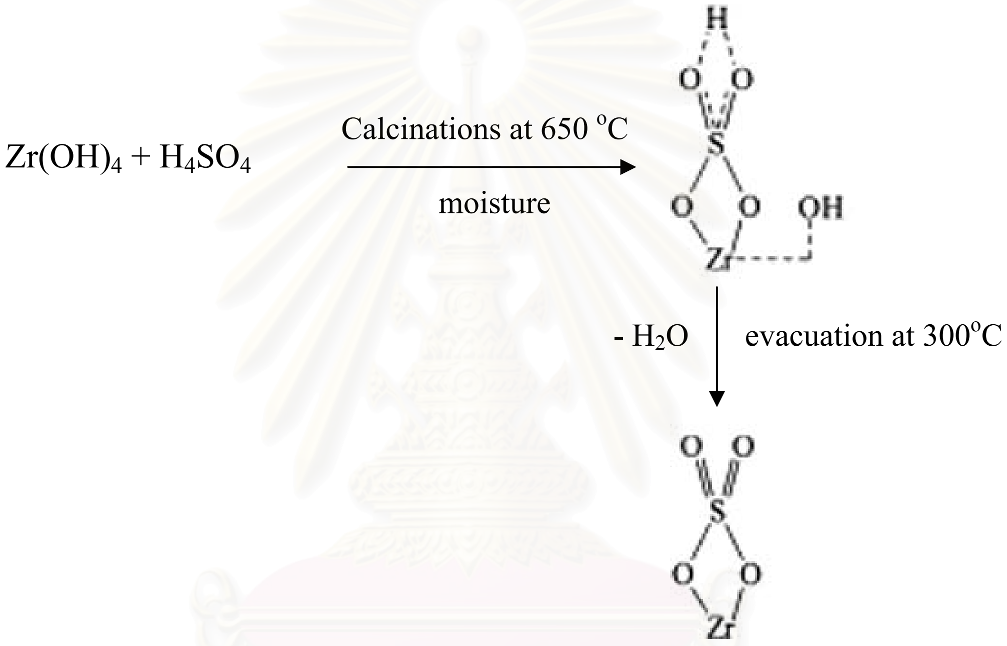

Figure 2.16 model of Sulfated Zirconia proposed by Kumbhar et al **(**Kumbhar,1989)

2.10 Mechanism of Cracking Processes

Cracking processes were assigned to two fundamental classes;

2.10.1 Thermal cracking

Thermal cracking, where free radicals (lacking one hydrogen atom on carbon atom in the hydrocarbon molecule) are intermediate species which cracked by a β- scission mechanism.

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The most successful present explanation of thermal cracking of hydrocarbon is rick free radical theory as modified by Kossiakoff and Rick. This will be called the "RK-theory" as follows to explain the cracking of normal paraffin:

The normal paraffin molecule loses a hydrogen atom by collision and reaction with a small free hydrocarbon radical of a free hydrogen atom, thereby becoming a free radical itself. This radical may immediately crack or may undergo radical isomerization prior to cracking. Radical isomerization presumably occurs through a coiled configuration of a single radical, in which the hydrogen donor and acceptor carbon atom much closely approach each other. Radical isomerization is a change of the position of hydrogen atom, usually to yield a more stable radical in order of teriary > secondary > primary free radical.

Cracking of either the original of isomerized radical then takes place at a carbon-carbon bond located in the β position to the carbon atom lackin one hydrogen atom. Cracking at the β position gives directly an alpha olefin and a primary radical (lacking one hydrogen atom on primary carbon atom); in this step no change of position of any hydrogen atom with respect to the carbon skeleton.

The primary radical derived from this step may immediately recrack at the β bone to give ethylene and another primary radical, or it may first isomerize. In the absence of radical isomerization, only primary radicals are derived form cracking reaction of normal paraffin; primary radicals are derived form cracking reaction of normal paraffin; primary radicals thus give only ethylene as the olefin product. Radical isomerization reduces the amount of ethylene, but it still remains the major product. By successive recracking, the radicals ultimately are reduced to methyl or ethyl fragments. These radicals then react with feedstock molecules to produce new free radicals and are themselves converted to methane or ethane. Thus, cracking is propagated as chain reaction.

1. Initiation

$$R_1CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2R_2 \longrightarrow R_1CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\ CH_2^{*} + R_2^{*} \qquad (2.1)$$

2. Chain carrying

2.1 beta fission

$$R_1CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\ CH_2^{*} \longrightarrow R_1CH_2CH_2\text{-}CH_2^{*} + CH_2{=}CH_2 \qquad (2.2)$$

$$R_1CH_2\text{-}\overset{\displaystyle H}{\overset{|}{C}}H\text{-}CH_2^{*} \longrightarrow R_1CH_2\text{-}CH{=}CH_2 + H^{*}$$

(2.3)

2.2 Chain Transfer

$$R_1CH_2\text{-}(CH_2)_4\text{-}CH_3 + H^{*} \longrightarrow R_1C^{*}\ H(CH_2)_4CH_3 \qquad (2.4)$$

3. Termination

$$R_1^{*} + R_2^{*} \longrightarrow R_1R_2 \qquad (2.5)$$

$$R_3CH_2\text{-}C^{*}H_2 + {}^{*}CH_2\text{-}\underset{\displaystyle H}{\underset{|}{C}}H\text{-}R_4 \longrightarrow R_3CH_2\text{-}CH_3 + CH_2{=}CH_2R_4$$

(2.6)

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2.10.2 Catalytic cracking

Catalytic cracking is the most important and widely used refinery process for converting heavy oil into more valuable Gasoline and lighter product. Originally cracking was accomplished thermally but the catalytic process has almost completely replaced thermal cracking because of more Gasoline having a higher octane and less heavy oil and unsaturated gases are produced.

Commercial cracking catalysts can be divided into three classes:

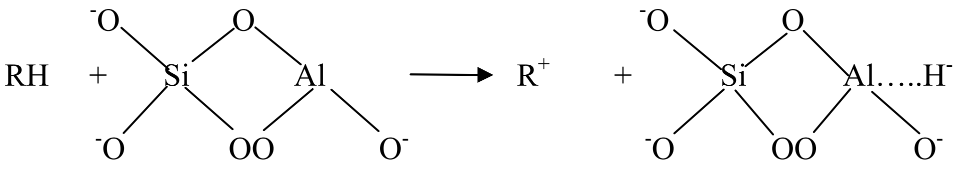
(1) Acid-treated natural aluminosillicated
(2) Amorphous synthetic silica-alumina
(3) Crystalline synthetic silica-alumina catalysts called zeolite or molecular sieves.

Most catalysts used in commercial units today are either class (3) or mixtures of classes (2) and (3) catalysts. The advantages of the zeolite catalysts over the natural and synthetic amorphous catalysts are:

- Higher activity
- Higher Gasoline yields at a given conversion
- Product of Gasoline containing a larger percentage of paraffinic and aromatic hydrocarbons
- Lower coke yield
- Increased isobutane production

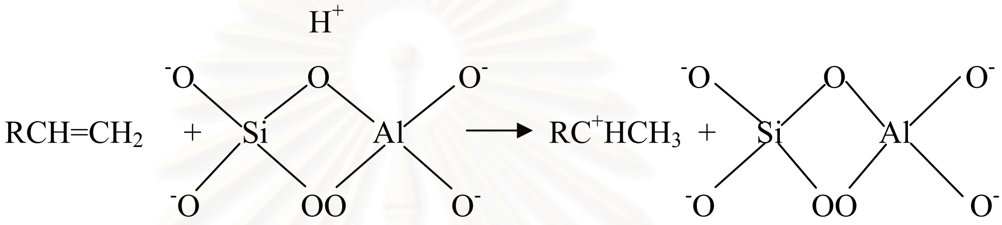
A major difference between thermal and catalytic cracking is that reactions through catalytic cracking occur via carbonium ion intermediate. Compared to the free radical intermediate in thermal cracking. Carbonium ions are longer lived and accordingly more selective than free radicals. Acid catalysts such as amorphous silica-alumina and crystalline zeolites promote the formation of carbonium ions. The following illustrates the different ways by which carbonium ions may be generated in the reactor :

1. Abstraction of a hydride ion by a Lewis acid site from a hydrocarbon



(2.7)

2. Reaction between a Bronsted acid site (H^+) and an olefin



(2.8)

3. Reaction of a carbonium ion formed from step 1 or step 2 with another hydrocarbon by abstraction of a hydride ion

$$R^+ + R\,CH_2CH_3 \longrightarrow RH + RC^+HCH_3 \tag{2.9}$$

Abstraction of hydride ion from a tertiary carbon is easier than from a secondary, which is easier than from a primary position. The formed carbonium ion can rearrange through a methide-hydride shift similar to what has been explained in catalytic reforming. This isomerization reaction is responsible for a high ratio of branched isomers in the products.

The most important cracking reaction, however, is the carbon-carbon β bond scission. A bond at a position beta to the positively-charged carbon breaks heterolytically.Yielding an olefin and another carbonium ion. This can be-represented by the following example:

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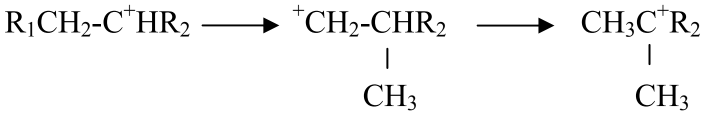
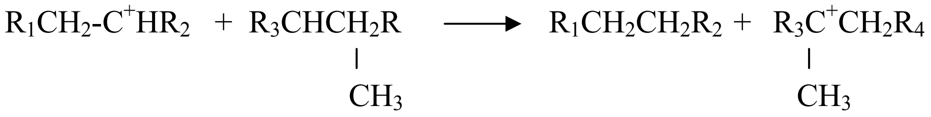


$$R_1CH_2\text{-}C^+HR_2 \longrightarrow {}^+CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HR_2 \longrightarrow CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}{}^+R_2$$

(2.10)

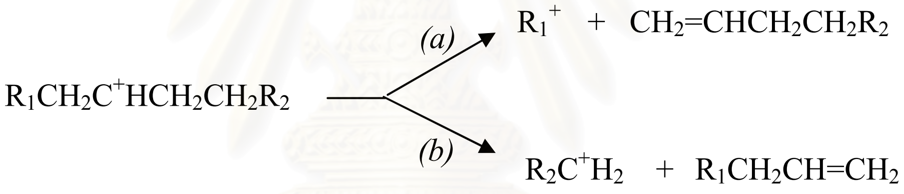


$$R_1CH_2\text{-}C^+HR_2 + R_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2R \longrightarrow R_1CH_2CH_2R_2 + R_3\underset{\displaystyle CH_3}{\underset{|}{C}}{}^+CH_2R_4$$

(2.11)

The new carbonium ion may experience another β scission , rearrange to a more stable carbonium ion, or react with a hydrocarbon molecule in the mixture and produce a paraffin

The carbon-carbon β scission may occur on either side of the carbonium ion, with the smallest fragment usually containing at least three carbon atoms. For example, cracking a secondary carbonium ion formed from a long chain paraffin could be represented as follows:



$$R_1CH_2C^+HCH_2CH_2R_2 \begin{cases} \xrightarrow{(a)} R_1{}^+ + CH_2{=}CHCH_2CH_2R_2 \\ \xrightarrow{(b)} R_2C^+H_2 + R_1CH_2CH{=}CH_2 \end{cases}$$

(2.12)

If R = H in the above example then according to the β scission rule (an empirical rule) only route *(b)* becomes possible, and propylene would be a product:

$$CH_3C^+HCH_2CH_2R \longrightarrow CH_3CH{=}CH_2 + {}^+RCH_2 \qquad (2.13)$$

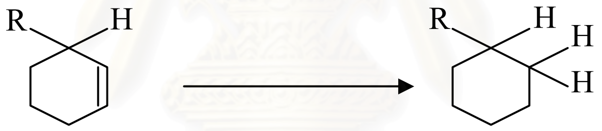
The propane may be protonated to an isopropyl carbonium ion

$$CH_3CH{=}CH_2 + H^+ \longrightarrow CH_3C^+HCH_3 \qquad (2.14)$$

An isopropyl carbonium ion cannot experience a β-fission (no C-C bond β to the carbon with the positive charge). It may either abstract a hydride ion from another hydrocarbon, yielding propane, or revert back to propene by eliminating a proton. This could explain the relatively higher yield of propene from catalytic cracking units than from thermal cracking units.

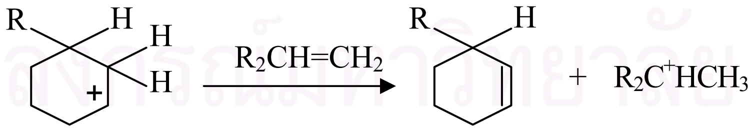
Aromatization of paraffins can occur through a dehydrocyclization reaction. Olefinic compounds formed by the β scission can form a carbonium ion intermediate with the configuration conductive to cyclization. For example, if a carbonium ion such as that shown below is formed (by any of the methods mentioned earlier), cyclization is likely to occur.

$$RCH_2CH_2CH_2CH_2CH{=}CH_2 \longrightarrow RC^{+}HCH_2CH_2CH_2CH{=}CH_2 \qquad (2.15)$$



(2.16)

Once cyclization has occurred, the formed carbonium ion can lose a proton, and a cyclohexene derivative is obtained. This reaction is aided by the presence of an olefin in the vicinity (R-CH=CH_2)



(2.17)

The next step is the abstraction of a hydride ion by a Lewis acid site from the zeolite surface to form the more stable allylic carbonium ion. This is again followed by a proton elimation to form a cyclohexadiene intermediate. The same sequence is followed until the ring is completely aromatized.

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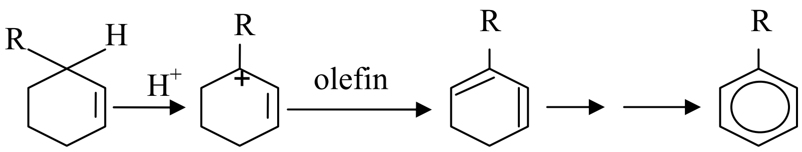

(2.18)

During the cracking process, fragmentation of sample polynuclear cyclic compounds may occur, leading to formation of simple cycloparaffins. These compounds can be a source of C_6, C_7 and C_8 aromatics through isomerization and hydrogen transfer reactions

Coke formed on the catalyst surface is thought to be due to polycondensation of aromatic nuclei. The reaction can also occur through a carbonium ion intermediate of the benzene ring. The polynuclear aromatic structure has a high C/H ratio.

2.11 Hydrocracking

Hydrocracking is essentially catalytic cracking in the presence of hydrogen, is a combination of catalytic cracking and hydrogenation and is carried out under substantial pressure. It is one of the most versatile petroleum refineing schemes adapted to process low value stock. The hydrogen hydrogenates coke precursors on the catalyst and thereby minimized the rate of coke formation such that a catalyst life of the order of a year or more can be achieved before regeneration is required. Hydrocracking processes were developed in 1930s to supply aviation Gasoline for military purposes in Germany. The catalyst consisted of various metal sulfide, unsupported, and metal supported, the dual functional catalysts used in hydrocracking provide high surface are such as cobalt, molybdenum, tungsten, vanadium, palladium, or rare earth element. In addition, high pressure was required. Hydrocracking were developed primarily to process feeds having a high content of polycyclic compounds, which are relatively unreactive in catalytic cracking such as heavy vacuum Gas Oil, Gas Oil, catalytic cycle oil, lubricating oils, diesel oil, fuel oil, and other chemicals. Furthermore, hydrogen gas adsorb with dissociation on a metal supported on an oxide and surface diffuse, it can cause reduction of an oxide at a distance from a supported metal crystallite and thereby reduce coke formation. On the other hand, the inverse effect may also occur dehydrogenation of a hydrocarbon may be accelerated by dissociate of hydrogen the migrated to a metal site where it recombines and is desorbed. This mechanism the role of metal is only to combine and desorbs hydrogen.

2.12Crude oil evaluation (Satterfield, 1991; Chaiyavech, 1997; Charusiri, 2001)

The first step in processing is to separate the crude oil by fractional distillation into cuts characterized by their boiling point range which is typically presented in term of fraction volatilized versus temperature as determined by a standard method which is usually simulated by a gas chromatograph procedure (ASTM D2887)

Table 2.5 Representative fraction from distillation of petroleum

Boiling oint range	**Fraction**	**Typical use**
Initial boiling point – 200 °C	Gasoline	Gasoline, blended into Gasoline
200 – 250 °C	Kerosene	Kerosene, Jet fuel, aviation fuel
250 – 350 °C	Light Gas Oil	Diesel fuel, blending stock for aviation fuel
350 – 370 °C	Gas Oil	Used as a feed to catalytic cracker or sold as heavy fuel oil
370 °C – Final boiling point	Long Residue	Used as a feed stock or burned to Energy

2.13 inetic Study (Boudart, 1984; Billaud, 2003)

For most kinetic model, a rate of reaction can be expression as a product of a temperature dependent function k(t) and a composition or conversion dependent function f(x)

Because of the complexity of reaction and the large number of components involved in the cracking mechanism. It is difficult to describe the kinetics model. Hence, the assumption to expression the mechanism of catalytic conversion of used vegetable oil to liquid fuels over the various catalysts are the reaction was continuously in the reactor and

rate of disappearance of B = the rate of the conversion of B per volume

$$-r_B = (-1/V)(dN_b/Dt) \qquad (2.19)$$

Suppose that N_{B0} is the initial amount of B in the reactor at time = 0, the N_B is the amount present at time t. Then, the conversion of B in constant volume system as

$$X_B = \frac{N_{B0} - N_B}{N_{B0}} = 1 - \frac{N_B/V}{N_{B0}/V} \qquad (2.20)$$

$$= 1 - \frac{C_B}{C_{B0}} \qquad (2.21)$$

At the constant volume;

$$-r_B = (-dC_b/dt) \qquad (2.22)$$

Thus, the equation for rate of reaction is expression in term of the function concentration and temperature as

$$-r_B = k_n C_B{}^n = (k_{n0}e^{-E/RT})C_B{}^n \qquad (2.23)$$

The equation (2.23) can expression in term of logarithm as

$$\ln(-r_B) = \ln(k_n) + n\ln(C_B) \qquad (2.24)$$

From this equation, A plotted of $\ln(-r_B)$ versus $\ln(C_B)$ gives a straight line with slope = n and intercept y-axis at $\ln(k_n)$

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At the constant volume; C_B and X_B can expression in term of

$$X_B = 1 - \frac{C_B}{C_{B0}} \tag{2.25}$$

And

$$dC_B = -C_{B0}dX_B \tag{2.26}$$

For the equation (2.25) and (2.26) integrating are obtain

$$\int_{o}^{t} dt = -\int_{C_{B0}}^{C_B} dC_B/(-rB) = C_{B0}\int_{0}^{X_B} dX_B/(-r_B) \tag{2.27}$$

Thus the time of reaction is

$$t = -\int_{C_{B0}}^{C_B} dC_B/(-rB) = C_{B0}\int_{0}^{X_B} dX_B/(-r_B) \tag{2.28}$$

Using integral method of analysis of data, where always puts a particular rate equation to the test by integrating and comparison the predicted C versus t curve with the experimental C versus t data. If the fit is unsatisfactory, another rate equation is guessed and tested.

If zero order reaction is obtain the relationship between $-r_B$ and C_B from the equation (2.28) as

$$(-dC_B/dt) = k_o \tag{2.29}$$

A plotted of C_B versus t gives the straight line with slope = k_o

If first order reaction is obtain the relationship between $-r_B$ and C_B from the equation (2.28) as

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$$(-dC_B/dt) = k_1 C_B \qquad (2.30)$$

$$-\int_{C_{B0}}^{C_B} dC_B / C_B = k_2 \int_0^t k_1 dt \qquad (2.31)$$

Integrating

$$\ln(C_B) - \ln(C_{B0}) = -k_1 t \qquad (2.32)$$

Thus

$$\ln(C_B) = \ln(C_{B0}) - k_1 t \qquad (2.33)$$

A plotted of $\ln(C_B)$ versus t gives the straight line with slope = $-k_1$

If second order reaction is obtain the relationship between $-r_B$ and C_B from the equation (2.28) as

$$(-dC_B/dt) = k_2 C_B^2 \qquad (2.34)$$

$$-\int_{C_{B0}}^{C_B} dC_B / C_B^{\;2} = k_2 \int_0^{t_B} dt \qquad (2.35)$$

Integrating

$$(1/C_B) - (1/C_{B0}) = k_2 t \qquad (2.36)$$

$$(1/C_B) = (1/C_{B0}) + k_2 t \qquad (2.37)$$

A plotted of $(1/C_B)$ versus t gives the straight line with slope = k_2

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Consideration to the rate constant and activation energy from Arrhenius's equation

$$k_n = k_{(n0)}e^{(-E/RT)} \quad (2.38)$$

The equation is expression in term of logarithm as following

$$\ln(k_n) = \ln(k_{n0}) - (E/R)/T \quad (2.39)$$

A plotted of $\ln(k_n)$ versus 1/T gives the straight line with the slope as (-E/R) and the intercept = $\ln(k_{n0})$ which uses to determine the activation energy (Ea) and pre-exponential (A) to predict the kinetic model of the reaction

2.14Literature Reviews

Prasad et.al. (1986) reported in his work concentrating to determine the effect of shape selective zeolite catalyst of the conversion of canola oil to liquid hydrocarbon fuels. The reaction temperature and oil space velocity were interested parameters on the statistical experiment design. The thermal cracking in empty reactor at 400 ^{o}C and oil flow rate at 4 g/h and time of reaction at 45 minutes obtained conversion of 14 wt% and small gaseous products. There was aliphatic C_6-C_{12} whereas no fraction of aromatic.

When HZSM-5 was used at the same condition of thermal cracking, the results showed the higher conversion with a large aromatic fraction. From the statistical test at 95% confidence level shows temperature and space velocity were mainly effect of the conversion to liquid hydrocarbon fuels which have aromatic fraction while the conversion was found to increase with an increase in reaction temperature and decrease space velocity and shows that nearly total conversion can be achieved at relatively lower temperature than those used in a typical fluid catalytic cracker. Furthermore, a short reaction period of 25 – 50 minute indicated that the catalyst deactivated fairly quickly. On the other hand, the aromatic content was significantly affected to the temperature and space velocity, selectivity towards the formation of aromatic hydrocarbon increased with increase in the reaction temperature and increased with decrease in the space velocity. It can be identified as deoxygenation cracking and aromatization with H-Transfer from catalytic cracking processes, deoxygenation can occur from decarboxylation and dehydration regarding the primary cracking of triglyceride which assumed that the predominantly by occur within the internal pore structure. The possibility is that the initial fragmentation can occur on the external surface of zeolite and followed by diffusion in to the pore. The subsequent reaction such as cyclization, isomerization, hydrogen transfer leading the formation of aromatic hydrocarbon. The higher selectivity towards aromatic content at about 370 ^{o}C. In addition, his work proposed that at about 300 ^{o}C the main reaction was dehydration between 340-375 ^{o}C the aromatic hydrocarbon formation was predominant, while above 400 ^{o}C the light olefin and CH_4 gaseous products became significant as a result of secondary cracking reaction.

At high space velocity, the results showed favor aromatic hydrocarbon formation and leading to formation of light gaseous predominant, if the higher space velocity shows the results in greater amount of aromatic and Gasoline boiling range C_6-C_{12} fraction also increased with increase in reaction temperature reached a maximum at 375 ^{o}C and gave later decrease. Furthermore, the C_6-C_{12} fraction represented the gasoline boiling range increased with increase in the space velocity. The highest gasoline fraction at of the temperature of 370 ^{o}C with space velocity of 4 h^{-1}. The amount of gaseous product was very small (0.5 – 5 wt%) shows that the gaseous product increased with increase the temperature and decrease space velocity. Propane and butane with small mostly consisted in the gaseous product while CO and CO_2 was observed to increased with increase the reaction temperature.

Adjaye et.al.(1995) studied the catalytic upgrading of bio-oil over various catalysts.HZSM-5, H-Y, H-mordenite, silicate and silica-alumina were obtained as a catalyst in a fixed bed reactor which carried out at atmospheric pressure, space velocity 1.8 – 3.6 h^{-1} and the reactor of temperature range of 290 – 410 ^{o}C. The experiment was to obtained high yield of hydrocarbon consisted mostly of C_6 – C_9, aromatic hydrocarbon, aliphatic hydrocarbon, small gases and coke formation. In order to determined the extent of thermal cracking where carried out at 410 ^{o}C and 1.8 h^{-1} space velocity without catalyst. The result showed that a large fraction of bio-oil was converted to char while deoxygenation and hydrocarbon formation were very low. In addition, the gaseous consisted of 5%wt of CO, 18 %wt of CO_2 and small amount of C_1-C_6 hydrocarbon gaseous. Where HZSM-5 was used as a catalyst, at of temperature increased to 370 and 410 ^oC, Organic liquid phase consisted mostly aromatic hydrocarbon and a few phenols while aliphatic and ketone were found in relatively low amount with absence of most of the oxygenated compound which indicated that the effect of HZSM-5 is able to converted all oxygenated compound to hydrocarbon. Furthermore, no residues was obtained, it seems that all non volatile compound of bio-oil were effectively converted over HZSM-5. The char was a solid carbonaceous material which formed over the catalyst and on the inner wall of reactor. It shows that a significant amount of bio-oil was converts to char before contacting the catalyst. As in the case of H-mordenite, the effect of temperature and space velocity were similar to HZSM-5. The amount of aliphatic was a maximum of 22.9 at 330 ^oC, 3.6 h^{-1} space velocity while the maximum of aromatic at 46.6 %wt at of 370 ^oC 1.8 h^{-1} and decreased to 39.4 %wt at 3.6 h^{-1} space velocity.

Silicate was used to determine the effect of acid site compared the results with HZSM-5, it has a uniform pore diameter and similar HZSM-5 exception being the absence of ion exchange and no acid site. The result showed that the yield of organic liquid phase was very low while char formation increased with temperature increase, On the other hand, the space velocity had very little effect on the yield, increasing the space velocity resulted in tar and coke formation. In order to the effect of H-Y, organic liquid phase were obtained a maximum at 28.4 at 3.6 h^{-1} while at 1.8 h^{-1} gave 25.5%wt , it showed that the yield was higher when upgrading was carried out at higher space velocity and lower temperature. However, the amount of aromatic was relatively low at about 6.5 to 20.6 %wt between 290 and 370 ^oC and jumped to 35.8%wt at 410 ^oC, it seemed that a transition occurs from aliphatic yield to aromatic hydrocarbon as the temperature increased. The low yield of organic liquid phase over silica-alumina which was carried out a higher space velocity, it has already been mentioned that the high yield was due to the lower retention of bio-oil components within the reactor during upgrading while the temperature was increase to 330 ^oC, tar fraction decreased drastically and coke formation also increased. At the space velocity of 1.8 h^{-1} and 370 ^oC gave the maximum of 56.9%wt of aliphatic hydrocarbons and decreased slightly to 55.8%wt at 410 ^oC. Furthermore, aromatic hydrocarbons were relatively low at about 4.6%wt. It appeared therefore that silica-alumina can be used to convert which is rich in aliphatic hydrocarbons.

Kantikaneni et.al. (1995) studied catalytic conversion of canola oil to liquid fuels and chemicals over various catalysts in a fixed-bed reactor under the condition of temperature range of 375 up to 500 ^{o}C, weight hourly space velocity of 1.8 and 3.6 h^{-1} at atmospheric pressure. The performance of each catalyst in term of pore size, acidity, crystallinity were obtained to determine the yield of organic liquid hydrocarbon product and optimized the coke formation in six types of catalyst such as HZSM-5, H-mordenite, H-Y, silicalile, alumina-pillared clay and silica alumina. In order to determine the effect of thermal cracking on the conversion of canola oil, the conditions were obtained of 400 ^{o}C and 1.8 h^{-1} WHSV, the conversion was 12 wt%, the liquid product consisted mostly C_6 up to C_9 aliphatic hydrocarbon and small gaseous. The result showed that thermal cracking was not enough to converted canola oil to light hydrocarbon fuels and aromatic fraction. Consequently, no catalytic cracking on the canola oil, no shape selectivity leading to low conversion in the effect of catalytic cracking, the conversion of canola oil increased with temperature and decreased with increased space velocity, Temperature has a strong influence. On the other hand, the conversion with silicate was lower than other catalyst was negligible acidity, thus it can be seen that the optimum operating temperature should be in range of 400 to 450 ^{o}C while the space velocity of 3.6 h^{-1} WHSV appears to be highest conversion for all type of catalysts. In order to HZSM-5 gave the highest organic liquid product yield of 63 wt%. The liquid products were consisted mainly methanol, acetone, and varies aliphatic and aromatic hydrocarbon which were within the Gasoline boiling range. The effect of catalyst shape selectivity could be examined by comparing the crystalline zeolite and silica-alumina. It seemed that crystalline zeolite were highly selective for C_7-C_9 aromatic hydrocarbon from the affected to shape selective property of zeolite while silica-alumina produced a high amount of hydrocarbons but the selectivity was not directed toward any particular hydrocarbon product. HZSM-5 was highly acidity while silicate was almost non-acidic so the conversion, hydrocarbon formation in HZSM-5 was higher than silicate from the Bronsted and Lewis acidic sites are responsible for deoxygenation, cracking and enhance useful hydrocarbon whereas the gaseous yield which cracked over HZSM-5 are due to higher extent of deoxygenation. Furthermore, the higher of hydrocarbon formation with HZSM-5 was due to subsequent acid catalyzed reaction such as secondary cracking oligomerization, cyclization and H-Transfer.

When the pore size of catalyst was increased, the conversion of canola oil and overall yield of hydrocarbons decreased accordingly. Moreover, the selectivity toward aromatic hydrocarbon decreased with increase in catalyst pore size, while the selectivity for aliphatic increased with the pore size. It seems that the cracking processes and deoxygenation which were the initial step and more enhance with medium pore size which more effective in aromatization of the intermediate olefin

Kantikaneni et.al. (1995) studied the conversion of canola oil over silica-alumina, HZSM-5 and hybrid catalyst which were prepared by adding H-Y to silica alumina and HZSM-5 to silica-alumina by varied ratio of thier catalysts. The experiment was setup in a fixed bed reactor at atmospheric pressure, temperature range of 400 – 550 ^{o}C and space velocity 1.8 to 3.6 h^{-1}. Hydrocarbon content of organic liquid product obtained with silica-alumina containing of 4 and 3 wt% aliphatic and 14 up to 58 wt% aromatic which mainly C_6-C_9 fuel range hydrocarbon. It seemed that the effect of temperature was increased the aliphatic content of liquid organic product decreased tremendously, whereas the aromatic increased. However, this result implied that it may be possible to obtain the desired ratio of aliphatic to aromatic just by increase the temperature. In addition the yield of organic liquid decreased with the space velocity was double from 1.8 to 3.6 h^{-1}. Thus, It should be operated at low space velocity.

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As for using HZSM-5, the effect of temperature and space velocity on the conversion was small, however the conversion increased with temperature gave the conversion at about 93 wt% at 400 ^{o}C and closed up to 100 wt% at 550 ^{o}C. On the other hand, it decreased when space velocity were double, the high conversion was probably due to the effectiveness of HZSM-5 to converted canola oil. HZSM-5 produced more aromatic than silica-alumina and highly selective for C_7-C_8 aromatic hydrocarbon whereas did not have a preferential selectivity in silica-alumina. The high aromatic hydrocarbon selectivity with HZSM-5 was due to its shape selective property, pore size and pore structure are known to enhance cyclization and aromatization while silica-alumina have acidity, pore size but no pore structure property and shape selectivity. Hence, the cracking over HZSM-5 were added to silica-alumina in order to enhance its cracking activity. When H-Y was added to silica-alumina, organic liquid product and coke formation were decreased, when amount of H-Y in silica-alumina was increased from ratio of 1:3 to 3:1 there was increased acidity of the hybrid catalyst are due to the presence of H-Y which imply increased deoxygenation by dehydration. Furthermore, hybrid catalyst obtained with physical mixing of silica-alumina and HZSM-5 shows the similar to those obtained with pure HZSM-5. There were mostly aromatic and small aliphatic hydrocarbon, it seemed that the addition of HZSM-5 to silica-alumina was a route to modified performance of catalytic cracking to aromatic fuels and could be increased more than used only silica-alumina. In 1996 they studied the performance of each catalyst in term of pore size, acidity and crytallinity were obtained to determine in yield of liquid hydrocarbon product and optimizated the coke formation in six types of catalysts such as HZSM-5, H-Mordenite, H-Y, silicalile, alumina-pillared clay (AL-OILC) and silica-alumina (Kantikaneni 1996). In order to determine the effect of thermal cracking on the conversion of canola oil, the condition was obtained at 400 C and 1.8 h^{-1} WHSV the conversion was 12 wt% The liquid products consisted mostly C_6-C_9 aliphatic hydrocarbon and small gaseous. The result showed that thermal cracking was not enough to converted canola oil to light hydrocarbon fuels.

Adjaye and co-workers (1996) were undertaken in order to investigate the effect of various mixture composition of silica-alumina and HZSM-5 on the yield and selectivity for liquid hydrocarbon fuels which performed in a fixed microreactor at atmospheric pressure, 1.8 – 7.2 h^{-1} space velocity and temperature of 330 – 410 ^{o}C. The results for the yield of organic liquid products increased with increasing the space velocity, however with increase in temperature reached a maximum yield at about 34.8 wt% at 370 ^{o}C. In order to the yield of organic liquid product over silica alumina processes, double space velocity gave to increased the yield of liquid product while increased with temperature, the organic liquid product decreased progressively. With the both HZSM-5 and Silica-alumina, converted at low temperature produced tar and residual matter, found that HZSM-5 produced far less residual compare to silica-alumina. In addition, the char fraction was high at low temperature but decreased drastically as the temperature was increased. However, Silica-alumina produced a relatively higher fraction of coke compared to the HZSM-5. Due to the mixture catalysts imply that by adding HZSM-5 to silica-alumina, it was possible to substantially increase the aliphatic hydrocarbon yield. However, a further increase in the HZSM-5 content resulted in a substantial increase in the aromatization activity. A reduction in coke formation, increase in the conversion of non-volatile of the bio-fuels and increased the yield of organic liquid products were gained when small amount of HZSM-5 are added to silica alumina.

