การแตกตัวของน้ำมันพืชใช้แล้วเป็นเชื้อเพลิงเหลวบนตัวเร่งปฏิกิริยาเอฟซีซีใช้แล้ว

นางสาวรติวรรณ ผาดไพบูลย์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

CRACKING OF USED VEGETABLE OIL TO LIQUID FUEL OVER SPENT FCC CATALYST

Miss Ratiwan Padpibool

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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Thesis Title	CRACKING OF USED VEGETABLE OIL TO LIQUID FUEL OVER SPENT FCC CATALYST
By	Miss Ratiwan Padpibool
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Professor Tharapong Vitidsant, Ph.D.

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รติวรรณ ผาดไพบูลย์ : การแตกตัวของน้ำมันพืชใช้แล้วเป็นเชื้อเพลิงเหลวบนตัวเร่งปฏิกิริยาเอฟซีซีใช้แล้ว. (CRACKING OF USED VEGETABLE OIL TO LIQUID FUEL OVER SPENT FCC CATALYST) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร.ธราพงษ์ วิทิตศานต์, 135 หน้า.

จุดมุ่งหมายของการวิจัยนี้คือเพื่อศึกษาการแตกตัวของน้ำมันพืชใช้แล้วให้เป็นเชื้อเพลิงเหลวบนตัวเร่งปฏิกิริยาเอฟซีซีใช้แล้วในเครื่องปฏิกรณ์ขนาด 70 มล. ตัวแปรที่ศึกษาประกอบไปด้วยอุณหภูมิ 380-450 องศาเซลเซียส เวลาในการทำปฏิกิริยา 30-60 นาที ความดันไฮโดรเจนเริ่มต้น 1-5 บาร์ น้ำหนักตัวเร่งปฏิกิริยาตัวเร่งปฏิกิริยาเอฟซีซีใช้แล้ว 1-5 % โดยน้ำหนัก และน้ำหนักของวัตถุดิบน้ำมันเริ่มต้นที่ 20 กรัม การศึกษาอิทธิพลของตัวแปรต่างๆที่ส่งต่อผลิตภัณฑ์น้ำมันและองค์ประกอบที่ดีที่สุด โดยใช้การทดลองแบบแฟกทอเรียลสองระดับศึกษาอิทธิพลของตัวแปรที่มีผลต่อร้อยละผลได้ของผลิตภัณฑ์น้ำมัน พบว่าอุณหภูมิของการเกิดปฏิกิริยา ปริมาณตัวเร่งปฏิกิริยาเวลาปฏิกิริยา ความดันเริ่มต้น ปฏิสัมพันธ์ของตัวเร่งปฏิกิริยา และความดันปฏิสัมพันธ์ของเวลาและความดันเป็นปัจจัยหลักที่มีผลต่อผลได้ผลิตภัณฑ์น้ำมันอย่างมีนัยสำคัญ เมื่อทำการวิเคราะห์ผลิตภัณฑ์น้ำมันโดยเทคนิคแก๊สโครมาโทกราฟีจำลองการกลั่น (Simulated Distillation Gas Chromatography) พบว่าภาวะที่เหมาะสมที่ได้จากการคำนวณด้วยโปรแกรม design-expert คืออุณหภูมิที่ในการทำปฏิกิริยา 400.49 องศาเซลเซียส เวลาในการทำปฏิกิริยา 60 นาที และความดันไฮโดรเจนเริ่มต้น 1 บาร์และน้ำหนักของตัวเร่งปฏิกิริยาเอฟซีซีใช้แล้วร้อยละ 5 โดยน้ำหนัก ซึ่งจากสภาวะที่เหมาะสมได้ร้อยละผลได้ผลิตภัณฑ์น้ำมัน 73.21 โดยน้ำหนัก แก๊สไฮโดรคาร์บอนร้อยละ 20.65 โดยน้ำหนัก และของแข็งร้อยละ 6.14 โดยน้ำหนัก และองค์ประกอบของของผลิตภัณฑ์น้ำมันมีปริมาณแนฟทาร้อยละ 19.88 และมีองค์ประกอบเป็นเคโรซีนร้อยละ 10.21 ดีเซลร้อยละ 31.02 และกากน้ำมันร้อยละ 12.10 จากการวิเคราะห์หมู่ฟังก์ชันด้วยเครื่อง Fourier Transform Infrared Spectrophotometer พบว่ามีหมู่ฟังก์ชันหลักที่เป็นสายโซ่อะโรมาติก (Long chain aromatic) จำนวนมากเป็นองค์ประกอบหลักคล้ายกับหมู่ฟังก์ชันของน้ำมันเบนซินที่ได้จากปิโตรเลียม

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....

ปีการศึกษา 2556 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....

5572198323 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: USED VEGETABLE OIL / PYROLYSIS / SPENT FCC CATALYST / BIODIESEL PRODUCTION / RENEWABLE ENERGY

RATIWAN PADPIBOOL: CRACKING OF USED VEGETABLE OIL TO LIQUID FUEL OVER SPENT FCC CATALYST. ADVISOR: PROF. THARAPONG VITIDSANT, Ph.D., 135 pp.

The aim of this research was to study the pyrolysis of used vegetable oil over spent FCC catalyst in a batch reactor of 70 ml. The process was performed at 380-450 ˚C, reaction time 30-60 min, initial hydrogen pressure 1-5 bars, containing 1-5 wt% of spent FCC catalysts. The two level factorial experimental designs were performed to investigate the effect of variables on oil yield. It found that temperature of reaction, the amount of catalyst, reaction time, initial pressure, catalyst and pressure of reaction interaction and pressure and time of reaction interaction were significant affect to oil yield product. Liquid products were analyzed by simulated distillation gas chromatography. The optimum condition was found that temperature of 400 ˚C, reaction time 60 min and initial hydrogen pressure 1 bars by using 5 wt% of spent FCC catalyst. The oil yield product was 73.21 wt%, 20.65 wt% of gaseous product and 6.14 wt% of solid and oil yield product was consisted of 19.88 wt% of naphtha, 10.21 wt% of kerosene, 31.02 wt% of diesel and 12.10 wt% of long residue. The analysis of functional groups with a Fourier Transform Infrared Spectrophotometer found a functional group of long chain aromatic in large amounts in main structure similar to the functional groups of gasoline petroleum fuel.

Field of Study: Petrochemistry and Polymer Science

Academic Year: 2013

Student's Signature ....

Advisor's Signature ....

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CHAPTER I

INTRODUCTION

One of the most attractive alternative fuels is Biodiesel from renewable resources since it is considered as a desirable chemical characteristics and low emissions such as being non-toxic, carbon neutral and biodegradable. Because of the sustainability and economic growth, biofuels has received more attention than ever. The renewable energy resources are prospective to take an increasing role in the future energy consumptions to reduce the environmental impacts with air and water quality and global warming, etc. Nowadays, the renewable energy is being considered as a significant energy. Because of up-to-date society is enormously dependent on combustion engines powering transport vehicles. Moreover, the threat of global warming motivate to development of renewable resources essential. This is urgency in the need to develop technologies manufacturing Biodiesel from renewable resources, for reducing the emission of CO_2 form petroleum fuel. Petroleum fuel are limited and emits pollutants such as nitrogen, sulphur and carbon oxides, lead, hydrocarbons, etc. [1]

The used vegetable oils is obtained after using several times for frying process such as palm oil, soybean oil, sunflower oils and rice bran oil. Vegetable oils are mostly consisted of triglycerides (about 90%) with lesser amounts of mono- and diglycerides, as well as free fatty acids [2]. The chemical and physical properties of used vegetable oil are slightly different from fresh oils properties since the chemical reaction during frying process. The growth in human population cause the large amounts of used vegetable oil generated by homes and restaurants are increasing rapidly. In addition, the increment in food consumption has also contributed to the production of large amounts of used vegetable oil. [3] For example, The United States alone generates approximately 10 million tons of used vegetable oil per years [4].

For catalytic cracking is the premier conversion process found in the refinery nearly 20% of all distilled crude oil is processed in catalytic cracking unit. Products from the unit are fuel gases, liquefied petroleum gas or LPG and gasoline-range naphtha. Fluid Catalytic Cracking (FCC) catalyst used for cracking heavy feedstock for improves yields of light olefin and quality of gasoline and diesel fuels. In petrochemical processing, zeolites are used as catalysts for FCC process, a process which transforms long-chain alkanes (heavy oil) into shorter ones (petrol), and to enhance the octane number of the petrol by producing branched species. The properties of shape selective catalysts control the product distribution in the process; acidity and selectivity of these catalysts are governed by several factors such as acidity and pore size [5]. Zeolites have shown the excellent performance as the acid catalyst for cracking middle hydrocarbon molecule because of their higher selectivity toward gasoline type [6]. The desirable properties of an FCC catalyst are good stability to high temperature and to steam high activity, large pore sizes, good resistance to attrition, low coke production and recycling. The use of fluid catalytic cracking (FCC) catalysts in the cracking process generates large quantities of spent FCC catalyst which is still active for other processes. Reuse of spent FCC catalyst would be economically advantageous [7].

The present work aims to determine the optimum condition for the cracking of used vegetable oil over spent FCC catalyst in a batch reactor. The effects of temperature, initial pressure of hydrogen gas, time of reaction and mass of catalyst on the oil yield conversion have been studied. The distribution of the yield oil product was investigated using by ASTM D2887 as naphtha, kerosene, gas oil, light gas oil, gas oil and long residue analyze with Simulated Distillation Gas Chromatograph.

The objectives of this study are:

1. To investigate the effects of experimental parameters on oil yield product from cracking of used vegetable oil over spent FCC catalyst such as effect of temperature, initial pressure of hydrogen gas, time of reaction and mass of catalyst.
2. To determine the optimum condition of cracking of used vegetable oil on spent FCC catalyst.

CHAPTER II

THEORY AND REVIEWS

2.1 Used vegetable Oil [4, 8]

The production of major vegetable oil increase every year to meet the increasing of demand for renewable resource. Vegetable oils are huge produced renewable resources, derived from the part of a wind variety plants. Their base materials are plant-based lipids, such as palm oil, soybean oil, corn oil, jathropa, coconut oil, olive oil, rice bran oil and canola oil and etc. The most common used vegetable oil is made from palm because of its low cost relative to other sources, such as coconut, corn or soybean plants. Used vegetable oil can be freely collected from restaurants and houses which may require public awareness campaigns preceding the collection process. Used vegetable oil generated in selected countries and the oil source also different quantity generated in various countries around the world as shown Table 2.1.

Table 2.1 Quantity of waste cooking oil generated in various countries around the world [4]

Country	Quanity (million tones/year)	Source of oil
United States	10	Soybean oil
China	4.5	Salad oil, animal fat
European	0.7-0.57	Rapeseed oil, sunflower oil
Japan	0.45-0.57	Soybean oil, palm oil, animal fat
Taiwan	0.07	Soybean oil, palm oil, beef oil, lard oil
Malaysia	0.5	Palm oil
Canada	0.12	Animal fat, canola oil
England	1.6	Soybean oil, canola oil
Ireland	0.153	Rapeseed oil

The term describes triglycerides of fatty acid consists of a straight chain of an even number of carbon atoms, with hydrogen atoms along the length of the chain and at one end of the chain and a carboxyl group (–COOH) at the other end which are liquid under ambient temperature and pressure. Vegetable oils are unstable at high temperature and non-volatile. These molecules have the form of a linear chain shown in Figure 2.1

Most naturally fatty acids have a chain of an even number of carbon atoms from 4 to 28 [9]. Vegetable oils almost all are usually mixture of naturally fatty acids in varying fraction as shown in Table 2.2. Properties of differ oil depending on the composition and nature kind of fatty acid in the triglyceride molecules [10]. The vegetable oils whose main composition is 95% of total weight of a triglyceride molecule with both saturated and unsaturated compounds as shown in Table 2 [11].

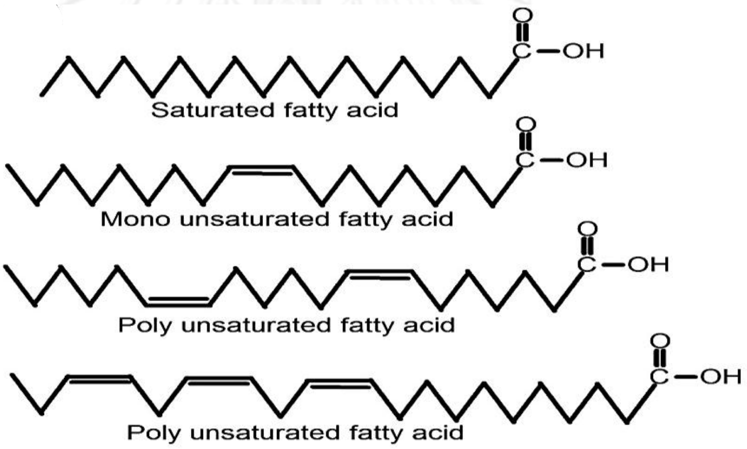


Figure 2.1 Compounds of vegetable oils (saturated fatty acid, mono unsaturated fatty acid and poly unsaturated fatty acid) [11]

Table 2.2 Mixture of naturally fatty acids in varying fraction in vegetable oil [9]

Fatty Acid	**Coconut oil**	**Rapeseed oil**	**Palm oil**	**Soybean Oil**
Caprylic C8:0	7.6	-	-	-
Capric C10:0	7.3	-	-	-
Lauric C12:0	48.2	-	0.1	-
Myristic C14:0	16.6	1	1.2	0.1
MyristoleicC14:1	-	-	-	-
Palmitic C16:0	8	25	46.8	10.5
Palmitoleic C16:1	1	0.7	3.8	-
Stearic C18:0	3.4	2.8	37.5	3.2
Oleic C18:1	5	17.1	10	22.3
Linoleic C18:2	2.5	52.7	-	54.5
Linolenic C18:3	-	-	-	8.3

Table 2.3 Representative the average composition of saturated and unsaturated fatty acid in vegetable oil [10]

Oil	Saturated fatty acid (%)	Unaaturated fatty acid (%)
Soybean oil	11.33	88.67
Sunflower oil	10.71	89.29
Corn oil	13	87
Rice bran oil	21.6	78.4
Palm olein	44.91	55.09
Palm oil	56.98	43.02
Coconut oil	90.52	9.48

The chemical and physical properties of used vegetable oil are slightly different from those of fresh oils because of the changes that occur during frying process as shown in Table 2.4 shows the chemical and physical properties of a used vegetable oil sample collected. [12]

Table 2.4 Properties of used vegetable oil [12]

Property	Units	Value
Palmitic acid	wt%	8.5
Stearic acid	wt%	3.1
Oleic acid	wt%	21.2
Linoleic acid	wt%	55.2
Linolenic acid	wt%	5.9
Other	wt%	4.2
Water content	wt%	1.9
Density	cm^3/g	0.91
Kinematic viscosity(40°C)	mm^2/s	4.2
Saponification value	mgKOH/g	207
Acid value	mgKOH/g	3.6
Iodine number	$gI^2\ 100g^{-1}$	83
Sodium content	mg/kg	6.9
Peroxide value	mg/kg	23.1

2.2 Catalyst [13]

2.2.1 Background and Properties of Catalysis

The catalyst change the reaction path by lowering its activation energy and consequently *the catalyst increase the rate of reaction*. A catalyst remains unchanged in the mass and chemical composition at the end of the reaction. A small quantity of the catalyst is generally sufficient. Catalyst reaction processes in a batch manner, reactants and catalysts are loaded together in reactor and catalytic reaction (homogenous or heterogeneous) take place in temperature and pressure for desired reaction time and conversion.

2.2.2 Type of catalyst

Catalysts may be classified generally according to ways catalyst work.
Catalysts can be classified into two types: homogeneous and heterogeneous as shown in Figure 2.2.

2.2.2.1 Homogeneous catalysis

Catalyst is of the same phase as the reactant and no phase boundary exists. Catalysts may be gases, liquids, or solids. In homogeneous catalysis, the catalyst is molecularly dispersed in the same phase (usually gaseous or liquid) as the reactants. Typically everything will be present as a gas or contained in a single liquid phase.

2.2.2.2 Heterogeneous catalysis

Catalyst is in the different phase from reactants and has the phase boundary. In heterogeneous catalysis the reactants and the catalyst are in different phases, separated by a phase boundary. Most commonly, heterogeneous catalysts are solids, and the reactants are gases or liquids. Heterogeneous divided to 2 main types are zeolite and non-zeolite. Non-zeolites are also divided to metal type and Oxides, Sulfides Etc. as shown in Figure 2.3. Typical examples involve a solid catalyst with the reactants as either liquids or gases.

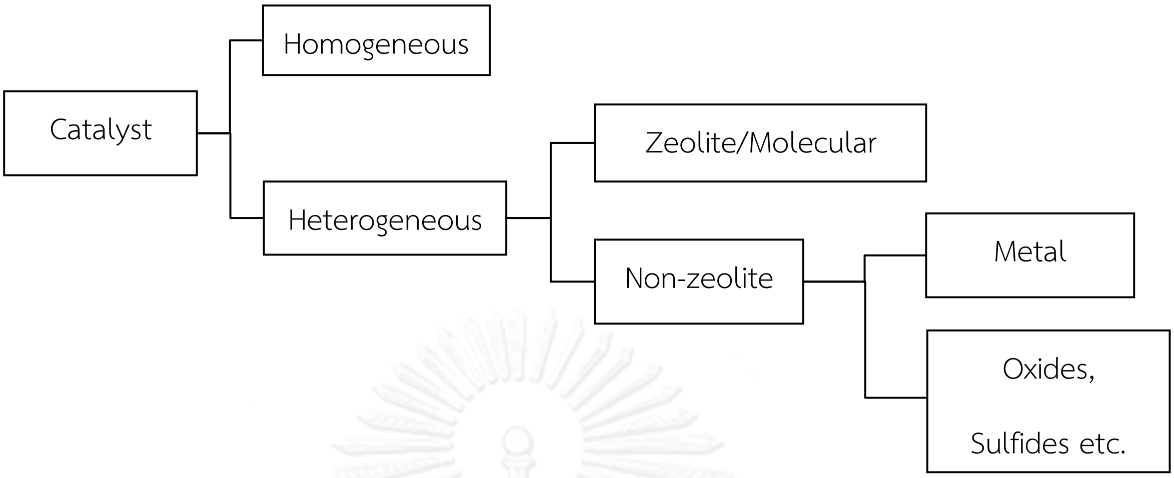


Figure 2.2 Types of catalyst [13]

2.2.3 External Diffusion Effects on Heterogeneous Reactions [4]

For heterogeneous catalytic reaction, the catalyst is usually in a different phase from the reactants. Commonly the catalyst is in the solid phase embedded in the reacting species which usually are in the liquid or gaseous phase. A heterogeneous catalyst is a substance that changes the rate of a chemical reaction due to its participation. It works when the reactants diffuse on its surface and are absorbed to it through formation of chemical bonds. After the reaction, the product desorbs from the surface of the catalyst and diffuses away. Most heterogeneous catalysts are solids and thus the surface area of the catalyst is very critical as it determines the catalytic site. Consequently, the reaction rate is principally relied on the mass transfer or diffusion between these phases. There are seven steps in a catalytic reaction as below:

1. Mass transfer (diffusion) of the reactant from the bulk fluid to the external surface of the catalyst pellet. This is the diffusion of the reactants from the bulk phase (boundary layer) to the external surface of the catalyst pellet (film diffusion or interphase diffusion).

2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface; the point where the chemical transformation occurs (pore diffusion or intraparticle diffusion)

3. The catalytic surface adsorption of reactants on the inner catalytic surface.

4. Reaction on the surface of the catalyst reaction at specific active sites on the catalyst surface.

5. Desorption of the products from the surface

6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface. Desorption of the products from the inner surface.

7. Mass transfer of the products from the external pellet surface to the bulk fluid.

2.4 Background of Zeolite [14]

Zeolites are form millions of years ago when volcanoes erupted enormous amount of ash composed of aluminosilicates of alkaline and alkaline earths. In all cases, the chemical reaction of volcanic ash and salt water results in the formation of natural zeolites.

Zeolites are microporous crystalline solids with well-defined structures as shown in Figure 2.5. Generally they contain silicon, aluminium and oxygen in their framework and cations, water or other molecules within their pores as shown in Figure 2.4. The main advantages of the micropores of zeolite molecular dimensions are their greatly high surface area and shape selectivity.

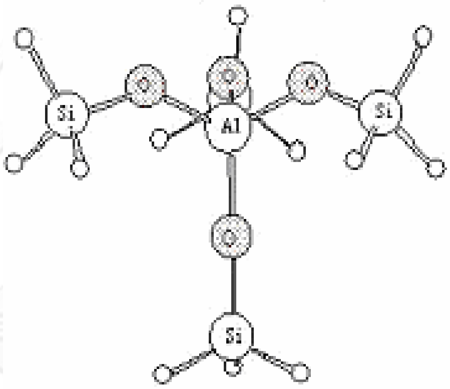


Figure 2.3 Subunit structure of the zeolite [14]

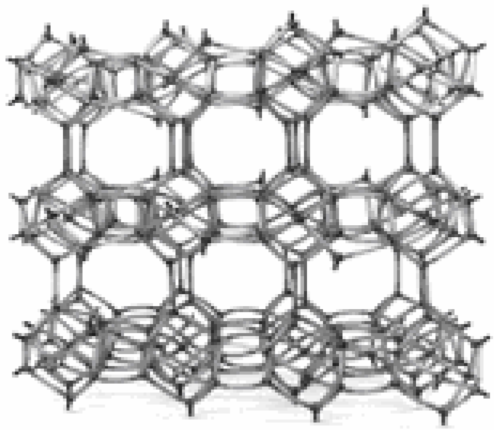


Figure 2.4 Crystalline structure of the zeolite species [14]

2.5 Properties of zeolites [15]

- Zeolites are crystalline solid material with microporous. Because of their unique porous properties, they are often also referred to as molecular sieves.
- Zeolites are negatively charges and they loosely hold positively charged cation (positive charge).
- Zeolites have high surface area and high cation exchange capacity.
- Zeolites have high thermal stability
- Zeolites exhibit particular shape and size selectivity.

2.6 Pore size and structure of the zeolites [16]

Zeolites are microporous materials with pore aperture dimensions (2–10 Å) closer to the molecular sizes. Zeolites are the original active compound of FCC catalysts. The fluid catalytic cracking of heavy gas oil is one of the most intensively used in refining processes; this process produces not only gasoline and diesel fuel but also light olefins. The pore size of zeolites is determined by the quantity of oxygen atoms that form the pore cavity and by the possible obstruction of the pores by cations.

The zeolite solid consists of framework of SiO_4 tetrahedral. The tetrahedral silicon ion sites in lattice are substituted by aluminum ions. The structure of faujasite or zeolite Y, a faujasite super cage is illustrated. The pore structure is 3-D and the pore size, determined by the 12-ring of oxygen atoms, is 0.74 nm as shown in Figure 2.6.

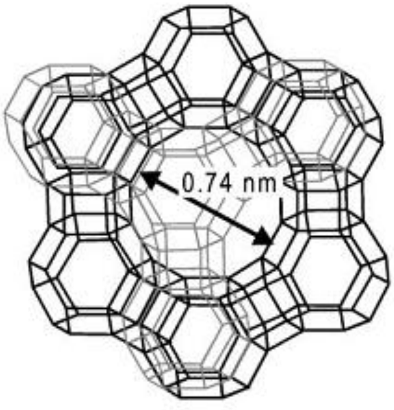


Figure 2.5 Structure of zeolite Y [16]

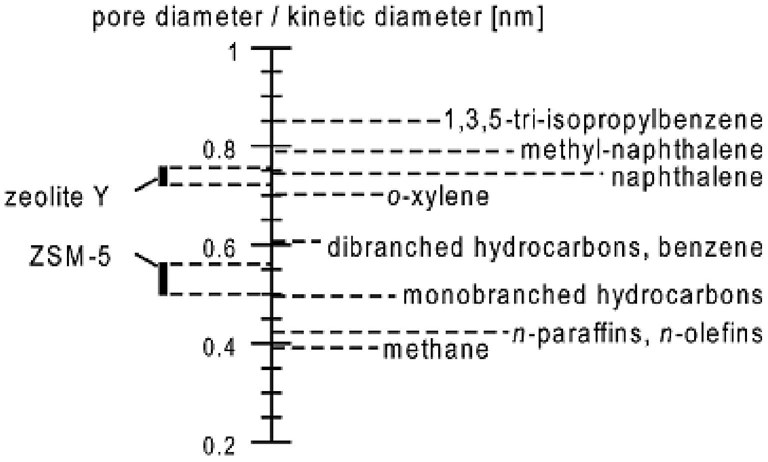


Figure 2.6 Comparison of pore sizes of zeolite Y and ZSM-5 with the kinetic diameters of some hydrocarbon molecules [16]

The comparison of pore diameters and kinetic diameter of HZSM-5 and zeolites Y is shown in Figure 2.7. By reason of the smaller pore size, only linear and monobranched hydrocarbonscan easily enter the pores of ZSM-5. In zeolite Y, molecules with two or more naphthenic rings enter the pore structure.

Zeolite is defined as a diverse group of inorganic, alkaline and hydrated crystalline aluminum-silicates, tetrahedral connecting neighboring corners by sharing their oxygen atoms (O-sites) forming a regular spatial arrangement of uniform cages, cavities or channels of molecular dimensions. The crystallographical structure of the siliceous zeolite silicalite (b-axis) as shown in Figure 2.7

The feature that is common to zeolite is that they all have a 3-dimensional, 4 connected framework structure constructed form corner-sharing TO_4 tetrahedra, where T is any tetrahedrally coordinated cation. The three-dimensional framework of 4-valent TO_4 unit cells (T=Si, Al, B, Ga, Ge, Fe, P and Co) [17].

Zeolites are 3-D porous material of idealized general formular as shown in equation 2.1.

$$M_{x/n}[Al_xSi_yO_{2(x+y)}].pH_2O \qquad ....2.1$$

M is (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is cation charge; y/x=1–6

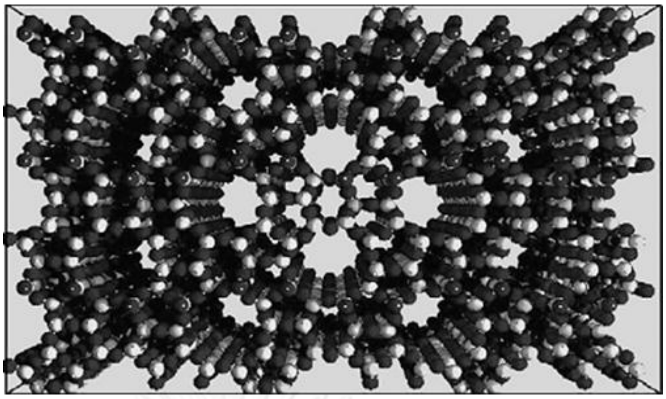


Figure 2.7 Crystallographical structure of the siliceous zeolite silicalite (b-axis) [17]