Kantikaneni and co-workers (1996) studied catalytic cracking of canola oil over HSZM-5 and potassium-impregnate. The result showed that canola oil conversion was decreased with increasing potassium concentration and space velocity as well as decreasing reaction temperature while the conversion was general decrease in the yield of organic liquid product with increasing reaction temperature and potassium concentration in the catalyst. The result of HZSM-5 which is the high acidity catalyst, formation C_2-C_4 from cracking residual oil occurs to a greater extent than oligomerization to aliphatic increased as catalyst acidity decrease by potassium impregnate. The effect of reaction temperature showed that C_2-C_4 olefin increases with reaction temperature, where is typical of highly endothermic thermal cracking which results in an increase in C-C bond scission of C_5+ aliphatic and consequent increase in C_2-C_4 olefin formed.

The effect of canola oil space velocity which was evaluated with lowest acid site and strong acid site which showed that the yield of C_2-C_4 olefin for runs at high canola oil space velocity was higher than at the low space velocity at reaction temperature of 500 ^oC. Therefore, favorable condition of maximum C_2-C_4 olefin were high reaction temperature, high space velocity and relatively low Bronsted and total acidity. However, the overall results showed that the maximum C_2-C_4 olefin yield of 25.8 wt% was obtained with HZSM-5 and 0.5% potassium impregnate at temperature of 500 ^oC and 18 h^{-1} space velocity.

Raphael et.al. (1997) studied catalytic conversion of canola oil over various types of catalysts to define the role of acidity, basicity and shape selectivity on product distribution of liquid fuels and chemicals. The thermal cracking shows that canola oil conversion were high and decreased drastically as the temperature increased with space velocity decreased, the liquid product consisted of C_1-C_5, dimethyl ether and hydrogen in gaseous products, aromatic and C_6+ aliphatic and residue oil consisting mainly of long chain unconverted hydrocarbons.

Role of catalyst shape selectivity

The primary cracking to long chain hydrocarbon and oxygenated was independent of catalyst characteristics. Subsequently, light olefin was occurs by the amorphous and non-shape selectivity of catalyst. On the other hand, the conversion of organic liquid products with HZSM-5 and silica-alumina were higher than those for the empty reactor that these was only limited secondary cracking which was sufficient to produced hydrocarbon and deoxygenated . Limited secondary cracking of long molecule may be contributed to the ability of long molecules to diffuse through the interconnecting pores of shape selective catalysts with only C-C bond scission. There was a selective of C_7-C_9 aromatic hydrocarbons obtained with HZSM-5 and silicate catalysts. The presence of aromatic hydrocarbons with HZSM-5 from the initial thermal cracking for the formation ethylene and butadiene which then undergo dehydrogenation to form diolefine, followed by cyclization and further dehydrogenation results in the formation of aromatic hydrocarbons.

Role of catalyst acidity

In order to uses HZSM-5, gave high yields of organic liquid product and aromatic hydrocarbons consisted C_6-C_{18} as compared to silica-alumina, y-alumina and empty reactor. The formation of aromatic over HZSM-5 was due to limited secondary cracking as well as a large degree of cyclization and aromatization that occur with it pores while compared to silica-alumina or γ-alumina showed that the only significant contribution of catalyst acidity to the modification of the thermal cracking is that of increasing the extent aromatization process.

Role of catalyst basicity

The runs over calcium oxide and magnesium oxide catalysts as well as those for the empty reactor were used to determined the role of basicity. The yield of residual oil were larger for runs with calcium oxide and magnesium oxide compared with empty reactor. It seemed that the initial thermal cracking and oxygenated hydrocarbons, subsequent secondary cracking of these heavy molecules appears to be inhibited by the presence of basic sites which is responsible for the formation of a large of residue oil and only small amount of gaseous. Moreover, the residual oil yield was lower for runs over magnesium oxide than calcium oxide, the results show that a higher degree of secondary cracking inhibition for calcium oxide can be attributed to the presence strong basic sites than magnesium oxide.

Meng et.al. (2001) studied the effect of the catalytic pyrolysis of the feedstock of Daqing atmospheric residue over a LCM-5 catalyst in a confined fluidized-bed reactor to the product distribution of light olefin. The experimental results obtained the influences of the reaction temperature, residence time and weight ratios of catalyst to oil and steam to oil were significant on light olefin yield.

The effect of reaction temperature on conversion and selectivity were obtained by the sum of yields of cracked product distribution of gas, Gasoline, diesel and coke and the mass of light olefins formed per unit mass of feedstock cracked respectively. The conversion of feedstock was above 90% and increased slightly with increasing reaction temperature, whereas the selectivity of light olefins shows a maximum.

The effect of reaction temperature on yield of cracked gas increase significantly with temperature but almost held when the temperature was over 963 K. On the contrary, the yield of Gasoline and diesel decreased greatly with temperature and then did not show an appreciable change with temperature at of 963 K. Moreover, the yield of coke was comparatively very low and increases gradually with temperature. The results indicated that the degree of catalytic pyrolysis was very high because cracked liquid was mainly composed of aromatic, including alkylbenzene, alkylnaphthalene, etc. The yield of alkylbenzene decreased with temperature, while that of alkylnaphthalene increased, which indicated that pyrolysis degree became deeper and the condensation degree of cracked liquid increased with an increase of temperature. Additionally, the effect of temperature was mainly effect to the gaseous products cracked, it could undergo secondary cracking, olefins could convert into alkane by hydrogen transforming reactions and could also convert into Gasoline and diesel by polymerization and aromatization reactions.

The effect of residence time which refered to the contact time of oil vapor with catalyst, the yield of overall light olefins decreased gradually with the residence time, while the yields of light gaseous such as ethylene, propylene, and butylene decrease very slightly. The results indicate that the yield of total light olefins does not increase by prolonging the residence time, and catalytic pyrolysis of heavy oils is suitable of operating at short residence time.

The effect of the weight ratio of catalyst to oil showed the yields of ethylene and overall light olefins increase slightly with increasing catalyst to oil weight ratio, while the yields of propylene and butylenes almost do not change. It seemed to the catlystic pyrolysis could not take place without acidity centers on catalysts. The pyrolysis reaction was mainly thermal pyrolysis, following the free radical mechanism from influence of temperature and creating much ethylene. When the catalyst was enough to offer energy and location for hydrocarbon pyrolysis, the effectiveness of the catalyst would become unimportant. Increasing the catalyst to oil weight ratio means high reaction rigor and high pyrolysis degree. After that Ming et.al.(2003) continued studies the kinetics of heavy oil catalytic pyrolysis were obtained the effects of reaction temperature, residence time and weight ratios of catalyst to oil and steam to oil on light olefin yielded and the product distribution of Daqing atmostpheric residue catalytic pyrolysis over a LCM-55 in fix-bed reactor to determined and developed a kinetic model.

Billaud et. al.(2001) studied catalytic cracking of octanoic acid over activated alumina (ALCAN), the effect of temperature and mass hourly space velocity (MHSV) were investigated, the main products obtained and analyzed by GC/MS were olefin C_6, C_9, C_{15}, 8-pentandecanone (symmetrical ketone) and 2-nonanone-8-methy ketone. Additionally, the conversion obtained at high temperature without a catalyst were low conversion about 4% whereas, at temperature of 450 ^oC with active alumina 40 grams the octanoic acid was almost entirely converted. At temperature of 350 ^oC with 40 grams of activated alumina, the octanoic acid was not effectively converted to symmetrical ketone, hence there were low proportions of C_6-C_7-C_9-C_{15} hydrocarbons, there was still a high proportion of unconverted 8-pentadecanone in the liquid organic. At temperature of 400^oC with 40 gram of catalyst, the reduction and dehydration reaction were favor to derived of hydrogen transfer and cracking of heavy hydrocarbon compounds into light compound molecules, while at temperature at of 500^oC with 40 gram of activated alumina, the proportion of C_{15} were decreased substantially whereas the proportion of C_6, C_7, C_8 compounds was higher than lower temperature, thus the temperature was mainly effected to introduced hydrogen transfer in catalytic cracking reaction. It confirms that the C_{15} proportion was decreased whereas the small compounds were increase substantially. The effect of mass of catalyst was investigated by varied the mass of activated alumina from 10 grams up to 40 grams; the products were obtained that increasing the mass of activated alumina resulted in increasing the conversion rate to symmetric ketone.

Twiaq and co-workers (2003) studied conversion of plant oil to liquid hydrocarbon fuels, this study obtained with modified mesoporous molecular sieve in proposed to increased surface area of catalysts. MCM-41 as a synthesized mesoporous molecular sieve and Mesoporous aluminosilicate with Si/Al ratio of 50 were synthesized to investigated catalytic cracking of Palm kernel oil and Palm olein oil in a fixed bed micro reactor which operated at atmospheric pressure, temperature of reaction at 723 K and weight hourly space velocity of 2.5 h^{-1}. Palm kernel and Palm olein oil having a difference molecular weight in their triglyceride structure were investigated in the activity and selectivity of H-MCM-41 having difference pore sizes. The synthesized MCM-41 was converted into H-form in order to increase the acidity of catalyst. The product distribution related to the low shape selectivity of the catalyst due to the large size of the pores compared to the size of the product such as Gasoline, Kerosene diesel. The C_{17} hydrocarbon, like diesel fraction are close to the size of the fatty acid from palm oil. The weak acidity of the mesoporous probably affected the ester group faster than the cracking reaction at high temperature by extracting CO_2 from the ester. The cracking reaction occurred as secondary cracking reaction of the linear chain of hydrocarbon, which has the length of C_{13}-C_{17} depending on the type of oil. While the conversion of palm oil was increased with the increase in surface area of the catalysts. Palm olein oil was found lower conversion compared to palm kernel probably due to larger molecular size and diffusion resistance. Comparing the conversion of palm kernel which average carbon number of 38 and palm olein (average carbon number of 54) found that palm kernel was higher converted to liquid hydrocarbon fuels about 85-98%wt because of easy accessibility of oil into the pores of the catalysts, the yield of diesel fraction decreased with conversion when the conversion was higher than 80 wt% showing the effect of secondary cracking reactions which led to cracking of middle hydrocarbon molecule into smaller fraction such as Kerosene, Gasoline and light hydrocarbon gases.

The coke formation from palm kernel oil cracking was increased with increase of surface area of the mesoporous modifier to MCM-41 whereas the formation of coke over palm olein cracking was about 10-12 wt% and lower compared to palm kernel oil. In addition, the coke formation obtain from cracking over mesoporous were much higher compare to the zeolite. They noted that the MCM-41 has lower activity when small size molecule was cracked while, the large molecule cracked, MCM-41 activity found to be the same activity of zeolite

The highest Gasoline yield was obtained from palm olein oil, the effect of pore size on the Gasoline selectivity was more pronounced with palm olein. While the pore size increased, the space available for reaction also increased where the active sites located inside the pores of MCM-41. The selectivity of Gasoline and Kerosene fraction were increased with increase in surface area of the catalyst, whereas the selectivity for diesel was independent with the change of surface area. In this year they (Farouq 2003) continued synthesize the composite materials containing microporous zeolite and mesoporous molecular sieve by coating HZSM-5 with a layer of mesoporous MCM-41 which were used as a catalysts in a palm oil cracking processes to the light hydrocarbon fuels and their performance was compared with those obtain HZSM-5 and MCM-41. The experiment were performed under nitrogen gas over the catalyst at atmospheric pressure un a fix bed reactor at temperature of 450 ^{o}C and weight hourly space velocity of 2.5 $h^{-1.}$

Performance of HZSM-5 was found to be almost constant with the change of Si/Al ratio. The removal of CO_2 from triglyceride was the first step of the cracking from the effect of thermal cracking whereas the acidity of HZSM-5 influence to the product distribution. On the other hand, the gas yielded significantly with an increased of Si/Al ratio of HZSM-5 which affected the role of the strength of the acid site. Furthermore, the Gasoline fraction increased with the increase in Si/Al ratio due to the increase in secondary cracking while increased in the gasoline and dropped in total aromatic were observed with the increased of Si/Al ratio.

Performance of MCM-41 which the both weak Bronsted and Lewis acid which led to cracking the fatty acid chain into linear paraffin and olefin without further isomerization to napthene. The result showed the both total conversion and the gas yield was much lower than HZSM-5 and gave more selective to the diesel fraction. The increase in Si/Al ratio still increased the selectivity of gaseous and coke formation whereas a little drop in the selectivity of total organic liquid product. In order to increase the acidity of siliceous MCM-41, the selectivity of Gasoline was higher at lower Si/Al ratio which was of low crystallinity and the results of increase in acid site within aluminosilicate increased the cracking activity resulting in the conversion.

Performance of composite catalyst was showed a good performance for product of Gasoline fraction. The composite of HZSM-5 of 10% and 20% of mesoporous layer gave higher conversion and dropped with further increase in thickness due to the low activity of the amorphous siliceous. The composite with 10% silica coating gave highest yield of gasoline fraction of 47 wt%. The yield of gasoline and the trend of gaseous decreased with the increase in the silica layer. On the other hand, the activity of aluminosilicate mesoporous coating affected to the conversion which was decreased because the BET surface area decrease from 504 to 141 m^2/grams, it was found to play the role in catalytic cracking and the results of product distribution was decreased with increase in the alumina content, though the conversion were high the yield of Gasoline were dropped notably with increase alumina content which the selectivity of diesel was increase at high alumina content in the coating. The catalyst prepared by coating HZSM-5 with low content of MCM-41 having low mesoporous coating gave higher conversion and yield of Gasoline compared to those having high mesoporous ratio coating. The presence of alumina in mesoporous decreased the crystallinity of the mesoporous coating because the higher crystallinity gave ability for palm oil access to the active site of microporous which played the role of shape selectivity and aromatization thus, the composite catalyst gave lower gaseous product, high liquid product and decrease in aromatic contents in the Gasoline fraction which compared with HZSM-5

CHAPTER III

EXPERIMENTAL

The emphasis in this research aims to investigate the parameters which affect to the conversion of used vegetable oil to liquid fuels over various type of catalyst, to analyze the liquid and gaseous products to the optimum condition where give the highest yield on Gasoline fraction, and investigate the kinetic parameter for each type of catalyst.

3.1 Starting material and chemicals

Used vegetable oil was obtained from fried chicken processing from KFC fast food (Pat-pong branch, Bangkok, Thailand) during March 2004. The spent oil was stored in the black bottle under the atmosphere of nitrogen gas to prevent the side reaction of oxidation and oxygenation. AOCS 1993Ce2-66Ce1-62 method is The American Oil Chemist Society's Standard to analyze the composition of fatty acid was obtain to analyzed of used vegetable oil comparison to fresh vegetable oil. Used vegetable oil was consist mainly total saturated fatty acid 43.97%wt and total unsaturated fatty acid 56.03%wt

HZSM-5 powder micro porous catalyst with the ratio of Si/Al 18 and surface areas were obtained by application of the Brunauer-Emmett-Teller (BET) procedure at of 393 m^2/gram.

Sulfated Zirconia as a commercial powder catalyst in range of 60 – 70 %wt metal support with surface area at of 133 m^2/gram.

Hybrid catalyst were prepared by thoroughly physically mixing in varies ratios of HZSM-5 and Sulfated Zirconia. In the ratio 0.1 : 0.9 to 0.8 : 0.2 gave the surface areas were determined by BET procedure at range of 191 m^2/gram to 385 m^2/gram

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Hydrogen gas (purity 99.5%) used to trace the effected of initial pressure of hydrogen gas which supplied by Enviromate Co., Ltd. Bangkok, Thailand.

Toluene (C_7H_8) is a commercial grade (purity 80% minimum) from S.R.Lab Co., Ltd. Bangkok, Thailand . This reagent was used without further purification

3.2 Catalyst Preparation

Preparation of HZSM-5

The seeding gel was prepared by dissolved 13.8 grams sodium hydroxide and 117.0 grams Tetrapropylamonium hydroxide into 710.3 grams distilled water and mix thoroughly followed by added 158.9 grams silicic acid into the obtained mixture under stirring to add silica in portion. Shake the mixture for 1 hour at ambient room temperature, then age the mixture at 100 ^{o}C for 16 hours. The seeding gel was obtained.

The synthesis gel was prepared by dissolved 8.8 grams sodium hydroxide and 10.3 grams sodium aluminate into 867.8 grams distilled water and mix thoroughly. 113.1 grams silicic acid was added under stirring to add silica in portion, followed by added 50 grams of seeding gel under stirring. Shake for 1 hour the synthesis gel was obtained at about 87 grams product. Then, the synthesis gel was placed into the vessel 50 ml PTFE-lined stainless steel autoclaves under temperature of 180 ^{o}C for 4 hours to crystallization. The obtained solid from the vessel was filtrated by vacuum filter and washed thoroughly with distilled water followed by drying on an oven at temperature of 105 ^{o}C. After drying for 24 hours, the crystallization product was pulverized dried in an agate mortar. HZSM-5 was obtained nearly equal to the Si/Al ratio at 18. The surface area was obtained by application of the Brunauer-Emmette-Teller (BET) procedure.

Preparation of Zirconia and Sulfated Zirconia

Zirconium oxynitrate [$ZrO(NO_3)_2$] was dissolved into a nitric acid solution, and aqueous ammonia was slowly added under stirring to precipitate zirconium hydroxide until the pH reached 11. The obtained solid was washed with water and calcined to prepare Zirconia at 573 K for 4 hours under atmospheric conditions.

Sulfate was loaded by an impregnation method, 5 grams of Zirconia was suspended in aqueous solutions containing various amounts of sulfuric acid with a constant volume of 100 cm^3, followed by drying on a hotplate. After drying for 2 hours. The obtained solid was calcined at 923 Kelvin for 4 hours under atmospheric conditions. BET surface area was determined from the amount of nitrogen adsorbed at 77 Kelvin under 30.39 kPa of nitrogen ($P/P^0 = 0.3$)

3.3 Apparatus

The 70 cm^3 microreactor, SS 316 stainless-steel pressure cylindrical reactor was used for this study on catalytic cracking of used vegetable oil to liquid fuels over various catalysts, and is shown in Figure 3.1. The microreactor composed a pressure gauge, safety valve, valve for admitting and releasing gases.

Figure 3.1 Stainless Steel Micro-reactor

Reaction experimental unit with the rotating machine, a speed motor was used to control the shaking of cylindrical stainless steel microreactor at 80 rpm. The reactor was heated by 400 watt injection heater at the heating rate of 20 ^{o}C /min, the temperature was measured by thermocouple type K having 1.6 mm. diameter with an accuracy of ± 5 ^{o}C by means of a programmable temperature controller.

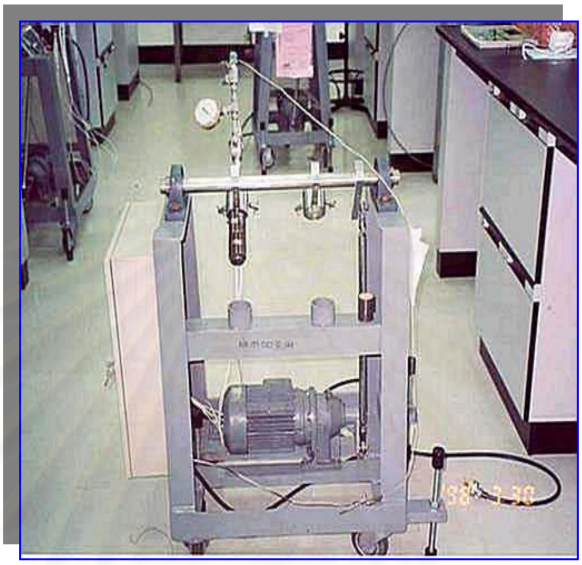

Figure 3.2 Reaction experimental unit

Vacuum filtration and 40 nm sieve filter uses to filtrate the liquid products and solid products from vacuum pump.

Figure 3.3 Vacuum pump (left) and set of vacuum filter (right)

3.4 Experiment procedures.

20 grams of used vegetable oil were put in the 316-stainless steel cylindrical micro-reactor volume of 70 cm^3. 0.2 grams of catalyst was added and hydrogen gas was supplied from a hydrogen tank to fill into inside the reactor. The reactor was constructed to reaction unit, with injection heater and insulator. The reactor was heated from the ambient room temperature to desired temperature and maintain at the desired temperature for any reaction times. The reaction temperature was controlled by a programmable temperature controller with K-type thermocouple was used as a temperature detector. After finish the reaction, the reactor was cooled to 30°C or ambient room temperature to prevent the effect of temperature gradient and solidification of residual oil. The gaseous products were analyzed by 3000MICROGC gas chromatograph. The liquid product was collected by vacuum filtration to separate the liquid oil products from solids. The liquid oil products were analyzed using a simulated distillation gas chromatograph (Variance Model CP-3800) by ASTM 2887-D86 method on a capillary glass column using FID detector. The oven temperature was programmed at a heating rate of 10°C /minutes in range of 30 – 320°C. The liquid oil compositions were defined according to the boiling point range of the petroleum products such as Gasoline (IBP-200°C) Kerosene (200-250°C) Light Gas Oil (250-300°C) Gas Oil (300 – 375°C) and Long Residue (375°C – FBP). A schematic diagram of this procedure is shown in Figure 3.4

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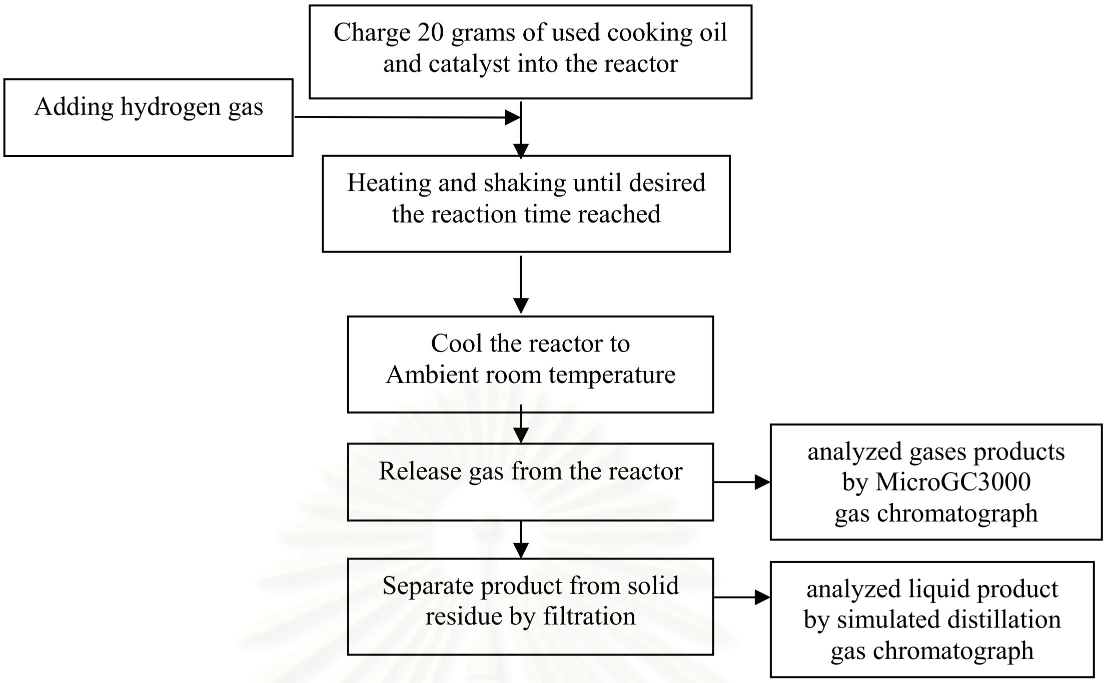

Figure 3.4 Schematic diagram for the catalytic cracking of used vegetable oil

3.5 Experiment design

To determine the significant factors for catalytic cracking of used vegetable oil , 2^k factorial design was used to design the experiment. This method is widely used for screening the factor for the system. The chosen factors for the catalytic cracking were temperature, initial pressure of hydrogen gas, time of reaction, weight of catalyst and ratio of HZSM-5 and Sulfated Zirconia in hybrid catalyst. In this experimental design method, there are two levels “low” coded (-1) and “high” coded (+1) level. In table 3.1 and 3.2 temperature, initial pressure of hydrogen gas, time of reaction, and weight of catalyst are represented as A, B, C, and D respectively. While table 3.3 temperature, initial pressure of hydrogen gas, time of reaction, and ratio of hybrid catalyst are represented as A, B, C, and D, respectively.

Table 3.1 Factors and level of variable of the catalytic cracking of used vegetable oil over HZSM-5

Factor	Low level (-)	High Level (+)
1. Temperature (^{o}C), A	400	430
2. Initial pressure of hydrogen gas (bar), B	10	20
3. Time of reaction (minute), C	45	75
4. %Weight of HZSM-5 (gram), D	0.1	1.0

Table 3.2 Factors and level of variable of the catalytic cracking of used vegetable oil over Sulfated Zirconia

Factor	Low level (-)	High Level (+)
1. Temperature (^{o}C), A	400	430
2. Initial pressure of hydrogen gas (bar), B	10	20
3. Time of reaction (minute), C	45	75
4. %Weight of Sulfated Zirconia (gram), D	0.1	1.0

Table 3.3 Factors and level of variable of the catalytic cracking of used vegetable oil over hybrid catalyst

Factor	Low level (-)	High Level (+)
1. Temperature (^{o}C), A	400	430
2. Initial pressure of hydrogen gas (bar), B	10	20
3. Time of reaction (minute), C	45	75
4. Ratio of HZSM-5 : Sulfated Zirconia, D	0.3 : 0.7	0.8 : 0.2

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3.6 Boiling range distribution

The boiling range distribution of the liquid product from catalytic cracking of used vegetable oil over various catalysts was determined by a simulated distillation gas chromatograph using the ASTM standard method D2787. The system consisted of VARIAN Model CP3800 gas chromatograph equipped with an automatic sampler, a flame ionization detector FID and a capillary column Model CP-SIL5CB internal diameter 0.25 mm Long 15 meter and film thickness 0.25 micron. Helium gas was obtained to a carrier gas at the flow rate of 1.5 μL/minutes, the split ration equal to 2. The oven temperature was programmed at a heating rate of 10°C /minutes in range of 30 – 320°C. Injector temperature at of 298 K. The column temperature or oven temperature consisted to 1 step temperature program. Liquid nitrogen was used a coolant to control the temperature from the initial of 30 °C in 0.01 minute which was program at constant heating rate at of 10°C /minutes to final temperature at 320 °C and constantly for 8.50 minutes. The gas chromatograph was calibrated by analyzing a mixture of normal paraffins with known boiling range. The sample of liquid product was prepared by dissolved 1 μL of liquid product into carbon disulfide CS_2 (analyze grade) to the volume of 100 ml.

Figure 3.6 Simulated Distillation Gas Chromatograph Varian CP-3800

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3.7 Gas composition analysis

The composition of the gas products were determined by gas chromatograph. The system consisted of a 3000Micro gas chromatograph equipped with a sampling loop and three columns. The detection of the separated components was performed using a flame ionization detector FID for hydrocarbon gases.

Figure 3.7 Micro Gas Chromatograph 3000MicroGC

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CHAPTER IV

RESULTS AND DISCUSSION

In this study, used vegetable oil was obtained from fried chicken processing from KFC fast food (Pat-pong branch, Bangkok, Thailand) during March 2004. AOCS 1993Ce2-66Ce1-62 method is American Oil Chemist Society's standard used to analyze the composition of fatty acid and physical properties were analyzed represented in table 4.1 and 4.2 respectively

Table 4.1 Comparison of the composition of used vegetable oil and fresh vegetable oil

Composition of fatty acid		Fresh oil	Used oil
C12:0	Lauric acid	1.58	0.32
C14:0	Myristic acid	1.35	0.93
C16:0	Palmitic acid	43.39	38.38
C18:0	Stearic acid	1.34	4.00
C20:0	Arachidic acid		0.34
Total saturated fatty acid		48.26	43.97
C16:1	Palmitoleic acid		0.25
C18:1	Oleic acid	41.00	45.59
C18:2	Linoleic acid	10.10	10.03
C18:3	Linolenic acid	0.41	0.16
Total unsaturated fatty acid		51.24	56.03

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Table 4.2 Comparison the physical properties of used vegetable oil and diesel fuels

Physical properties	**Used vegetable oil**	**Diesel fuels**
Specific gravity at 15.6 ^{o}C (g/ml) ASTM D1298	0.92	0.81 – 0.87
Viscosity at 40^{o}C (mm^2/s) ASTM D2270	44.56	1.8 – 4.1
Flash point (^{o}C) : ASTM D93	318	52
Pour point (^{o}C) : ASTM D97	6	10 – 16
Carbon residue (%) : ASTM D189	0.2305	0.05
Ash (%) : ASTM D482	0.0023	0.01

4.1 Performance of HZSM-5

4.1.1 The 2^4 Experimental Design

2^k experimental design is an effective method to determine how various reaction parameters affect the system. It is very useful in the primary experimental study when there are many factor effects to determine. The interesting parameters in the study for catalytic cracking of used vegetable oil over HZSM-5 are temperature, initial pressure of hydrogen gas, time of reaction, and weight of HZSM-5. For the two level factorial design, the yield of liquid product were defined as the response by a change in the level of these factors. The treatment combination in standard order can be written as (1), a, b, ab, c, ac, bc, abc, d, ad, bd, abd, cd, acd, bcd, and abcd. The experiments were designed to run a single replicate to obtain the response data as the yield of liquid product represented in Table 4.3

Table 4.3 Yield of liquid product from catalytic cracking of used vegetable oil over HZSM-5

Treatment	Factor				%yield of Liquid		Factor Level	
	A	B	C	D			Low (-)	High (+)
1	-	-	-	-	91.97	A (^oC)	400	430
2	+	-	-	-	75.77	B (bar)	10	20
3	-	+	-	-	91.18	C (min)	45	75
4	+	+	-	-	75.51	D (wt%)	0.05	0.1
5	-	-	+	-	78.23			
6	+	-	+	-	74.09			
7	-	+	+	-	77.97			
8	+	+	+	-	73.65			
9	-	-	-	+	89.48			
10	+	-	-	+	74.85			
11	-	+	-	+	89.98			
12	+	+	-	+	74.95			
13	-	-	+	+	77.18			
14	+	-	+	+	73.12			
15	-	+	+	+	75.25			
16	+	+	+	+	71.76			

The procedure to analyze the data from a single factorial design is providing through examination of a normal probability plot. The contrast constants for the 2^4 design were calculated and the normal probability plot is illustrated in Figure 4.1. From the normal probability plot, all of the effects that lie along the line are negligible, whereas larger effects deviate from the straight line. Therefore, the important effects that emerge from this analysis are the main effect of temperature (A), time of reaction (C), weight of HZSM-5 (D) and temperature-time of reaction interaction (AC) as define in table 4.3

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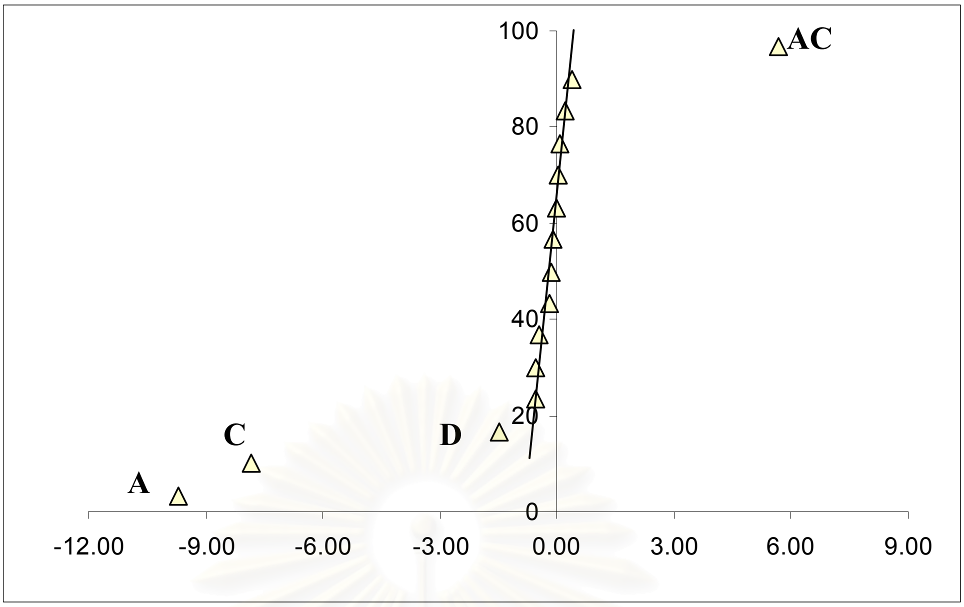

Figure 4.1 Normal probability plot

Figure 4.1 is a normal probability plot of the effects which shows the effect of temperature (A), time of reaction (C), %wt of HZSM-5 (D), and temperature-time of reaction interaction (AC) are significant to the catalytic cracking of used vegetable oil to liquid yield. The analysis of variance (ANOVA) display for this model is shown in Table 4.4 and the test statistic F_o shows the effect of temperature, time of reaction, %wt of HZSM-5, and temperature-time of reaction interaction are significant to liquid yield at 95 % confidence interval.

Table 4.4 Analysis of Variance for 2^k experimental design in catalytic cracking of used vegetable oil over HZSM-5

Source of Variation	Sum of Square	df	Mean Square	F_0	$F_{0.025,1,11}$
A	375.778	1	375.778	974.678	> 6.72
C	243.672	1	243.672	632.027	> 6.72
AC	129.504	1	129.504	335.903	> 6.72
D	8.702	1	8.702	22.572	> 6.72
Error	4.241	11	0.386		
Total	761.898	15			

4.1.2 Univariate study for the catalytic cracking of used vegetable oil to liquid fuels over HZSM-5

4.1.2.1 The effect of temperature

In order to investigate the extent of thermal cracking of used vegetable oil, a blank run was performed without the catalyst in the condition of 400 ^{o}C. Low conversion of used vegetable oil cracked was observed at temperature of 400 ^{o}C for the time of reaction of 60 minutes. When the experiments were conducted without catalyst usage, the amount of gaseous in the product distribution largely increased whereas the Gasoline fraction insignificant increased. The product yield without catalyst usage is summarized in figure 4.2. On the other hand, when HZSM-5 was introduced, the amount of gaseous in the reaction with catalyst usage decreased significantly

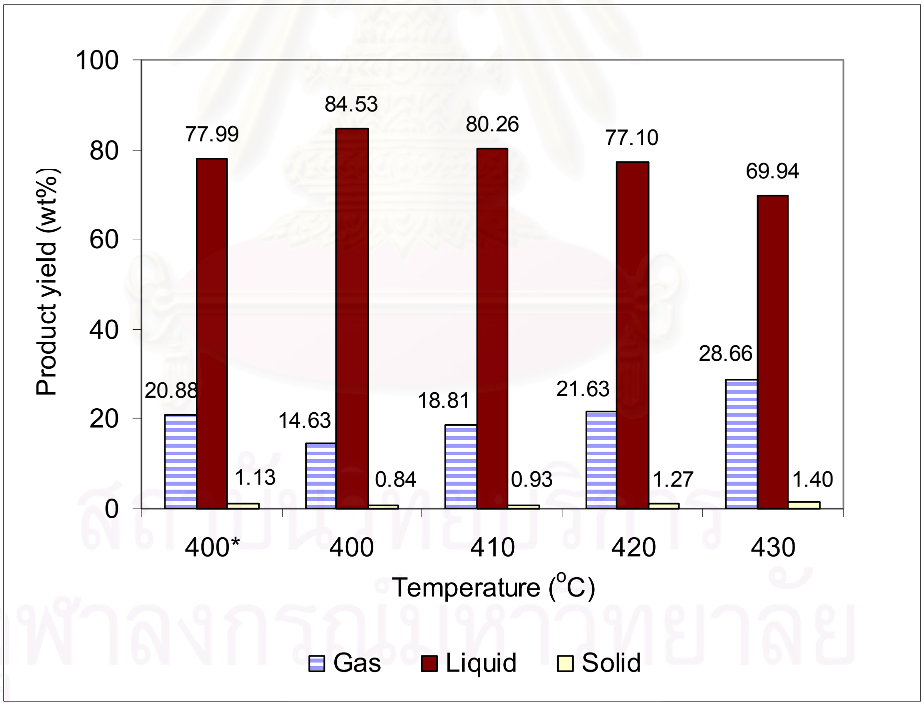

Figure 4.2 The effect of temperature on product yield where initial hydrogen pressure of 10 bar, reaction time 60 minutes over HZSM-5 and comparison to the product yield where without HZSM-5 ; (*) not use HZSM-5

The conversion of used vegetable oil in an empty catalyst at 400 °C pressure of hydrogen gas at of 10 bar and time of reaction of 60 minutes was about 20.88 wt%, 77.99 wt%, and 1.13 wt% in liquid product, gas product, and solid respectively. In addition, the liquid product gave the product distribution which determined from simulated distillation gas chromatograph about 6.74 wt% gasoline, 7.93 wt% of kerosene, 24.18 wt% of light gas oil, 15.02 wt% of gas oil and 24.12 wt% long residue

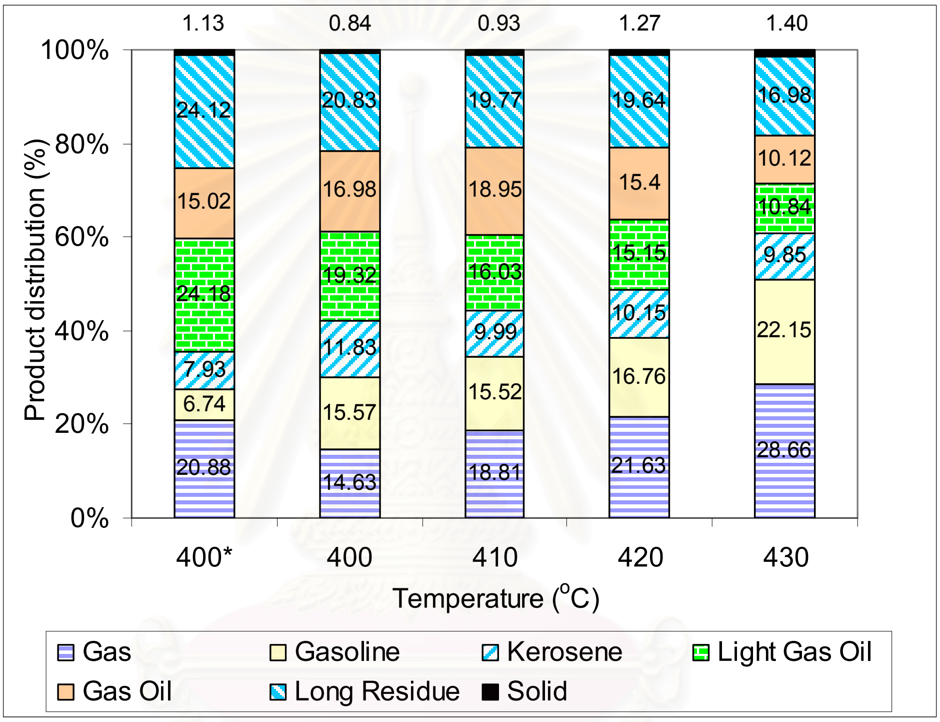

Figure 4.3 The effect of temperature on the product distribution where initial hydrogen pressure 10 bars, time of reaction 60 minutes over HZSM-5 ; (*) not use HZSM-5

The reaction of catalytic cracking over HZSM-5, the liquid yield was decreased with increase of temperature whereas the yield of Gasoline fraction increased with increase temperature. A possible reason for this behavior is that the higher temperature (400°C) accelerated the thermal cracking and hence changing the long chain of hydrocarbon molecule from thermal cracking into a middle hydrocarbon molecule such as Kerosene and diesel fraction. Thereafter Kerosene, Light Gas Oil and Gas Oil were catalytically cracked at the surface of HZSM-5, converting them into gasoline and gaseous (normally C_1-C_4). It can be identified as deoxygenation cracking and aromatization with H-Transfer from catalytic cracking processes, deoxygenation can occur from decarboxylation and dehydration regarding the primary cracking of triglyceride which assumed that the predominantly by occur within the internal pore structure which was reported by Kantikaneni (1996). In addition, Adjaye (1996) reported that when HZSM-5 was used as a catalyst at temperature to 410 ^{o}C, the liquid products consisted mostly of aromatic. HZSM-5 is able to converted all oxygenated compound to aromatic hydrocarbon. Therefore, the possibility is that the initial fragmentation can occur on the external surface of zeolite and followed by diffusion into the pore. The subsequent reaction such as cyclization, isomerization, hydrogen transfer leading the formation of aromatic hydrocarbon. On the contrary the total solids increased with the reaction time which meant that coking also occurred during the same reaction time. When the temperature reached to 430^{o}C, a large amount of gaseous products have been observed to increase substantially. It seemed that when higher temperature was used, light hydrocarbon could be cracked more, because thermal cracking was faster than catalytic cracking. The result of this effect showed that temperature of 430^{o}C gave the appropriate fraction of Gasoline, the liquid yield of 69.94 % was obtained with the composition of gasoline 22.15 wt%, kerosene 9.85 wt%, light gas oil 10.84 wt %, gas oil 10.12 wt% and long residue 16.98 wt% whereas the light gases by product of 28.66 wt% and solids of 1.40 wt% were obtained.

The amount of gaseous product increases with increasing temperature. For instant, the gaseous yield for HZSM-5 was 14.63 wt% at 400 ^{o}C for reaction time of 60 minutes and increased to 28.66 wt% at temperature of 430 ^{o}C for the reaction time of 60 minutes. Figure 4.4 shows the composition of the gaseous product. It consisted of C_1-C_4 hydrocarbon such as CH_4, C_2H_6, C_3H_8, C_4H_{10}, and CO_2.

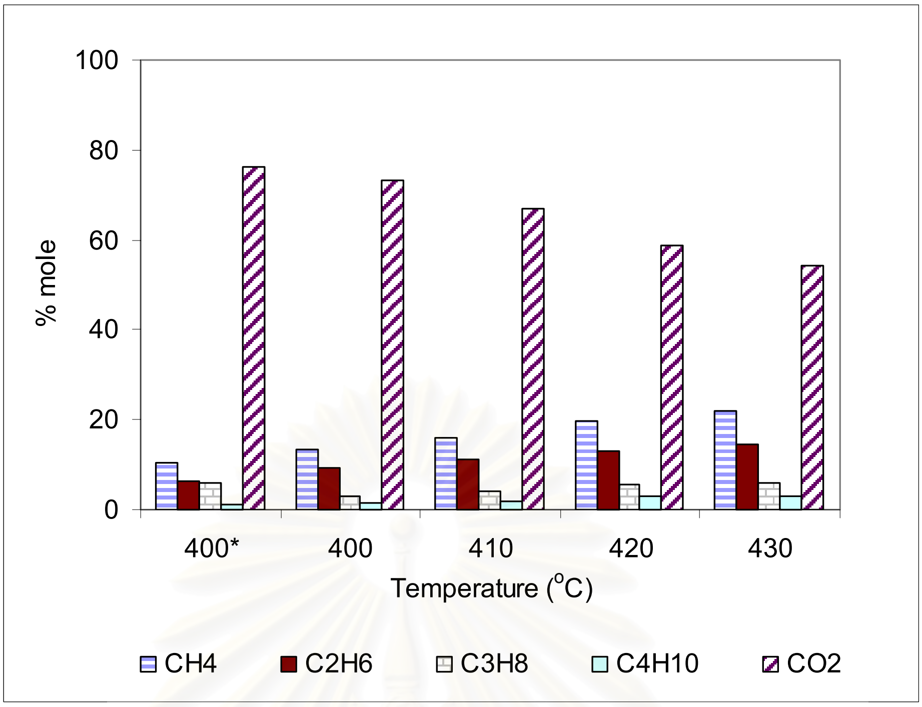

Figure 4.4 The effect of temperature on the fraction of gaseous product where initial hydrogen pressure of 10 bar, reaction time of 60 minute over 0.1 wt% of HZSM-5 ; (*) not use HZSM-5

Figure 4.4 shows the effect of temperature to the gaseous product, gaseous yield was increased with an increase of temperature. A possible reason for this behavior is that the higher temperature (400^{o}C) accelerated the thermal cracking and hence changing the long chain of hydrocarbon molecule from thermal cracking into a middle hydrocarbon molecule and light hydrocarbon molecules (Adjaye 1996). Thereafter light hydrocarbon molecules were thermally and catalytically cracked converting them into gaseous product. The results at temperature of 400 ^{o}C shown the composition of gaseous product consisted of CH_4, C_2H_6, C_3H_8, C_4H_{10}, and CO_2 at about 13.45, 9.17, 2.81, 1.40 and 73.17 %mole respectively. If the temperature was increased, the effect of thermal cracking was mainly significant to increase the light molecule and converted them to gaseous product. The composition of gaseous product at temperature of 430 ^{o}C, initial hydrogen pressure of 10 bars and reaction time of 60 minutes over 0.1 wt% of HZSM-5 obtained the composition of CH_4 22.03 %mole, C_2H_6 14.50 %mole C_3H_8 6.04 %mole, C_4H_{10} 3.10 %mole, and CO_2 54.33 %mole. Furthermore, the high concentration of CO_2 indicated that a significant fraction of oxygen from triglyceride fatty acid in used vegetable oil was removal from the effect of temperature in the first step as a result to produce CO_2. The step of oxygen removal was important for obtaining high hydrocarbons yield since the hydrogen content of the used vegetable oil was low. Therefore, the removal of oxygen as CO_2 were favorable for hydrocarbon formation and converted for long chain triglyceride to light hydrocarbon molecules compared to oxygen removal as H_2O.

4.1.2.2 The effect of initial hydrogen pressure

Figure 4.5 shows the effect of initial hydrogen pressure range of 10 – 30 bar comparison to blank run, without the pressure of hydrogen gas. It seems that initial hydrogen pressure is responsible to the catalytic cracking of used vegetable oil. It was noticed that when the pressure of hydrogen increasing from atmospheric pressure to 10 bar, the liquid yield was increased significantly from 64.22 wt% to 69.94 wt%. Whereas, the effect of variation of initial hydrogen pressure ranging from 10 – 30 bar was insignificant for liquid yield. At the temperature 430 ^{o}C initial hydrogen pressure of 10 bars and reaction time of 60 minute, gave the yield of liquid, gaseous, and solid of 69.94, 28.66, and 1.40 wt%, respectively.

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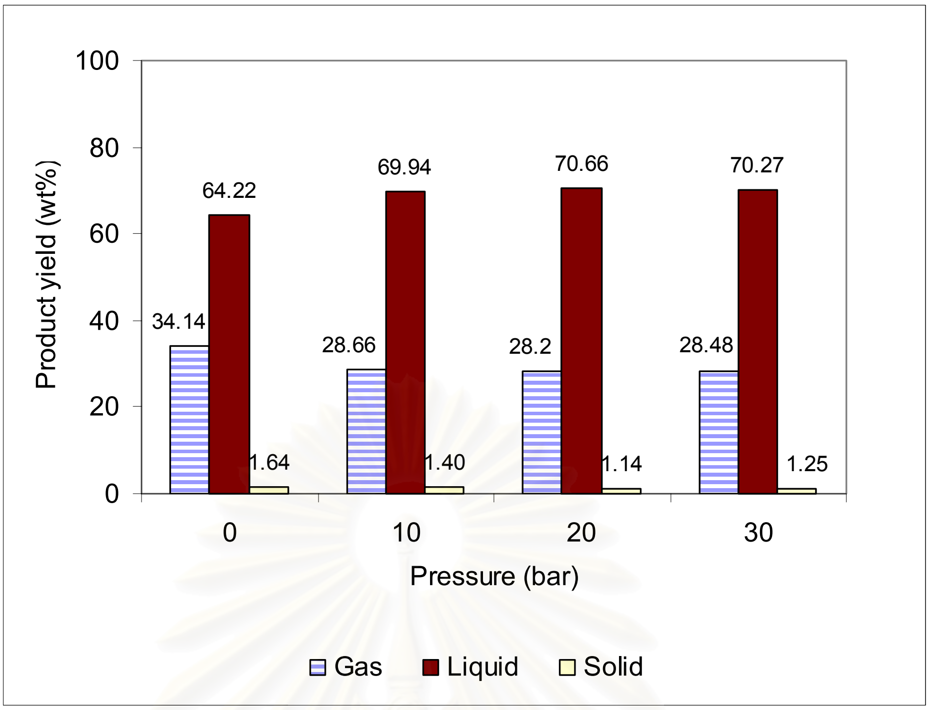

Figure 4.5 The effect of initial hydrogen pressure on product yield where temperature reaction time 60 minutes over HZSM-5

Figure 4.6 shows the effect of initial pressure of hydrogen gas on the products distribution. The catalytic cracking takes place very well by given the pressure of hydrogen. Normally HZSM-5 gave protons from the structural surface of HZSM-5 to the long chain hydrocarbon for cracking and this hydrogen compensated at the surface by hydrogen feed (Adjaye 1996, and Twaiq 1999). But the effect of initial hydrogen pressure was insignificant for the product distributuion. The initial hydrogen pressure was responsible for the catalytic cracking step. It was noticed that when the pressure was increased, the yields gasoline, kerosene, light gas oil, and solid small also increased. In both cases the initial pressure was high enough so that similar results were reached. It seemed that pressure of 10 bars was enough to gave gasoline fraction amounting to 22.15%, while kerosene 9.85 wt%, light gas oil 10.84 wt%, gas oil 10.12wt%, long residue 16.98 wt% were obtained

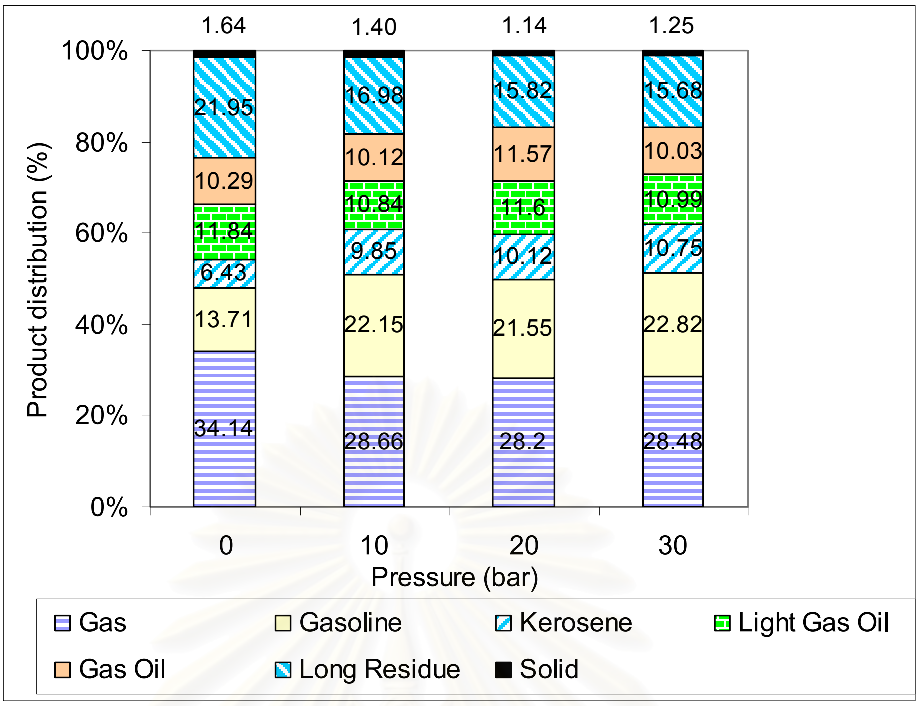

Figure 4.6 the effect of initial hydrogen pressure on the product distribution where temperature of 430 °C, time of reaction 60 minutes over HZSM-5

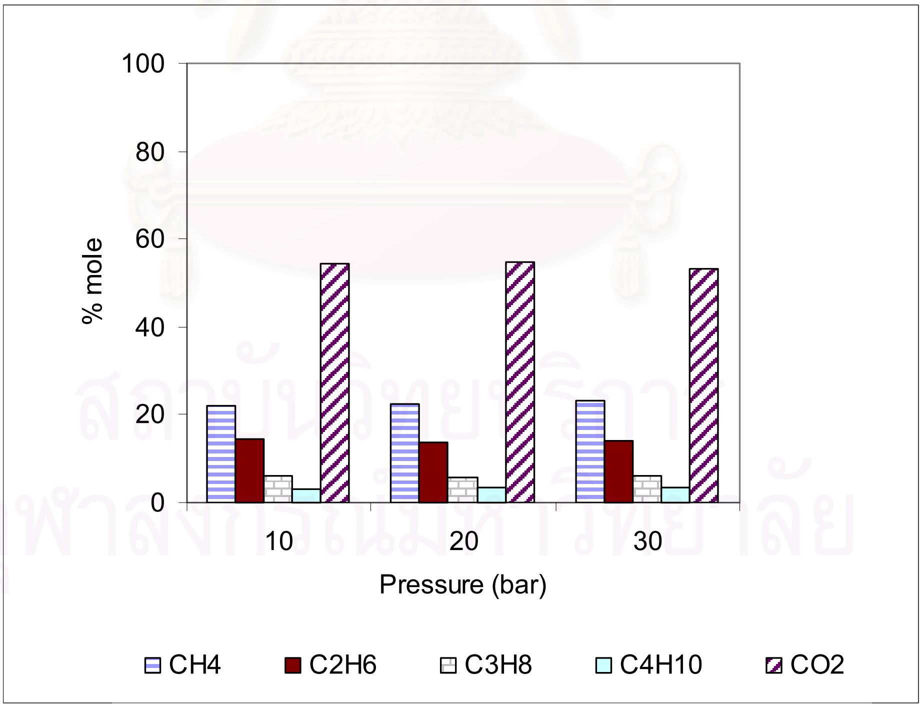

Figure 4.7 The effect of initial hydrogen pressure on the composition of gaseous product where temperature of 430 °C, reaction time of 60 minute over 0.1 wt% of HZSM-5

The effect of initial hydrogen pressure in the catalytic cracking of used vegetable oil to liquid fuels gave the gaseous product of 28.66 %wt. The gaseous composition shows in Figure 4.7, it consisted of C_1 – C_4 hydrocarbon and CO_2. While, CO_2, CH_4, and C_2H_6 were major product at temperature of 430 ^oC, initial pressure of 10 bars, time of reaction at 60 minutes gave the composition of CO_2, CH_4, and C_2H_6 at amount 54.33, 22.03, and 14.5 %mole respectively. It seemed that the compositions of gaseous produced were the same in variation of initial hydrogen pressure ranging of 10 - 30 bars. The results show that the effect of initial hydrogen pressure was insignificantly to the product distribution and gaseous compositions.

4.1.2.3 The effect of reaction time

Time of reaction contributed mainly to the liquid yield and product distribution, Figure 4.8 shows that the yield of liquid was increased with increasing reaction time from 45 – 60 minutes and decreased with increasing reaction time from 75 – 90 minutes. It seems that in the first of reaction, used vegetable oil begins crack and undergoes more cracking when the reaction time is continues, and hence, the light hydrocarbon molecules were produced in greater from the effect of thermal cracking (Adjaye 1996, and Twaiq 1999). If time of reaction si short, the product distribution probably shifted to heavier hydrocarbon molecules and the reaction for this could be the new arrangement of the hydrocarbon structure due to cross-linking after the reaction at low temperature and short time of reaction (Manos 2002). Hence, at the condition of 400 ^oC reaction time of 10 to 30 minutes found the product like bitumen. When the time of reaction is continued the liquid yield which consisted of the fraction of light hydrocarbon was continued cracking to the gaseous product. Hence, the gaseous product increased with increasing the time of reaction. The yield of liquid product was decreased from 76.37 wt% to 62.76 wt% in ranging of increased the reaction time of 45 minutes to 90 minutes

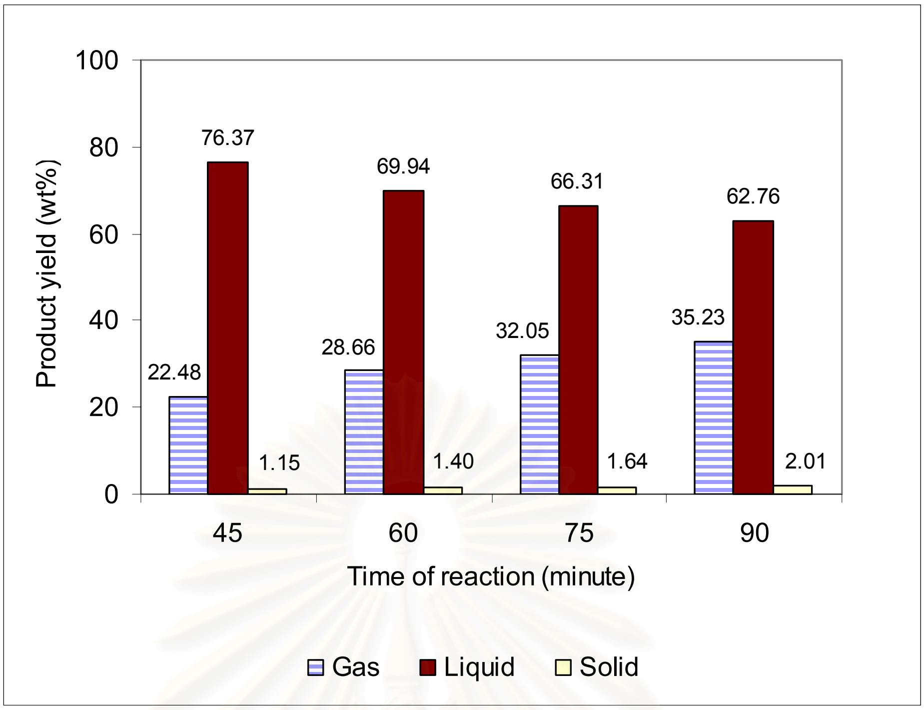

Figure 4.8 The effect of time of reaction on the yield where temperature 430 °C initial pressure of hydrogen gas 10 bars over HZSM-5

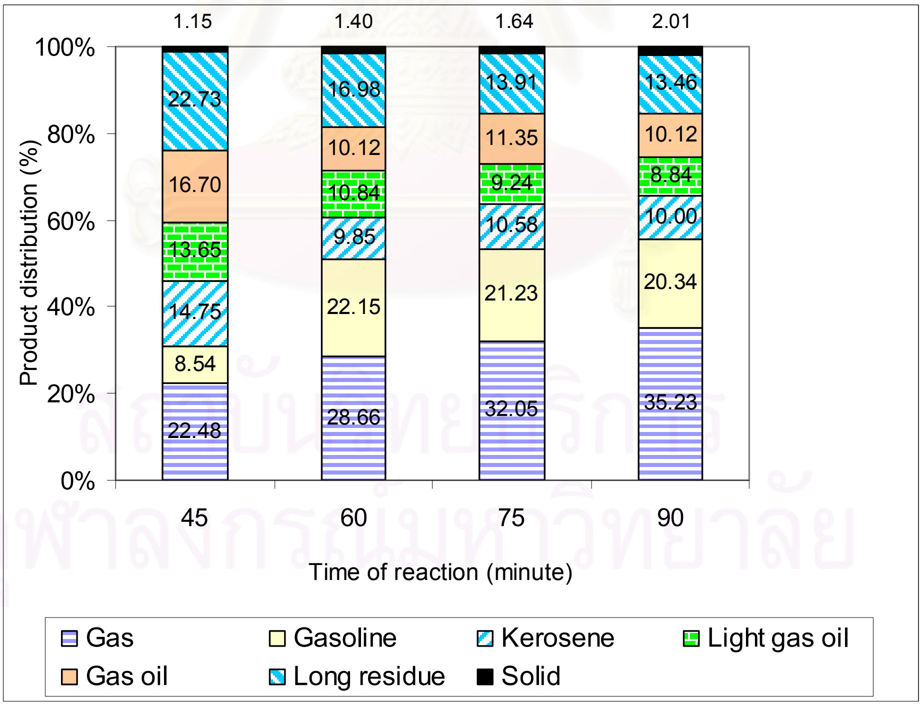

Figure 4.9 The effect of reaction time to the product distribution where temperature of 430 °C initial pressure of hydrogen gas 10 bars over HZSM-5

Figure 4.9 shows the effect of reaction time on the product distribution. It seemed that temperature was mainly affecting the thermal cracking of long chain hydrocarbon molecules into light molecules and continued cracking led to light hydrocarbon gaseous with increasing the reaction time. The result of increase reaction time shows that the gaseous products increased whereas the product distribution such as Gasoline, Kerosene, Light Gas Oil and Gas Oil decreased. The time of reaction was found to favor aromatic hydrocarbon formation and leading to formation of light gaseous predominant (Adjaye 1996, and Twaiq 1999) the effect of reaction time shows the results in greater amount of aromatic and Gasoline boiling range fraction also increased with increase in reaction temperature reached a maximum at 430 °C and gave later decrease. Furthermore, the gasoline fraction represents the boiling range 0 – 200 °C fraction which was increased with increase in the reaction of time from 45 to 60 minutes and was dropped at the time of reaction more than 60 minutes. At the conditions of temperature 430°C, initial hydrogen pressure of 10 bars and reaction time of 60 minutes, the liquid yield of 69.94 % was obtained with the composition of gasoline 22.15%, kerosene 9.85%, light gas oil 10.84%, gas oil 10.12% and long chain hydrocarbon molecule 16.98% whereas the light gaseous products of 28.66 % and solids of 1.40 % were obtained.

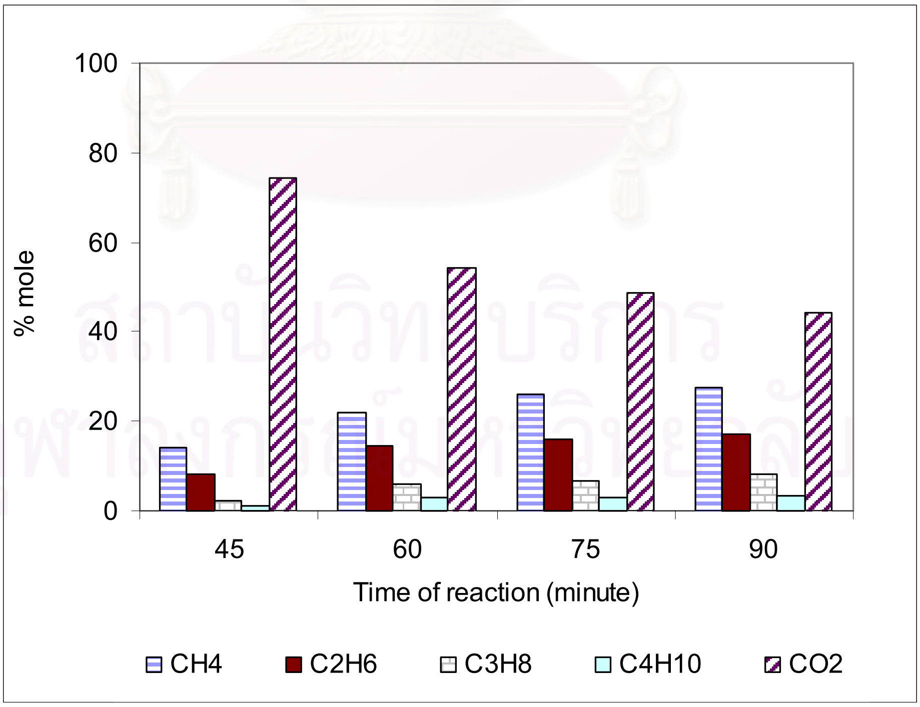

Figure 4.10 The effect of time of reaction on the composition of gaseous product where temperature of 430 °C initial hydrogen pressure of 10 bar, over 0.1 wt% of HZSM-5

The yield of gaseous product increased monotonically with temperature from the effect of thermal cracking and catalytic cracking to light hydrocarbon molecule. The effect of temperature was significantly effect on liquid product and gas yield. Where the time of reaction was continued, the temperature affected to cracking small hydrocarbon molecule to the gases. The gaseous products consisted mostly C_1-C_2 and CO_2. As can be seen, the CH_4 yield increased dramatically with increasing time of reaction ranging from 45 minutes to 90 minutes, it is noticeable that thermal cracking and catalytic cracking were affected to light hydrocarbon gases. If the reaction time continues, they will crack to small hydrocarbon gases and increased continuously with increase the time of reaction. At the temperature of 430 ^oC, initial pressure of 10 bars and time of reaction at 60 minutes, the catalytic cracking of used vegetable oil to liquid fuels gave the composition of gaseous products which consisted of CH_4 22.03 %mole, C_2H_6 14.5 %mole, C_3H_8 6.04 %mole, C_4H_{10} 3.1 %mole and CO_2 54.33 %mole

4.1.2.4 The effect of the mass of HZSM-5

The investigate of catalytic cracking of used vegetable oil in an empty catalyst at 430 ^oC, pressure of hydrogen gas at of 10 bar and time of reaction of 60 minutes was about 36.63 wt%, 61.69 wt%, and 1.68 wt% in liquid product, gas product, and solid respectively. It seems that the effect of temperature mainly removed CO_2 from triglyceride fatty acid and cracked long chain hydrocarbon to the middle molecule and continuously cracked to light hydrocarbon gases. Whereas using variation of the mass of %wt HZSM-5 shows the trend of gaseous yield increased with increasing the mass of %wt HZSM-5 ranging of 0.05 – 0.2 wt% Hence, the mass of HZSM-5 in the catalytic cracking was significant on the yield of gases is due to the acid sites in the catalyst promotes the cracking reactions responsible for the formation of gaseous product. In addition, the light hydrocarbon molecules from thermal and catalytic cracking were converted to light gases. The yield of gas, liquid, and solid shows in Figure 4.11

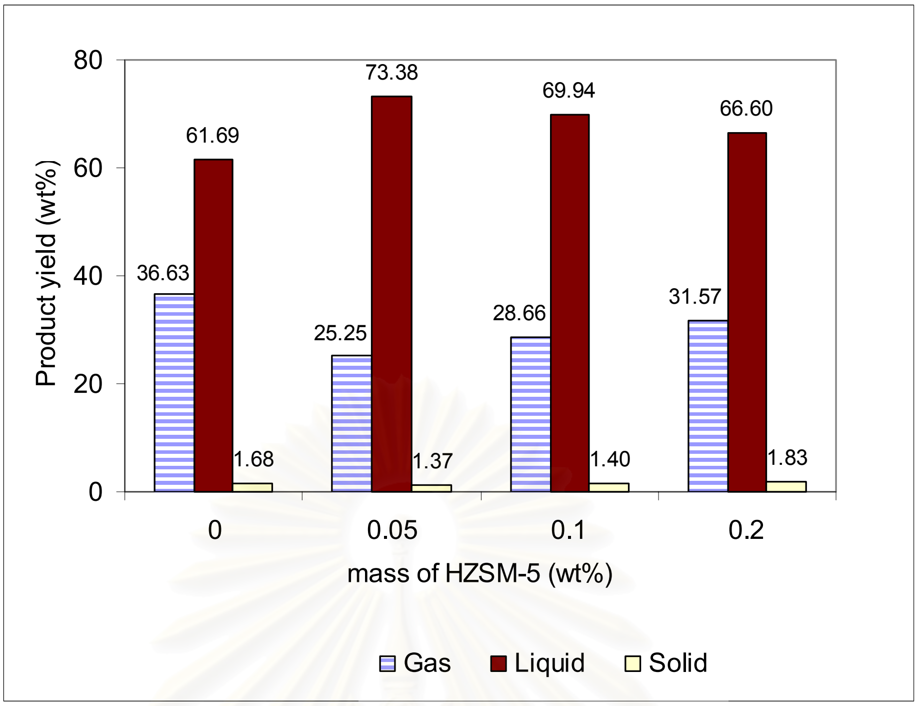

Figure 4.11 The effect of the mass of HZSM-5 on the yield where temperature 430 °C initial hydrogen pressure of 10 bars and reaction time of 60 minutes

The product distribution which was determined from simulated distillation gas chromatograph about 22.15 wt% gasoline, 9.85 wt% of kerosene, 10.84 wt% of light gas oil, 10.12 wt% of gas oil and 16.98 wt% long residue for the run of temperature of 430 °C, initial hydrogen pressure of 10 bar and time of reaction of 60 minute over the mass of HZSM-5 of 0.1 wt%. The effect to mass of catalyst from ranging of 0.05 – 0.2 %wt shows the difference of fraction of gasoline, kerosene, and long residue. A possible reason for this behavior is that the mass of HZSM-5 may correlation to the HZSM-5 concentration. Hence, HZSM–5 concentration increases the selectivity to gasoline fraction increases while that of long residue decreases, with the exception of the light gas oil and gas oil which presented a small increase in the selectivity. Therefore, an increase in the mass of HZSM-5 increased the acid sites in the catalyst promotes the cracking reactions, and also responsible for the formation of gaseous products. High concentration of HZSM–5 in the catalyst is in effect equivalent to an increase in the contact time of the reactants and products distribution with the acid sites and is therefore contrary to the liquid yield preservation. The selectivity increase toward the

Gasoline fraction at high zeolite contents can be due to the formation of these products, which is favored at high HZSM-5 contents. Furthermore, this results relatively an increase in the number of zeolite acid site in the catalyst promotes the cracking reaction responsible for the formation of light hydrocarbon molecule which was reported by Gonzalez. (2001) The condition of reaction at temperature of 430 °C, initial pressure of 10 bar, time of reaction of 60 minutes over 0.2 wt% of HZSM-5 gave the highest gasoline fraction of 24.84 wt% But it also small increased compared with used 0.1 wt% of HZSM-5. Therefore, the catalytic cracking of used vegetable oil over 0.1 wt% HZSM-5 was enough to gave gasoline fraction amounting 22.15 wt% while, kerosene 9.85 wt%, light gas oil 10.84 wt%, gas oil 10.12 wt%, and long residue 16.98 wt% were obtained.