2.7 Zeolites Acid site [15, 18]

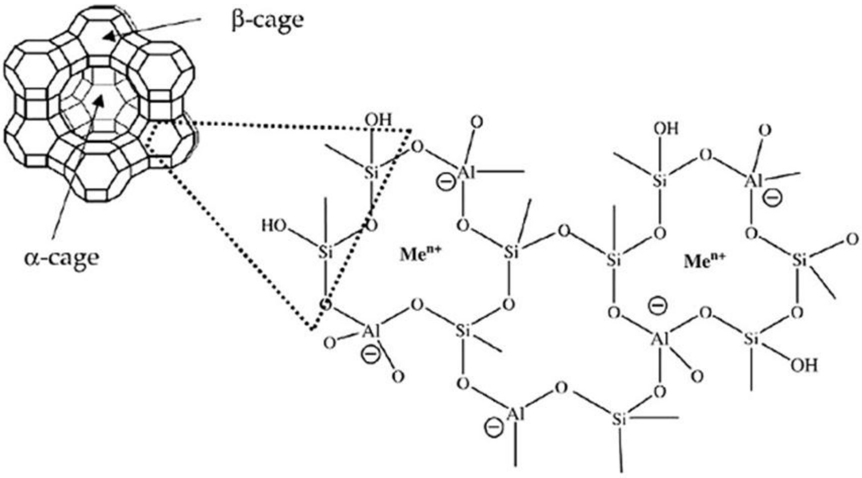
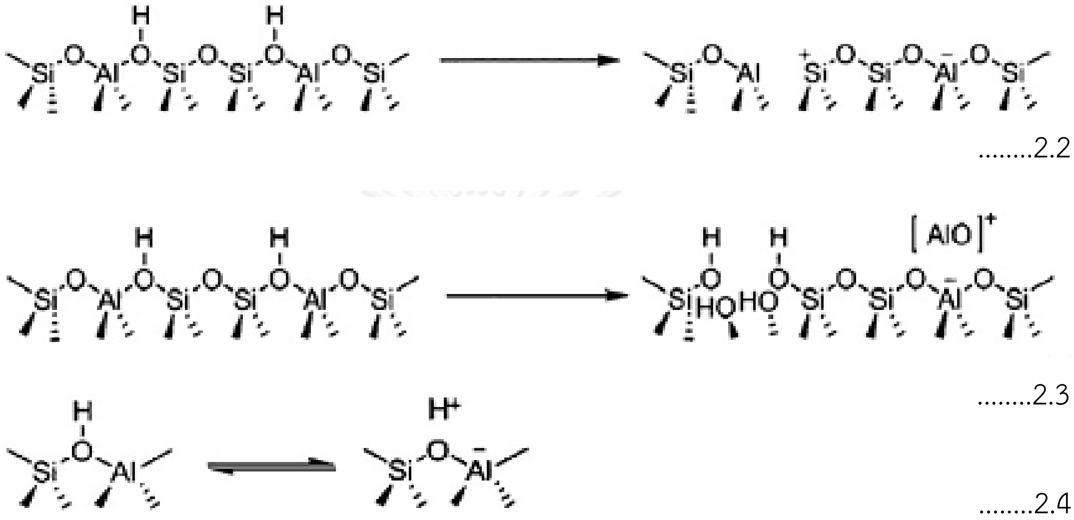


Figure 2.8 Three and two-dimensional representations of the framework structure of zeolites [17]

Zeolite's crystallographical pentasil ring as shown in Fig 2.8 has Silanol (Si–OH) function group generated by the occurrence of bond deficiencies between silicon and oxygen atoms during crystal growth, Lewis acid formed by dehydration of two acidic hydroxyl groups under vacuum at 750 K as shown in equation 2.2 and Bronsted acid hydroxyl groups bridging Si–OH–Al structure as shown in equation

2.3 - 2.4 are featured by its great hydrogen bonding, polarized attraction forces (**π**–electrons), induced dipole-dipole moment and electrostatic interactions as shown in Fig 2.10.



........2.2

........2.3

........2.4

Figure 2.9 Diagram of the surface of zeolite framework [15]

2.8 Shape selectivity [18]

Shape selectivity in catalysis and separations is an important property of zeolites. Attempts to explain observations of catalytic selectivity in highly ordered materials with different pore dimensions and different degrees of pore interconnectedness have driven the general theoretical development of shape selectivity in molecular sieves. Fresh theories have emerged with the discovery of new molecular sieves, or as newly found catalytic importance have shifted attention back onto older materials. Highly evolved random and molecular dynamic models are able to accurately represent the primary effects of shape selectivity.

Most of the shape selectivity phenomena encounters belong to one of following 3 categories:

1. **Reaction Selectivity**

It takes place when zeolite catalyst as a molecular sieve and excludes certain molecular sizes and aperture structures from intracrystalline void, only certain smaller molecules and excludes larger molecules **[18]**.

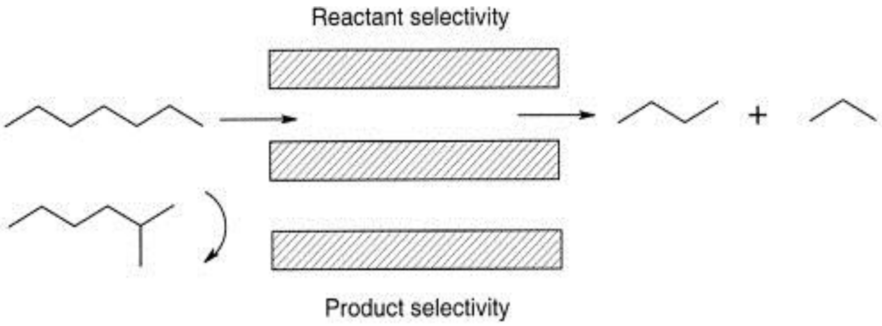


Figure 2.10 Reactant selectivity [19]

2. Product Selectivity

It is the result of discrete diffusivities of the different reaction products in the pores of the zeolite crystal intensively are the isomerization reaction. This selectivity not only depend on the pore size but also the intracrystalline size of catalyst particles. This selectivity kind of “molecular traffic control” has been involves to describe transportation of molecules with different shape and size in catalyst **[18]**.

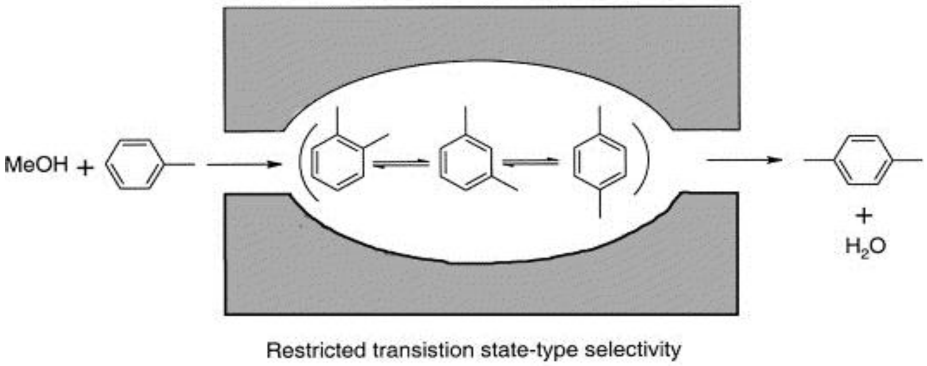


Figure 2.11 Product selectivity [19]

3. Transient state shape selectivity

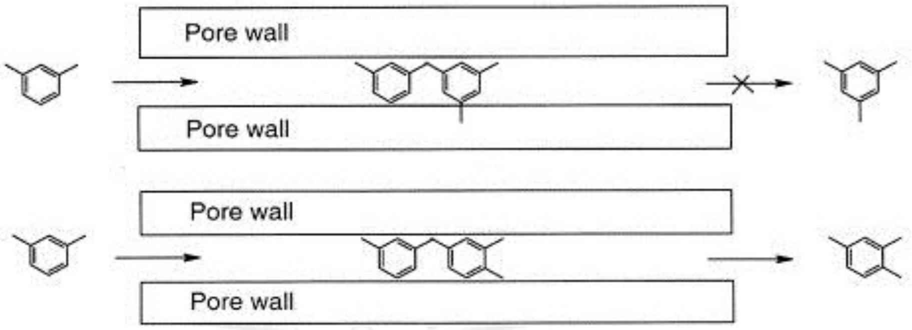


Figure 2.12 Transient state selectivity [19]

Product shape selectivity occurs when the spatial configuration around a reaction intermediate located in the intracrystalline as slowly diffusion that only certain configuration are possible**[18]**. Hence, a product shapes selective as slowly diffusing molecule unable to access through the crystal pores and undergoes secondary reaction [19].

2.8 Application of zeolite [20]

Zeolites are used in a variety of applications with a global market of several million tons per annum. In the western world, major uses are in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. They are often also referred to as molecular sieves. And variety the other applications as below:

- Additive in fertilizer production
- Water and other liquid purification and clarification.
- Odor abatement
- Oxygen production and gas separation
- Ion exchange
- Absorption and adsorption
- Nitrogen (ammonia or ammonium) abatement
- Hydrocarbon abatement
- Abatement of certain toxic waste and acid wastes

2.9 Catalyst deactivation [20]

Catalyst deactivation is the loss over time of catalytic activity and selectivity. It is a problem of great and continuing concern in the practice of industrial catalytic processes. They can be classified into 4 distinct types.

- Poisoning contaminants in the reactor feed
- Fouling thermal degradation such as sintering, evaporation and volatilization leaching by the reaction mixture
- Coking (formation of deposits) coverage of the surface by coke or carbon from undesired reactions of hydrocarbon reactants, intermediates and products.
- Mechanical damage

2.10 Characterization [21]

Catalyst characterization to examine the properties of the catalyst both of physical and chemical to determine the physical properties of the catalyst often focused on the issue of surface area of the catalyst. Popular methods used to analyze the surface area and adsorption methods (BET) gas technique and examine the structure of the catalyst can be achieved by the physics technique including X-Ray Powder Diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) etc. This research will study adsorption technique BET, X-Ray Powder Diffraction (XRD) and X-Ray Fluorescence Spectrometry (XRF).

2.10.1. BET gas adsorption [22, 23]

The BET theory to measure total surface area, nonspecific physical adsorption is required, aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. Most physical adsorption isotherms may grouped into five types. The grouping has generally been termed the Brunauer, Emmet and Teller (BET).

The common method of measuring surface area delveloped by Brunauer, Emmet and Teller. The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses that adsorbed molecules are classical objects localized on their adsorption site, adsorption taken place either on surface sites or on the top of molecules already adsorbed but not between positions. And the first layer only interacts with the surface; all other layers have interparticle interaction with the same energy as would apply in the liquid state, and involving only nearest neighbors in the vertical stack of adsorbed atom in each site and adsorbed molecules do not intersct laterally.

The heat of adsorption for all layers except the first layer is assumed to be equal to the heat of liquefraction of the adsorbed gas. Summation over an infinite numbers of adsorbed gives the final expression as follow:

$$\frac{P}{V(P_0-P)} = \frac{I}{V_mC} + \frac{(C-1)P}{VmC\ P_0}$$

Where P = Pressure of adsorbate

P_o = saturation pressure of adsorbate gas at the experimental temperature

V = Volume of gas adsorbed at pressure P

V_m = Volume of gas adsorbed in monolayer same unit as V

C = A constant relates exponentially to heat of adsorption and liquefaction of the gas

$$\mathbf{C = C^{(q1-qL)/RT}} \qquad \text{......... 2.5}$$

Where q1 = heat of adsorption on the first layer

qL = heat of liquefaction of adsorbed gas all other layers

R = the gas constant

2.10.2. X-ray Diffractrometer (XRD) [9]

An x-ray diffraction technique (XRD) was the non-destructive identification method by using the diffraction of X-rays to indicate the different angles on the crystal surface. The results will be compared with the database to identify the phase composition of the samples.

Analysis is that the material is a crystalline material has interplanar spacing (d) in different value; the distance varies depending on the nature of the crystal.

Terms of diffraction of the radiation:

$$AB + BC = n\lambda$$

And $AB = BC = d \sin \theta$

Then $d \sin \theta = n\lambda$ 2.6

Equation 2.6 is "Bragg's Equation"

When d = interplanar spacing, Å

λ = wavelength, Å

θ = angle between the lattice plane and X- Ray, degree

n = Integer

Because the compounds are different element or structures cause diffraction angle of radiation with different degrees. Information can indicate the type of compounds and inspect the detail of their structure.

2.10.3. X-Ray Fluorescence Spectrometry (XRF) [9]

X-ray fluorescence (XRF) is a powerful quantitative and qualitative analytical tool for elemental analysis of materials. It is ideally suited to the measurement of film thickness and composition, determination of elemental concentration by weight of solids and solutions, and identification of specific and trace elements in complex sample matrices. X-rays form part of the electromagnetic spectrum and are expressed in terms of their energy or wavelength. XRF (X-ray Fluorescence) is a consequence of changes that take place within an atom. A stable atom comprises a nucleus and the electrons orbiting it. Orbiting electrons are organized into shells: each shell is made up of electrons with the same energy. When a high energy incident (primary) X-ray collides with an atom it disturbs this stability. An electron is ejected from a low energy level and a space is created. As a result an electron from a higher energy level falls into this space. The difference in energy produced as the electron moves between these levels is released as secondary X-rays which are characteristic of the element.

XRF analysis is used extensively in many industries including semiconductors, telecommunications, microelectronics, metal finishing and refining, food, pharmaceuticals, cosmetics, agriculture, plastics, rubbers, textiles, fuels, chemicals, and environmental analysis. The method is fast, accurate, non-destructive, and usually requires only minimal sample preparation. Currently XRF spectrometry is very widely applied in many industries and scientific fields. The steel and cement industries routinely utilize XRF devices for material development tasks and quality control.

2.11 Cracking of hydrocarbon reaction [20, 24]

Cracking of hydrocarbon reaction divided into 3 main types.

2.11.1 Thermal cracking

Thermal cracking is a free radical chain reaction. A free radical, in which lacking one hydrogen atom on carbon atom in the hydrocarbon molecule ,is very reactive and often difficult to control. Thermal cracking, the free radicals are intermediate species which cracked by a β-scission mechanism. It is their mode of reaction that determines the product distribution obtained during thermal cracking. A significant feature of hydrocarbon free radicals is their resistance to isomerization.

Thermal cracking typically involves the following chemical reaction:

1.) ***Initiation reaction***, the single paraffin molecule breaks into two free radical and reaction with small free hydrocarbon radicals of a free hydrogen atom becoming a free radical itself as shown in the equation 2.6.

$$\text{R-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-R} \xrightarrow{\text{Heat, h}\nu} \text{R-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2^{\bullet} + \text{R}^{\bullet} \qquad ...2.6$$

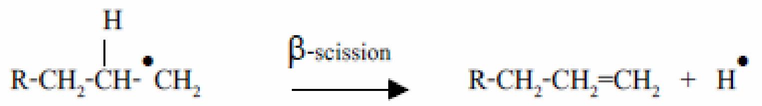
Radical isomerization is a change of the position of hydrogen atom, usually to yield a more stable radical in order of tertiary > secondary > primary free radical.

2.) ***Propagation step*** caused by free radicals in the process. *Hydrogen abstraction reaction* in which the free radical abstracts a hydrogen atom from another molecule located in β position.

Cracking at the β position decomposes into alkene and a primary radical in this step no change of position of any hydrogen atom with respect to the carbon skeleton. The primary radical react with an alkene to form a single, larger free radical as shown in equation 2.7.

β-fission

$$\mathrm{R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}{}^{\bullet}CH_2} \xrightarrow{\beta\text{-scission}} \mathrm{R\text{-}CH_2\text{-}CH_2\text{-}{}^{\bullet}CH_2 + CH_2{=}CH_2}$$



$$\mathrm{R\text{-}CH_2\text{-}\overset{\displaystyle H\atop|}{C}H\text{-}{}^{\bullet}CH_2} \xrightarrow{\beta\text{-scission}} \mathrm{R\text{-}CH_2\text{-}CH_2{=}CH_2 + H^{\bullet}}$$

Chain transfer

$$\mathrm{R\text{-}CH_2\text{-}(CH_2)_4\text{-}CH_3 + H^{\bullet}} \longrightarrow \mathrm{R^{\bullet}\text{-}CH\text{-}(CH_2)_4\text{-}CH_3}$$

...2.7

3. ***Termination reaction*** in which two free radical react with each other to produce a final product. The termination reaction is *recombination reactions* and *disproportionation reactions*, which one radical transfer a hydrogen atom to the other to produce an alkene and an alkane as shown in equation 2.8.

$$\mathrm{R^{\bullet} + R^{\bullet}} \longrightarrow \mathrm{R\text{-}R}$$

$$\mathrm{R\text{-}CH_2\text{-}{}^{\bullet}CH_2 + {}^{\bullet}CH_2\text{-}CH\text{-}R} \longrightarrow \mathrm{R\text{-}CH_2\text{-}CH_3 + CH_2{=}CH\text{-}R}$$

...2.8

2.11.2 Catalytic cracking [20, 24, 25]

Catalyst is a process helping to crack the large hydrocarbon molecule into the desired smaller and structures. Gasoline produced by the catalytic cracking is richer in branched paraffins, cycloparaffins and aromatics, which all increase its quality.

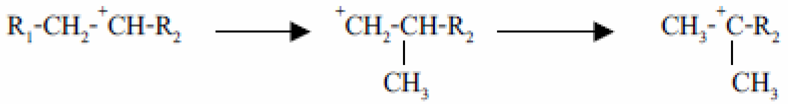
Catalytic cracking is an ionic process involving carbocations, which are hydrocarbon ions having a positive charge and are produced by:

1. Absrtaction of hydride ion from a hydrocarbon by the acid catalyst, or by another carbocation as shown in equation 2.9.

$$\begin{aligned} R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 &\longrightarrow R_1\text{-}CH{=}CH\text{-}R_2 + H_2 \\ R_1\text{-}CH{=}CH\text{-}R_2 + H^+ &\longrightarrow R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 \end{aligned} \qquad ...2.9$$

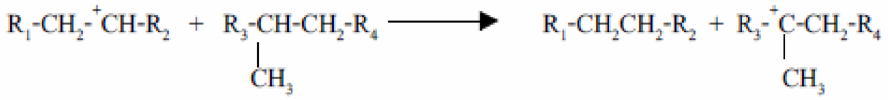
Abstraction of hydride ion from tertiary carbon is easier than from secondary, which also easier than the primary carbon.

2. Chain propagation involves isomerization reaction by hydride ion or methyl group shift occurs readily. The reaction is the stabilization of the carbocation. This reaction is responsible for a high ratio of branched isomer in the products as shown in equation 2.10



$$R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 \longrightarrow {}^+CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}\text{-}R_2 \longrightarrow CH_3\text{-}{}^+\underset{\displaystyle CH_3}{\underset{|}{C}}\text{-}R_2 \qquad ...2.10$$

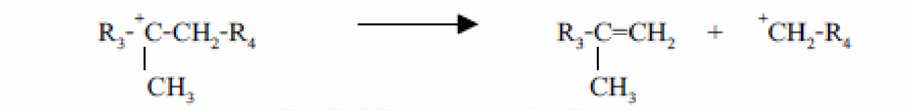
And hydride transfer by reaction between carbocation and molecules of hydrocarbon chain as shown in equation 2.11



$$R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 + R_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}\text{-}CH_2\text{-}R_4 \longrightarrow R_1\text{-}CH_2CH_2\text{-}R_2 + R_3\text{-}{}^+\underset{\displaystyle CH_3}{\underset{|}{C}}\text{-}CH_2\text{-}R_4 \qquad ...2.11$$

The major reaction exhibited by paraffins is the carbon-carbon β bond scission into lighter hydrocarbon molecule.

The primary rule is the carbon-carbon cleavage occurs at the position one carbon atom away from carbocation. The new carbocation may experience another β-scission to stable of the carbocation, or react with a hydrocarbon molecule as shown in equation 2.12.

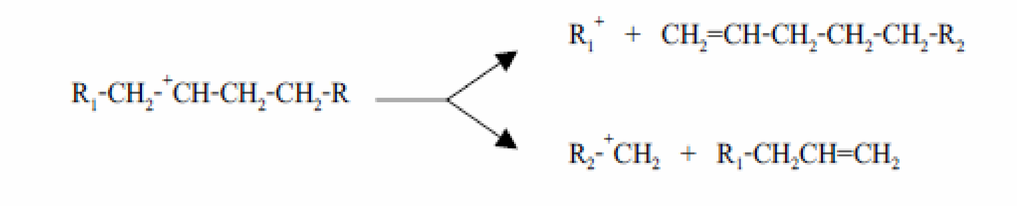


$$R_3\text{-}\overset{+}{C}(CH_3)\text{-}CH_2\text{-}R_4 \longrightarrow R_3\text{-}C(CH_3){=}CH_2 + {}^{+}CH_2\text{-}R_4$$

...2.12

A hydride shift then converts the primary carbocation formed into a secondary carbocation.

Supsequent step involve future β-scission and hydride transfer and proceed unit the chain become so short that cracking at the β position is no longer a rapid reaction. For example, the secondary carbocation cracking from a long chain paraffin as in equation 2.13.



$$R_1\text{-}CH_2\text{-}{}^{+}CH\text{-}CH_2\text{-}CH_2\text{-}R \longrightarrow R_1^{+} + CH_2{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R_2$$

$$R_1\text{-}CH_2\text{-}{}^{+}CH\text{-}CH_2\text{-}CH_2\text{-}R \longrightarrow R_2\text{-}{}^{+}CH_2 + R_1\text{-}CH_2CH{=}CH_2$$

...2.13

The reaction model of hydrocarbon cracking if R_1 = H in the equation 2.13 then according to route (b), propylene would be a product as shown in the equation 2.14

$$CH_3\text{-}{}^{+}CH\text{-}CH_2\text{-}CH_2\text{-}R \longrightarrow CH_3\text{-}CH{=}CH_2 + {}^{+}R\text{-}CH_2$$

...2.14

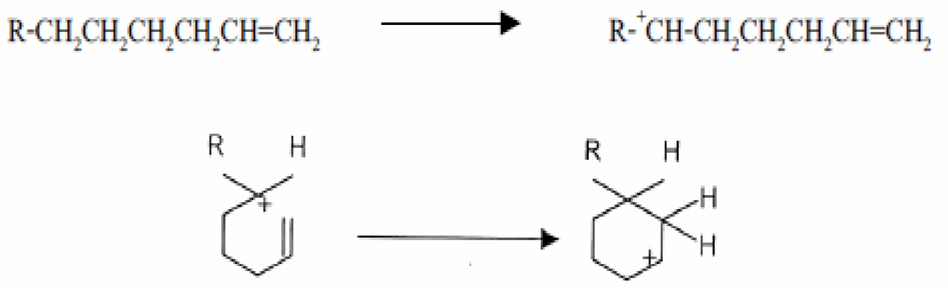
An isopropyl carbonium ion was protonated by propane as shown in equation 2.15

$$CH_3\text{-}CH{=}CH_2 + H^+ \longrightarrow CH_3\text{-}\overset{+}{C}H\text{-}CH_3$$

(isopropyl carbonium ion)

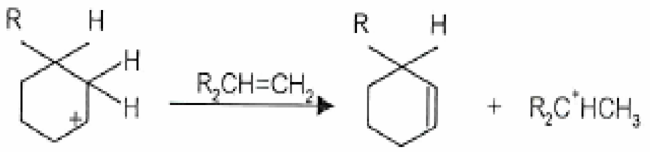
...2.15

Aromatic hydrocarbon exhibit wide variations in their suspectibility to catalytic cracking. Aromatization of paraffins can occur through a dehydrocyclization reaction. Olefin compound formed by the beta scission can form a carbocation intermediate with the configuration conductive to cyclization as shown in equation 2.16.



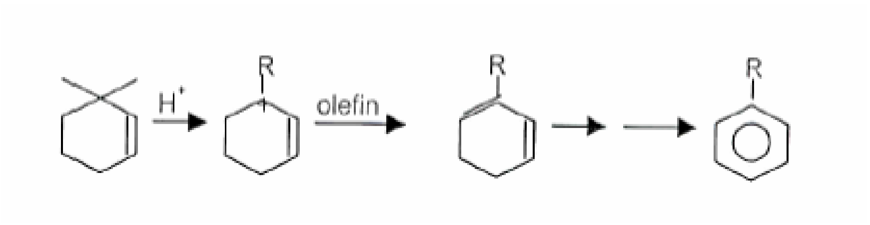
...2.16

Once cyclization has occurred, the formed carbocation can lose a proton, and a cyclohexene derivative is obtained. This reaction is aid by the presence of an olefin in vicinity (R-CH=CH_2) as shown in equation 2.17.



...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 from a cyclohexadiene intermediate. The same sequence is followed unit the ring is completely aromatized as shown in equation 2.18.



...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 reaction.

2.12 Hydrocracking [20, 25]

Hydrocracking is a thermal process in which hydrogenation accompanies cracking. Relatively high pressures are employed. The reactions are catalyzed by dual function is to help cracking the bonding of carbon – carbon of hydrocarbon molecules function and provide by the hydrogenation function. The product has many branching as paraffin and naphtha was occurring. Often contain crystalline silica - alumina could help to break the bond of carbon and hydrogenated at the same time. The reaction starts when olefins occur on the metal position of catalyst surface. Olefins cause carbonium ion on the acid site surface then cracking happen and hydrogenate at the acid site surface. Hydrogenated achieve the saturated product. Moreover, the reaction of an acid and hydrogenated catalyst will help to clean the surface of the catalyst. Because hydrogenated clear coke from the catalyst surface.

The process hydrocracking was the exothermic reaction caused the temperature increase in the reactor .The increase in the temperature has to control as well, because if the temperature is too high can cause coke and catalyst will lose the ability. Reactor has been damaged and achieve undesired product. Hydrocracking is an established petroleum refining process. Traditionally, heavy petroleum fractions serve as feedstock of a hydrocracker unit to produce a range of products, including

LPG, gasoline, diesel, kerosene, and lubricant bases. A more recent application is hydrocracking of very long n-alkanes produced in Fischer Tropsch (FT) processes running in wax mode for producing diesel range product. Catalytic hydro processing is an alternative technology for biofuels production technology which employs the existing infrastructure of petroleum refineries and has already several industrial applications. The technology has significant potential as the produced hydro treated vegetable oils have better fuel properties than the biodiesel produced via trans esterification, and their use improves engine fuel economy Hydro processing of raw vegetable oil – heavy vacuum gas oil mixtures have been explored by employing hydro treating and hydrocracking catalysts at nominal operating conditions. Nevertheless, this technology has only been applied to raw vegetable oil feedstock.

2.13 Coking [20, 26]

Coke formation is an undesirable side reaction of catalytic cracking. Primary coke is highly structured but when reaction take long period of time cause hydrogen is reduced. The coke found in every reaction involving hydrocarbon reactions as dehydrogenation, isomerization, reforming, catalytic cracking. 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 benzene ring. The polynucleas aromatic has a high C/H ratio.

2.14 Crude oil evaluation [25, 27]

The crude oil can be separated by physical methods, in this case by fractional distillation, because they have different boiling and condensation points. The crude oil is heated to evaporated or boiled and the vapor passed into the fractionating column. The fraction volatilized versus temperature as determined by a standard method which usually by gas chromatograph procedure (ASTM D2887) as shown in Table 2.5.

Table 2.5 Representative fractions from distillation of petroleum [25, 27]

Boiling point range ($^{\circ}$C)	**Composition**	**Physical properties and typical use**
Initital boiling point – 200	Gasoline (Naphtha)	valuable source of organic molecules to make other things, cracked to make more petrol and alkenes
200-250	Kerosene	less flammable than petrol, domestic heating fuel, (paraffin) aircraft jet fuel
250-350	Light gas oil	car and larger vehicle fuel (diesel), central heating fuel, cracked to make more petrol and alkenes
350-370	Gas oil	
370- Final boiling point	Long Residue	not as flammable, safe to store, fuel oil for power stations and ships, quite viscous (sticky) and can also be used for lubricating oils, clear waxes and polishes

2.15 Literature review

Niken and co-workers [6] studied the catalytic of waste cooking palm oil to biofuel in fixed bed reactor. This research was studied over different type of nanocrystalline zeolites such as zeolite Y, HZSM-5 and zeolite Beta. The research study at temperature range 400-500˚C, catalyst ratio range 6-14 and catalyst pore size different type of nanocrystalline range 0.54-0.80 nm to studied yield of organic liquid product, the conversion of waste cooking palm oil and yield of gasoline. The optimum condition determines that maximum conversion as well as maximum yield organic liquid product and gasoline yield by using design expert program following central composite design (CCD). The product distribution was influenced by the acidity of the catalyst and the pore structure. From the research found that nanocrystalline ZSM-5 gave the highest gasoline fraction yield and the optimum reaction temperature of 458°C with oil/catalyst ratio over the Nano crystalline zeolite Y with pore size 0.67 nm gave 86.4 wt% oil conversion, 46.5 wt% of OLP yield and 33.5 wt% of gasoline fraction yleid.