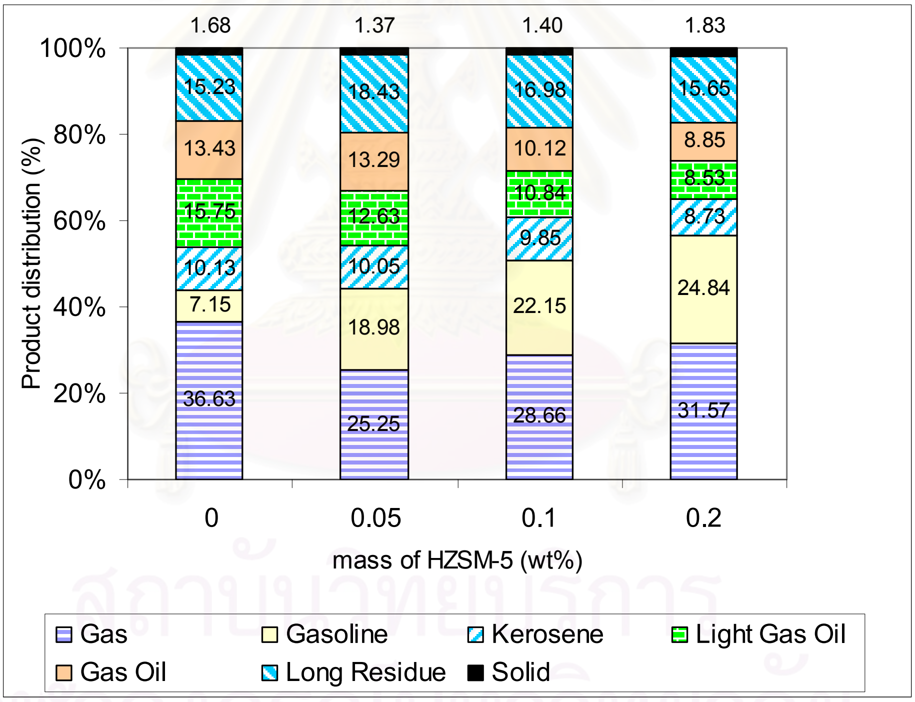

Figure 4.12 The effect of the mass of HZSM-5 on the product distribution where temperature 430 °C initial hydrogen pressure of 10 bars and reaction time of 60 minutes

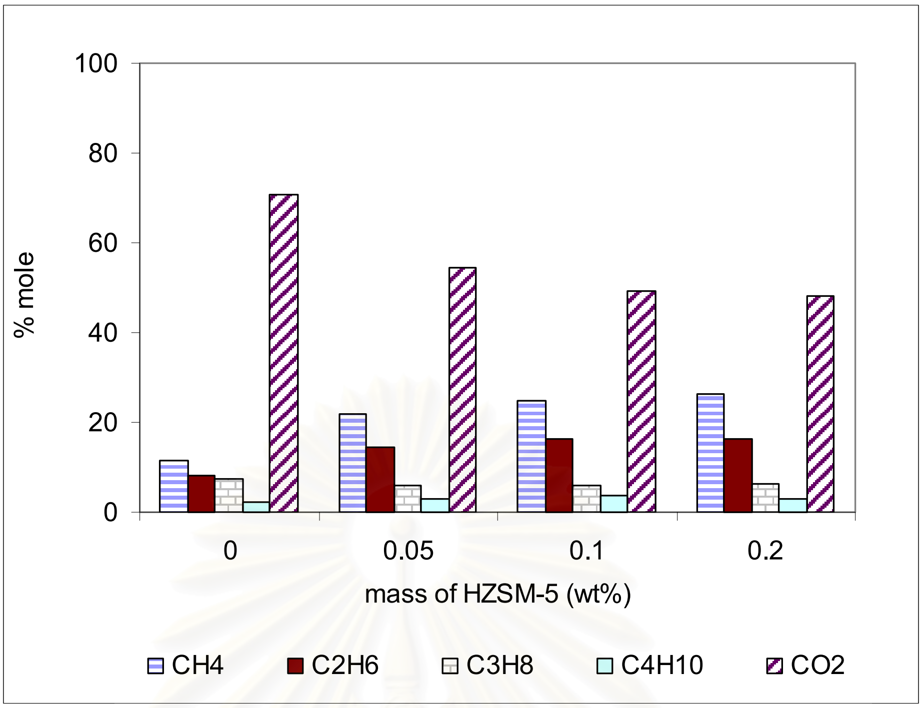

Figure 4.13 The effect of the mass of HZSM-5 on the composition of gaseous product where temperature 430 °C, initial hydrogen pressure of 10 bars and reaction time of 60 minutes

Figure 4.13 shows the gaseous product obtained with increased the mass of HZSM-5 consisted of a high composition of CH_4, C_2H_6, and CO_2. Initially, CO_2 was removed from the fatty acid in the first step of cracking reaction. The composition of small hydrocarbons gases, CH_4 increased dramatically with the mass of HZSM-5 increasing and ranging of 0.05 – 0.1 wt% and small change where concentration of HZSM-5 of 0.2 wt%. Thus, the HZSM-5 concentration with high are probably able to crack small molecule and light hydrocarbon gases to CH_4 easier than low concentration of catalyst The gaseous composition for the reaction at temperature of 430 °C, initial hydrogen pressure of 10 bar, time of reaction of 60 minutes over 0.1 wt% of HZSM-5 contained 24.88 wt% CH_4, 16.12 wt% C_2H_6, 5.95 wt% C_3H_8, 3.81 wt% C_4H_{10} and 49.24 wt% CO_2

4.2. Performance of Sulfated Zirconia

4.2.1 The 2^4 Experimental Design

2^k experimental design is used to investigate the interesting parameters in the performance of Sulfated Zirconia, which are temperature, initial hydrogen pressure, time of reaction, and the mass of Sulfated Zirconia. For the two level factorial design, the yield of liquid product were defined as the response by a change in the level of these factors. The experiments were designed to obtain the response data as the yield of liquid product represented in Table 4.4

Table 4.4 Yield of liquid product from catalytic cracking of used vegetable oil over Sulfated Zirconia

Treatment	Factor				%yield of Liquid		Factor Level	
	A	B	C	D			Low (-)	High (+)
1	-	-	-	-	93.75	A (°C)	400	430
2	+	-	-	-	78.79	B (bar)	10	20
3	-	+	-	-	92.34	C (min)	45	75
4	+	+	-	-	79.05	D (wt%)	0.05	0.1
5	-	-	+	-	84.85			
6	+	-	+	-	75.48			
7	-	+	+	-	82.94			
8	+	+	+	-	73.03			
9	-	-	-	+	92.34			
10	+	-	-	+	76.38			
11	-	+	-	+	90.99			
12	+	+	-	+	78.94			
13	-	-	+	+	82.08			
14	+	-	+	+	75.37			
15	-	+	+	+	80.91			
16	+	+	+	+	72.03			

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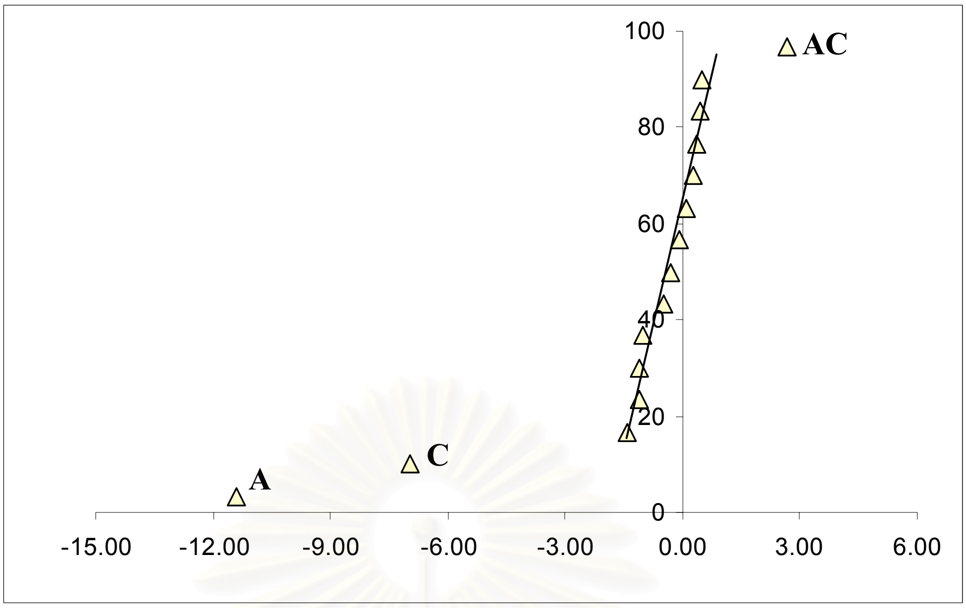

Figure 4.14 Normal probability plot for the effect estimated for catalytic cracking over Sulfated Zirconia

Table 4.5 Analysis of Variance of the experiment

Source of Variation	Sum of Square	df	Mean Square	F_0	$F_{0.025,1,12}$
A	519.042	1	519.042	240.823	> 6.55
C	195.231	1	195.231	90.582	> 6.55
AC	28.596	1	28.596	13.268	> 6.55
Error	25.863	12	2.155		
Total	768.732	15			

A normal probability plot and the analysis of variance were obtained from the 2^k experimental design, The contrast constants for the 2^4 design were calculated and the normal probability plot represented in Figure 4.14, which shown the larger effects deviate from the straight line. Therefore, the important effects that emerge from this analysis are the main effect of temperature (A), time of reaction (C), and temperature-time of reaction interaction (AC), whereas the mass of Sulfated Zirconia is negligible The ANOVA shown in Table 4.5 and the test statistic F_o shows the effect of temperature, time of reaction, and temperature-time of reaction interaction are significant to liquid yield at 95 % confidence interval.

4.2.2 Univariate study for the catalytic cracking of used vegetable oil to liquid fuels over Sulfated Zirconia

4.2.2.1 The effect of temperature

This observed the product yield for the thermal cracking of used vegetable oil, which performed without Sulfated Zirconia at the condition of 400 ^{o}C. initial pressure of 10 bar, and time of reaction of 60 minutes. The result shows that the amount of gases in the product yield largely increased while comparison where used Sulfated Zirconia gave lower gaseous product. A possible reason of these results could be claimed that the effect of temperature in thermal cracking was significantly in the first step of cracking to remove CO_2 from triglyceride. At the condition without used Sulfated Zirconia were obtained gaseous, liquid, and solid yield of 20.88 wt%, 77.84 wt%, and 1.28 wt% respectively and the product distribution which SIMDIS analyzed were consisted of gasoline 6.74 wt%, kerosene 7.78 wt%, light gas oil 24.18 wt%, gas oil 15.02 wt%, and long residue 24.12 wt%

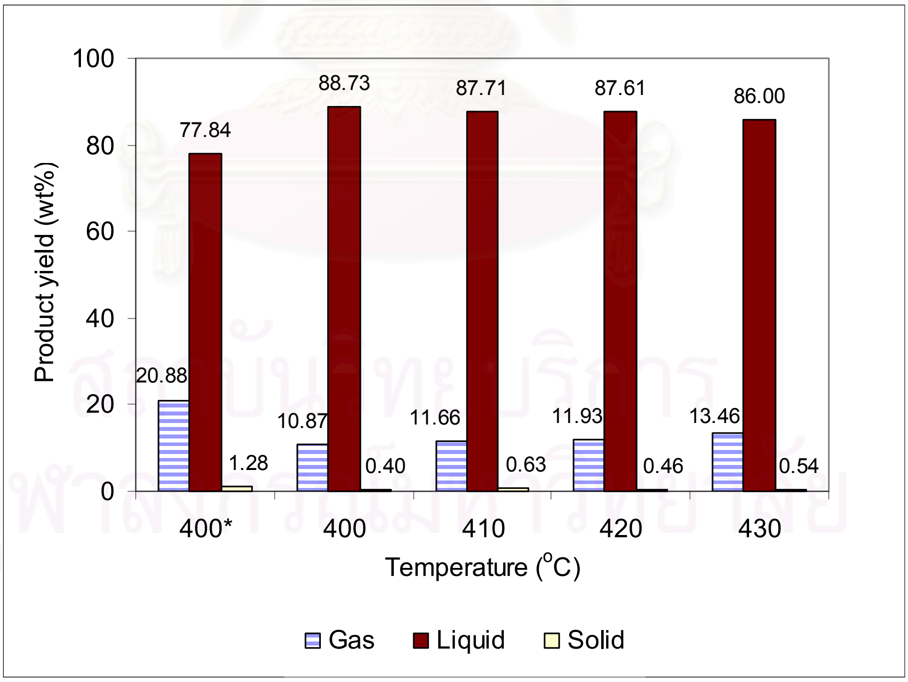

Figure 4.15 The effect of temperature on product yield where initial hydrogen pressure of 10 bar, reaction time 60 minutes over Sulfated Zirconia and comparison on the product yield where without Sulfated Zirconia; (*) not use Sulfated Zirconia

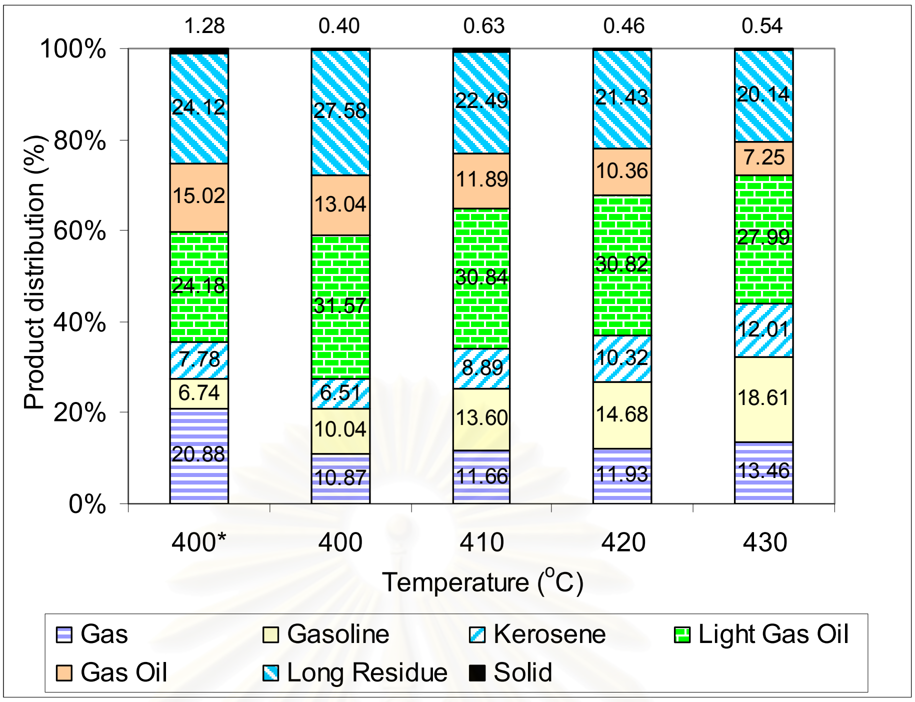

Figure 4.16 The effect of temperature on the product distribution where initial pressure 10 bars, time of reaction 60 minutes over Sulfated Zirconia; (*) not use Sulfated Zirconia

For the effect of catalytic cracking over Sulfated Zirconia, the liquid yield was decreased with increase of temperature whereas the yield of gasoline fraction increased with increase temperature. A possible reason for this behavior is that the higher temperature (400°C) accelerated the thermal cracking and hence changing the long chain of hydrocarbon molecule from thermal cracking into a middle hydrocarbon molecule. Thereafter kerosene, light gas oil and gas oil were catalytically cracked at the surface of Sulfated Zirconia, converting them into light hydrocarbon fraction and gases. It can be identified as deoxygenation cracking with H-Transfer from the properties of metal support catalyst over Sulfated Zirconia in catalytic cracking processes (Jiang 2002).The subsequent reaction such as isomerization, cyclization, and hydrogen transfer leading the formation of aromatic hydrocarbon. (Jaing 2002, and Zhou 2003) At the temperature of 430°C, a large amount of gaseous products have been observed. It seemed that when higher temperature was used, light hydrocarbon could be cracked continually. The result of this effect showed that temperature of 430°C gave the appropriate fraction of gasoline. The product yield consisted of 13.46 %wt of gases, and 0.54 wt% of solid. In addition 86.00 wt% liquid product was obtained. The composition of gasoline 18.61 wt%, kerosene 12.01 wt%, light gas oil 27.99 wt%, gas oil 7.25 wt% and 20.14 wt% of long residue. Furthermore, the gaseous product increases with increasing temperature. At the temperature of 430 °C, initial hydrogen pressure of 10 bars for the reaction time of 60 minutes. Figure 4.17 shows the composition of the gaseous product. It consisted of mainly C_1-C_4 hydrocarbon such as CH_4, 18.15 %mole, C_2H_6 9.15 %mole, and CO_2 64.33 %mole

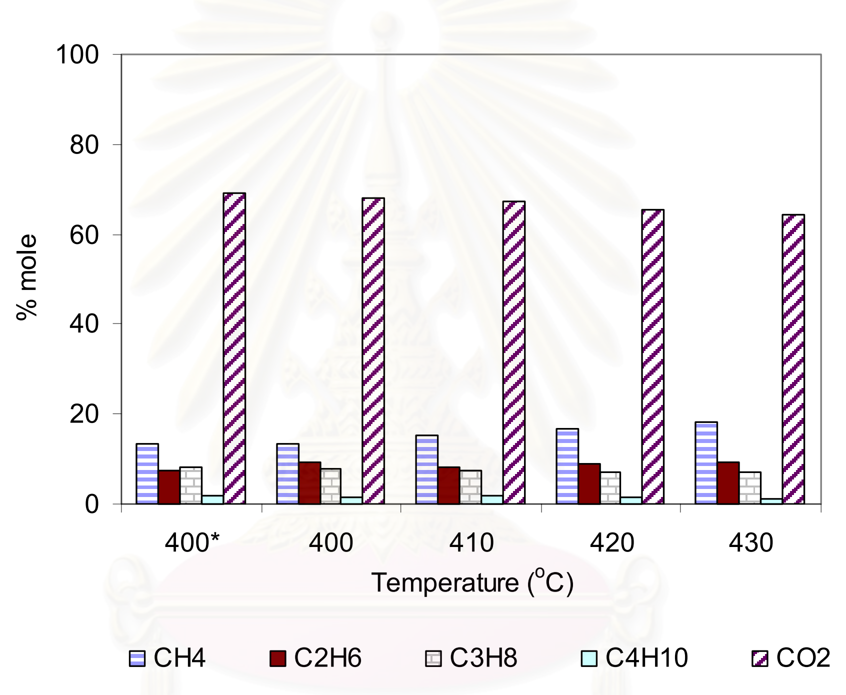

Figure 4.17 The effect of temperature to the fraction of gaseous product where initial hydrogen pressure of 10 bar, reaction time of 60 minute over 0.1 wt% of Sulfated Zirconia; (*) not use Sulfated Zirconia

4.2.2.2 The effect of initial hydrogen pressure

Figure 4.18 shows the effect of initial hydrogen pressure ranging of 10 – 30 bars compare to the blank run, without the pressure of hydrogen gas. It seems that initial hydrogen pressure is responsible to the catalytic cracking of used vegetable oil. It was noticed that when the pressure of hydrogen increasing from atmospheric pressure to 10 bar, the liquid yield was increased significantly from 64.92 wt% to 86.00 wt%. On the contrary, the effect of variation of initial hydrogen pressure ranging from 10 – 30 bars was insignificant with increasing pressure. At the temperature 430 °C initial hydrogen gas of 10 bars and reaction time of 60 minute, gave the yield of liquid, gases, and solid of 13.46, 86.00, and 0.54 wt% respectively.

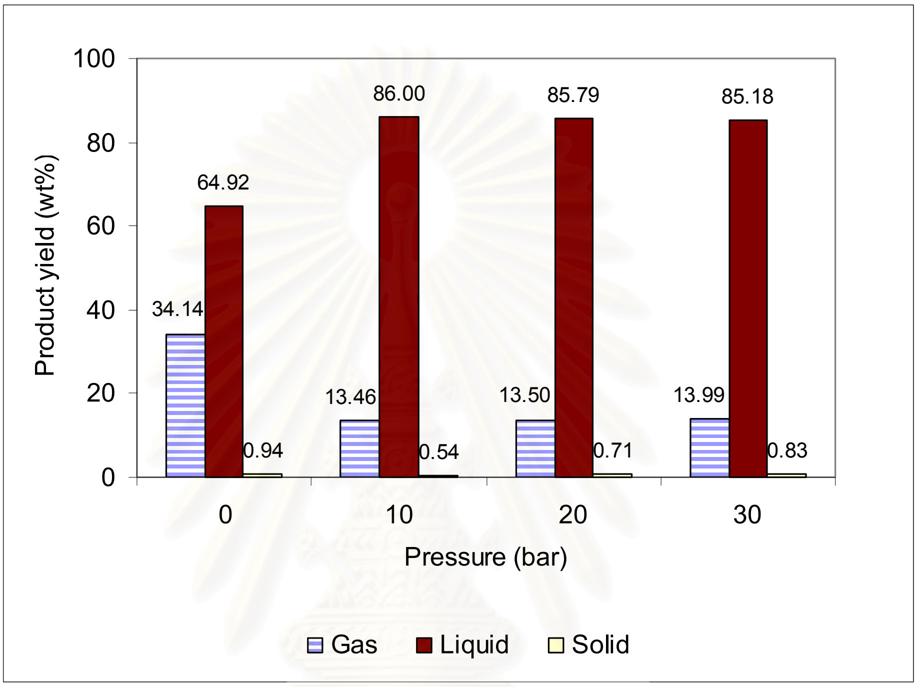

Figure 4.18 The effect of variation of initial hydrogen pressure on product yield where temperature reaction time 60 minutes over Sulfated Zirconia

Figure 4.19 shows the effect of initial pressure of hydrogen gas on the products distribution. The catalytic cracking takes place very well by given the pressure of hydrogen. Normally Sulfated Zirconia gave protons from the structural surface of metal support catalyst to the long chain hydrocarbon for cracking and this hydrogen compensated at the surface by hydrogen feed.(Jaing 2002, and Hamache 2003) But the effect of initial hydrogen pressure was insignificant with increasing pressure. The initial hydrogen pressure was responsible for the catalytic cracking step and hydrogenation and hydrocracking were possible to the cracking and rearrangement of light hydrocarbon molecule. Thus, the yields Gasoline, Kerosene, Light Gas Oil, and solid small also increased with pressure increasing. 10 bars of initial hydrogen pressure was high enough to gave Gasoline fraction amounting to 18.61 wt% of gasoline, 12.01 wt% kerosene, 27.99 wt% light gas oil, 7.25 wt% gas oil, and 20.14 wt% of long residue.

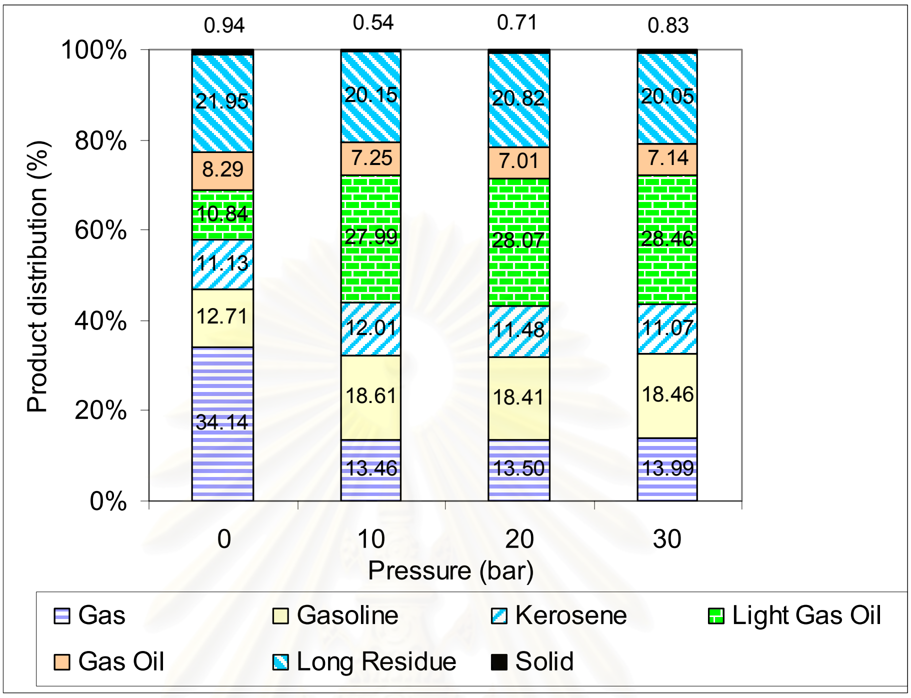

Figure 4.19 The effect of initial hydrogen pressure on the product distribution where temperature of 430 °C, time of reaction 60 minutes over Sulfated Zirconia

In order to study the effect of initial hydrogen pressure on the gaseous product, 13.46 wt% of gaseous products consisted of CO_2, CH_4, and C_2H_6 at amount 54.33, 22.03, and 14.5 %mole respectively. It seems that the compositions of gaseous product are the same in variation of initial hydrogen pressure ranging of 10 - 30 bars. The results show that the effect of initial hydrogen pressure was insignificantly to the product distribution and gaseous compositions.

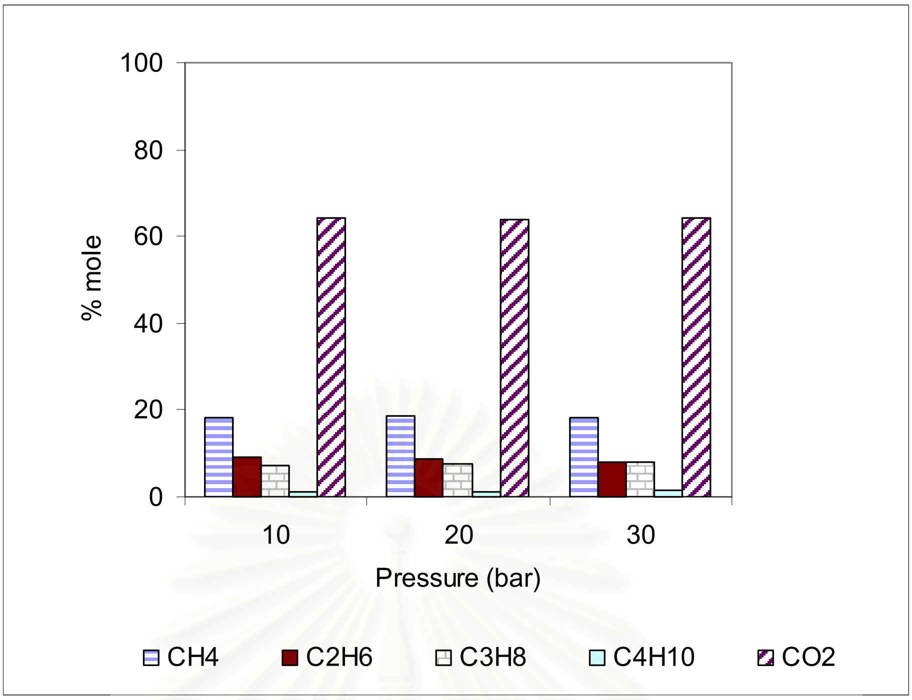

Figure 4.20 The effect of initial hydrogen pressure to the composition of gaseous product where initial hydrogen pressure of 10 bar, reaction time of 60 minute over 0.1 wt% of Sulfated Zirconia

4.2.2.3 The effect of reaction time

Time of reaction contributed mainly to the liquid yield and product distribution, the yield of liquid also small decreased with the reaction time ranging from 45 minute to 60 minutes and dropped with reaction time from 75 – 90 minutes. As the results are claimed that used vegetable oil begins crack and undergoes more cracking when the reaction time is continues. Therefore, the light hydrocarbon molecules were produced from the effect of thermal cracking. When the time of reaction is continued the liquid yield which consisted of the fraction of light hydrocarbon was continued cracking to the gaseous product. On the contrary, the results as confirmed that the gases were produced dramatically increased with increasing the time of reaction. The product yield was shown in Figure 4.21

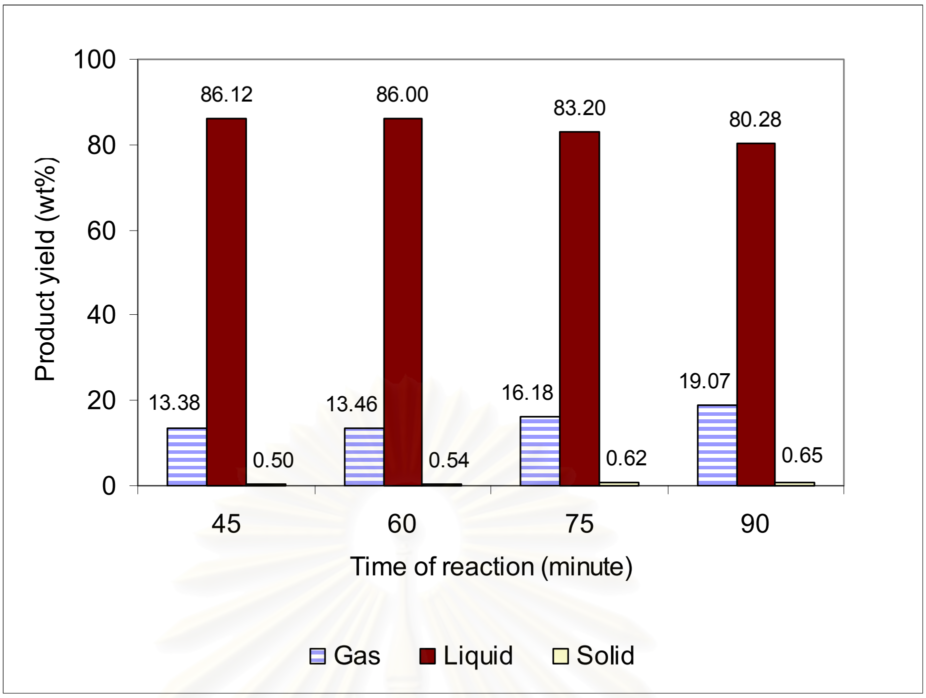

Figure 4.21 The effect of time of reaction on the yield where temperature 430 °C initial hydrogen pressure 10 bars over Sulfated Zirconia

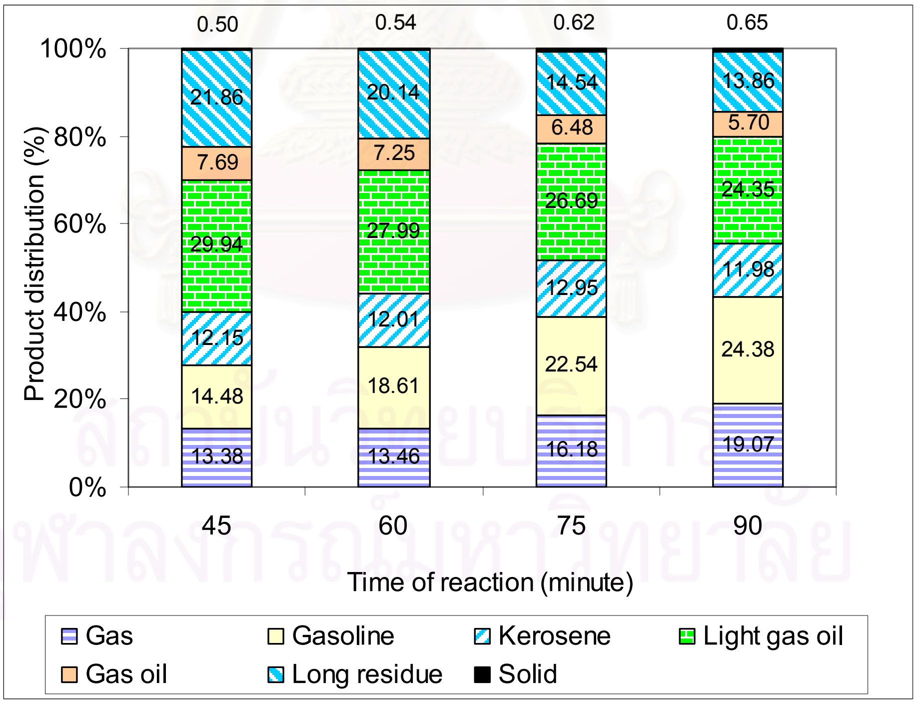

Figure 4.22 The effect of reaction time to the product distribution where temperature of 430 °C initial hydrogen pressure 10 bars over Sulfated Zirconia

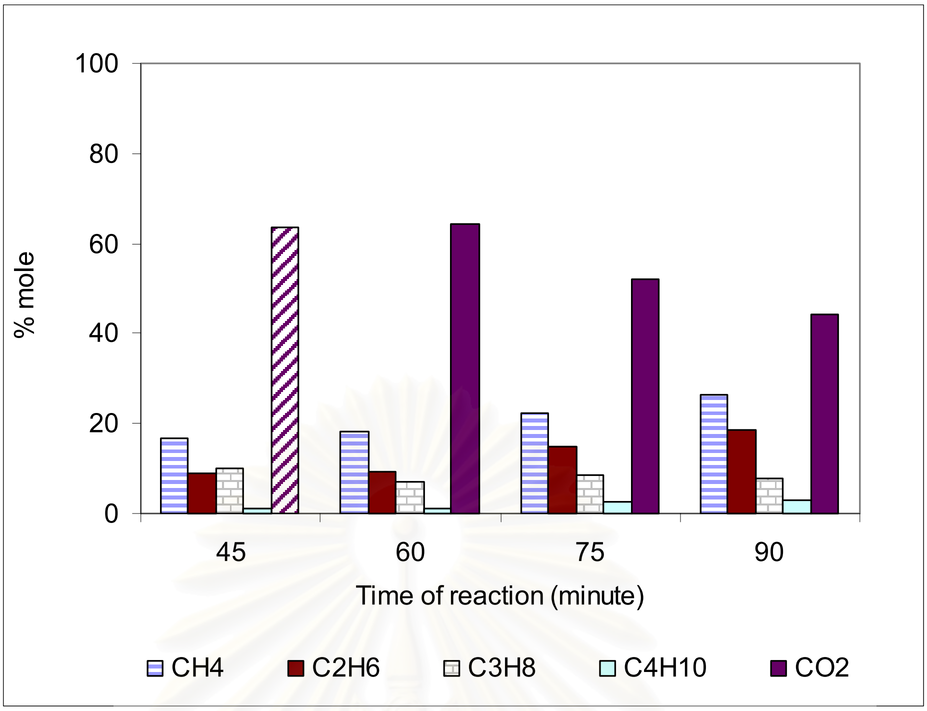

Figure 4.23 The effect of time of reaction to the composition of gaseous product where temperature of 430 °C initial hydrogen pressure of 10 bar, over 0.1 wt% of Sulfated Zirconia