Eduard and co-workers [28] studied of rapeseed oil cracking in the presence of zeolite catalysts over different type of nanocrystalline zeolites such as NaY, HY, NH_4Y, Na-ZSM5, H-ZSM5 and CL order to determine the composition of liquid fraction and the properties of liquid yield that close to fossil diesel in batch arrangement at temperatures between 350 and 440 ℃. And determination viscosities, acid values and densities by using the chromatographic methods GL and GC/MS. The analysis gave a yield of liquid condensate 85 to 90 wt% when non-catalyst to give a percentage of the product of the liquid product is low, but high gaseous product. The results showed that the zeolite catalyst to effect the catalytic cracking of rapeseed oil is NaY, HY and CL which is the percentage of liquid product over a period of 20-30 minutes at 85-90 analyzed the composition of the fluid by GC / MS showed that the composition of paraffin and olefin carboxylic acid was similar to that of fossil diesel fuel. When use the different type of catalysts the composition still same.

Hanna et.al. [2] stuied the pyrolysis of palm, olive, rapeseed and castor oils at temperature reaction 750°C for 20 s. Gas chromatography with mass selective and flame ionisation detection (Py-/MSD and FID) to clarify their thermochemical behaviors. Organic liquid yield from palm oil, olive oil and rapeseed oil mostly consist of alkene a chain (up to C_{19}) and alkanes (up to C_{17}), both species are similar to those found in gasoline (C_4 - C_{10}) and diesel fuel (C_{11} - C_{22}) which is similar petroleum fuel. While in the case of castor oil found amount of undesired oxygen containing products such as ketones and phenols. The obtained data on reaction mechanisms can also be utilised in applications where various biofuels are produced.

Eduard et.al. [1] studied of the catalytic cracking of vegetable oil and animal fat as a fuel catalyst zeolite (NaY and Clinoptilolite) of rapeseed oil. Sunflower oil, Jatropha and used cooking oil. The conditions used in the study is the temperature 350-440 °C, the reaction time of 20-30 min the type of oil and animal fat does not influence the catalytic cracking process because of the products of fuel from rapeseed oil, sunflower oil, jatropha and used cooking oil gave 85-90 percent by weight , which is similar. Analysis of oil products in a reaction properties and composition found that similar to petroleum products. Treated condensates blended with fossil diesel (5–7% of the condensate by volume) are compliant with the EN 590 standard and can thus be used as a component of diesel fuels.

M. Mongkol [10] studied the catalytic cracking of used vegetable oil to liquid fuels on HZSM-5 and Fe/active carbon in fixed bed microreactor. This research studied at reaction temperature range of 400-430 ˚C, reaction time 45-60 mins, the amount of Fe/active carbon 0.5-2.0 g with initial hydrogen pressure 10-30 bars and amount of HZSM-5 0.05-0.2 g with 10-20 bars of initial hydrogen pressure. The reported that the highest yield of gasoline concluded that the optimum condition were temperature of 430 ˚C, reaction time 60 min and initial hydrogen pressure 10 bars by using 0.5 percent by weight of Fe/AC. The design expert program by using two level factorial experimental investigate the reaction temperature, reaction time and mass of Fe/active carbon were significantly affected to organic liquid product. The oil yield was 79.74 wt%, 28.14 wt% of Gasoline, 16.56 wt% of Kerosene, 21.86 wt% of light gas oil, 3.26 wt% of Gas oil and 9.91 wt% of long residue. And the optimum condition were temperature of 430 °C, reaction time 60 min and initial hydrogen pressure 1 bars by using 0.05 percent by weight of HZSM-5. The experimental design investigates the reaction temperature and reaction times were significantly affected to organic liquid product. The oil yield was 83.60 wt%, 26.75 wt% of Gasoline, 13.79 wt% of Kerosene, 22.99 wt% of light gas oil, 3.26 wt% of Gas oil and 16.30 wt% of long residue.

K. Pinweha [26] studied the used lubricating oil was used to convert to light oil product by pyrolysis with spent FCC catalyst. The motivation is the amount of used lubricating oils has been increasing every year. The main objective of this research was to study the pyrolysis of used lubricating oil with spent FCC catalyst in a micro reactor of 250 ml. the temperature was varied from 400-450°C, 1-5 bars of initial hydrogen pressure, the mass of spent FCC catalyst ranging from 1-5 % by weight and 25-75 minutes of reaction time. Research found that temperature of 410 °C, reaction time 60 min and initial hydrogen pressure 5 bars by using 1 percent by weight of spent FCC catalyst gave highest yield. The two level experimental designs investigates the reaction temperature, reaction time and mass of spent FCC were significantly affected to organic liquid product. The optimum condition was shown in 72.94 wt% of oil yield, 23.86 wt% of gas, and 3.24 % wt% of solid and was composed of 33.08 wt% of naphtha, 11.46 wt% of kerosene, 16.65 wt% of light gas oil, 2.70 wt% of gas oil and 9.05 wt% of long residue. And also found the organic liquid yield consist of aromatic hydrocarbon comparing with the structure of gasoline from fossil fuel was similar show that the oil product from the cracking liquid products can be instead of fuel.

W. Charusiri [20] studied catalytic cracking of the used vegetable oil was used to convert to light oil product by pyrolysis using over HZSM-5, Sulfates Zirconia and hybrid of HZSM-5 and Sulfates Zirconia catalyst. The aim of this research was to study the pyrolysis of used vegetable oil with HZSM-5, Sulfates Zirconia and hybrid of HZSM-5 and Sulfates Zirconia catalyst in a batch reactor of 70 ml. The process was performed at 400-450°C, reaction time 45-90 min, initial hydrogen pressure 10-30 bars to produce the optimum yield of product. Liquid products were analyzed by Simulated Distillation Gas Chromatography and found that temperature of 430°C, reaction time 90 min and initial hydrogen pressure 10 bars by using hybrid catalyst mixing of HZSM-5 and Sulfated Zirconia at ratio of 0.3:0.7 gave highest yield of gasoline. The product was shown in 26.57 wt% of gasoline, 10.65 wt% of kerosene, and 23.02 wt% of light gas oil , 6.05 wt% of gas oil and 12.88 wt% of long residue whereas the gaseous product is 20.20 wt% and solid of 0.63 wt%. The activation energy of 116.072 $kJmol^{-1}$ and pre-exponential factor (A) = $2.67\ x10^{5}\ s^{-1}$ of catalytic cracking used vegetable oil to liquid over hybrid catalyst.

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N. Wongsawat [29] studied of the cracking of vegetable oil on calcium oxide and magnesium in continuous reactor of 1250 mL was performed operating variable the temperature was varied from 390-440°C, feedstock's flowing rate 2-5 gram/minute and the mass of catalyst ranging from 1-5 wt%. It was found that catalytic cracking used vegetable oil on calcium oxide catalyst is temperature of 424°C, feedstock's flowing rate 2.21 gram/minute by using 1 wt% of calcium oxide catalyst gave highest yield of naphtha. The oil yield product was 32.26 wt% and oil yield product was composed of 11.54 wt% of naphtha. The catalytic cracking used vegetable oil on magnesium oxide catalyst is temperature of 422°C, feedstock's flowing rate 2.90 gram/minute by using 5 wt% of magnesium oxide catalyst gave highest yield of naphtha. The oil yield product was 31.19 wt% and oil yield product was composed of 12.16 wt% of naphtha.

C. Wannawong [30] studied the pyrolysis of jatropha to liquid fuel over spent FCC catalyst in a batch reactor of 70 ml. The process was performed at 380-440°C, reaction time 30-60 min, initial hydrogen pressure 1-5 bars and containing 1-5 wt% of spent FCC catalysts. The two level factorial experimental designs were performed to investigate the effect of variables on oil yield. It found that temperature of reaction, the amount of catalyst, reaction time were significant affect to oil yield product. Liquid products were analyzed by Simulated Distillation Gas Chromatography. The optimum condition was found that temperature of 410.24°C, reaction time 30 min and initial hydrogen pressure 1 bars by using 1 wt% of spent FCC catalyst. The oil yield product was 88.60 wt%, 9.26 wt% of gaseous product and and oil yield product was composed of 15.62 wt% of naphtha 7.93 wt% of kerosene, 40.15 wt% of diesel.

CHAPTER III

EXPERIMENTAL

3.1 Starting material and chemicals

1. Used vegetable oil from fried food processing in Nonthaburi market, Nonthaburi Province, Thailand during January 2013
2. Toluene (Commercial grade: pure 80% minimum)
3. Hydrogen gas 99.99% from TIG Trading
4. Spent FCC catalyst from Thai oil public limited company

3.2 Raw material preparation

3.2.1 The spent FCC catalyst preparation

This catalyst is spent FCC catalysts from Thai oil public company that all distilled crude oil is processed in catalytic cracking unit. The metals are typically vanadium, nickel, iron, sodium and coke entrapped in the catalyst pore. Before reuse, The FCC catalyst was prepared by thermally treated spent FCC catalyst at 550 °C for 4 hours. Properties of spent FCC catalysts characterized by XRF, XRD and N_2-BET analyzer.

3.2.2 Used vegetable oil preparation

Used vegetable oil generated by homes and restaurants. The used oil was stored in the black bottle under the atmosphere of nitrogen gas to prevent the side reaction of oxidation and oxygenation. Used vegetable oil was prepared by filtering to remove solids and other impurities left over from the fryer process by vacuum filtration then press in oven to eliminate water content by heated to above 100°C. The boiling range distribution of used vegetable oil was determined by DGC (Simulated Distillation Gas Chromatography).

3.3 Apparatus and Instruments

3.3.1 The cracking unit

The 70 cm^3 micro-reactor is a stainless-steel (SS 316) pressure cylindrical reactor was used for this study on cracking of used vegetable oil to liquid fuels over spent FCC and is shown in Figure 3.1. The micro reactor set a pressure gauge, safety valve, valve for admitting and releasing gases.

Figure 3.1 Micro-reactor volume of 70 ml

The cracking process experimental unit with the rotating machine, the shaking of micro-reactor was controlled by speed motor at 80 rpm. The reactor was heated by 400 watt injection heater at the heating rate 20 °C/min, Temperature was controlled and measured by thermocouple type K (diameter 1.6 mm.) with accuracy of ± 10°C by means of a programmable temperature controller as shown in Figure 3.2.

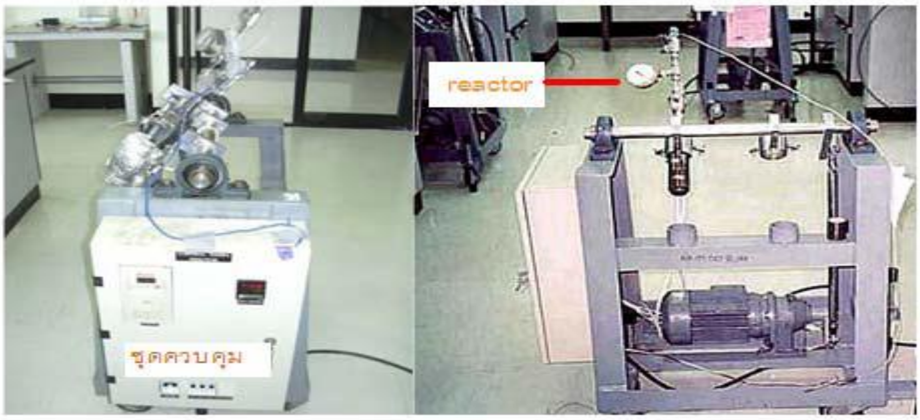


Figure 3.2 Experimental set consists digital temperature control and the shaker

3.3.2 Vacuum pump

The liquid products and solid product was separated by vacuum filtration with pressure 1 kg/cm^3 and 40 nm of sieve filter.

Figure 3.3 The filter vacuum

3.4 Characterization

3.4.1. Gas Chromatography Simulated Distillation

Gas Chromatography Simulated Distillation (DGC) from Agilent Technologies Model GC7890A for analyze the boiling range distribution of liquid product from cracking of used vegetable oil over spent FCC catalyst by a simulation distillation gas chromatograph using the ASTM standard method 2887.

Figure 3.4 Simulated Distillation Gas Chromatography

3.4.2. The X-Ray Fluorescence Spectrometer (XRF)

X-ray fluorescence (XRF) spectrometry is an elemental analysis technique in science and industry. XRF is based on the principle that individual atoms, when excited by an external energy source, emit X-ray photons of a characteristic energy or wavelength. By counting the number of photons of each energy emitted from a sample, the existing elements present may be identified and quantitated.

Figure 3.5 X-Ray Fluorescence Spectrometry (XRF)

3.4.3. The X-ray Diffractrometer (XRD)

X-ray powder diffraction (XRD) is analytical technique primarily used for phase identification of a crystalline material and provides information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (minerals, inorganic compounds).

Figure 3.6 X-ray Diffractrometer (XRD)

3.4.4. The total pore surface area (BET surface area)

The physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material.

Figure 3.7 BET surface area

3.4.5. Fourier Transform Infrared Spectrophotometer

Fourier Transform Infrared, the preferred method of infrared spectroscopy. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

Figure 3.8 Fourier Transform Infrared Spectrophotometer (FT-IR)

3.4.6. Gas Chromatography Mass Spectrometry

Gas chromatography mass spectrometry from Agilent Technologies Model GC7890A could identification and quantitation of volatile and semivolatile organic compounds in complex mixtures. It is useful for the determination of molecular weights and the elemental compositions of unknown organic compounds in complex mixtures.

Figure 3.9 Gas Chromatography-Mass Spectrometry (GC-MS)

3.5 Experimental procedures

The 20 grams of used vegetable oil with the proper mass of spent FCC catalyst were filling in the reactor. Hydrogen gas was supplied from hydrogen tank to fill inside the reactor. The reactor was set up at the shaking stand and attached with heater and insulator. The reactor was heated from room temperature to desired temperature. The reaction temperature was controlled by K-type thermocouple. After finish the reaction, the oil product was separate from the solid waste by vacuum filtration. The gas product was analyzed by using gas chromatography. The oil product was analyzed by using Simulated Distillation Gas Chromatography to analysis the boiling range distribution. The oil product composition were defined according to boiling in the range 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

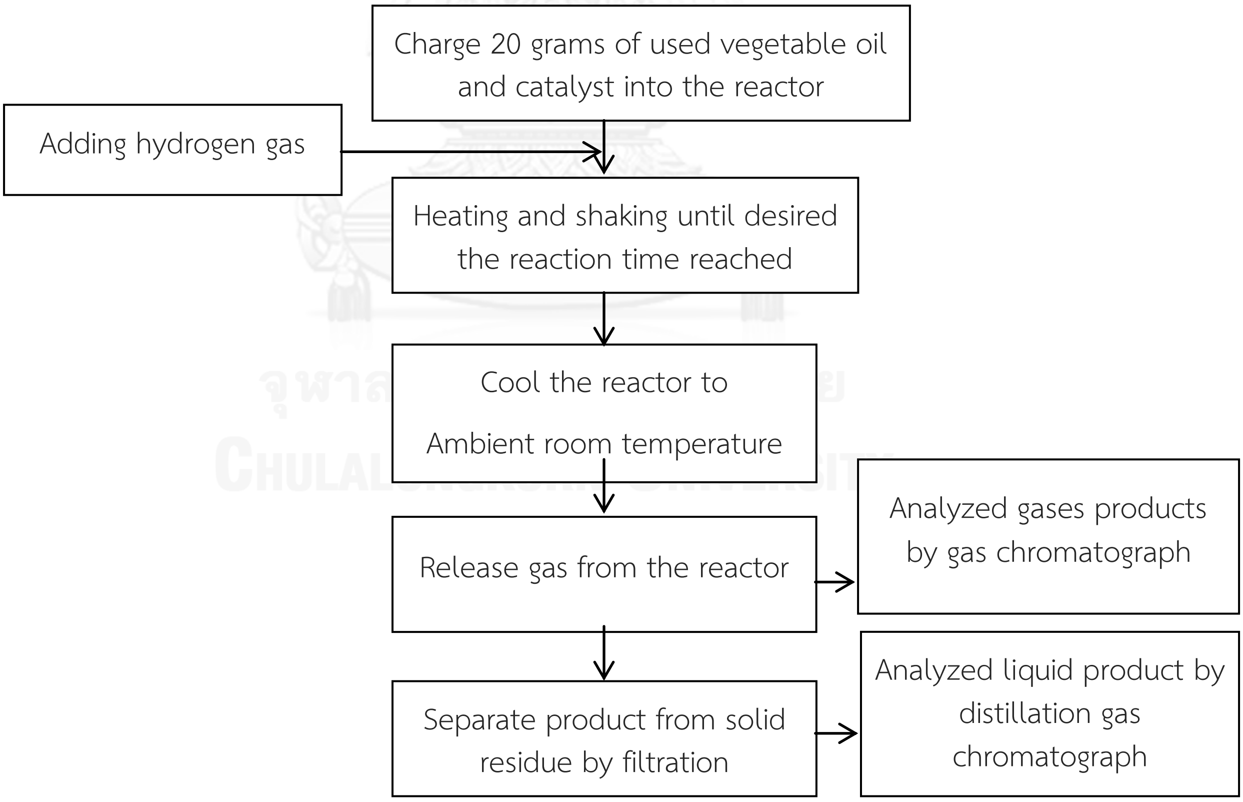


Figure 3.10 A schematic diagram of cracking of used vegetable oil over spent FCC catalyst

3.6 Experimental design

2^k factorial designs are use to design the experiment. This method is widely used for screening the factor for the system. It is useful to determine the significant factors for the cracking of used vegetable oil to liquid fuel over spent FCC catalyst, The experimental design factorial two level four parameters variables studied were temperature, weight of spent FCC catalyst time, initial pressure of hydrogen gas and reaction time were represented as A, B, C and D respectively. There are two levels "low" coded (-1) and "high" coded (+1) level as shown in table 3.1 and table 3.2

Table 3.1 Factor and level of variable of cracking of used vegetable oil over spent FCC catalyst.

Factor		**Level**		**Unit**
		Low (-)	High (+)	
A =	Temperature	380	450	°C
B =	% weight of spent FCC	1	5	wt%
C =	initial pressure of hydrogen gas	1	5	Bar
D =	Time of reaction	30	60	minutes

3.6 Determination of condition effects

To determine the optimum condition of cracking of used vegetable oil over spent FCC catalyst to light oil product. The distribution of oil product analyze by GC Simulated Distillation by ASTM D2887 specification of Naphtha, Kerosene, Light gas oil, Gas oil and heavy oil residue.

Investigation of the cracking of used vegetable oil over spent FCC catalyst under the following conditions:

- Reaction temperature as follows: 380, 415 and 450 °C.
- The reaction time as follows: 30, 45 and 60 minutes.
- Mass of spent FCC catalyst as follows: 1, 3, and 5 wt% and without addition of catalyst in reaction.
- Initial hydrogen pressure as follows: 1, 3 and 5 bar and without hydrogen atmosphere.

Table 3.2 Number of experimental factorial two-level design

Factor			
Temperature (°C)	% weight of spent FCC (percent weight)	Initial pressure of hydrogen gas (bar)	Time of reaction (minutes)
450	5	5	60
450	5	1	60
450	1	5	60
450	1	1	60
450	5	5	30
450	5	1	30
450	1	5	30
450	1	1	30
380	5	5	60
380	5	1	60

Factor			
Temperature (°C)	% weight of spent FCC (percent weight)	Initial pressure of hydrogen gas (bar)	Time of reaction (minutes)
380	1	5	60
380	1	1	60
380	5	5	30
380	5	1	30
380	1	5	30
380	1	1	30
415	3	3	45
415	3	3	45
415	3	3	45

CHAPTER IV
RESULTS AND DISCUSSION

This research aims to study the cracking of used vegetable oil to liquid fuel over spent FCC catalyst in a batch reactor of 70 ml. The cracking process of 20 grams of used vegetable oil are perform at 380-450 ˚C, reaction time 30-60 mins, initial hydrogen pressure 1-5 bars and containing 1-5 wt% of FCC catalyst.

4.1 Properties of raw material

4.1.1 Used vegetable oil

4.1.1.1 The distribution of used vegetable oil was analyzed by Gas Chromatography Simulated Distillation (DGC).

Table 4.1 The distribution composition of used vegetable oil

Boiling Point (˚C)	Composition	% Recovery
IBP - 200	Naphtha (C_5 - C_{12})	3.11
200 - 250	Kerosene (C_{12} - C_{15})	2.09
250 - 350	Light gas oil (C_{15} - C_{25})	15.5
350 - 370	Gas oil (C_{25} - C_{33})	32.21
370 - FBP	Long Residue (>C_{33})	47.09

Analysis of the periodic boiling point of used vegetable oil before pyrolysis cracking was determined by DGC standard ASTM D2887 as shown in Table 4.1. These analyses showed that the large quantity of long residue is 47% whereas quantity of gasoline is only 3%.

The most abundant fractions of used vegetable oil are large hydrocarbon molecules and still need to be improved to reach this purpose. Therefore,the cracking of used vegetable oil over spent FCC catalyst to liquid fuel is being considered.

4.1.1.2 Thermal analysis of used cooking oil by Thermogravimetric Analyzer (TGA) technique

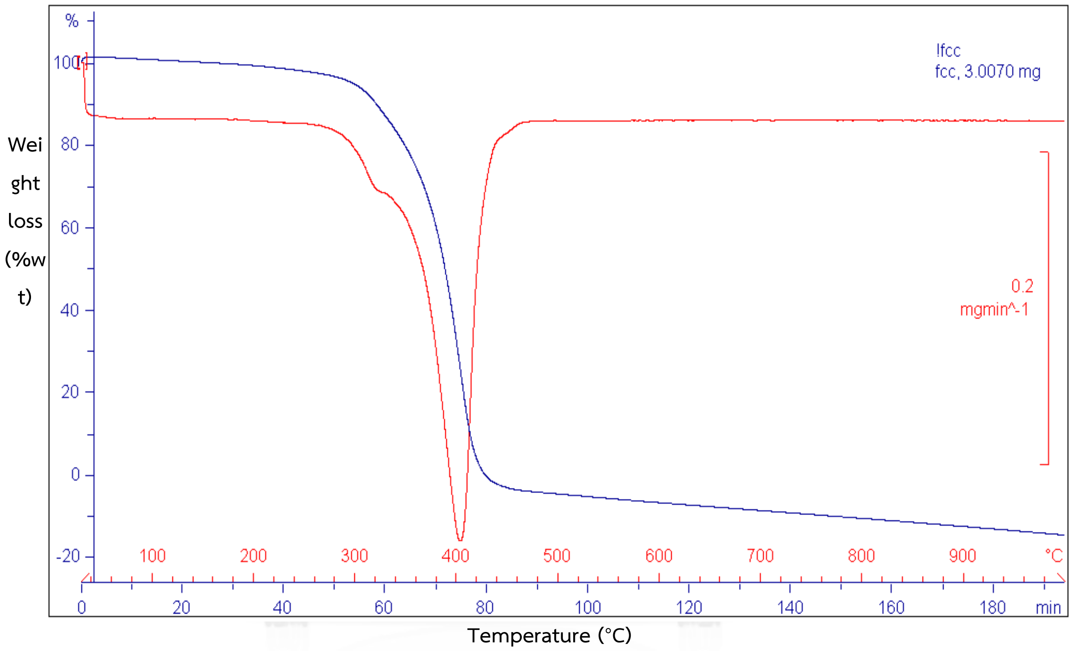


Figure 4.1 The decomposition temperature range of used vegetable oil by Thermogravimetric Analyzer (TGA) technique

The used vegetable oil was characterized by thermal analysis to elucidate the decomposition temperature of used vegetable oil. The analysis of the decomposition temperature of used vegetable oil by using TGA techniques as shown in Figure 4.1. The result showed the used vegetable oil represents the decomposition temperature ranges 350-450 °C and maximum decomposition temperature is 410 °C.

4.1.1.3 The composition of fatty acid

The composition of used vegetable oil was determined in the terms of different types of fatty acid represented in Table 4.2. The result showed majority fraction of 35.69% of Palmitic acid (C16:0) in saturated and 45.96% Oleic acid (C18:1) in unsaturated fatty acid.

Table 4.2 Composition of fatty acid of used vegetable oil

Composition of fatty acid (%)		
C12 : 0	Lauric acid	0.31
C14 : 0	Myristic acid	0.87
C16 : 0	Palmitic acid	35.69
C18 : 0	Steric acid	4.58
C20 : 0	Arachidic acid	0.34
Total saturated fatty acid		**41.79**
C16 : 1	Palmitoleic acid	0.25
C18 : 1	Oleic acid	45.96
C18 : 2	Linoleic acid	11.84
C18 : 3	Linolenic acid	0.16
Total unsaturated fatty acid		**58.21**

4.1.2 Properties of Spent FCC catalysts

4.1.2.1 Analysis composition of spent FCC catalysts by technique XRF

The spent FCC catalyst was prepared by thermal treatment of spent FCC catalyst at 550 °C for 5 hours to remove the nitrate or ammonium group. The concentration of metal in spent FCC catalyst was determined by XRF containing 40.30% and 42.03% of Al and Si respectively as shown in Table 4.3.

Table 4.3 %Concentration of metal in spent FCC catalyst before and after calcination at 550°C

Spent FCC catalyst		Spent FCC catalyst after calcination at 550°C	
Element	**% Concentration**	**Element**	**% Concentration**
Na	0.58	Na	0.31
Al	42.07	Al	40.30
Si	40.13	Si	42.03
P	0.12	P	0.20
S	0.30	S	0.49
K	0.32	K	0.24
Ca	0.40	Ca	0.37
Ti	2.67	Ti	3.08
V	0.34	V	0.34
Mn	0.20	Mn	0.19
Fe	3.12	Fe	3.29
Ni	1.65	Ni	1.27
Cu	0.08	Cu	0.11
Zn	0.07	Zn	0.07
La	6.29	La	7.06
Ge	0.49	Ge	0.64
Ga	0.04	Ga	0.02

The analysis by the XRF technique shows the majority concentration of Si and Al in the spent FCC catalyst expected that the spent FCC catalyst is one type of the zeolites. For type identification of the zeolitic, spent FCC catalyst was analyzed by using XRD technique.

4.1.2.1 Analysis of the structure of crystalline spent FCC catalyst by technique XRD

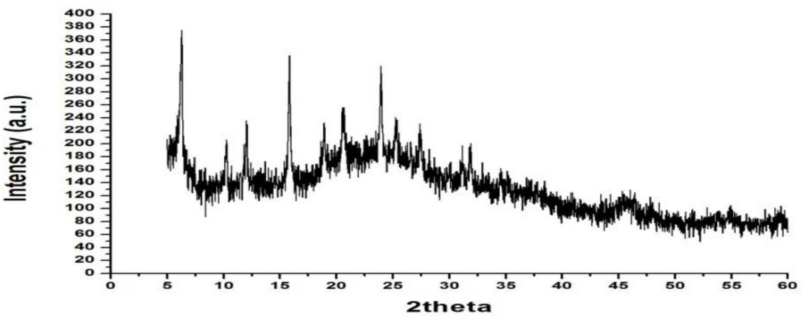


Figure 4.2 XRD pattern of spent FCC catalysts

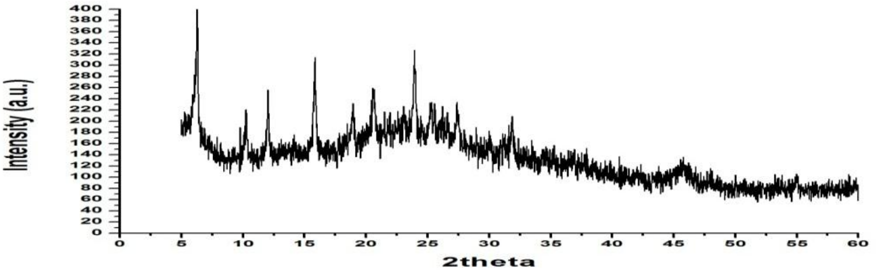


Figure 4.3 XRD pattern spent FCC catalyst after calcination at 550°C

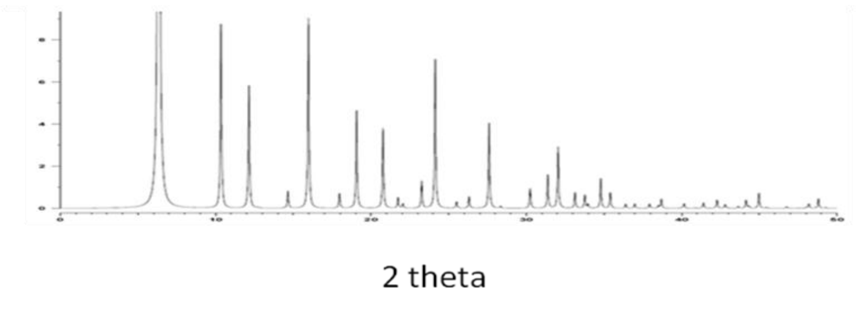


Figure 4.4 XRD pattern of Ultrastable Y, Dehydrated Dealuminated Catalyst

The results of the XRD technique showed XRD pattern of the catalyst spent FCC catalyst before and after calcination at 550°C as shown in Figure 4.4 and Figure 4.5, respectively. The result showed the peak appeared closely with the XRD pattern of the catalysts in Figure 4.6, which is Ultrastable Y, Dehydrated Dealuminated. It can be concluded that FCC catalyst used in this study is a zeolite type USY.