Figure 4.22 shows the effect of reaction time on the product distribution. It seemed that the temperature also mainly significant affecting the conversion of long chain hydrocarbon molecules into light molecules and continued cracking led to light hydrocarbon gases with increasing the reaction time. The result of increase reaction time shows that the gaseous products increased whereas the product distribution such as kerosene, light gas oil and gas oil decreased. The time of reaction was found to favor aromatic hydrocarbon formation and leading to formation of light gases predominant, the effect of reaction time shows the results in greater amount of aromatic and gasoline boiling range fraction also increased with increase in reaction temperature reached a maximum at 430 °C and gave later decrease. Furthermore, the gasoline fraction represented the boiling range 0 – 200 °C which was increased with the reaction of time was continued. These results show that, in termed of optimum yield and product distribution, at the reaction time of 90 minute, temperature of 430 °C, initial hydrogen pressure 10 bars over 0.1 wt% Sulfated Zirconia produced a higher gasoline fraction than lower time of reaction, the liquid yield consisted of gasoline 24.38 wt%, kerosene 11.98 wt%, light gas oil 24.35 wt%, gas oil 5.70 wt%

and long residue 13.86% while the light gases produced amount of 19.07 wt% and solids of 0.65 %

Figure 4.23 shows the composition of gaseous product. Also, the yield of gaseous product largely increased with increase the time of reaction, the effect of temperature is a possible reason to claimed that the effect of thermal cracking and catalytic cracking to light hydrocarbon molecule when the temperature was maintained while the time of reaction was continued, the temperature affected to cracking small hydrocarbon molecule and continually cracked its to light gaseous. Therefore, at the temperature of 430 ^{o}C, initial pressure of 10 bars and time of reaction at 60 minutes, gave the composition of gaseous products which consisted of CH_4 26.23 %mole, C_2H_6 18.67 %mole, C_3H_8 7.99 %mole, C_4H_{10} 2.9 %mole and CO_2 44.21 %mole

4.2.2.4 The effect of the mass of Sulfated Zirconia

The effect of the mass of Sufated Zirconia in catalytic cracking of used vegetable oil in an empty catalyst runs at 430 ^{o}C pressure of hydrogen gas at of 10 bar and time of reaction of 60 minutes containing of 36.63 wt%, 61.74 wt%, and 1.63 wt% in liquid product, gaseous product, and solid respectively. With Sulfated Zirconia, the yield of gases around at 13.25 – 15.74 %wt in ranging of 0.05 – 0.20 wt% Sulfated Zirconia. Hence, the effect of catalyst was affected to the yield of product. On the contrary, increasing the mass of Sulfated Zirconia was insignificant on the product yield. The yield of gas, liquid, and solid shows in Figure 4.24

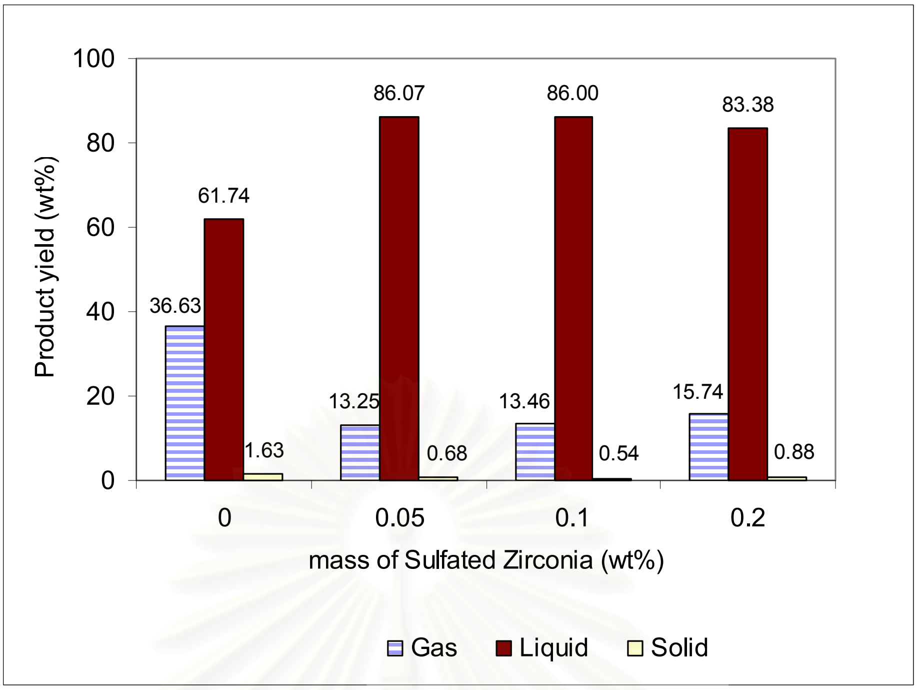

Figure 4.24 The effect of the mass of Sulfated Zirconia on the yield where temperature 430 °C initial hydrogen pressure of 10 bars and reaction time of 60 minutes

The product distribution obtained the run of temperature of 430 °C, initial hydrogen pressure of 10 bars and time of reaction of 60 minute over the mass of Sulfated Zirconia of 0.1 wt%. shown gasoline amount of 18.61 wt%, 12.01 wt% of kerosene, 27.99 wt% of light gas oil, 7.25 wt% of gas oil and 20.14 wt% long residue, whereas the effect to mass catalyst from ranging of 0.05 – 0.2 wt% shown the similar of fraction of Gasoline, Kerosene, and Long Residue in range 0.05 – 0.1 wt% and small increased where 0.2 wt% Sulfated Zirconia. Furthermore, when increasing the concentration of catalyst was increased the product distribution with the small changing, from the reason that increased contact time of reactant and also responsible to formation of the light hydrocarbon molecule. Therefore the condition of reaction at temperature of 430 °C, initial hydrogen pressure of 10 bars, time of reaction of 60 minutes over 0.1 wt% of Sulfated Zirconia was enough to the product distribution amounting 18.61 wt% gasoline, 12.01 wt% kerosene, 27.99 wt% light gas oil, 7.25 wt% gas oil, and 20.14 wt% long residue.

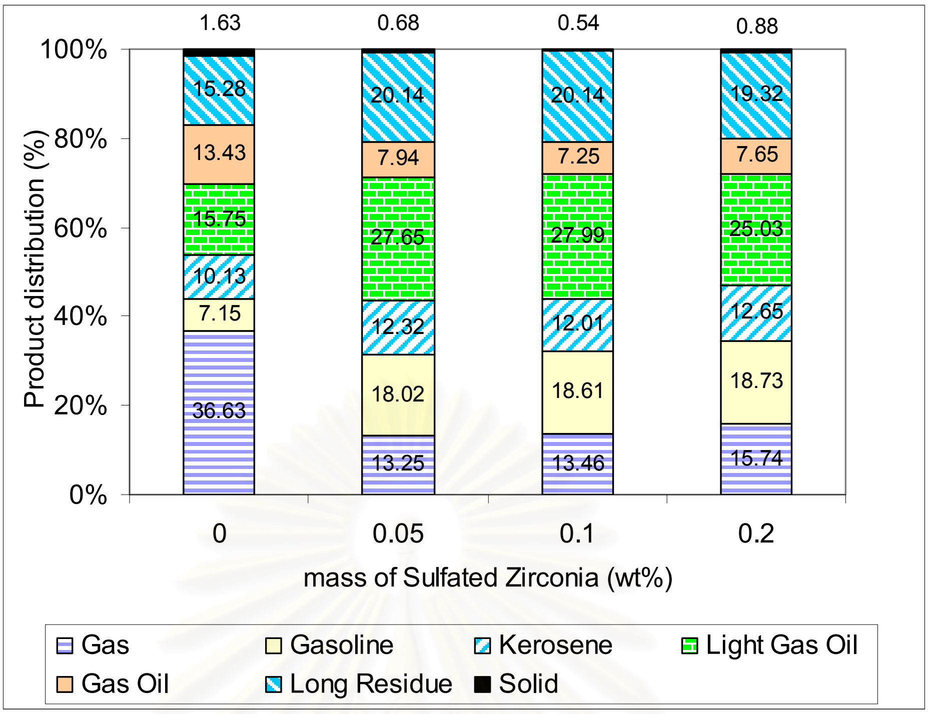

Figure 4.25 The effect of the mass of Sulfated Zirconia on the product distribution where temperature 430 °C initial hydrogen pressure 10 bars and reaction time of 60 minutes

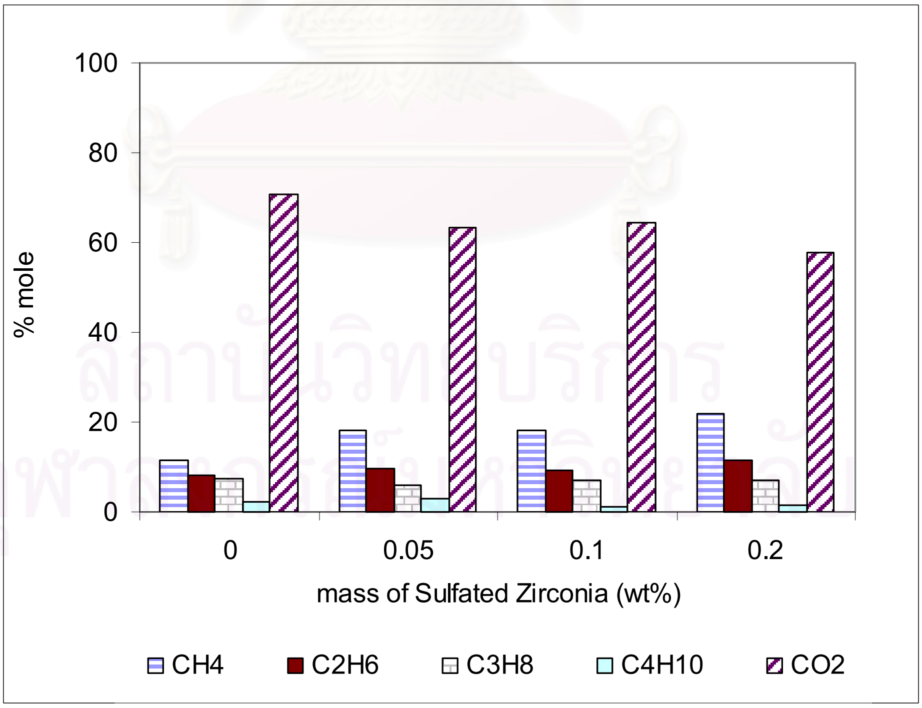

Figure 4.26 The effect of the mass of Sulfated Zirconia on the composition of gaseous product where temperature 430 °C, initial hydrogen pressure of 10 bars and reaction time of 60 minutes

4.3 Performance of Hybrid catalyst

The catalytic properties of HZSM-5 are strong acids site, properties of pore size effect and shape selective which was beneficial for cracking and aromatization whereas Sulfated Zirconia is a metal support catalyst which have relatively low hydrothermal stability and weaker acidity compare with HZSM-5. The hybrid catalyst were prepared by thoroughly physically mixing in varies ratios of HZSM-5 and Sulfated Zirconia.

4.3.1 The 2^4 Experimental Design

To investigate the significant factors which were affected to liquid yield of used vegetable oil to liquid fuels. The application of 2^K experimental design is used to determine the effect of temperature, initial hydrogen pressure, time of reaction, and ratio of HZSM-5 : Sulfated Zirconia. Factors levels were chosen by considering the operating limits of the experiment apparatus and the properties of used vegetable oil with the catalyst. The upper temperature level, 430°C was determined by the results of catalytic cracking over HSZM-5 and Sulfated Zirconia, both indicated that the higher temperature gave much more gaseous whereas the small hydrocarbon molecule was unwanted desire product and the lower temperature was 400°C, since lower temperature would required to initial the catalytic cracking of used vegetable oil. In addition the results claimed that the use of higher pressure obviously increase the conversion and largely increase the cost of the process, the upper and lower initial of hydrogen gas pressure were 10 and 20 bar respectively. The reaction time was agreeable to the trend of temperature, hence 45 and 75 minutes were investigated to the upper and lower level of reaction time. The hybrid catalysts were prepared by thoroughly physically mixing in varies ratios of HZSM-5 and Sulfated Zirconia in ranging of 0.3 : 0.7 to 0.8 : 0.2. Table 4.6 shows the experimental matrix for the 2^k factorial design. Real and coded level (±1) were assigned for the two factors. Furthermore, the order in which the runs were made was randomized to avoid systematic errors.

Table 4.6 Yield of liquid product from catalytic cracking of used vegetable oil over Hybrid catalyst

Treatment	Factor				%yield of Liquid
	A	B	C	D	
1	-	-	-	-	92.55
2	+	-	-	-	83.69
3	-	+	-	-	92.06
4	+	+	-	-	83.75
5	-	-	+	-	85.07
6	+	-	+	-	78.94
7	-	+	+	-	86.33
8	+	+	+	-	78.85
9	-	-	-	+	89.48
10	+	-	-	+	75.33
11	-	+	-	+	89.54
12	+	+	-	+	78.68
13	-	-	+	+	77.19
14	+	-	+	+	72.88
15	-	+	+	+	82.03
16	+	+	+	+	71.45

	Factor Level	
	Low (-)	High (+)
A (^{o}C)	400	430
B (bar)	10	20
C (min)	45	75
D	0.3 : 0.7	0.8 : 0.2

D : HZSM-5 : Sulfated Zirconia

The procedure to analyze the data from 2^k factorial design is providing through examination of a normal probability plot. The contrast constants for the 2^4 design were calculated and the normal probability plot is illustrated in Figure 4.27 From the normal probability plot, all of the effects that lie along the line are negligible, whereas larger effects deviate from the straight line. Therefore, the important effects that emerge from this analysis are the main effect of temperature (A), time of reaction (C), ratio of HZSM-5 : Sulfated Zirconia (D) are define in Table 4.7

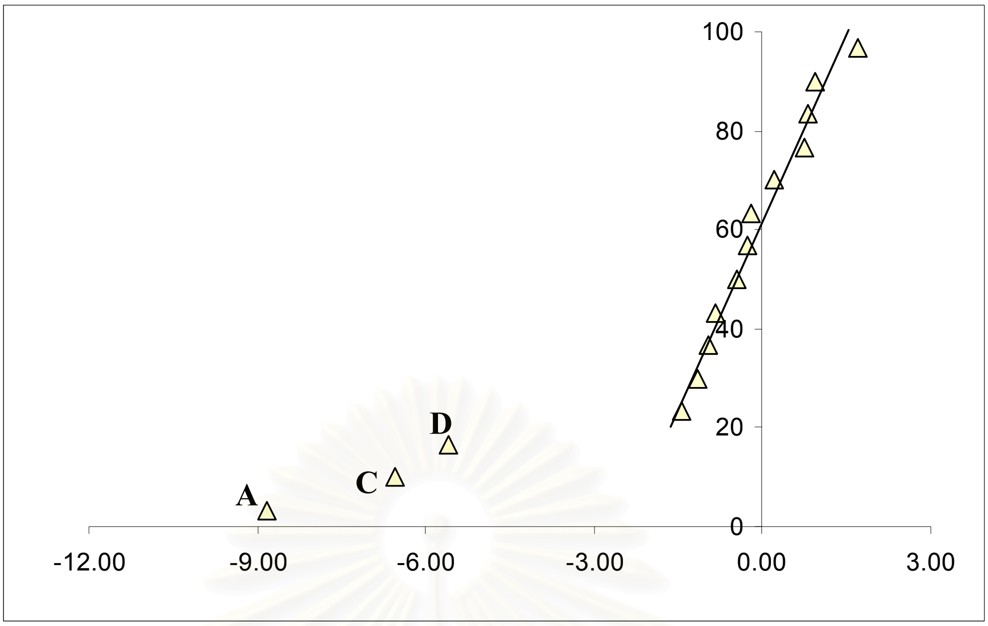

Figure 4.27 Normal probability plot

In Figure 4.27, temperature (A), time of reaction (C), and ratio of hybrid catalyst (D) are significant to the catalytic cracking of used vegetable oil to liquid yield. The analysis of variance at 95 % confidence interval is shown in Table 4.7 The test statistic F_o shows the effect of temperature, time of reaction, ratio of hybrid catalyst are significant to liquid yield.

Table 4.7 Analysis of Variance for 2^k experimental design in catalytic cracking of used vegetable oil over Hybrid catalyst.

Source of Variation	Sum of Square	df	Mean Square	F_0	$F_{0.025,1,12}$
A	312.229	1	312.229	90.085	> 6.55
C	171.217	1	171.217	49.400	> 6.55
D	124.657	1	124.657	35.966	> 6.55
Error	41.591	12	3.466		
Total	649.695	15			

4.3.2 Univariate study for the catalytic cracking of used vegetable oil to liquid fuels over Hybrid catalyst

4.3.2.1 The effect of hybrid catalyst

Figure 4.28 shows the effect of hybrid catalyst at various ratio of HZSM-5 and Sulfated Zirconia ranging 0.1 : 0.9 to 0.8 : 0.2 where the condition at temperature of 430 °C, initial hydrogen pressure 10 bar, time of reaction at 60 minutes. It seems that the effect of ratio of hybrid catalyst were significant to the gaseous yield and, the gaseous product largely increased with increasing amount of HZSM-5. The results imply that by adding small amounts of HZSM-5 to Sulfated Zirconia, it is possible to substantially increased the liquid yield, when HZSM-5 is continued to add, the effect of HZSM-5 in acid strength, pore and shape selectivity are significant to gaseous yield. At temperature of 430 °C, initial hydrogen pressure 10 bar, time of reaction 60 minutes and, ratio of HZSM-5 : Sulfated Zirconia at 0.3 : 0.7, the yields of gaseous, liquid, and solid are 13.46 wt%, 86.11 wt% and 0.43 wt% respectively

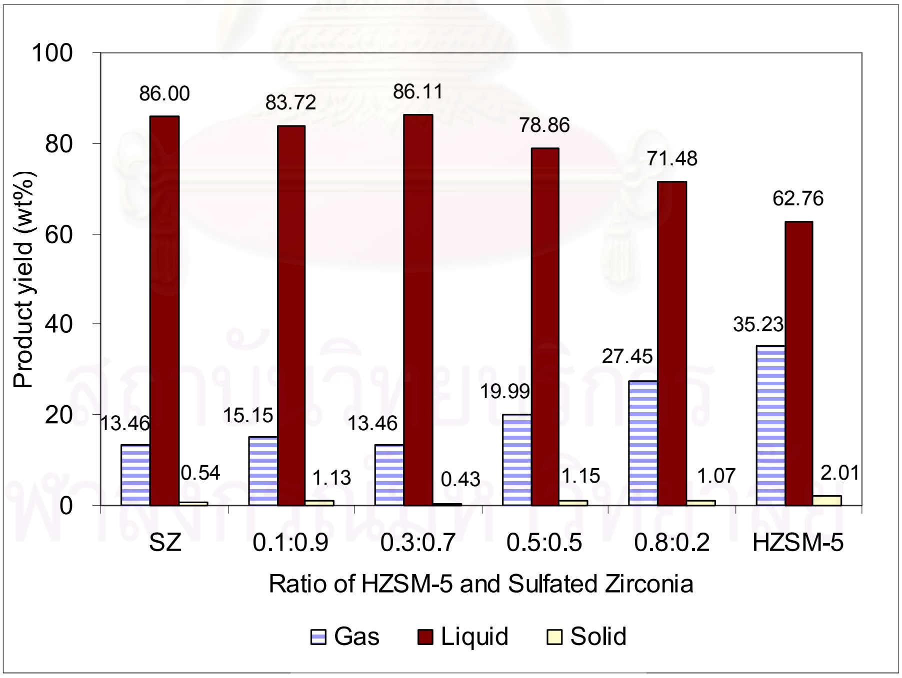

Figure 4.28 The effect of various ratio of HZSM-5 and Sulfated Zirconia on the yield where temperature 430 °C initial hydrogen pressure of 10 bars and reaction time of 60 minutes

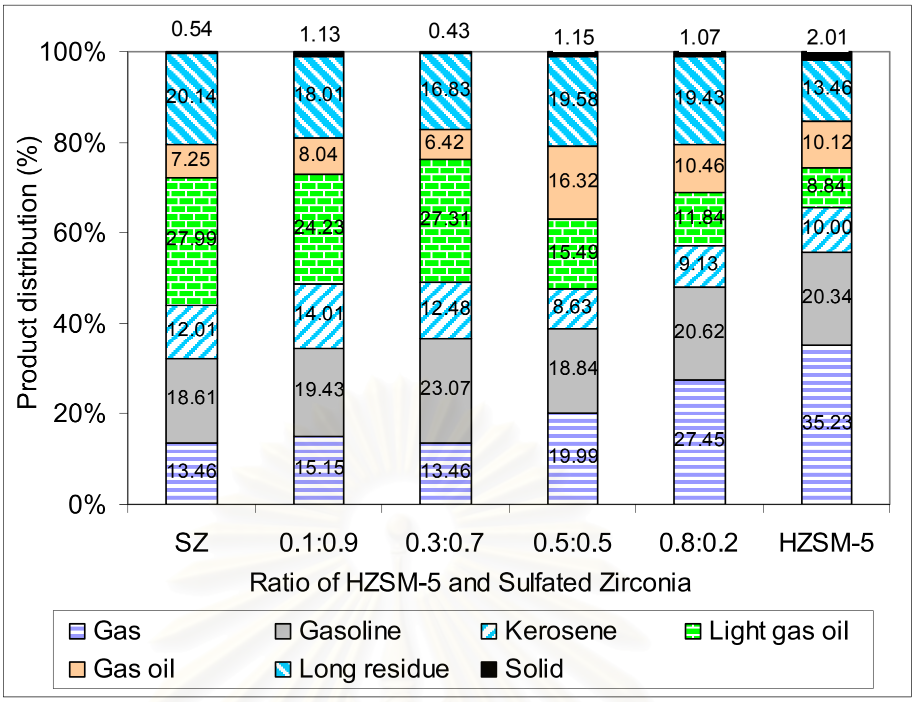

Figure 4.29 The effect of various ratio of HZSM-5 and Sulfated Zirconia on product distribution where temperature 430 ^{o}C initial hydrogen pressure of 10 bars and reaction time of 60 minutes

Due to the physical mixing catalysts imply that by adding HZSM-5 to Sulfated Zirconia, it is possible to substantially increase the aromatic hydrocarbon yield. At the ratio 0.3 : 0.7 of HZSM-5 and Sulfated Zirconia 23.07 wt% of gasoline and 12.48 wt% of kerosene were obtained. The high gasoline fraction with HZSM-5 was due to its shape selective, pore structure were enhance to cyclization and aromatization while Sulfated Zirconia have strong acidity but no pore structure property. Hence, the cracking over HZSM-5 was added to Sulfated Zirconia in order to enhance its cracking activity. There was increased acidity of the hybrid catalyst are due to the presence of HZSM-5 which imply increased deoxygenation by dehydration.(Kantikaneni 1996) While Adjaye (1996) was reported that the adding of small amount of HZSM-5 to silica-alumina is possible to substantially increase aliphatic and a further increase HZSM-5 content results in a substantial increase in aromatization activity. Hence, hybrid catalyst obtained with physical mixing of HZSM-5 and Sulfated Zirconia showed mostly aromatic and small aliphatic hydrocarbon, it seems that the addition of HZSM-5 to Sulfated Zirconia was a route to modify performance of catalytic cracking to aromatic fuels and could be increased more than used only Sulfated Zirconia. The result of this effect showed that temperature of 430^{o}C, initial of hydrogen pressure 10 bars, time of reaction 60 minutes, and ratio of HZSM-5 and Sulfated Zirconia 0.3 : 0.7 gave the appropriate fraction of Gasoline, the liquid yield of 86.11 % was obtained with the composition of gasoline 23.07 wt%, kerosene 12.48 wt%, light gas oil 27.13 wt %, gas oil 6.42 wt% and long residue 16.83 wt% whereas the light gaseous by product of 13.46 wt% and solids of 0.43 wt% were obtained.

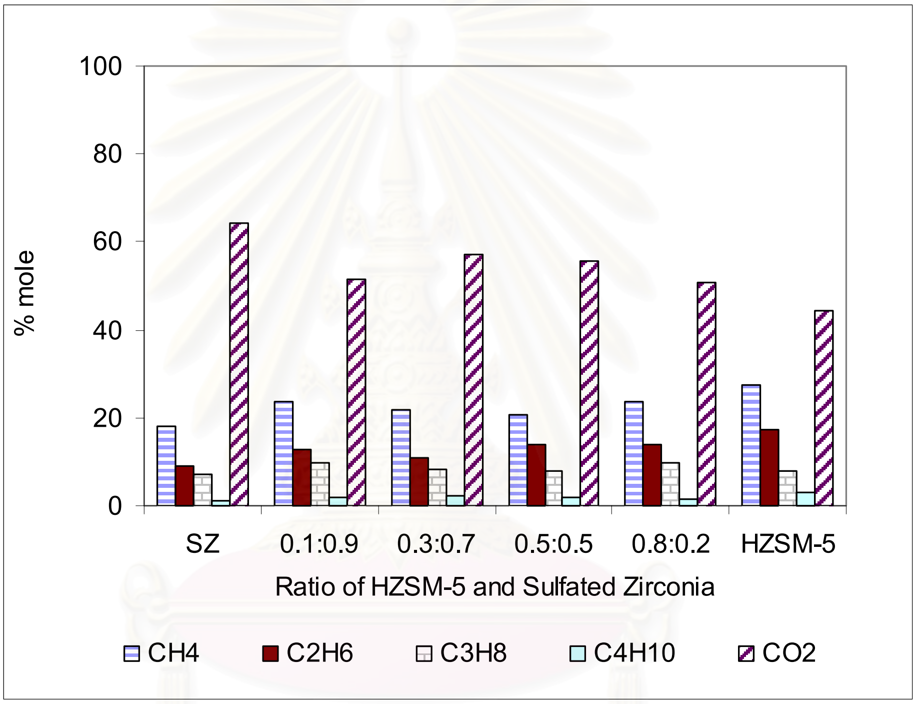

Figure 4.30 The effect of various ratio of HZSM-5 and Sulfated Zirconia on the composition of gaseous roduct where temperature 430 ^{o}C initial hydrogen pressure of 10 bars and reaction time of 60 minutes

Figure 4.30 shows the composition of gaseous product. Also, the yield of gaseous product dramatically increased with increased amount of HZSM-5 into Sulfated Zirconia, the effect of hybrid catalyst is a possible reason claimed that the effect of acid strength and pore properties are possibly reason to cracking to long chain hydrocarbon to light hydrocarbon gaseous.(Kantikaneni 1996, and Twaiq 2003) In addition the temperature affected to cracking small hydrocarbon molecule and continually cracked its to light gaseous. Therefore, at the temperature of 430 ^{o}C, initial hydrogen pressure of 10 bars and time of reaction at 60 minutes, at the ratio of HZSM-5 and Sulfated Zirconia 0.3 : 0.7 gave the composition of gaseous products which consisted of CH_4 21.63 %mole, C_2H_6 11.05 %mole, C_3H_8 8.13 %mole, C_4H_{10} 2.14 %mole and CO_2 57.05 %mole

4.3.2.2 The effect of temperature

The effect of temperature on the product yield, in a blank run was performed without the hybrid catalyst in the condition of 400 ^{o}C. initial hydrogen pressure of 10 bar, and time of reaction 60 minute indicated that low amount of liquid yield because of the thermal cracking was significantly effect to cracked medium and small hydrocarbon to light gaseous. On the contrary, hybrid catalyst at the ratio of HZSM-5 and Sulfated Zirconia 0.3 : 0.7 which are the results of an appropriate conditions at the various temperature, the gaseous product dramatically increased with increasing the temperature. An empty catalyst run at 400 ^{o}C, initial hydrogen pressure of 10 bars and time of reaction of 60 minutes was about 20.88 wt%, 77.99 wt%, and 1.13 wt% in liquid product, gas product, and solid respectively. In addition, the liquid product gave the product distribution which determined from simulated distillation gas chromatograph about 6.74 wt% gasoline, 7.93 wt% of kerosene, 24.18 wt% of light gas oil, 15.02 wt% of gas oil and 24.12 wt% long residue

Catalytic cracking over 0.3 : 0.7 HZSM-5 and Sulfated Zirconia, the liquid yield was decreased with increase of temperature whereas the yield of gasoline fraction increased with increase temperature. A possible reason for this behavior is that the higher temperature (400^{o}C) accelerated the thermal cracking and hence changing the long chain of hydrocarbon molecule from thermal cracking into a middle hydrocarbon molecule such as kerosene and diesel fraction. Thereafter kerosene, light gas oil and gas oil were catalytically cracked at the surface of Sulfated Zirconia and HSZM-5, the pore structure and shape selective of HZSM-5 can converting medium hydrocarbon molecule into convert to gasoline (Raphael, 1997; Twaiq, 2003) and gases (normally C_1-C_4) . It can be identified as deoxygenation cracking and aromatization with H-Transfer from catalytic cracking processes, deoxygenation can occur from decarboxylation and dehydration regarding the primary cracking of triglyceride

(Adjaye, 1996; Twaiq, 1999) which assumed that the predominantly by occur within the internal pore structure. The possibility is that the initial fragmentation can occur on the external surface of HZSM-5 and followed by diffusion in to the pore. The subsequent reaction such as cyclization, isomerization, hydrogen transfer leading the formation of aromatic hydrocarbon. When the temperature reached to 430°C, a large amount of gaseous products have been observed to increase substantially. It seemed that when higher temperature was used, light hydrocarbon could be cracked more. The result of this effect showed that temperature of 430°C gave the appropriate fraction of gasoline, the liquid yield of 86.11 wt% was obtained with the composition of gasoline 23.07 wt%, kerosene 12.48 wt%, light gas oil 27.31 wt %, gas oil 6.42 wt% and long residue 16.83 wt% whereas the light gases by product of 13.46 wt% and solids of 0.43 wt% were obtained.

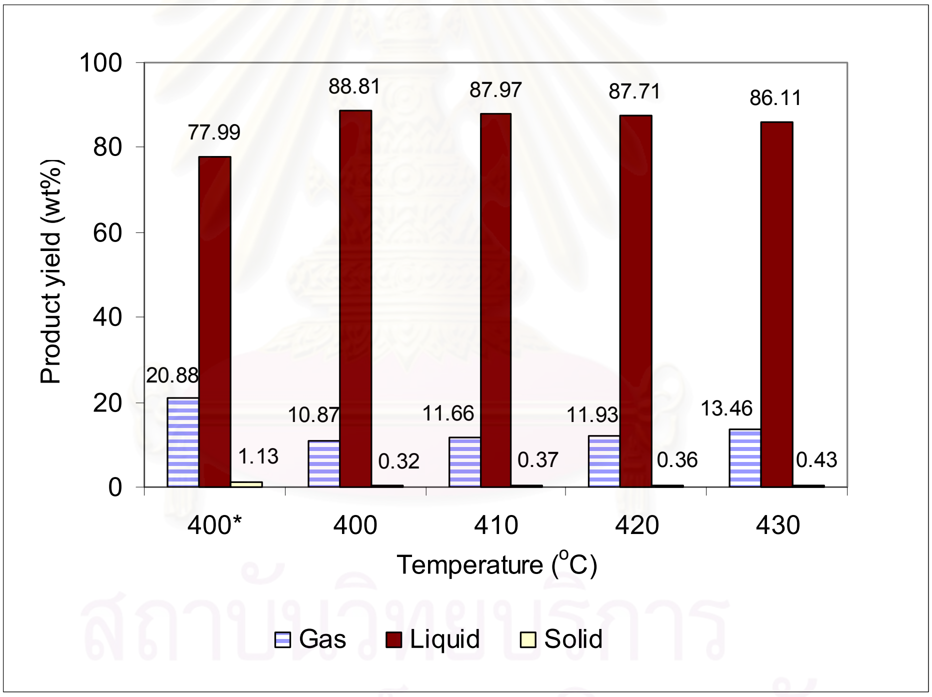

Figure 4.31 The effect of temperature on product yield where initial hydrogen pressure of 10 bars, reaction time 60 minutes over 0.3 : 0.7 HZSM-5 : Sulafted Zirconia hybrid catalyst and comparison to the product yield where without catalyst; (*) not use hybrid catalyst

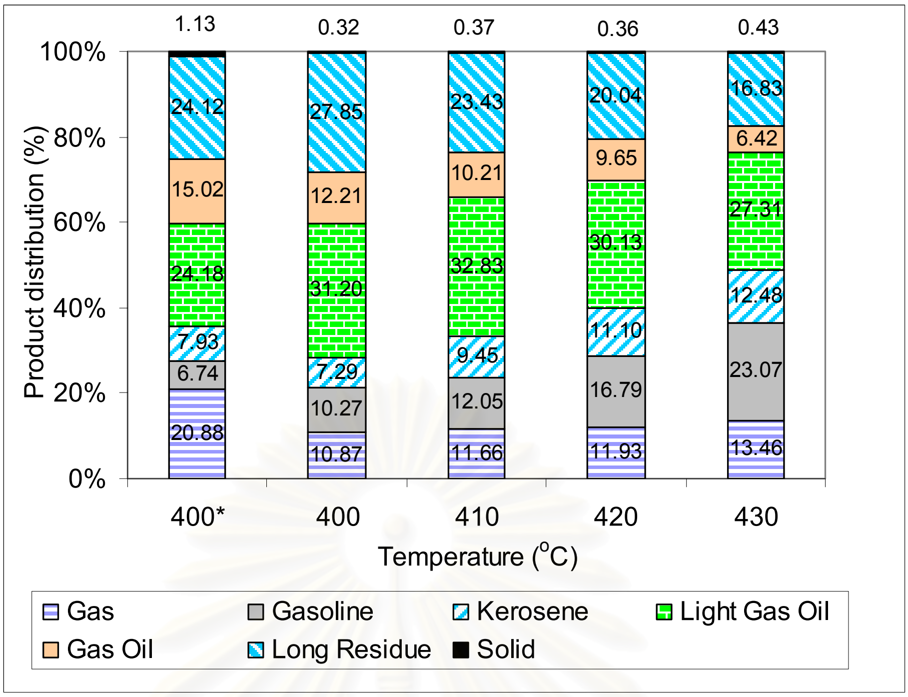

Figure 4.32 The effect of temperature on the product distribution where initial hydrogen pressure 10 bars, time of reaction 60 minutes over 0.3 : 0.7 HZSM-5 and Sulfated Zirconia ; (*) not use hybrid catalyst.