4.1.2.3 BET surface area of the spent FCC catalyst before and after calcination at 550 °C.

Table 4.4 The BET surface area of the spent FCC catalyst before and after calcination at 550 °C.

Sample	Surface area (S_{BET}) M^2/g	Average Pore Size Nm	Pore volume Cm^3/g
Spent FCC catalyst	79.84	6.92	0.13
Spent FCC catalyst after calcination at 550°C	103.65	8.89	0.15

the BET surface area of the spent FCC catalyst before calcination was compared with the spent FCC catalyst after calcination at 550°C (Table 4.2). The result showed that the BET surface area of the spent FCC catalyst after calcination was increased from 79.84 to 103.65 m^2/g, due to the decoking and elimination of some impurities on the pore surface.

4.1.2.4. Analysis of the acidity of spent FCC catalyst before and after calcination at 550°C.

In addition, due to replacement of aluminum by silicon atom during calcination, the ratio of silicon to aluminum is higher than the spent FCC catalyst before calcination. The higher ratio of silicon to aluminum atom increases the acidity of spent FCC catalyst as shown in Table 4.3.

Table 4.5 Acidity of spent FCC catalyst before and after calcination at 550°C.

Catalyst	**Acid value (mmol H^+/g)**
Spent FCC catalyst	0.23
Spent FCC catalyst after calcined at 550°C	0.35

4.2 Univarate study for the cracking of used vegetable oil to liquid fuels over spent FCC.

This part was the studied of parameters affecting to cracking of used vegetable oil over spent FCC catalyst. The parameters were temperature, reaction time, mass of catalyst and initial hydrogen pressure.

4.2.1 Effect of reaction temperature

The study of reaction temperature on the cracking of used vegetable oil over spent FCC catalyst was performed by operating in various temperatures: 380, 415 and 450°C by using 5 wt% of spent FCC catalyst, 1 bar of initial hydrogen pressure and 60 minutes of reaction time.

Normally the higher temperature favors for the thermal cracking reaction, as results found the gaseous product increased with increasing temperature which long chain hydrocarbon as broken into middle chain and small chain hydrocarbon as C_1-C_4 hydrocarbon molecules whereas the lower of liquid yield. The product composition was showed in Figure 4.5. The result shows that the amount of gaseous product increased continuously while the liquid yield was decreased with the increase of temperature. At the temperature 380°C the amount of liquid yield, gaseous product and solid yield were 75.99 wt%, 20.02 wt% and 3.99 wt%, respectively, When the temperature was increased to 450°C the amount of liquid yield, gaseous product and solid yield was 66.92 wt%, 28.48 wt%. and 4.60 wt% respectively (Figure 4.7).

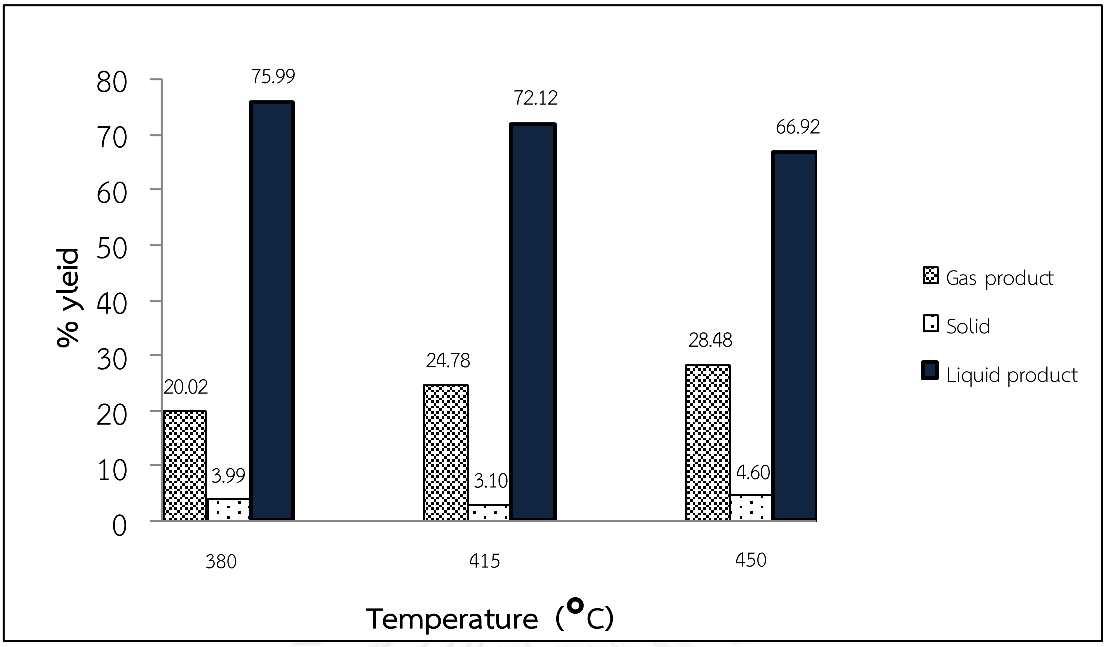


Figure 4.5 Effect of reaction temperature range of 380-450°C on product composition at 5.0 wt% of spent FCC catalyst, 1 bar of initial hydrogen pressure and 60 minutes of reaction time

A possible reason for this behavior is that the higher temperature (450°C) accelerates the thermal cracking of middle hydrocarbon molecule such as kerosene, light gas oil and heavy gas oil fraction converting them into light hydrocarbon fraction such as naphtha and gaseous product (normally C1-C4) by catalytically cracked at the surface of FCC catalyst. It can be concluded that deoxygenation cracking and aromatization with H-Transfer from catalytic cracking processes, deoxygenation occur from dehydration and decarboxylation regarding the cracking of triglyceride fatty acid by occur within the internal pore of catalyst [31].

It is generally assumed that the reaction predominantly occur within the internal pore structure of zeolite catalyst [34] and subsequent reaction such as isomerization, cyclization and hydrogen transfer leading to formation of aromatic hydrocarbon also occur in pores of zeolite catalyst [35]. At cracking temperatures 450 °C, high yields of gaseous products are achieved. It seemed that when higher temperature was increased, light hydrocarbon could be cracked continually due to thermal cracking.

The distribution of fraction in liquid product was determined by simulated distillation gas chromatograph. It notice at temperature 380°C, 415°C and 450°C have naphtha fraction as 16.72 wt%, 23.73 wt% and 27.44 wt% respectively as shown in Figure 4.6. It found that naphtha fraction increased with increased temperature.

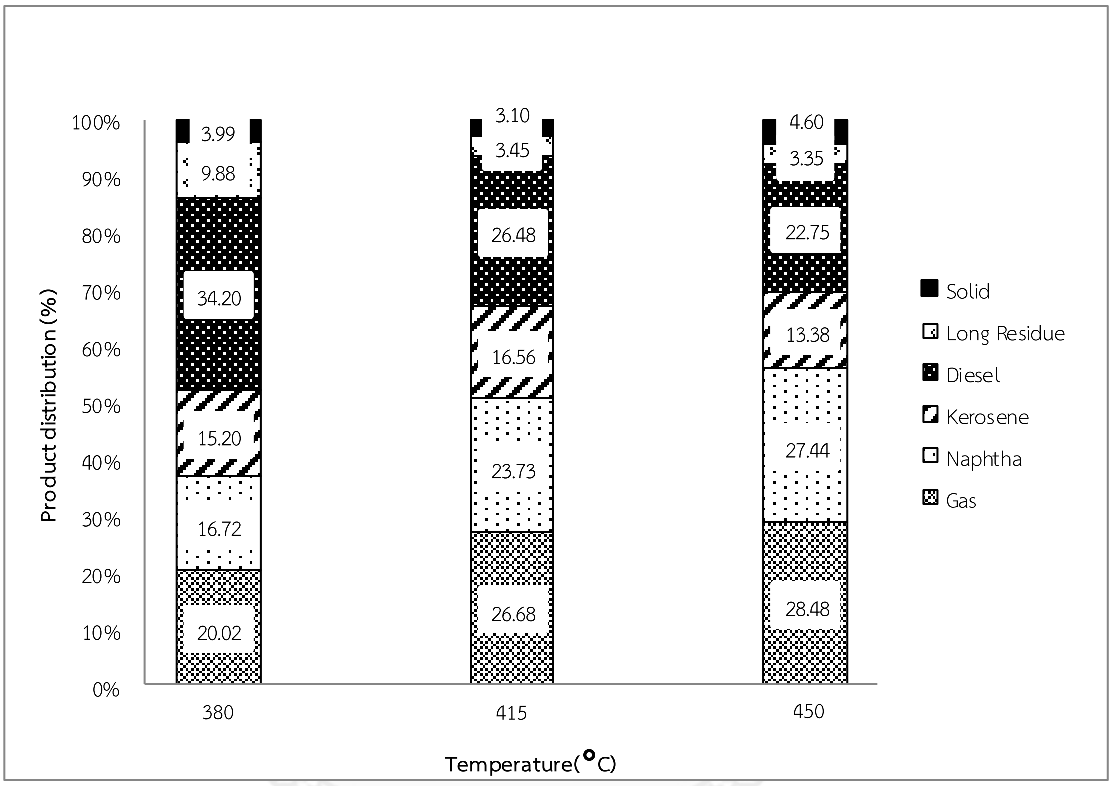


Figure 4.6 Effect of reaction temperature range of 380-450°C on product distribution where 5.0 wt% of spent FCC catalyst, 1 bar of initial hydrogen pressure and 60 minutes of reaction time

From the study of temperature reaction effect, the optimum temperature was 450°C because of the highest percentage yield of liquid and naphtha. The product were liquid, gas and solid yield as 66.92 wt%, 28.48 wt% and 4.60 wt%, respectively while the product composition were naphtha 27.44 wt%, kerosene 13.38 wt%, diesel 22.75 wt% and long residue 3.35 wt%, respectively.

4.2.2 Effect of reaction time

The study of the reaction on the cracking of used vegetable oil over spent FCC catalyst was performed by operating with various reaction times: 30. 45 and 60 minutes at 450°C of reaction temperature, 1 bar of initial hydrogen pressure and 5.0% by wt. FCC catalyst as shown in Figure 4.9

According to Figure 4.7 and 4.8 temperatures was mainly affecting the thermal cracking of long chain hydrocarbon to smaller hydrocarbon and continued cracking to gaseous with increase reaction time due to temperature produce free radical to convert long chain hydrocarbon molecules into smaller molecules [31, 32]. At the condition of 450 °C, when reaction time increased from 30 to 60 minutes found the oil yield product was decrease due to light hydrocarbon was continued cracking to the gaseous product (normally C_1-C_4) by thermal cracking. As the result, the gaseous product increased with increasing the time of reaction.

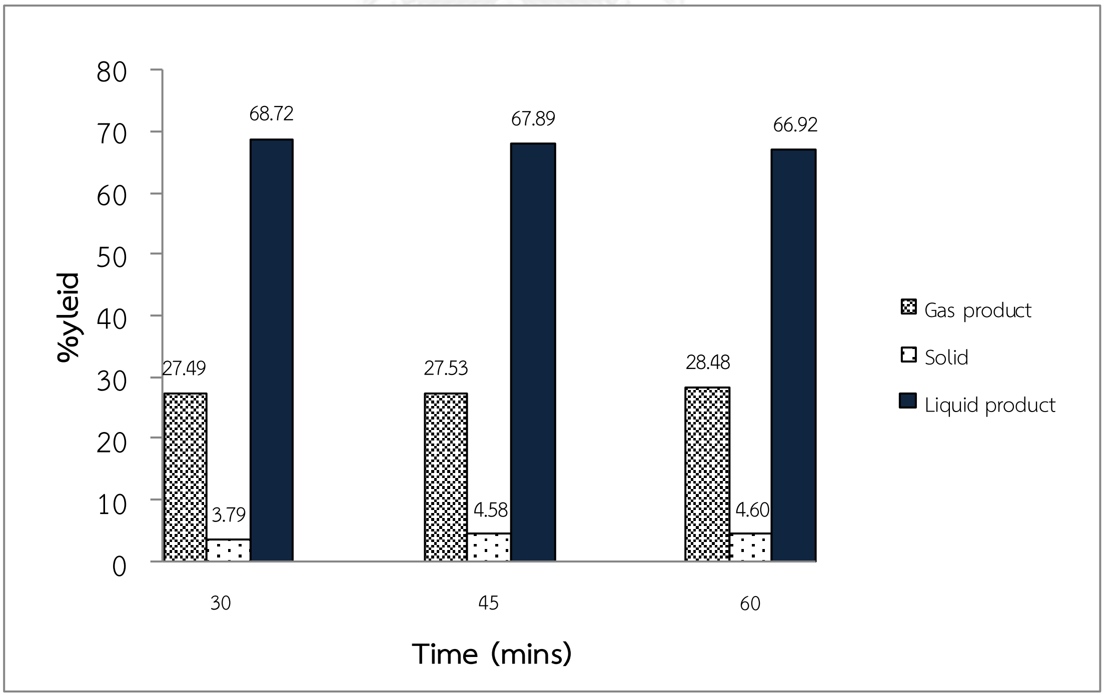


Figure 4.7 Effect of reaction time on product composition at 450°C of reaction temperature, 1 bar of initial hydrogen pressure and 5.0 wt% of spent FCC catalyst

The liquid yield were obtained from cracking process at reaction time 30, 45 and 60 minutes was about 68.72 wt%, 67.89 wt% and 66.92 wt% respectively.