In order to study the effect of temperature to the gaseous product, gaseous yield was increased with increase of temperature. A possible reason for this behavior is that the higher temperature (400^{o}C) accelerated the thermal cracking and hence changing the long chain of hydrocarbon molecule from thermal cracking into a middle hydrocarbon molecule and light hydrocarbon molecules. Thereafter light hydrocarbon molecules were thermally and catalytically cracked converting them into gaseous product. The results shown the composition of gaseous product consisted of CH_4, C_2H_6, C_3H_8, C_4H_{10}, and CO_2 at about 10.98, 9.23, 6.94, 1.98 and 70.87 %mole respectively whereas an appropriated condition which gave the highest Gasoline fraction at temperature of 430 ^{o}C gave the composition of gaseous product consisted of 21.63 %mole of CH_4, 11.05 %mole of C_2H_6, 8.13 %mole of C_3H_8, 2.14 % mole of C_4H_{10}, and 57.05 %mole of CO_2. It seems that at the higher temperature gave more amount of small gaseous products such as CH_4 and C_2H_6 from the effect of temperature.

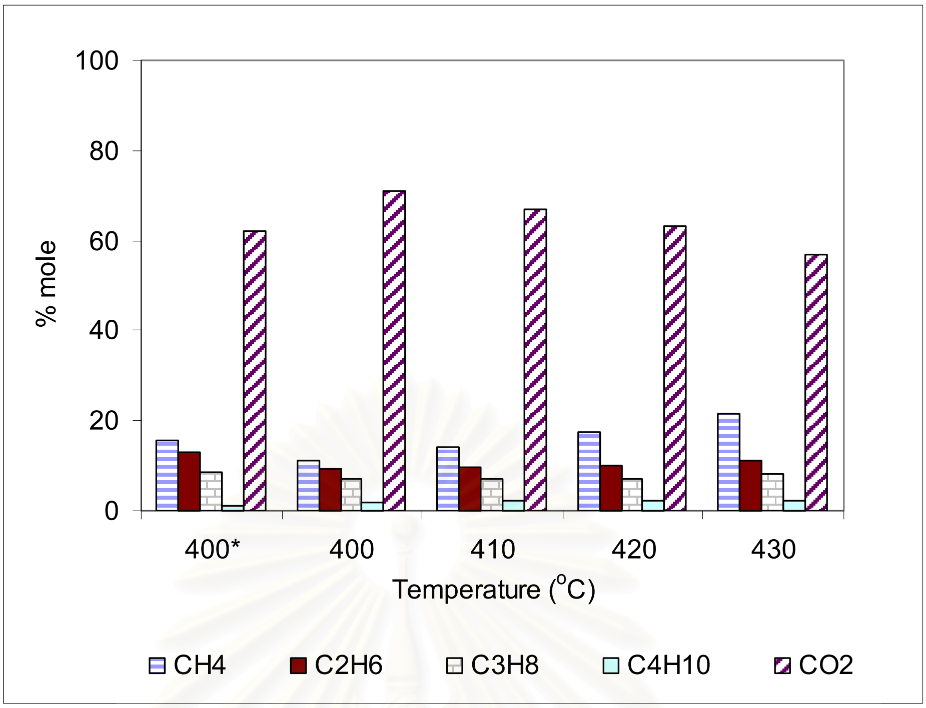

Figure 4.33 The effect of temperature on the gaseous product where initial hydrogen pressure 10 bars, time of reaction 60 minutes over 0.3 : 0.7 HZSM-5 and Sulfated Zirconia

4.1.2.2 The effect of initial hydrogen pressure

Figure 4.34 shows the effect of initial hydrogen pressure range of 10 – 30 bars comparison to blank run, without atmosphere hydrogen gas. It seems that initial hydrogen pressure is responsible to the catalytic cracking of used vegetable oil. It was noticed that when the pressure of hydrogen increasing from atmospheric pressure to 10 bars, the liquid yield was large increased from 64.92 wt% to 86.00 wt%. Whereas, the effect of variation of initial hydrogen pressure ranging from 10 – 30 bars was insignificant with increasing pressure. At the temperature 430 ^oC initial hydrogen gas of 10 bars and reaction time of 60 minute, gave the yield of liquid, gaseous, and solid of 86.00, 13.46, and 0.54 wt% respectively.

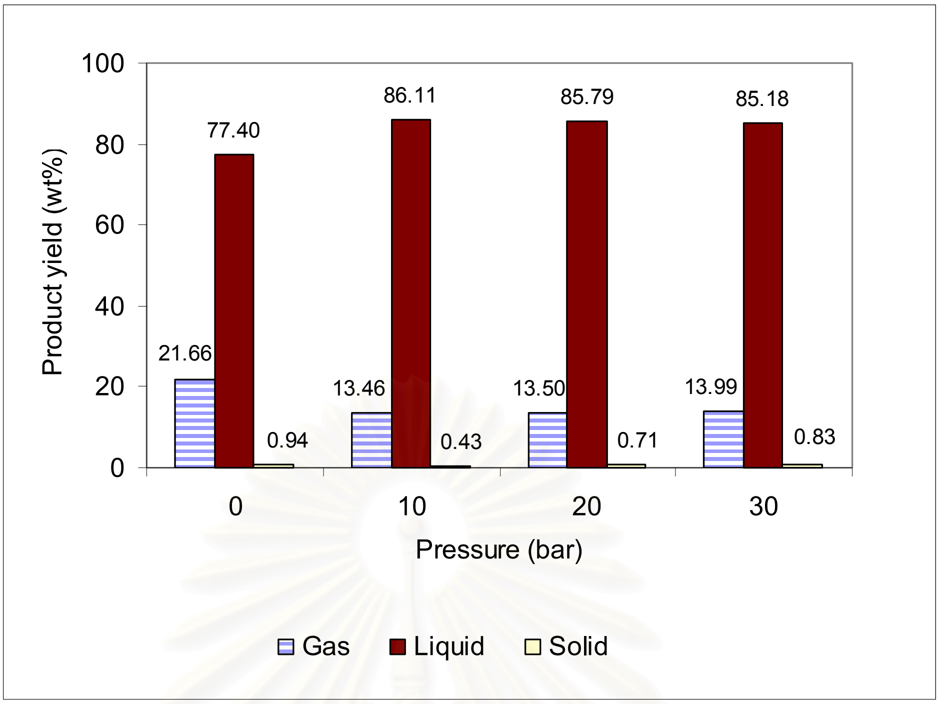

Figure 4.34 The effect of initial hydrogen pressure to the product yield where temperature of 430 ^{o}C, reaction time of 60 minutes over 0.3 : 0.7 HZSM-5 and Sulfated Zirconia

Figure 4.35 shows the effect of initial pressure of hydrogen gas on the products distribution. The catalytic cracking takes place very well by given the pressure of hydrogen. Both Sulfated Zirconia and HZSM-5 have the Bronsted acid strength which gave protons from the structural surface of catalyst to the long chain hydrocarbon for cracking and this hydrogen compensated at the surface by hydrogen feed. But the effect of initial hydrogen pressure was insignificant with increasing pressure. The initial hydrogen pressure was responsible for the catalytic cracking step. It was noticed that when the pressure was increased, the yields gasoline, kerosene, light gas oil, and solid were slightly increased. In both case the initial pressure was high enough so that similar results were reached. It seemed that a pressure of 10 bars was enough to gave gasoline fraction amounting to 23.07 wt%, while kerosene 12.48 wt%, light gas oil 27.31 wt%, gas oil 6.42 wt%, long residue 16.83 wt% were obtained

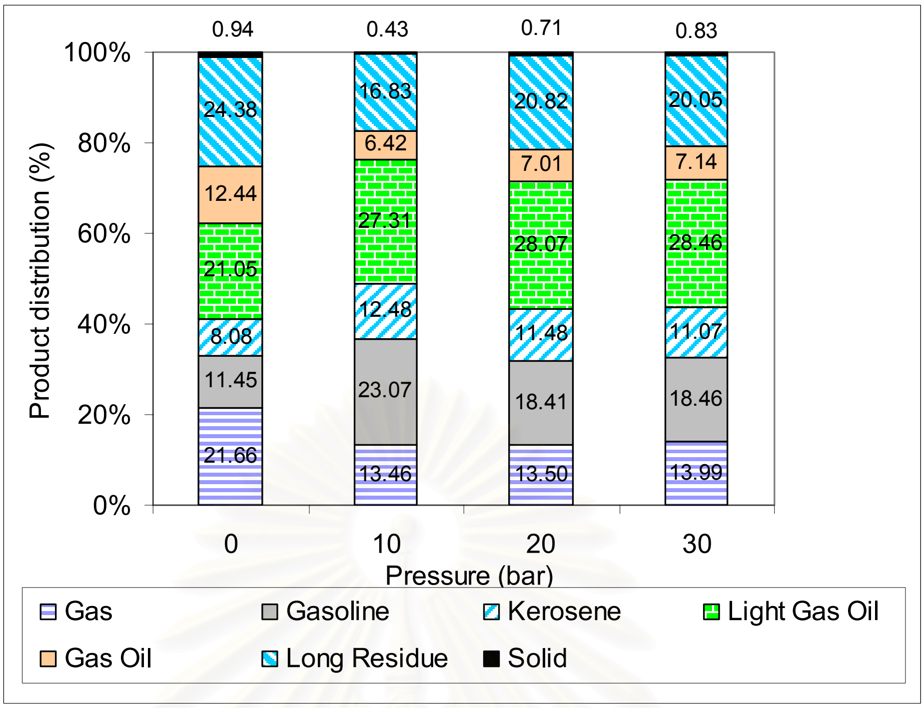

Figure 4.35 The effect of initial hydrogen pressure to the product distribution where temperature of 430 °C, reaction time of 60 minute over 0.3 : 0.7 HZSM-5 and Sulfated Zirconia

In addition, the effect of initial hydrogen pressure in the catalytic cracking of used vegetable oil to liquid fuels gave the same composition of the gaseous product at the variation of initial hydrogen pressure. At the lowest initial hydrogen pressure 10 bars, temperature of 430 °C and time of reaction of 60 minute over 0.3 : 0.7 HZSM-5 and Sulfated Zirconia consisted of mainly CO_2, CH_4, and C_2H_6 at amount of 57.05, 21.63 and 11.05 %mole respectively. The results of the variation of initial hydrogen pressure on gaseous composition shown in Figure 4.36

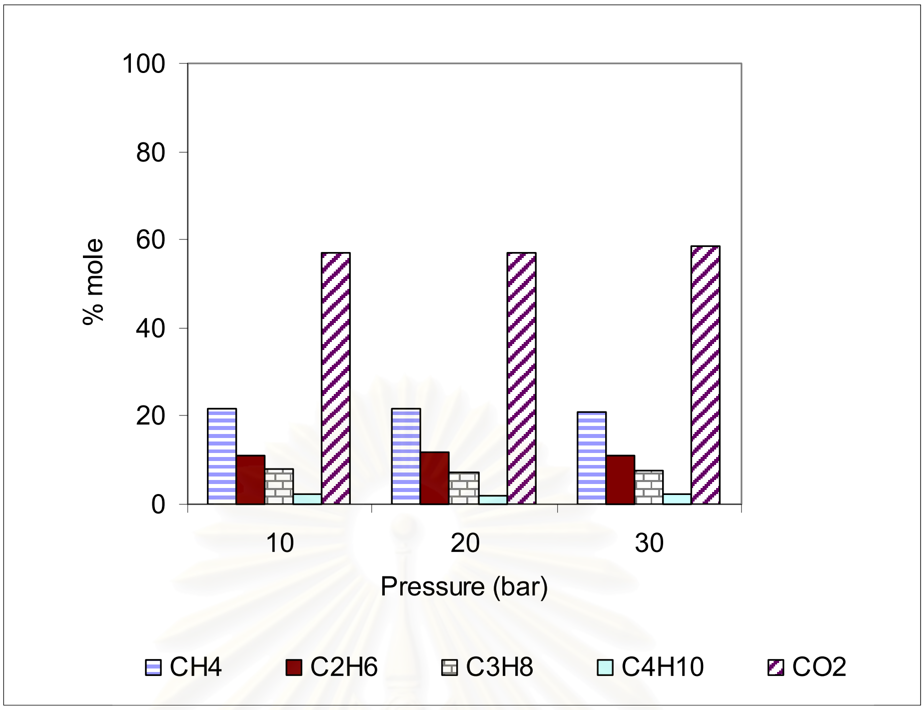

Figure 4.36 The effect of initial hydrogen pressure to the gaseous composition where temperature of 430 °C, reaction time of 60 minute over 0.3 : 0.7 HZSM-5 and Sulfated Zirconia

4.1.2.3 The effect of reaction time

The time of reaction contributed mainly to the liquid yield and product distribution, Figure 4.37 shows that the yield of liquid was increased with increasing reaction time from 45 – 60 minutes and decreased with decreasing reaction time from 75 – 90 minutes. It seems that in the first of reaction, used vegetable oil begins crack by the effect of thermal cracking and undergoes more cracking when the reaction time continued, the liquid yield which consisted of the fraction of light hydrocarbon continued cracking to the gaseous product. Hence, the gaseous product increased with increasing the time of reaction. The yield of liquid product was decreased from 86.68 wt% to 79.17 wt% in ranging of increased the reaction time of 45 minutes to 90 minutes

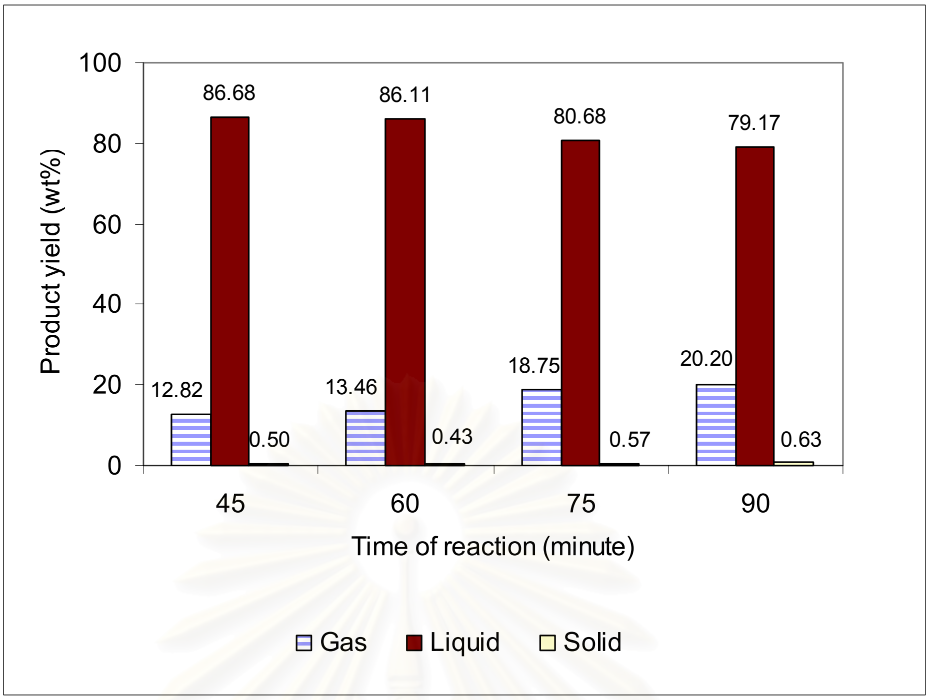

Figure 4.37 The effect of time of reaction to the product yield where temperature of 430 °C, initial hydrogen pressure of 10 bars over 0.3 : 0.7 HZSM-5 and Sulfated Zirconia

Figure 4.38 shows the effect of reaction time on the product distribution. The results shown temperature was mainly affecting the thermal cracking of long chain hydrocarbon molecules into light molecules and continued cracking led to light hydrocarbon gaseous with increasing the reaction time. If maintained the time of reaction , the temperature was affected to more cracked to light hydrocarbon gaseous The result of increase reaction time shows that the gaseous products increased whereas the product distribution such as gasoline, kerosene, light gas oil, and gas oil decreased. The time of reaction was found to favor aromatic hydrocarbon formation and leading to formation of light gaseous predominant, the effect of reaction time shows the results in greater amount of aromatic and gasoline boiling range fraction also increased with increase in reaction temperature reached a maximum at 430 °C and gave later decrease.

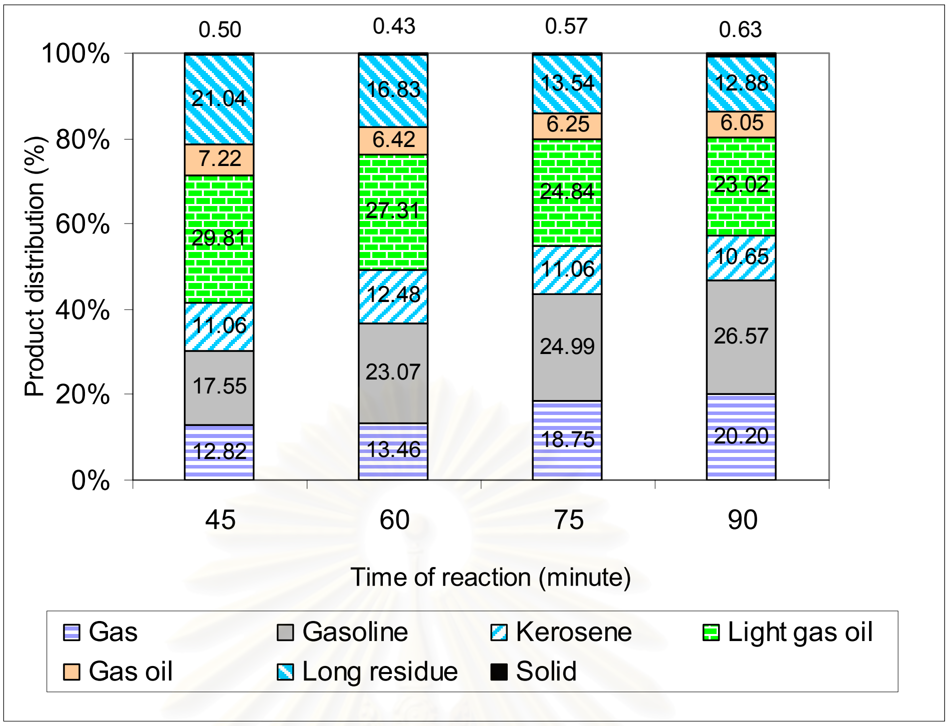

Figure 4.38 The effect of time of reaction to the product distribution where temperature of 430 °C, initial hydrogen pressure of 10 bars over 0.3 : 0.7 HZSM-5 and Sulfated Zirconia

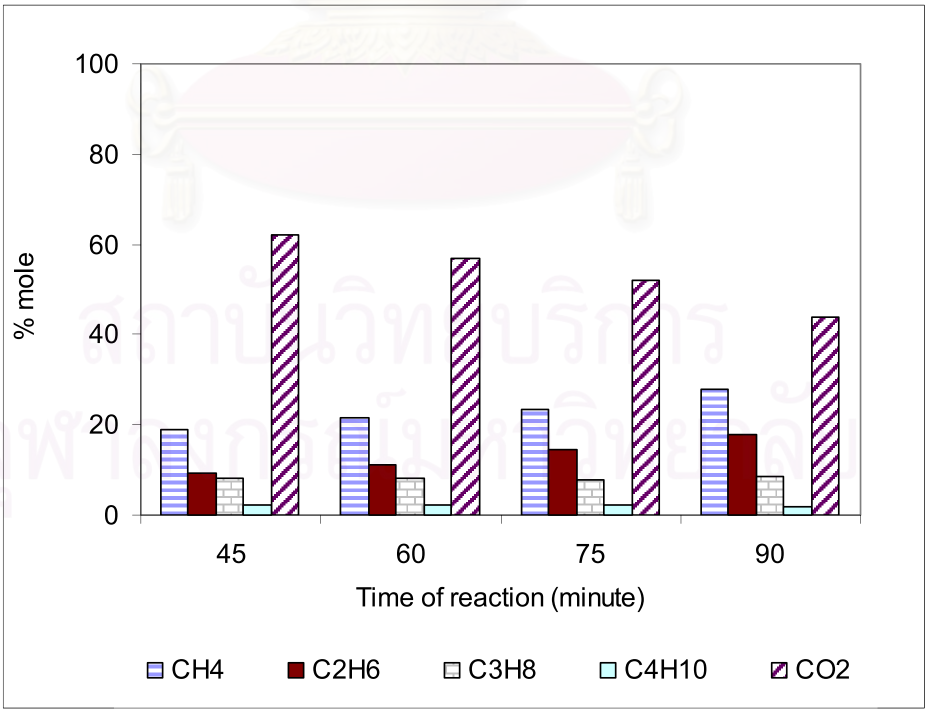

Figure 4.38 The effect of time of reaction to the gaseous composition where temperature of 430 °C, initial hydrogen pressure of 10 bars over 0.3 : 0.7 HZSM-5 and Sulfated Zirconia

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At the conditions of temperature 430°C, initial hydrogen pressure of 10 bars and reaction time of 90 minutes, the liquid yield of 79.17 % was obtained with the composition of gasoline 26.57 wt%, kerosene 10.65 wt%, light gas oil 23.02 wt%, gas oil 6.05 wt%, and long residue 12.88 wt% whereas the light gases by product of 20.20 wt% and solids of 0.63 wt% were obtained.

The yield of gaseous product increased with maintained the temperature of 430 °C and increased time of reaction to 90 minutes. The gaseous products consisted mostly C_1-C_2 and CO_2. As can be seen, the CH_4 yield increased dramatically with increasing time of reaction ranging from 45 minutes to 90 minutes, it is noticeable that thermal cracking and catalytic cracking were affected to light hydrocarbon gaseous. If the reaction time was continued, they will cracked to small hydrocarbon gaseous and increased continuously with increased the time of reaction. At the temperature of 430 °C, initial pressure of 10 bars and time of reaction at 60 minutes, the composition of gaseous products consisted of CH_4 21.63 %mole, C_2H_6 11.05 %mole, C_3H_8 8.13 %mole, C_4H_{10} 2.14 %mole and CO_2 57.05 %mole whereas increased the time of reaction reached to 90 minutes, the small light gaseous such as CH_4 and C_2H_6 were increased to 27.82 %mole and 17.94 %mole respectively.

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4.4 Kinetic Study

The cracking mechanism was the mostly complex and slight in expression, then the assumption to expression the mechanism of catalytic conversion of used vegetable oil to liquid fuels over the various catalysts are the reaction was continuously in the reactor which could be represented by the following scheme Figure 4.40

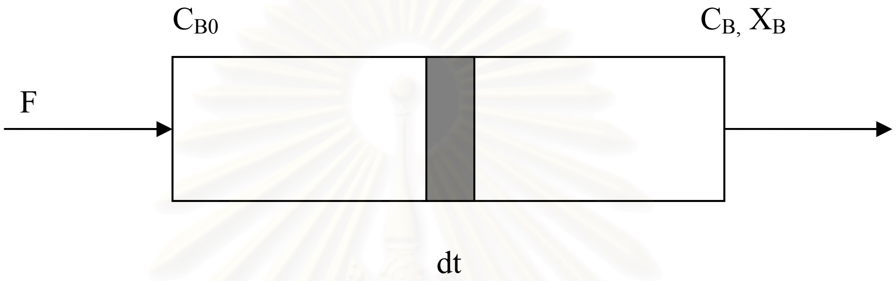

Figure 4.40 Schematic diagram represented of the reactor

The experimental parameters are ambient room temperature : Ta = 30 C, and initial pressure of hydrogen gas fed to the reactor : Pa = 10 bars. Furthermore, the following assumptions are accepted:

The kinetic study for each experiment was performed in the batch reactor, the assumption of kinetic model as following; the feed of reactant (F) is constant, the reactor is isothermal at the desired temperature for each batch at the temperature of T under the pressure of 10 bars hydrogen gas (loss of changes negligible), the conversion for each desired temperature could be calculated from the analysis of Long Residue fraction at time = 0 where the reaction undergo to desire temperature (X_{B0}) and complete reaction at the final time of reaction (X_B).

For example, the fraction of Long Residues which performed at temperature of 400 ^{o}C could represented the initial Long Residue by the results from analyze of the reaction of ambient room temperature to 400 ^{o}C reached and remarked that this reaction time during ambient room temperature to reached desire temperature is t_{B0} and the conversion of Long Residue is X_{B0}. In the similar, the conversion of Long

Residue at the reaction completely could represented by the isothermal reaction at desired temperature until the end of reaction, Long Residue were analyzed by simulated distillation gas chromatograph. The fraction of Long Residue was represented at the final time of reaction X_B. The conversion of Long Residue at any time could be represented by

$$\% \text{ Conversion} = \frac{X_{B0} - X_B}{X_{B0}} \times 100 \qquad (4.1)$$

Thus, the gray part of the reactor (from Figure 4.40) could be represented by the equation

rate of disappearance of B = the rate of the conversion of B per volume (4.2)

$$-r_B = (-1/V)(dN_b/dt) \qquad (4.3)$$

Suppose that N_{B0} is the initial amount of B in the reactor at time = 0, that N_B is the amount present at time t. Then, the conversion of B in constant volume system is as follow

$$X_B = \frac{N_{B0} - N_B}{N_{B0}} = 1 - \frac{N_B/V}{N_{B0}/V} \qquad (4.4)$$

$$= 1 - \frac{C_B}{C_{B0}} \qquad (4.5)$$

At the constant volume;

$$-r_B = (-dC_b/dt) = k_n C_B^n \qquad (4.6)$$

If first order reaction is obtain the relationship between $-r_B$ and C_B from the equation 4.6 as follow

$$(-dC_B/dt) = k_1 C_B \qquad (4.7)$$

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$$-\int_{C_{B0}}^{C_B} dC_B / C_B \quad = \quad k_2 \int_0^t k_1 dt \tag{4.8}$$

Integrating

$$\ln(C_B) - \ln(C_{B0}) \quad = \quad -k_1 t \tag{4.9}$$

Thus

$$\ln(C_B) \quad = \quad \ln(C_{B0}) - k_1 t \tag{4.10}$$

A plotted of $\ln(C_B)$ versus t gives the straight line with slope = - k_1

If second order reaction is obtain the relationship between $-r_B$ and C_B from the equation 4.6 as

$$(-dC_B/dt) \quad = \quad k_2 C_B^2 \tag{4.11}$$

$$-\int_{C_{B0}}^{C_B} dC_B / C_B^{\;2} \quad = \quad k_2 \int_0^{t_B} dt \tag{4.12}$$

Integrating

$$(1/C_B) - (1/C_{B0}) \quad = \quad k_2 t \tag{4.13}$$

$$(1/C_B) \quad = \quad (1/C_{B0}) + k_2 t \tag{4.14}$$

A plotted of $(1/C_B)$ versus t gives the straight line with slope = k_2

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Table 4.8 The conversion of Long Residue at the variation of reaction time where the catalytic cracking of used vegetable oil over HZSM-5

Temperature (^{o}C)	Time (min)	Long Residue (wt)%	Conversion	ln(1-x)	x/(1-x)
400	0	55.94	0.0000	0.0000	0.0000
	30	35.31	0.3688	-0.4601	0.5843
	40	31.73	0.4328	-0.5670	0.7630
	50	28.42	0.4920	-0.6772	0.9683
	60	27.41	0.5100	-0.7133	1.0406
	70	25.63	0.5419	-0.7806	1.1828
	80	23.64	0.5774	-0.8613	1.3662
	90	21.35	0.6184	-0.9634	1.6206
410	0	55.88	0.0000	0.0000	0.0000
	30	27.45	0.5088	-0.7109	1.0359
	40	25.71	0.5399	-0.7763	1.1735
	50	24.37	0.5638	-0.8297	1.2927
	60	22.69	0.5940	-0.9014	1.4630
	70	20.62	0.6310	-0.9969	1.7100
	80	18.19	0.6746	-1.1226	2.0727
	90	17.18	0.6925	-1.1792	2.2518
420	0	53.95	0.0000	0.0000	0.0000
	30	26.83	0.5027	-0.6985	1.0108
	40	23.69	0.5610	-0.8232	1.2778
	50	21.49	0.6017	-0.9205	1.5105
	60	19.07	0.6465	-1.0400	1.8291
	70	15.80	0.7072	-1.2282	2.4149
	80	14.00	0.7405	-1.3491	2.8538
	90	12.91	0.7607	-1.4301	3.1790
430	0	50.63	0.0000	0.0000	0.0000
	30	25.26	0.5011	-0.6954	1.0045
	40	21.44	0.5766	-0.8595	1.3619
	50	18.14	0.6418	-1.0267	1.7917
	60	15.52	0.6935	-1.1826	2.2629
	70	12.98	0.7437	-1.3614	2.9017
	80	11.98	0.7634	-1.4415	3.2269
	90	10.95	0.7838	-1.5314	3.6246

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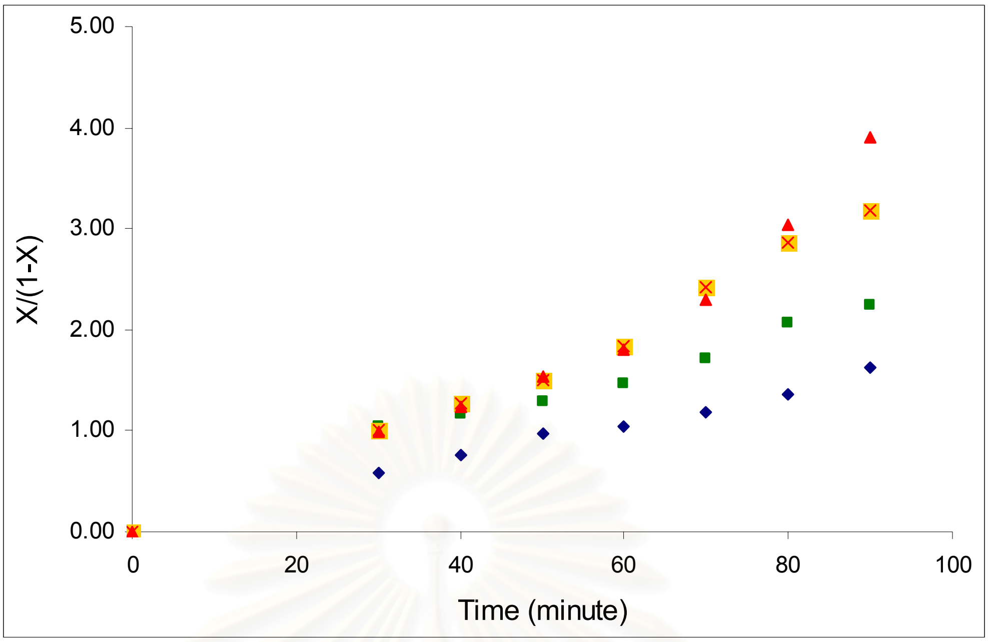

Figure 4.41 Conversion vs. Time of reaction [(◆) 400 C; (■) 410 C; (☒) 420 C ; (Δ) 430°C]

Figure 4.41 allowed to determine the reaction order of catalytic cracking of used vegetable oil over HZSM-5 at various temperature of 400, 410, 420 and 430°C : Eight point of the graph from time of reaction during 0 to 90 minutes gave correctly a straight line with a good regression constant near by 1.00 than the first order reaction, thus the Figure 4.41 shown the conversion of long residue of used vegetable oil to liquid fuels is the second order, thus the equation (4.6) become

$$(1/C_B) - (1/C_{B0}) = k_2t \qquad (4.15)$$

$$(1/C_B) = (1/C_{B0}) + k_2t \qquad (4.16)$$

Rearrange in term of conversion

$$X = 1 - (C_B/C_{B0}) \qquad (4.17)$$

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Thus

$$K_2C_{Bo}t \quad = \quad (1/(1\text{-}X)) - 1 \qquad (4.18)$$

Consideration the rate constant at the various temperature and plot the correlation between $\ln(k_2)$ and 1/T from Arrhenius's equation

$$k_n \quad = \quad k_{(n0)}e^{(-E/RT)} \qquad (4.19)$$

The equation is expression in term of logarithm as following

$$\ln(k_n) \quad = \quad \ln(k_{n0}) - (E/R)/T \qquad (4.20)$$

A plotted of $\ln(k_n)$ versus 1/T gives the straight line with the slope as (-E/R) and the intercept = $\ln(k_{n0})$ which uses to determine the activation energy (Ea) and Pre-exponential (A), respectively.

Table 4.9 Represented of $\ln(k_n)$ versus 1/T at the variation of reaction tempearture

Temperature (K)	1/T (K^{-1})	k_2 (min^{-1})	k_2 (s^{-1})	$\ln(k_2)$
400	1.4856×10^{-3}	0.0177	2.95×10^{-4}	-8.1285
410	1.4638×10^{-3}	0.0257	4.28×10^{-4}	-7.7556
420	1.4427×10^{-3}	0.0339	5.65×10^{-4}	-7.4787
430	1.4222×10^{-3}	0.0392	6.53×10^{-4}	-7.3334

Figure 4.42 shows ln k versus 1/T could be traced. So Ea, the activation energy could be obtained by the slope of the straight line and also, $\ln(k_0)$ as an intercept which determined the pre-exponential (A) from equation (4.20).

Thus

$$Ea = 118.757 \text{ kJ mol}^{-1} \text{ ; } A = 4.80 \times 10^{5} \text{ s}^{-1}$$

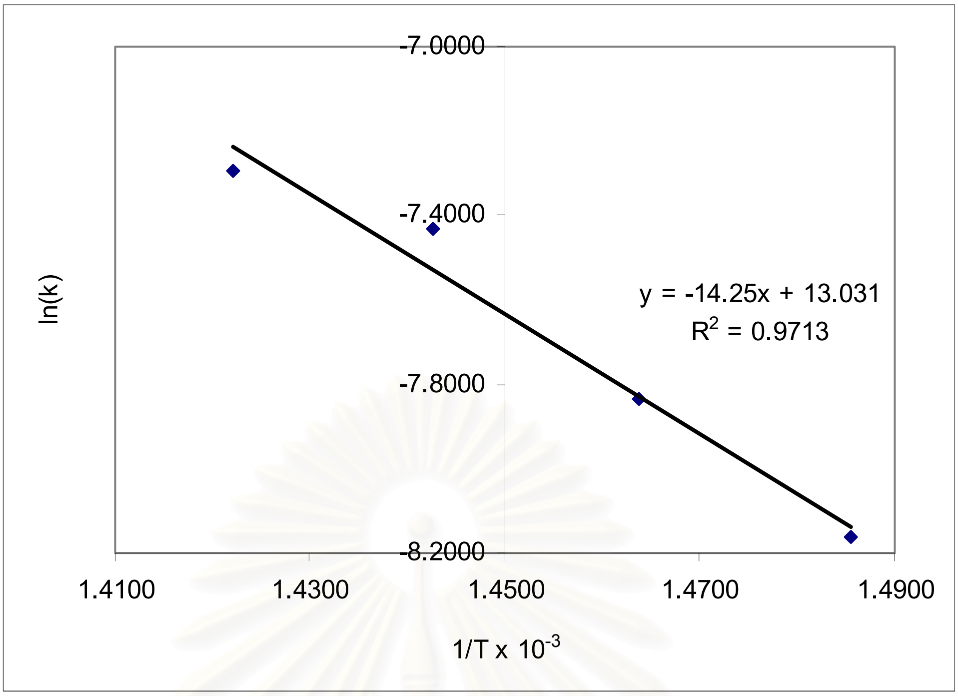

Figure 4.42 Plot of values of logarithmic specific reaction rate constant against the reciprocal of the reaction temperature

Table 4.10 The conversion of Long Residue at the variation of reaction time where the catalytic cracking of used vegetable oil over Sulfated Zirconia

Temperature (^{o}C)	Time (min)	Long Residue (wt)%	Conversion	ln(1-x)	x/(1-x)
400	0	55.94	0.0000	0.0000	0.0000
	30	35.31	0.3688	-0.4601	0.5843
	40	31.73	0.4328	-0.5670	0.7630
	50	28.42	0.4920	-0.6772	0.9683
	60	27.41	0.5100	-0.7133	1.0406
	70	25.63	0.5419	-0.7806	1.1828
	80	23.64	0.5774	-0.8613	1.3662
	90	21.35	0.6184	-0.9634	1.6206
410	0	55.88	0.0000	0.0000	0.0000
	30	27.45	0.5088	-0.7109	1.0359
	40	25.71	0.5399	-0.7763	1.1735
	50	24.37	0.5638	-0.8297	1.2927
	60	22.69	0.5940	-0.9014	1.4630
	70	20.62	0.6310	-0.9969	1.7100
	80	18.19	0.6746	-1.1226	2.0727
	90	17.18	0.6925	-1.1792	2.2518

<u>Table 4.10 (continue)</u> The conversion of Long Residue at the variation of reaction time where the catalytic cracking of used vegetable oil over Sulfated Zirconia

Temperature (^{o}C)	Time (min)	Long Residue (wt)%	Conversion	ln(1-x)	x/(1-x)
420	0	53.95	0.0000	0.0000	0.0000
	30	26.83	0.5027	-0.6985	1.0108
	40	23.69	0.5610	-0.8232	1.2778
	50	21.49	0.6017	-0.9205	1.5105
	60	19.07	0.6465	-1.0400	1.8291
	70	15.80	0.7072	-1.2282	2.4149
	80	14.00	0.7405	-1.3491	2.8538
	90	12.91	0.7607	-1.4301	3.1790
430	0	50.63	0.0000	0.0000	0.0000
	30	25.26	0.5011	-0.6954	1.0045
	40	21.44	0.5766	-0.8595	1.3619
	50	18.14	0.6418	-1.0267	1.7917
	60	15.52	0.6935	-1.1826	2.2629
	70	12.98	0.7437	-1.3614	2.9017
	80	11.98	0.7634	-1.4415	3.2269
	90	10.95	0.7838	-1.5314	3.6246

Figure 4.43 implies that the conversion of Long Residues to liquid fuels over Sulfated Zirconia are validate at temperature 400, 410, 420 and 430 ^{o}C: time of reaction during 0 to 90 minutes gave correctly a straight line with a good regression constant near by 1.00. Hence, this reaction is the second order

The rate constant at the various temperatures are plotted to find a correlation between ln(k_2) and 1/T from Arrhenius's equation in equation (4.19) in term of logarithm becomes; $\ln(k_n) = \ln(k_{n0}) - (E/R)/T$

A plotted of ln(k_n) versus 1/T gives straight line with the slope as (-E/R) and the intercept = ln(k_{n0}) which uses to determine the activation energy and ln(k_{n0}) to predict the kinetic model of the reaction

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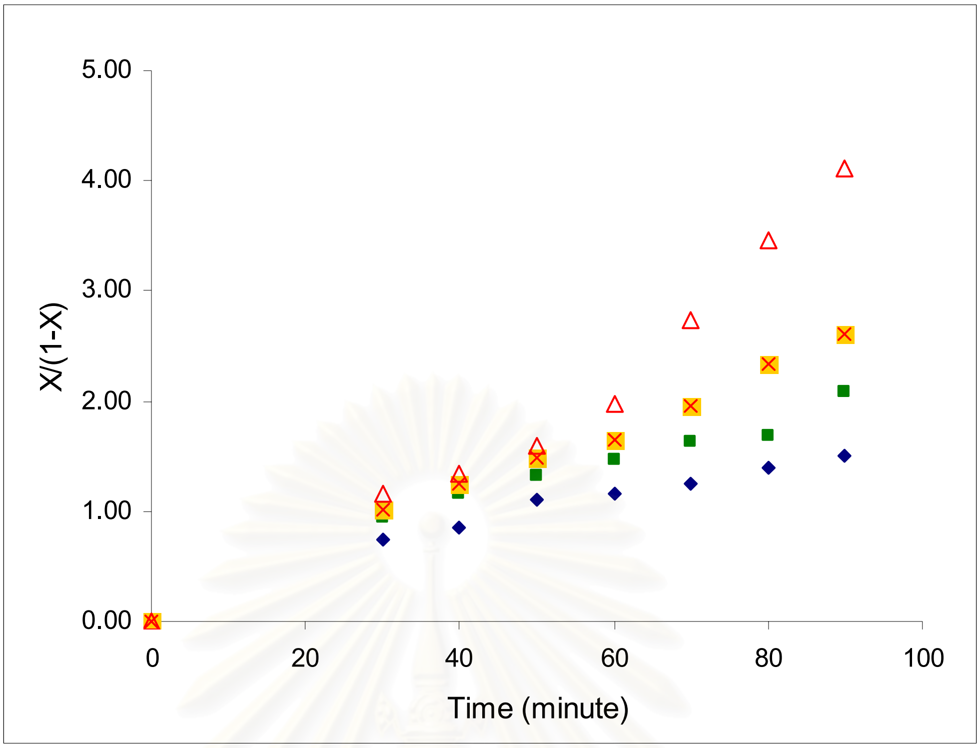

Figure 4.43 Conversion vs. Time of reaction [(◆) 400 C; (■) 410 C; (☒) 420 C ; (Δ) 430°C]

Table 4.11 Represented of ln(k_n) versus 1/T at the variation of reaction tempearture

Temperature (K)	1/T (K^{-1})	k_2 (min^{-1})	k_2 (s^{-1})	ln(k_2)
400	1.4856 x 10^{-3}	0.0159	2.65 x 10^{-4}	-8.2358
410	1.4638 x 10^{-3}	0.0209	3.48 x 10^{-4}	-7.9624
420	1.4427 x 10^{-3}	0.028	4.67 x 10^{-4}	-7.6699
430	1.4222 x 10^{-3}	0.0443	7.38 x 10^{-4}	-7.2111

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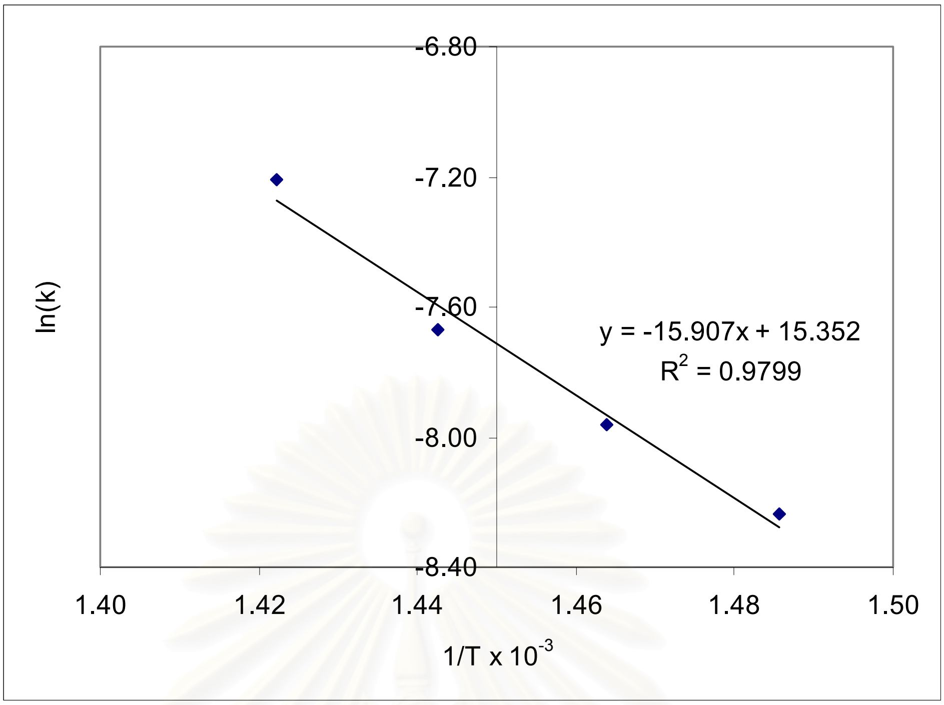

Figure 4.44 Plot of values of logarithmic specific reaction rate constant against the reciprocal of the reaction temperature

Figure 4.44 shows the plot of ln k versus 1/T could be traced. So Ea, the activation energy could be obtained from the slope of the straight line and also, the pre-exponential factor are; Ea = 132.251 kJ mol^{-1} ; A = 4.65 x 10^5 s^{-1}

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Table 4.12 The conversion of Long Residue at the variation of reaction time where the catalytic cracking of used vegetable oil over Hybrid catalyst of 0.3 : 0.7 HSZM-5 and Sulfated Ziconia

Temperature (^{o}C)	Time (min)	Long Residue (wt)%	Conversion	ln(1-x)	x/(1-x)
400	0	55.94	0.0000	0.0000	0.0000
	30	35.31	0.3688	-0.4601	0.5843
	40	31.73	0.4328	-0.5670	0.7630
	50	28.42	0.4920	-0.6772	0.9683
	60	27.41	0.5100	-0.7133	1.0406
	70	25.63	0.5419	-0.7806	1.1828
	80	23.64	0.5774	-0.8613	1.3662
	90	21.35	0.6184	-0.9634	1.6206
410	0	55.88	0.0000	0.0000	0.0000
	30	27.45	0.5088	-0.7109	1.0359
	40	25.71	0.5399	-0.7763	1.1735
	50	24.37	0.5638	-0.8297	1.2927
	60	22.69	0.5940	-0.9014	1.4630
	70	20.62	0.6310	-0.9969	1.7100
	80	18.19	0.6746	-1.1226	2.0727
	90	17.18	0.6925	-1.1792	2.2518
420	0	53.95	0.0000	0.0000	0.0000
	30	26.83	0.5027	-0.6985	1.0108
	40	23.69	0.5610	-0.8232	1.2778
	50	21.49	0.6017	-0.9205	1.5105
	60	19.07	0.6465	-1.0400	1.8291
	70	15.80	0.7072	-1.2282	2.4149
	80	14.00	0.7405	-1.3491	2.8538
	90	12.91	0.7607	-1.4301	3.1790
430	0	50.63	0.0000	0.0000	0.0000
	30	25.26	0.5011	-0.6954	1.0045
	40	21.44	0.5766	-0.8595	1.3619
	50	18.14	0.6418	-1.0267	1.7917
	60	15.52	0.6935	-1.1826	2.2629
	70	12.98	0.7437	-1.3614	2.9017
	80	11.98	0.7634	-1.4415	3.2269
	90	10.95	0.7838	-1.5314	3.6246

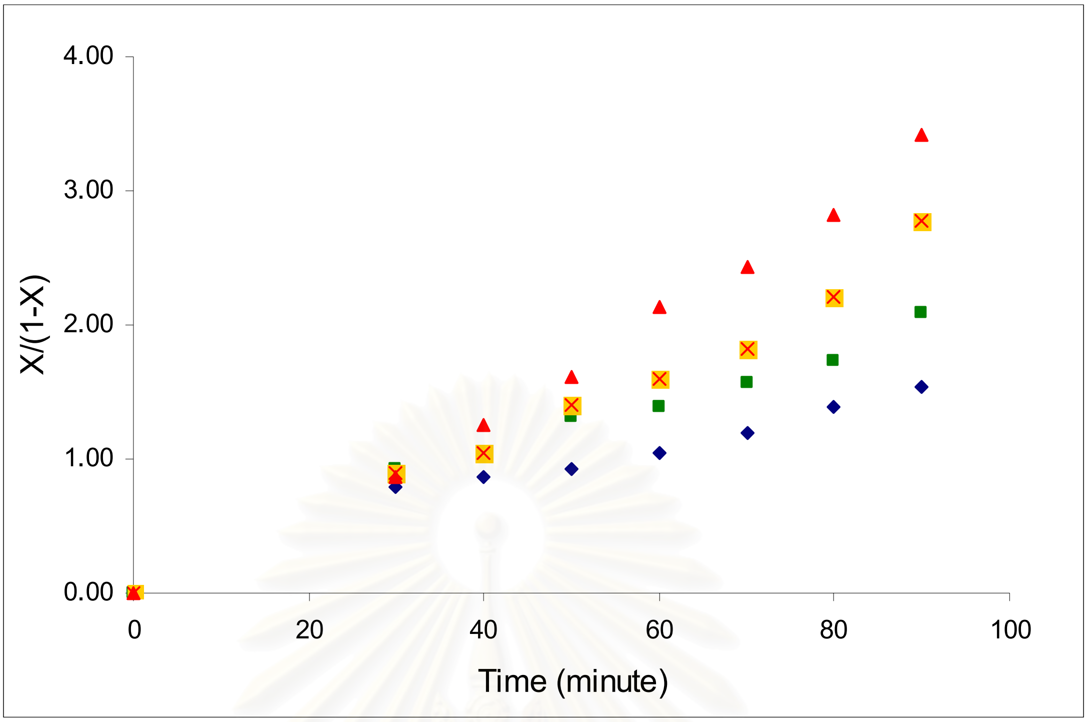

Figure 4.45 Conversion vs. Time of reaction [(◆) 400 C; (■) 410 C; (☒) 420 C ; (Δ) 430°C]

Figure 4.45 illustrated that the conversion of Long Residues to liquid fuels over 0.3 : 0.7 HZSM-5 and Sulfated Zirconia Hybrid catalyst are validate at temperature 400, 410, 420 and 430°C : time of reaction during 0 to 90 minutes gave correctly a right line with a good regression constant near by 1.00. Hence, this reaction is the second order

Table 4.13 Represented of $\ln(k_n)$ versus 1/T at the variation of reaction tempearture

Temperature (K)	1/T (K^{-1})	k_2 (min^{-1})	k_2 (s^{-1})	$\ln(k_2)$
400	1.4856×10^{-3}	0.0157	2.62×10^{-4}	-8.2484
410	1.4638×10^{-3}	0.0213	3.55×10^{-4}	-7.9434
420	1.4427×10^{-3}	0.0289	4.82×10^{-4}	-7.6383
430	1.4222×10^{-3}	0.0379	6.32×10^{-4}	-7.3671

The rate constant at various temperatures are plotted the correlation between $\ln(k_2)$ and 1/T from Arrhenius's equation in equation (4.19) in term of logarithm becomes; $\ln(k_n) = \ln(k_{n0}) - (E/R)/T$

A plotted of $\ln(k_n)$ versus 1/T gives the straight line with the slope as (-E/R) and the intercept = $\ln(k_{n0})$ which uses to determine the activation energy and pre-exponential (A) to predict the kinetic model of the reaction

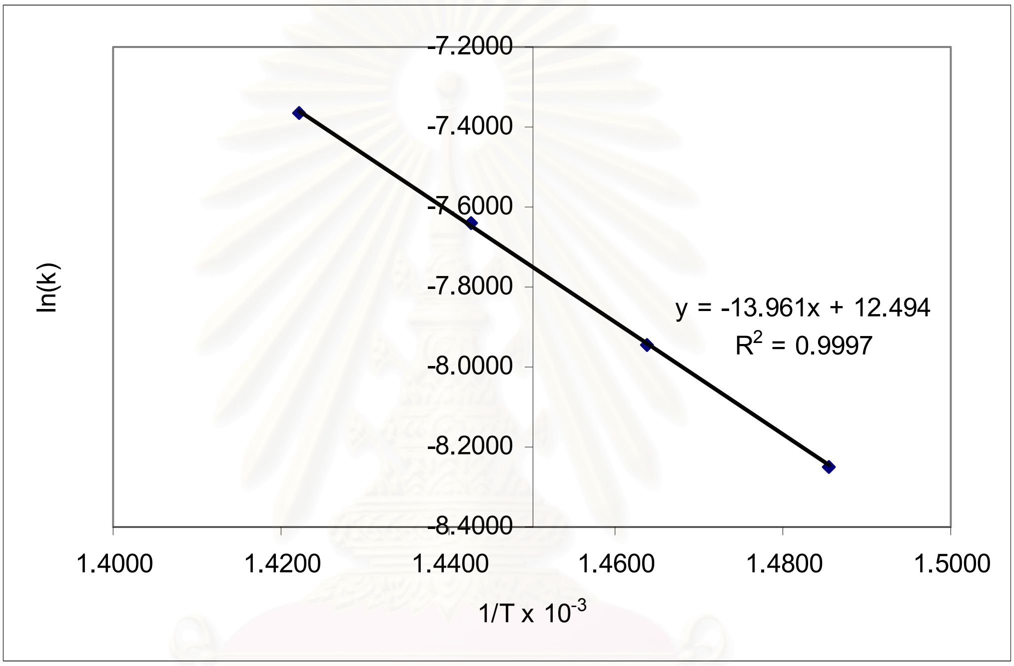

Figure 4.46 Plot of values of logarithmic specific reaction rate constant against the reciprocal of the reaction temperature

Figure 4.46 shows ln k versus 1/T traced. So Ea, the activation energy could be obtained by the slope of the right line and also, A the pre-exponential factor ;
Ea = 116.072 kJ mol^{-1} ; A = 2.67×10^5 s^{-1}

4.5 Comparison the appropriated condition and kinetic model for the catalytic cracking of used vegetable oil to liquid fuels over various catalysts

Table 4.14 The appropriated condition and represented kinetic model in each type of catalyst.

Condition	**HZSM-5**	**Sulfated Zirconia**	**Hybrid Catalyst**
Temperature	430 °C	430 °C	430 °C
Initial hydrogen pressure	10 bars	10 bars	10 bars
Time of Reaction	60 min	90 min	90 min
Catalysts	0.1 wt%	0.1 wt%	0.1 wt% of the ratio 0.3 : 0.7 HZSM-5 : Sulfated Zirconia
%wt of liquid yield	69.94 wt%	80.28 wt%	79.17 wt%
%wt of Gasoline fraction	22.15 wt%	24.38 wt%	26.57 wt%
Kinetic Model			
Order of reaction	Second	Second	Second
Ea (KJ/mol)	118.757	132.251	116.072
Pre-exponential (s^{-1})	4.80×10^{-5}	4.65×10^{-5}	2.67×10^{-5}

4.6 Comparison the results to the previous works

In 2003, Farouq and co-worker (2003) studied conversion of palm oil to liquid hydrocarbon fuels, This study used HZSM-5 to investigate catalytic cracking of Palm kernel oil and Palm olein oil in a fixed bed micro reactor which operated at atmospheric pressure, temperature of reaction at 350 °C

In addition, M. Mongkol (2003) were studied catalytic cracking of used vegetable oil to liquid fuels over Fe/Active carbon and HZSM-5, her studies was performed in batch reactor, temperature of 400 – 430 °C, initial hydrogen pressure 10 – 20 bar, time of reaction 45 – 75 miniute were investigated the significant parameters affected to the cracking of used vegetable oil. Table 4.15 represented the comparison this study and the other research

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Table 4.15 Comparison the results of this study and other research

	Twaiq 1999	**Mongkol** 2003	**This study**
Temperature	350 °C	430 °C	430 °C
Initial hydrogen pressure	-	10 bar	10 bar
Time of Reaction	-	90 min	90 min
Catalysts	HZSM-5	0.1 wt%	0.1 wt% of the ratio 0.3 : 0.7
		Fe/Active Carbon	HZSM-5 : Sulfated Zirconia
%wt of liquid yield	43.60	83.60	79.17
%wt of Gasoline fraction	22.15	26.75	26.57
% wt of gaseous yield	41.80	15.30	20.20
% wt of solid	15.60	0.10	0.63

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CHAPTER V

CONCLUSION

The conversion of used vegetable oil to liquid fuels through physical and chemical remain highly interested. Used vegetable oil is attracting increasingly interest because they have great potential to be used as diesel substitutes or direct upgrading to clean premium transportation fuels using catalytic cracking. This work furnishes leads to methods to obtain liquid fuels from used vegetable oil from fried chicken fast food. The products can be in the range of Gasoline, middle distillates, and Long Residues.

1. A maximum liquid product of 84.53 wt%, 88.73 wt%, and 88.81 wt% were obtained with the condition of 400 C, 10 bar of initial hydrogen pressure, the time of reaction of 60 minutes over HZSM-5, Sulfated Zirconia, and 0.3 : 0.7 HZSM-5 and Sulfated Zirconia, respectively. The highest gasoline fraction from these catalysts was 26.57 wt% over 0.1 wt% of 0.3 : 0.7 HZSM-5 and Sulfated Zirconia hybrid catalyst at the condition of 430 ^{o}C, initial hydrogen pressure 10 bars and time of reaction of 90 minutes. Compared with HZSM-5 and Sulfated Zirconia, Hybrid Catalyst providing a higher gasoline fraction whereas HZSM-5 providing a high gaseous yield. The gaseous products consisted mainly of $C_1 – C_4$ hydrocarbon gases. Methane, Ethane, Propane, Butane, and CO_2 were the major products

2. The cracking capability of Sulfated Zirconia could be increased by interaction between Sulfated Zirconia and HZSM-5, which are physically combined with it in hybrid catalysts. It has been shown that using appropriate hybrid catalyst with small amount of HZSM-5 added into Sulfated Zirconia can be increased liquid yield and increased gasoline fraction and affect conversion from long residue to the other chemical. In the HZSM-5/Sulfated Zirconia (0.3:0.7) hybrid catalysts was more active than HZSM-5 and

Sulfated Zirconia in the gasoline fraction, obtained selective can be related to the acid strength of HZSM-5 and Sulfated Zirconia, pore structure and shape selective of HZSM-5 in a hybrid catalyst may affect conversion of used vegetable oil. Thus, the higher Gasoline had been produced.

3. In order to the gaseous products, a direct relationship between the gas product and the strength of the acid sites is observed. The results indicate that long-chain hydrocarbon cracking reaction was favored by the enhancement of the catalytic acid strength. Hence, HZSM-5 shows the highest yield of gaseous products toward C_1-C_4 products.

4. The conversion of Long Residues of used vegetable oil to liquid fuels over HZSM-5 and Sulfated Zirconia (0.3 : 0.7) Hybrid catalyst are validate at temperature 400, 410, 420 and 430 ^{o}C, time of reaction during 0 to 90 minutes under initial hydrogen pressure of 10 bar. The reaction can be claimed to the second order, the activation energy and pre-exponential factor are 116.072 kJ mol^{-1} and 2.67 x 10^{5} s^{-1}, respectively.

Recommendations

For the improving of catalytic cracking of used vegetable oil to liquid fuels, further study should be given to the following aspect.

1. The study should be obtained with modified catalysts in proposed to increased surface area of catalysts. A synthesized mesoporous or changing of Si/Al ratio of HZSM-5 were synthesized to investigated catalytic cracking of used vegetable oil and other waste oil including to the waste plastic.

2. Scale-up of this process in the continuous reactor should be investigated.

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APPENDICES

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APPENDIX A

The Product Yield and Product Distribution

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Table A-1 The product yield and product distribution; Analyzed by Variance CP3800 Simulate Distillation Gas Chromatograph

Temperature (^oC)	Initial Pressure (bar)	Time of Reaction (min)	Catalyst	Gas	Gasoline	Kerosene	Light Gas Oil	Gas Oil	Long Residue	Solid
400	10	60	no catalyst	20.88	6.74	7.93	24.18	15.02	24.12	1.13
400	10	60	0.1 wt% HZSM-5	14.63	15.57	11.83	19.32	16.98	20.83	0.84
410	10	60	0.1 wt% HZSM-5	18.81	15.52	9.99	16.03	18.95	19.77	0.93
420	10	60	0.1 wt% HZSM-5	21.63	16.76	10.15	15.15	15.40	19.64	1.27
430	10	60	0.1 wt% HZSM-5	28.66	22.15	9.85	10.84	10.12	16.98	1.40
430	0	60	0.1 wt% HZSM-5	34.14	13.71	6.43	11.84	10.29	21.95	1.64
430	10	60	0.1 wt% HZSM-5	28.66	22.15	9.85	10.84	10.12	16.98	1.40
430	20	60	0.1 wt% HZSM-5	28.20	21.55	10.12	11.60	11.57	15.82	1.14
430	30	60	0.1 wt% HZSM-5	28.48	22.82	10.75	10.99	10.03	15.68	1.25
430	10	45	0.1 wt% HZSM-5	22.48	8.54	14.75	13.65	16.70	22.73	1.15
430	10	60	0.1 wt% HZSM-5	28.66	22.15	9.85	10.84	10.12	16.98	1.40
430	10	75	0.1 wt% HZSM-5	32.05	21.23	10.58	9.24	11.35	13.91	1.64
430	10	90	0.1 wt% HZSM-5	35.23	20.34	10.00	8.84	10.12	13.46	2.01
430	0	0	non catalyst	36.63	7.15	10.13	15.75	13.43	15.23	1.68
430	0.05	0.05	0.05 wt% HZSM-5	25.25	18.98	10.05	12.63	13.29	18.43	1.37
430	0.1	0.1	0.1 wt% HZSM-5	28.66	22.95	9.85	10.84	9.32	16.98	1.40
430	0.2	0.2	0.2 wt% HZSM-5	31.57	24.84	8.73	8.53	8.85	15.65	1.83

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Table A-1 (Continue) The product yield and product distribution; Analyzed by Variance CP3800 Simulate Distillation Gas Chromatograph

Temperature (°C)	Initial Pressure (bar)	Time of Reaction (min)	Catalyst	Gas	Gasoline	Kerosene	Light Gas Oil	Gas Oil	Long Residue	Solid
400	10	60	no catalyst	20.88	6.74	7.78	24.18	15.02	24.12	1.28
400	10	60	0.1 wt% SZ	10.87	10.04	6.51	31.57	13.04	27.58	0.40
410	10	60	0.1 wt% SZ	11.66	13.60	8.89	30.84	11.89	22.49	0.63
420	10	60	0.1 wt% SZ	11.93	14.68	10.32	30.82	10.36	21.43	0.46
430	10	60	0.1 wt% SZ	13.46	18.61	12.01	27.99	7.25	20.14	0.54
430	0	60	0.1 wt% SZ	34.14	12.71	11.13	10.84	8.29	21.95	0.94
430	10	60	0.1 wt% SZ	13.46	18.61	12.01	27.99	7.25	20.14	0.54
430	20	60	0.1 wt% SZ	13.50	18.41	11.48	28.07	7.01	20.82	0.71
430	30	60	0.1 wt% SZ	13.99	18.46	11.07	28.46	7.14	20.05	0.83
430	10	45	0.1 wt% SZ	13.38	14.48	12.15	29.94	7.69	21.86	0.50
430	10	60	0.1 wt% SZ	13.46	18.61	12.01	27.99	7.25	20.14	0.54
430	10	75	0.1 wt% SZ	16.18	22.54	12.95	26.69	6.48	14.54	0.62
430	10	90	0.1 wt% SZ	19.07	24.38	11.98	24.35	5.70	13.86	0.65
430	0	0	non catalyst	36.63	7.15	10.13	15.75	13.43	15.28	1.63
430	0.05	0.05	0.05 wt% SZ	13.25	18.02	12.32	27.65	7.94	20.14	0.68
430	0.1	0.1	0.1 wt% SZ	13.46	18.61	12.01	27.99	7.25	20.14	0.54
430	0.2	0.2	0.2 wt% SZ	15.74	18.73	12.65	25.03	7.65	19.32	0.88

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Table A-1 (Continue) The product yield and product distribution; Analyzed by Variance CP3800 Simulate Distillation Gas Chromatograph

Temperature (^{o}C)	Initial Pressure (bar)	Time of Reaction (min)	Catalyst	Gas	Gasoline	Kerosene	Light Gas Oil	Gas Oil	Long Residue	Solid
430	10	90	0.1:0.9 HZSM-5:SZ	15.15	19.43	14.01	24.23	8.04	18.01	1.13
430	10	90	0.3:0.7 HZSM-5:SZ	13.46	23.07	12.48	27.31	6.42	16.83	0.43
430	10	90	0.5:0.5 HZSM-5:SZ	19.99	18.84	8.63	15.49	16.32	19.58	1.15
430	10	90	0.8:0.2 HZSM-5:SZ	27.45	20.62	9.13	11.84	10.46	19.43	1.07
400	10	60	non catalyst	20.88	6.74	7.93	24.18	15.02	24.12	1.13
400	10	60	0.3:0.7 HZSM-5:SZ	10.87	10.27	7.29	31.20	12.21	27.85	0.32
410	10	60	0.3:0.7 HZSM-5:SZ	11.66	12.05	9.45	32.83	10.21	23.43	0.37
420	10	60	0.3:0.7 HZSM-5:SZ	11.93	16.79	11.10	30.13	9.65	20.04	0.36
430	10	60	0.3:0.7 HZSM-5:SZ	13.46	23.07	12.48	27.31	6.42	16.83	0.43
430	0	60	0.3:0.7 HZSM-5:SZ	21.66	11.45	8.08	21.05	12.44	24.38	0.94
430	10	60	0.3:0.7 HZSM-5:SZ	13.46	23.07	12.48	27.31	6.42	16.83	0.43
430	20	60	0.3:0.7 HZSM-5:SZ	13.50	18.41	11.48	28.07	7.01	20.82	0.71
430	30	60	0.3:0.7 HZSM-5:SZ	13.99	18.46	11.07	28.46	7.14	20.05	0.83
430	10	45	0.3:0.7 HZSM-5:SZ	12.82	17.55	11.06	29.81	7.22	21.04	0.50
430	10	60	0.3:0.7 HZSM-5:SZ	13.46	23.07	12.48	27.31	6.42	16.83	0.43

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Table A-1 (Continue) The product yield and product distribution; Analyzed by Variance CP3800 Simulate Distillation Gas Chromatograph

Temperature (^oC)	Initial Pressure (bar)	Time of Reaction (min)	Catalyst	Gas	Gasoline	Kerosene	Light Gas Oil	Gas Oil	Long Residue	Solid
430	10	75	0.3:0.7 HZSM-5:SZ	18.75	24.99	11.06	24.84	6.25	13.54	0.57
430	10	90	0.3:0.7 HZSM-5:SZ	20.20	26.57	10.65	23.02	6.05	12.88	0.63

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APPENDIX B

The composition of gaseous products

Table A-2 The composition of gaseous products; Analyzed by MICROGC3000 Gas Chromatograph

Temperature (^{o}C)	Initial Pressure (bar)	Time of Reaction (min)	Catalyst	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO_2
400	10	60	no catalyst	10.48	6.23	6.01	0.99	76.29
400	10	60	0.1 wt% HZSM-5	13.45	9.17	2.81	1.4	73.17
410	10	60	0.1 wt% HZSM-5	15.97	11.04	4.15	1.93	66.91
420	10	60	0.1 wt% HZSM-5	19.75	12.99	5.48	2.89	58.89
430	10	60	0.1 wt% HZSM-5	22.03	14.5	6.04	3.1	54.33
430	10	60	0.1 wt% HZSM-5	22.03	14.5	6.04	3.1	54.33
430	20	60	0.1 wt% HZSM-5	22.58	13.74	5.68	3.24	54.76
430	30	60	0.1 wt% HZSM-5	23.14	13.98	6.17	3.44	53.27
430	10	45	0.1 wt% HZSM-5	14.01	8.28	2.13	1.26	74.32
430	10	60	0.1 wt% HZSM-5	22.03	14.5	6.04	3.1	54.33
430	10	75	0.1 wt% HZSM-5	25.88	15.83	6.74	3.01	48.54
430	10	90	0.1 wt% HZSM-5	27.42	17.11	8	3.19	44.28
430	0	0	non catalyst	11.64	8.01	7.45	2.15	70.75
430	10	0.05	0.05 wt% HZSM-5	22.03	14.5	6.04	3.1	54.33
430	10	0.1	0.1 wt% HZSM-5	24.88	16.12	5.95	3.81	49.24
430	10	0.2	0.2 wt% HZSM-5	26.17	16.4	6.12	2.99	48.32
400	10	60	no catalyst	13.48	7.54	8.13	1.78	69.07
400	10	60	0.1 wt% SZ	13.45	9.17	7.81	1.36	68.21
410	10	60	0.1 wt% SZ	15.23	8.04	7.46	1.93	67.34
420	10	60	0.1 wt% SZ	16.75	8.99	7.02	1.67	65.57
430	10	60	0.1 wt% SZ	18.15	9.15	7.15	1.22	64.33
430	10	60	0.1 wt% SZ	18.15	9.15	7.15	1.22	64.33
430	20	60	0.1 wt% SZ	18.58	8.74	7.68	1.24	63.76
430	30	60	0.1 wt% SZ	18.14	8.09	8.12	1.44	64.21
430	10	45	0.1 wt% SZ	16.6	8.88	9.88	1.08	63.56
430	10	60	0.1 wt% SZ	18.15	9.15	7.15	1.22	64.33
430	10	75	0.1 wt% SZ	22.15	14.75	8.63	2.47	52
430	10	90	0.1 wt% SZ	26.23	18.67	7.99	2.9	44.21

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Table A-2 (Continue) The composition of gaseous product; Analyzed by MICROGC3000 Gas Chromatograph

Temperature (°C)	Initial Pressure (bar)	Time of Reaction (min)	Catalyst	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO_2
430	0	0	no catalyst	11.64	8.01	7.45	2.15	70.75
430	10	0.05	0.05 wt% SZ	18.03	9.63	5.95	2.94	63.45
430	10	0.1	0.1 wt% SZ	18.15	9.15	7.15	1.22	64.33
430	10	0.2	0.2 wt% SZ	22.01	11.65	6.99	1.48	57.87
430	10	90	0.1:0.9 HZSM-5:SZ	23.53	12.93	9.86	2.06	51.62
430	10	90	0.3:0.7 HZSM-5:SZ	21.63	11.05	8.13	2.14	57.05
430	10	90	0.5:0.5 HZSM-5:SZ	20.66	13.75	8.05	1.88	55.66
430	10	90	0.8:0.2 HZSM-5:SZ	23.65	13.88	9.9	1.67	50.9
400	10	60	no catalyst	15.55	12.84	8.55	1.13	61.93
400	10	60	0.3:0.7 HZSM-5:SZ	10.98	9.23	6.94	1.98	70.87
410	10	60	0.3:0.7 HZSM-5:SZ	14.23	9.65	7.02	2.12	66.98
420	10	60	0.3:0.7 HZSM-5:SZ	17.62	10.18	7.02	2.08	63.1
430	10	60	0.3:0.7 HZSM-5:SZ	21.63	11.05	8.13	2.14	57.05
430	10	60	0.3:0.7 HZSM-5:SZ	21.63	11.05	8.13	2.14	57.05
430	20	60	0.3:0.7 HZSM-5:SZ	21.77	11.68	7.29	2.07	57.19
430	30	60	0.3:0.7 HZSM-5:SZ	20.98	10.95	7.44	2.23	58.4
430	10	45	0.3:0.7 HZSM-5:SZ	18.85	9.13	8.04	2.08	61.9
430	10	60	0.3:0.7 HZSM-5:SZ	21.63	11.05	8.13	2.14	57.05
430	10	75	0.3:0.7 HZSM-5:SZ	23.48	14.67	7.64	2.27	51.94
430	10	90	0.3:0.7 HZSM-5:SZ	27.82	17.94	8.49	2.01	43.74

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APPENDIX C

Analysis the production distribution in the boiling range

The product distribution was determined by Simulated Distillation Gas Chromatograph (DGC) followed by ASTM D2887 to classified the product distribution in petroleum boiling range

The specification and the condition of DGC in this research are following

Open tubular column cappiraly columns :	RTX 2887
Initial temperature	40 ^oC
Final temperateure	350 ^oC
Detector	FID detector
Sample size	1 µL
Carrier gas	helium
Programming Rate	10 ^oC/min

The chromatograph from simulated distillation chromatograph shows the percentage of recovery of the product distribution which could be proposed in the petroleum product boiling range definitions. In the oil industry, a distillate fraction from C_5 to material boiling at about 200 ^oC is called gasoline; kerosene boils from 200 to 250 ^oC; light gas oil boiling ranges is from 250 to 300 ^oC; gas oil boils from 300 to 370 ^oC; and over at about 370 ^oC is definition to the long residue.

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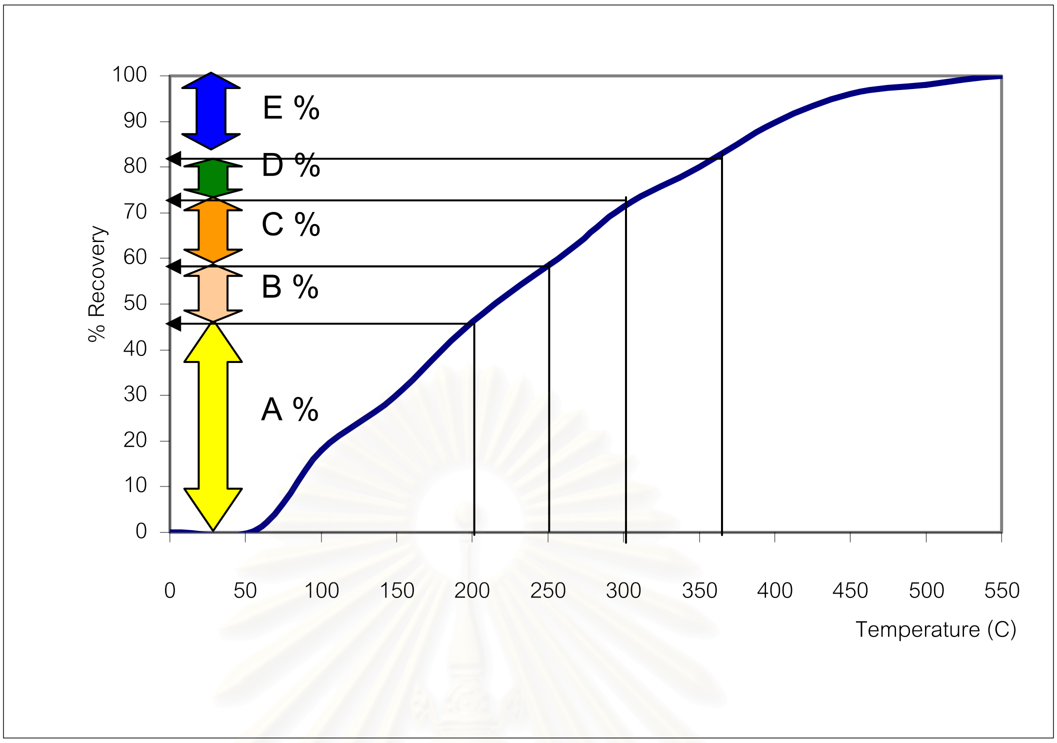

Figure A-1 Determine product boiling range from simulated distillation gas chromatograph

The chromatograph is definition the product distribution from the % recovery and boiling range as following

The %recovery of Gasoline in chromatograph A %

Hence, %wt of Gasoline fraction in the liquid W gram $= \frac{A \times W}{100}$

The %recovery of Kerosene in chromatograph B %

Hence, %wt of Kerosene fraction in the liquid W gram $= \frac{B \times W}{100}$

The %recovery of Light Gas Oil in chromatograph C %

Hence, %wt of Light Gas Oil fraction in the liquid W gram $= \frac{C \times W}{100}$

The %recovery of Gas Oil in chromatograph D %

Hence, %wt of Gas Oil fraction in the liquid W gram = $\frac{D \times W}{100}$

The %recovery of Long Residue in chromatograph E %

Hence, %wt of Long Residue fraction in the liquid W gram = $\frac{E \times W}{100}$

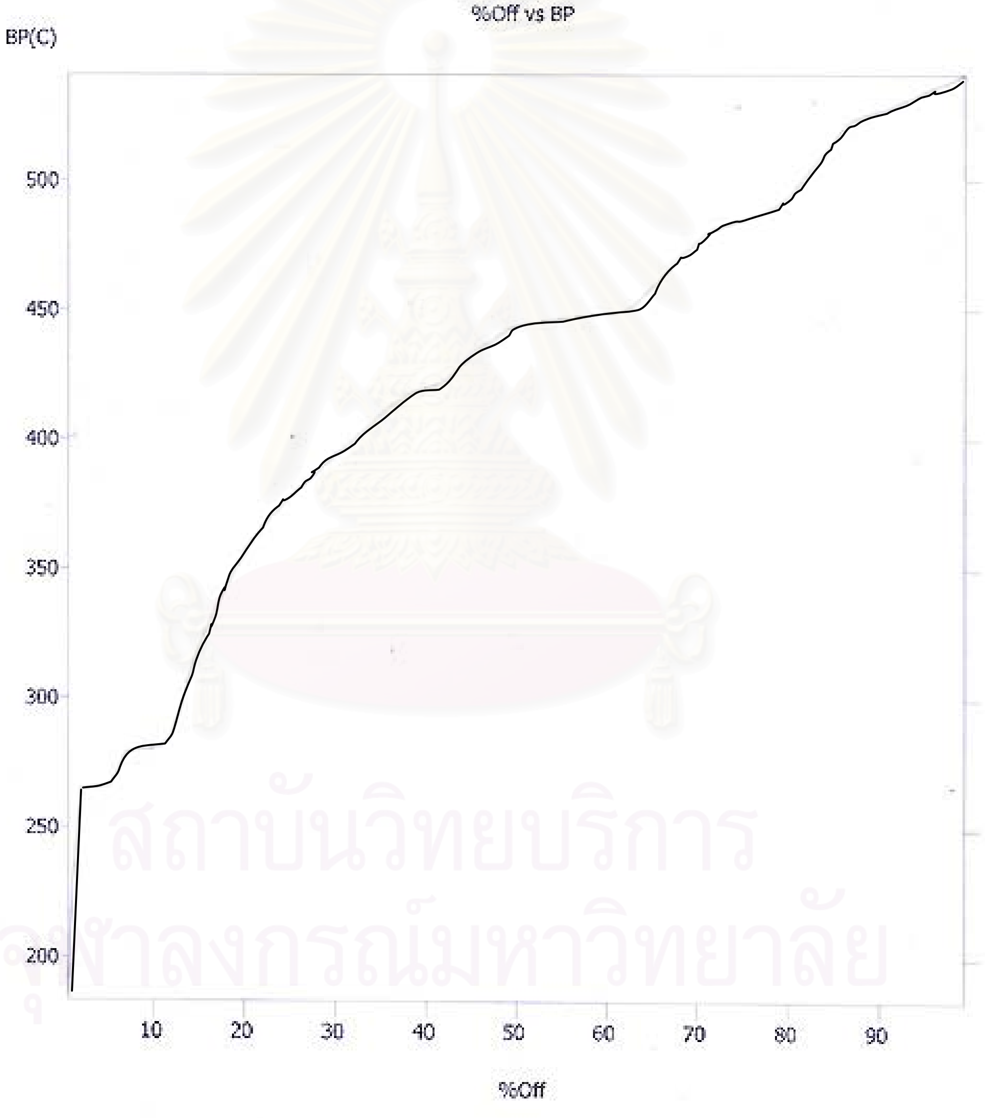

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Figure A-2 Simulated Distillation gas chromatograph of used vegetable oil before cracked shows only the fraction of Light Gas Oil at about 15%; Gas Oil of 10% and Long Residue 75%

APPENDIX D

Product distribution for the runs to proposed a kinetic model over various catalysts

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Table A-3 Product distribution for the runs to proposed a kinetic model over HZSM-5

Temperature (^oC)	Time (min)	Gas (%)	Liquid (%)	Gasoline (%)	Kerosene (%)	Light gas oil (%)	Gas oil (%)	Long Residue (%)	SOLID (%)	Conversion (X)	ln(1-X)	X/(1-X)
400	0	3.36	96.31	0.00	0.28	30.67	8.44	55.94	0.39	0.0000	0.0000	0.0000
	30	11.38	88.25	7.10	5.34	30.05	15.85	35.31	0.37	0.3688	-0.4601	0.5843
	40	12.43	87.19	8.70	5.72	29.88	14.12	31.73	0.38	0.4328	-0.5670	0.7630
	50	13.26	86.33	9.13	6.17	30.03	12.59	28.42	0.41	0.4920	-0.6772	0.9683
	60	13.88	85.72	11.14	6.52	30.01	10.64	27.41	0.40	0.5100	-0.7133	1.0406
	70	15.07	84.44	13.16	7.07	30.09	8.49	25.63	0.49	0.5419	-0.7806	1.1828
	80	15.99	83.45	14.80	8.95	29.30	6.77	23.64	0.56	0.5774	-0.8613	1.3662
	90	16.75	82.61	16.19	10.31	29.34	5.42	21.35	0.64	0.6184	-0.9634	1.6206
410	0	4.99	94.68	0.00	0.37	28.78	9.65	55.88	0.37	0.0000	0.0000	0.0000
	30	11.44	88.20	8.58	6.91	30.49	14.76	27.45	0.36	0.5088	-0.7109	1.0359
	40	13.46	86.16	9.68	7.13	31.38	12.26	25.71	0.38	0.5399	-0.7763	1.1735
	50	14.40	85.13	11.93	7.46	31.24	10.13	24.37	0.47	0.5638	-0.8297	1.2927
	60	15.51	84.03	13.42	8.43	30.33	9.17	22.69	0.46	0.5940	-0.9014	1.4630
	70	16.28	83.18	15.10	9.09	30.60	7.77	20.62	0.54	0.6310	-0.9969	1.7100
	80	16.88	82.55	18.18	9.78	29.33	7.07	18.19	0.57	0.6746	-1.1226	2.0727
	90	17.10	82.34	21.28	9.58	28.66	5.64	17.18	0.56	0.6925	-1.1792	2.2518
420	0	7.36	92.30	0.17	1.23	27.11	9.85	53.95	0.36	0.0000	0.0000	0.0000
	30	12.67	86.97	9.58	8.32	32.20	10.04	26.83	0.36	0.5027	-0.6985	1.0108
	40	13.74	85.94	12.75	8.91	32.54	8.05	23.69	0.32	0.5610	-0.8232	1.2778
	50	14.98	84.67	15.22	9.86	30.90	7.21	21.49	0.35	0.6017	-0.9205	1.5105
	60	15.92	83.71	15.92	10.95	30.67	7.10	19.07	0.37	0.6465	-1.0400	1.8291
	70	16.53	83.06	18.98	11.08	30.77	6.43	15.80	0.41	0.7072	-1.2282	2.4149
	80	17.78	81.77	21.38	11.45	29.08	5.86	14.00	0.45	0.7405	-1.3491	2.8538
	90	18.03	81.50	23.91	12.95	26.63	5.09	12.91	0.47	0.7607	-1.4301	3.1790

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Table A-3 (continue) Product distribution for the runs to proposed a kinetic model over HZSM-5

Temperature (^oC)	Time (min)	Gas (%)	Liquid (%)	Gasoline (%)	Kerosene (%)	Light gas oil (%)	Gas oil (%)	Long Residue (%)	SOLID (%)	Conversion (X)	ln(1-X)	X/(1-X)
430	0	8.13	91.51	0.25	1.81	30.10	8.72	50.63	0.36	0.0000	0.0000	0.0000
	30	14.98	84.62	15.51	9.32	28.62	5.91	25.26	0.40	0.5011	-0.6954	1.0045
	40	15.02	84.53	20.16	10.21	27.95	4.77	21.44	0.45	0.5766	-0.8595	1.3619
	50	16.38	83.12	21.35	10.76	28.29	4.58	18.14	0.50	0.6418	-1.0267	1.7917
	60	17.66	81.80	23.05	10.84	26.21	6.18	15.52	0.54	0.6935	-1.1826	2.2629
	70	18.14	81.31	25.01	11.68	26.07	5.58	12.98	0.55	0.7437	-1.3614	2.9017
	80	20.47	78.91	28.19	11.08	23.52	4.13	11.98	0.62	0.7634	-1.4415	3.2269
	90	23.53	75.82	28.06	11.43	21.51	3.87	10.95	0.65	0.7838	-1.5314	3.6246

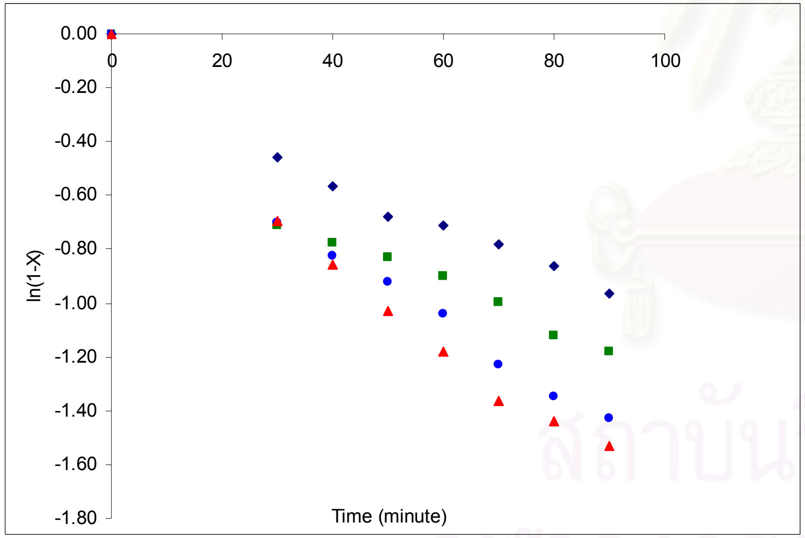

Figure A-3 plot of ln(1-X) versus Time for hypothesis order = 1

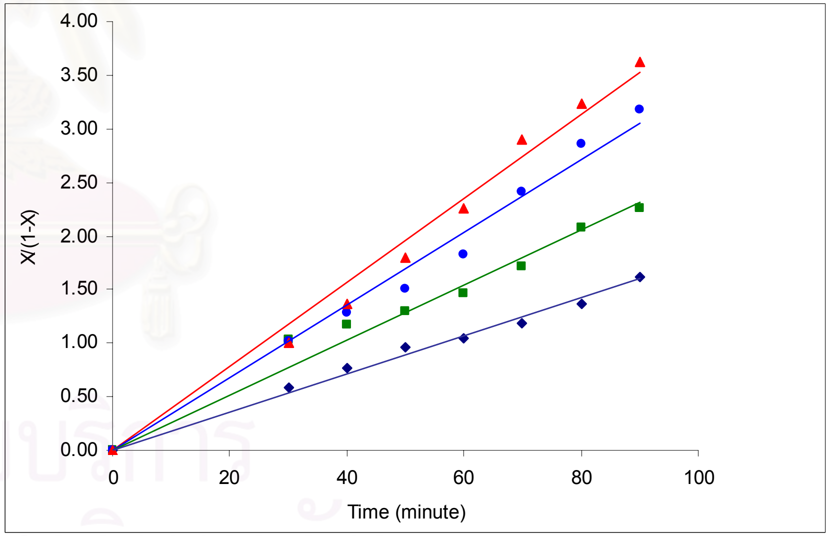

Figure A-4 plot of X/(1-X) versus Time for hypothesis order = 2

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Table A-4 Product distribution for the runs to proposed a kinetic model over Sulfated Zirconia

Temperature (^oC)	Time (min)	Gas (%)	Liquid (%)	Gasoline (%)	Kerosene (%)	Light gas oil (%)	Gas oil (%)	Long Residue (%)	SOLID (%)	Conversion (X)	ln(1-X)	X/(1-X)
400	0	3.29	96.38	0.00	0.00	30.27	7.72	59.34	0.33	0.0000	0.0000	0.0000
	30	6.68	92.96	5.65	6.23	31.46	15.65	33.98	0.36	0.4274	-0.5576	0.7465
	40	7.23	92.39	7.49	6.82	31.35	14.59	32.14	0.38	0.4583	-0.6131	0.8462
	50	8.88	90.71	9.45	6.46	32.96	13.71	28.13	0.41	0.5260	-0.7465	1.1096
	60	9.57	90.03	10.49	6.51	32.42	13.04	27.58	0.40	0.5353	-0.7664	1.1519
	70	10.66	88.85	11.53	7.90	31.28	11.67	26.47	0.49	0.5540	-0.8074	1.2420
	80	10.81	88.63	12.92	8.84	31.06	10.95	24.86	0.56	0.5811	-0.8700	1.3869
	90	11.41	87.95	14.63	9.22	30.11	10.27	23.73	0.64	0.6001	-0.9166	1.5008
410	0	4.87	94.80	0.00	0.00	30.01	7.02	57.76	0.33	0.0000	0.0000	0.0000
	30	6.97	92.69	10.24	6.97	34.70	11.17	29.61	0.34	0.4875	-0.6684	0.9511
	40	7.92	91.70	12.59	7.34	33.64	11.41	26.73	0.38	0.5372	-0.7705	1.1609
	50	10.63	88.90	13.34	7.60	32.40	10.63	24.92	0.47	0.5686	-0.8407	1.3180
	60	11.72	87.82	14.52	8.33	32.18	9.36	23.43	0.46	0.5944	-0.9023	1.4652
	70	11.48	87.98	16.10	8.70	32.30	8.86	22.02	0.54	0.6188	-0.9643	1.6230
	80	11.82	87.61	17.29	8.87	31.79	8.15	21.52	0.57	0.6275	-0.9875	1.6845
	90	12.10	87.34	19.14	10.62	31.65	7.19	18.73	0.56	0.6757	-1.1260	2.0832
420	0	5.48	94.18	0.00	0.55	29.79	6.91	56.93	0.34	0.0000	0.0000	0.0000
	30	8.08	91.56	12.05	7.65	33.89	9.82	28.15	0.36	0.5056	-0.7045	1.0228
	40	9.43	90.25	13.07	7.68	33.71	10.42	25.37	0.32	0.5544	-0.8083	1.2441
	50	10.93	88.72	14.76	8.11	33.07	9.81	22.97	0.35	0.5965	-0.9077	1.4786
	60	11.69	87.94	15.71	8.82	33.07	8.84	21.50	0.37	0.6223	-0.9737	1.6478
	70	12.90	86.69	17.06	10.05	32.12	8.24	19.22	0.41	0.6624	-1.0859	1.9622
	80	13.70	85.85	19.53	10.58	32.09	6.61	17.04	0.45	0.7007	-1.2062	2.3408
	90	13.98	85.55	21.00	11.20	31.53	6.07	15.75	0.47	0.7234	-1.2850	2.6148

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Table A-4 (continue) Product distribution for the runs to proposed a kinetic model over Sulfated Zirconia

Temperature (^oC)	Time (min)	Gas (%)	Liquid (%)	Gasoline (%)	Kerosene (%)	Light gas oil (%)	Gas oil (%)	Long Residue (%)	SOLID (%)	Conversion (X)	ln(1-X)	X/(1-X)
430	0	6.56	93.08	0.61	0.93	27.03	7.71	56.81	0.36	0.0000	0.0000	0.0000
	30	10.68	88.92	14.02	9.64	29.74	8.72	26.79	0.40	0.5284	-0.7516	1.1203
	40	11.74	87.81	15.33	8.80	29.24	8.22	26.22	0.45	0.5384	-0.7731	1.1665
	50	12.07	87.43	17.21	11.15	29.76	7.45	21.86	0.50	0.6152	-0.9551	1.5990
	60	12.71	86.75	18.61	12.01	28.74	7.25	20.14	0.54	0.6454	-1.0368	1.8201
	70	13.08	86.37	20.59	12.54	28.47	7.66	17.11	0.55	0.6988	-1.2000	2.3201
	80	15.74	83.64	22.54	12.95	27.13	6.48	14.54	0.62	0.7441	-1.3630	2.9078
	90	18.05	81.30	24.38	11.98	25.37	5.70	13.86	0.65	0.7560	-1.4105	3.0981

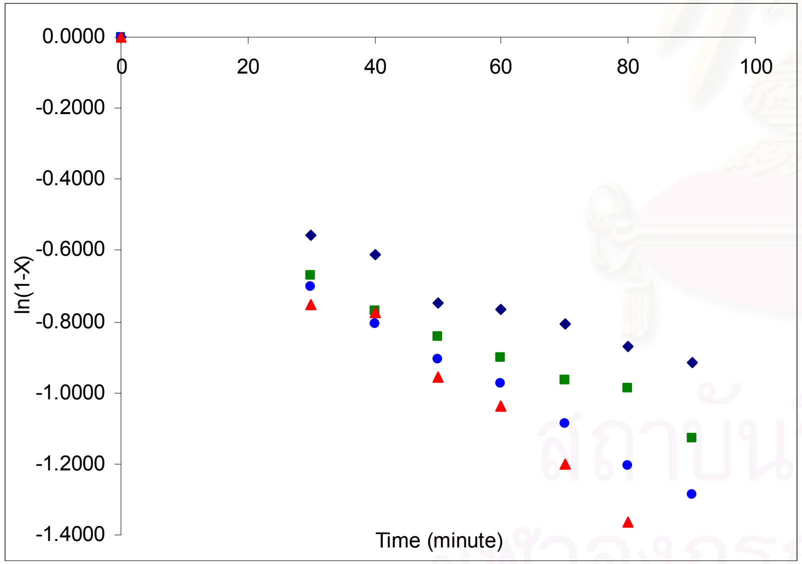

Figure A-5 plot of ln(1-X) versus Time for hypothesis order = 1

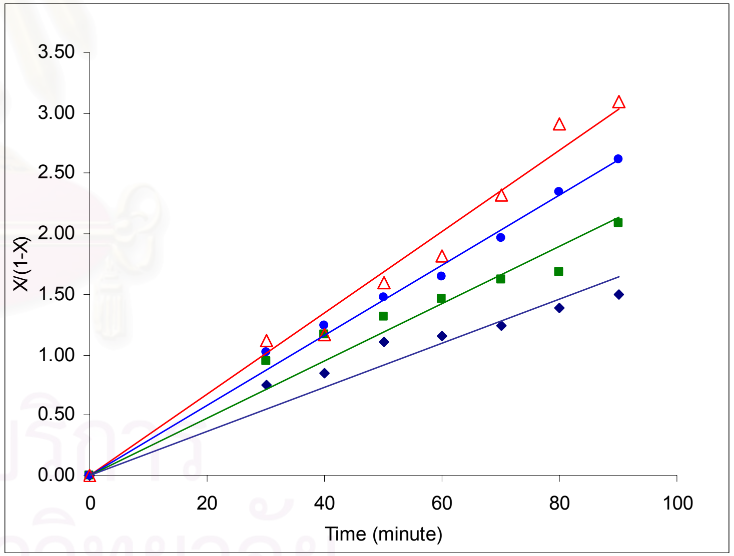

Figure A-6 plot of X/(1-X) versus Time for hypothesis order = 2

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Table A-5 Product distribution for the runs to proposed a kinetic model over Hybrid catalysts of 0.3 HZSM-5 and 0.7 Sulfated Zirconia

Temperature (^{o}C)	Time (min)	Gas (%)	Liquid (%)	Gasoline (%)	Kerosene (%)	Light gas oil (%)	Gas oil (%)	Long Residue (%)	SOLID (%)	Conversion (X)	ln(1-X)	X/(1-X)
400	0	3.30	96.39	0.00	0.00	30.59	8.32	57.48	0.31	0.0000	0.0000	0.0000
	30	7.72	91.97	7.44	5.76	32.31	14.42	32.04	0.31	0.4425	-0.5843	0.7938
	40	8.32	91.37	8.60	5.75	31.85	14.35	30.83	0.31	0.4636	-0.6230	0.8644
	50	9.15	90.53	9.81	6.71	31.23	12.87	29.90	0.32	0.4798	-0.6535	0.9222
	60	10.59	89.09	10.27	7.29	31.20	12.21	28.13	0.32	0.5107	-0.7147	1.0436
	70	11.98	87.67	12.42	7.03	29.86	12.11	26.25	0.35	0.5433	-0.7838	1.1897
	80	13.58	86.05	13.36	7.26	29.60	11.69	24.14	0.37	0.5801	-0.8676	1.3813
	90	14.24	85.38	14.51	7.28	29.49	11.51	22.59	0.38	0.6069	-0.9338	1.5442
410	0	4.74	94.94	0.00	0.00	30.84	8.05	56.05	0.32	0.0000	0.0000	0.0000
	30	8.40	91.25	8.33	7.77	33.41	12.55	29.20	0.35	0.4791	-0.6521	0.9196
	40	9.21	90.43	9.94	8.36	33.26	11.31	27.56	0.36	0.5083	-0.7098	1.0336
	50	10.62	89.01	11.24	9.35	34.25	9.93	24.23	0.37	0.5678	-0.8388	1.3135
	60	11.33	88.30	12.05	9.45	33.16	10.21	23.43	0.37	0.5819	-0.8721	1.3919
	70	12.36	87.24	13.43	9.59	32.42	10.02	21.78	0.40	0.6114	-0.9451	1.5731
	80	13.39	86.19	15.88	10.20	30.72	8.82	20.56	0.42	0.6331	-1.0027	1.7256
	90	15.10	84.47	18.57	10.10	29.24	8.40	18.14	0.43	0.6763	-1.1279	2.0893
420	0	5.99	93.66	0.00	1.29	29.70	7.95	54.72	0.35	0.0000	0.0000	0.0000
	30	8.70	90.94	9.08	8.82	32.91	11.32	28.81	0.36	0.4735	-0.6414	0.8992
	40	9.47	90.17	10.57	9.88	32.11	10.79	26.82	0.36	0.5099	-0.7131	1.0404
	50	10.97	88.65	13.24	10.82	31.56	10.27	22.76	0.38	0.5841	-0.8773	1.4044
	60	12.08	87.56	14.79	11.10	31.00	9.65	21.02	0.36	0.6158	-0.9565	1.6027
	70	13.90	85.72	15.61	11.53	29.18	10.04	19.36	0.38	0.6461	-1.0387	1.8256
	80	14.23	85.39	19.20	12.24	27.97	8.93	17.05	0.38	0.6883	-1.1659	2.2087
	90	15.54	84.05	21.00	12.49	28.28	7.80	14.48	0.41	0.7353	-1.3293	2.7783

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Table A-5 (continue) Product distribution for the runs to proposed a kinetic model over Hybrid catalysts of 0.3 HZSM-5 and 0.7 Sulfated Zirconia

Temperature (^{o}C)	Time (min)	Gas (%)	Liquid (%)	Gasoline (%)	Kerosene (%)	Light gas oil (%)	Gas oil (%)	Long Residue (%)	SOLID (%)	Conversion (X)	ln(1-X)	X/(1-X)
430	0	6.88	92.74	0.81	1.47	27.83	9.78	52.85	0.38	0.0000	0.0000	0.0000
	30	9.58	90.04	15.27	9.22	29.15	8.06	28.34	0.38	0.4637	-0.6231	0.8646
	40	10.38	89.22	16.37	10.02	31.49	7.84	23.49	0.40	0.5555	-0.8109	1.2498
	50	11.12	88.46	20.20	12.19	29.69	6.20	20.18	0.42	0.6182	-0.9629	1.6193
	60	13.35	86.22	22.87	12.79	27.31	6.42	16.83	0.43	0.6816	-1.1443	2.1403
	70	17.79	81.77	25.44	10.97	24.60	5.36	15.40	0.44	0.7087	-1.2333	2.4326
	80	21.02	78.53	24.91	11.50	23.72	4.59	13.81	0.45	0.7386	-1.3419	2.8262
	90	21.58	77.96	26.54	11.09	23.79	4.58	11.96	0.46	0.7737	-1.4860	3.4195

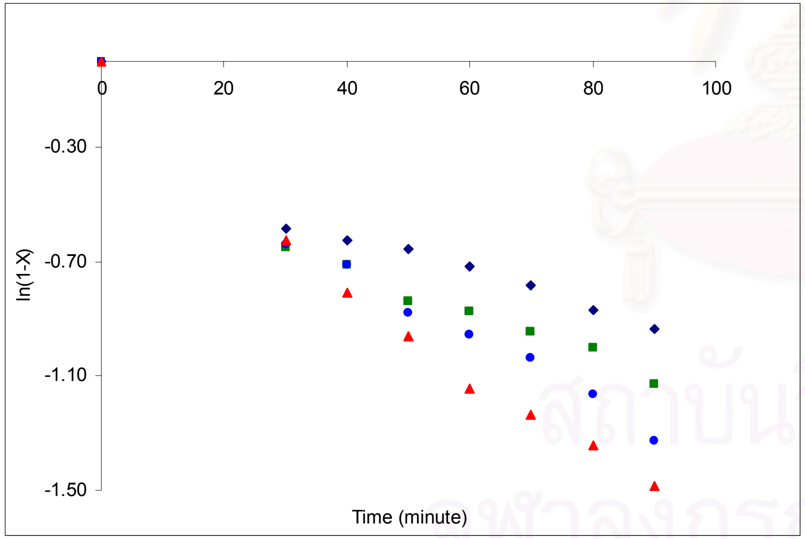

Figure A-7 plot of ln(1-X) versus Time for hypothesis order = 1

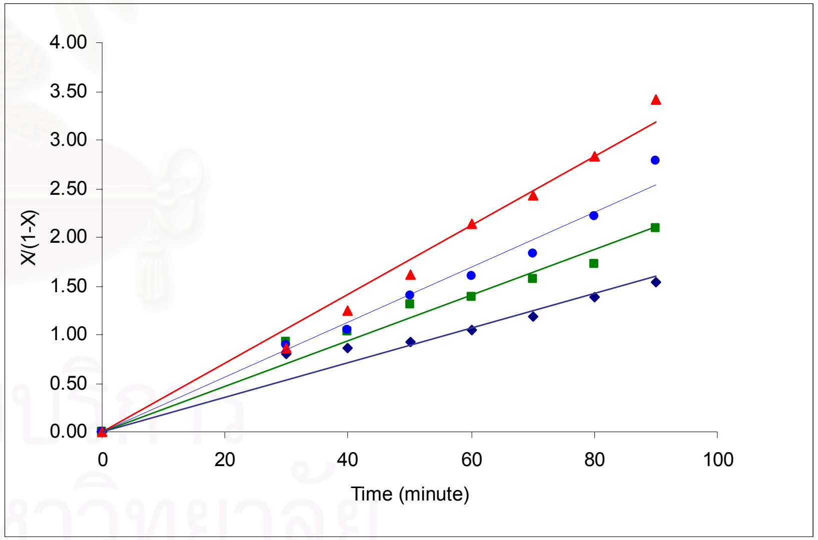

Figure A-8 plot of X/(1-X) versus Time for hypothesis order = 2

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Biography

Witchakorn Charusiri graduated his Bachelor from Faculty of Science majoring chemistry in 1997. He started working as a junior researcher at Energy Research Institute of Chulalongkorn University right after he had graduated. He studied his Master's degree in Chemical Technology and completed the program in 2001. He has continued study toward his Doctor's degree at Department of Chemical Technology, Faculty of Science, Chulalongkorn University. He has interested in renewable energy as well as developing energy from waste and potential study of renewable energy.

During 2004, he had opportunity to participated The 19th World Energy Congress and presented the paper on "Sizing and Location of Electrical Power Generation from Rice husk in Thailand" at Sydney, Australia. In addition, he presented the paper on "Conversion of Used Cooking Oil to Liquid Fuels on HZSM-5, Sulfated Zirconia and Hybrid Catalysts" in 32nd CHEMECA Conference on 25 – 28 September 2004 at Sydney, Australia.

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