The mainly affecting the thermal cracking of long chain hydrocarbon into middle hydrocarbon molecules continued cracking leading to lighter hydrocarbon molecules and gaseous hydrocarbon with increasing the reaction time. The result of increase reaction time shows that the gaseous products increased whereas the product distribution such as kerosene and long residue decreased included found the favors formation of aromatic hydrocarbon [20, 32]. The effect of reaction time shows the results in greater amount of naphtha boiling range fraction and also increased with increase in reaction temperature reached a maximum at 450 °C and gave later decrease.

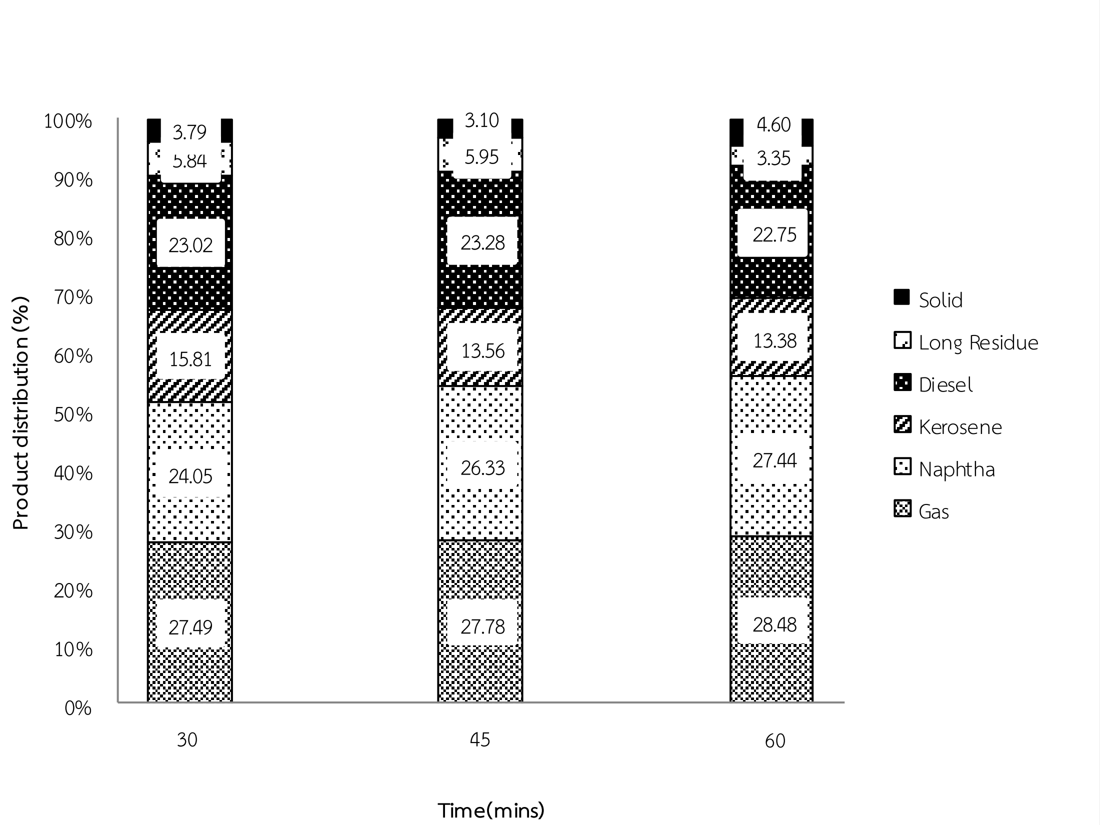


Figure 4.8 Effect of reaction time range of 30-60 minutes on product distribution where 450°C of reaction temperature, 1 bar of initial hydrogen pressure and 5.0 wt% of spent FCC catalyst

The liquid product provides the product distribution which determined from simulated distillation gas chromatograph. The product distribution such as naphtha was increased significantly. The middle hydrocarbon such as kerosene, light gas oil and heavy gas oil were decreased. The effect of reaction time shows the results in greater amount naphtha at 450°C of reaction temperature, 1 bar of initial hydrogen pressure and 5.0% by wt. FCC catalyst as shown in Figure 4.10.

The reaction time of 60 minutes provides the optimal condition as high as 66.92 wt% liquid yield where 450°C of reaction temperature, 1 bar of initial hydrogen pressure. the liquid yield of 66.92 wt% gave The product distribution of naphtha were 27.44 wt%, kerosene 13.38 wt%, diesel 22.75 wt% and long residue 3.35 wt% whereas the gaseous product was 28.48 wt% and solid yield was 4.60 wt%

4.2.3 Effect of mass of catalyst

The study of mass of catalyst on cracking of used vegetable oil with spent FCC catalyst was performed by operating in various mass of catalyst: 1, 2.5, 4 and 5 wt% using as catalyst at 450°C of reaction temperature, 1 bar of initial hydrogen pressure and 60 minutes of reaction time comparing with non-using catalyst as shown in Figure 4.9

A possible reason for this behavior is that the first step the effect of temperature mainly affect to cracking long chain by decarboxylation of fatty acid from used vegetable oil, the decarboxylation reaction were occurred to remove CO_2 form triglyceride fatty acid. And the effect of the temperature mainly cracked long chain hydrocarbon to middle hydrocarbon molecule and continuously cracked to light hydrocarbon. In addition, the light hydrocarbon molecules from thermal and catalytic cracking were converted to light gases. The catalytic cracking reaction was significant on the yield of gases is because of the acid site in the catalyst promote the cracking reaction responsible for the formation of gaseous product [15].

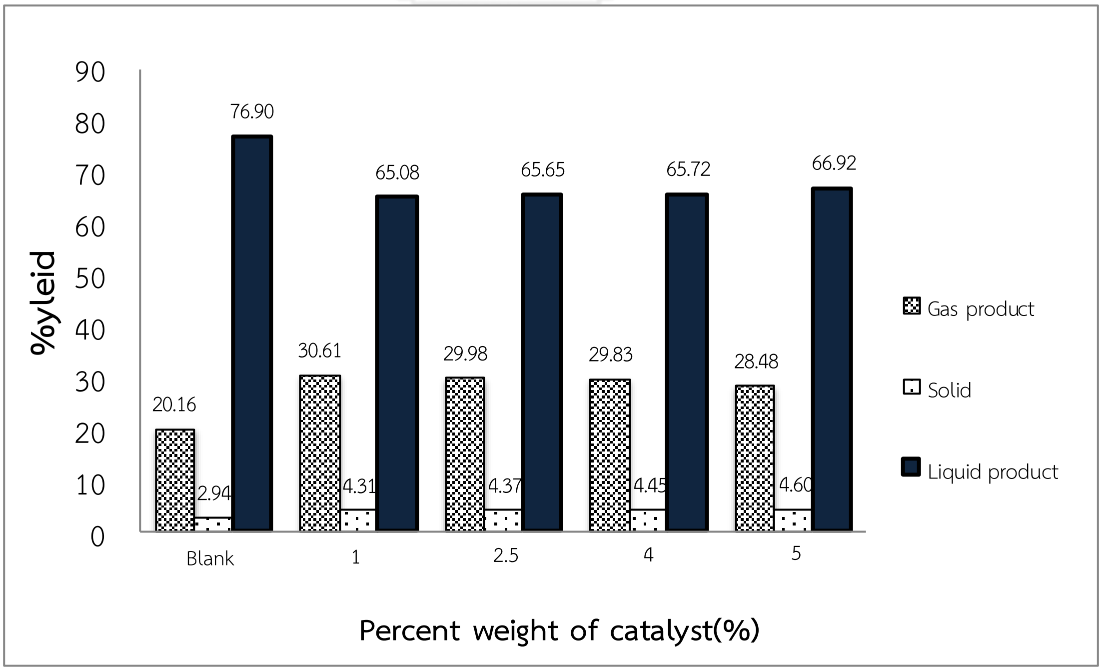


Figure 4.9 Effect of mass of spent FCC catalyst on product composition at 450°C of reaction temperature, 1 bar of initial hydrogen pressure and 60 minutes of reaction time

Due to the acid sites in the catalyst promotes the cracking reactions responsible for the formation of gaseous product. Hence, the mass of FCC in the catalytic cracking reaction was significantly affected to gaseous product. Furthermore, the light hydrocarbon molecules from thermal and catalytic cracking were converted to light gases.The investigation of used vegetable oil without catalyst at 1 bar and time of reaction 60 minutes showed 20.16 wt% of gas product, 76.90 wt% of liquid product and 2.94 wt% of solid. When the addition of spent FCC catalyst was increased from 1--5 wt%, the liquid product was decreased from 76.90 wt% to 65.08 wt% at, while gas product was increased from 20.16 wt% to 30.61 wt%. While the effects of mass of FCC catalyst between 1-5% on liquid, gas and solid yield were not significantly different.

A possible reason for this behavior is that the mass of the FCC catalyst increases the number of zeolite acid site to promote the cracking reaction to generate the lighter hydrocarbon molecule and also responsible for the formation of gaseous products. Zeolites have shown the excellent performance as acid catalyst for cracking middle hydrocarbon molecule because of their higher selectivity toward naphtha type[6]. The mass of FCC catalyst may correlation to the FCC catalyst concentration. Therefore, concentration of FCC catalyst increase the selectivity to naphtha fraction increase during long residue and diesel decreased. The selectivity increase to yield of naphtha product at high zeolite contents because of the formation of these products, which is favored at high zeolite catalyst contents[20].

The product distribution was determined by simulated distillation gas chromatograph shown as Figure 4.9. It found the increasing of naphtha from 14.54 wt% of blank condition to 19.52 wt%, kerosene from 8.97 to 13.02 wt% and decreasing of diesel 34.20 to 22.78 wt% and long residue from 19.19 to 9.76 wt% using 1% by mass of catalyst. As the results noticed that the product distribution by using mass catalyst between 1-5% was not significantly different.

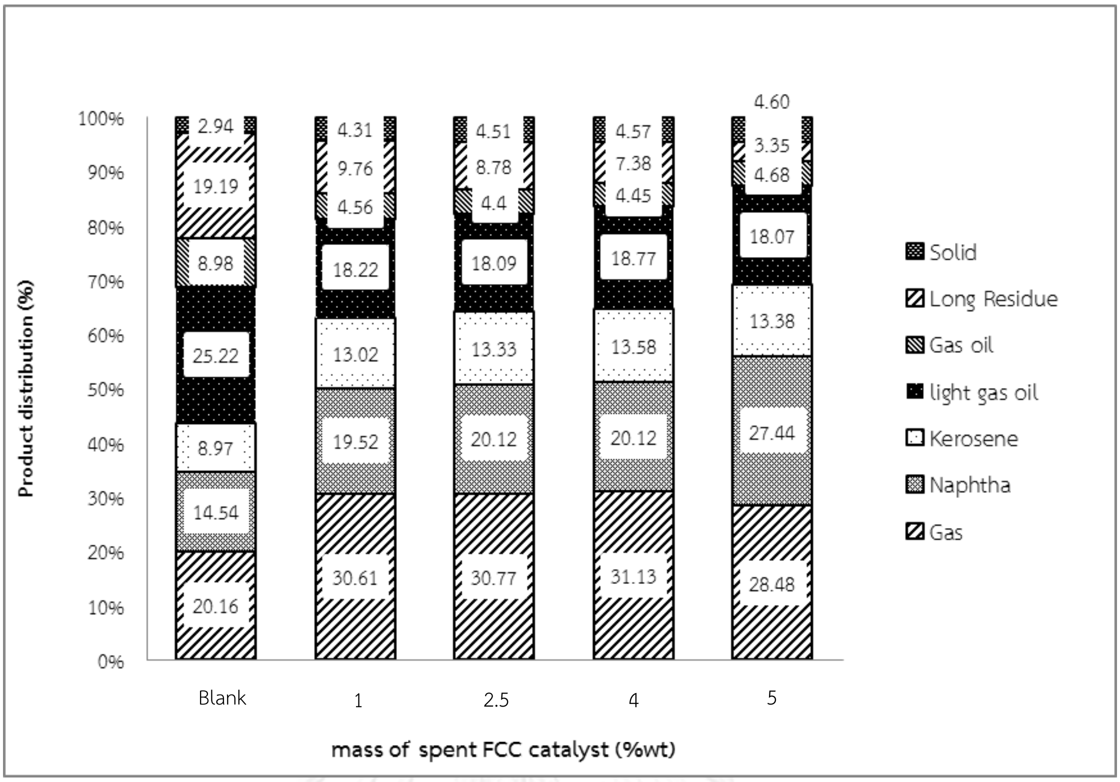


Figure 4.10 Effect of mass of spent FCC catalyst on product distribution at 450°C of reaction temperature, 1 bar of initial hydrogen pressure and 60 minutes of reaction time

In conclusion, Figure 4.10 showed that when the amount of spent FCC catalyst 1-5 percent by weight were used. The amount of liquid product yield was decreased with increased percent of catalyst, while the distribution of oil products naphtha fraction was increased steadily. Therefore, the condition 450°C of reaction temperature, 1 bar of initial hydrogen pressure and 60 minutes of reaction time over 5 wt% of spent FCC catalyst gave the highest naphtha fraction of 27.44 wt%, kerosene 13.38 wt%, diesel 22.75 wt% and long residue 3.35 wt% whereas the liquid yield of 66.92 wt%. The gaseous product was 28.48 wt% and solid yield was 4.60 wt%.

4.2.4 Effect of initial hydrogen pressure

The study of effects of initial hydrogen pressure on product composition was performed at 450°C of reaction temperature 5.0% by wt. of FCC catalyst and 60 minutes of reaction time was performed by operating in various initial hydrogen pressure; blank, 1 and 5 bars (pressure gauge). It was observed that the gas product increased 26.78 wt% at the atmospheric pressure to 31.69 wt% at 5 bars of initial hydrogen pressure, whereas the liquid product decreased form 69.43 wt% to 63.88 wt% (Figure 4.11). Normally the role of hydrogen supports cracking mechanism of hydrocarbon by hydrogenation. The Fluid catalytic (FCC) catalyst promote hydrogen transfer reaction to catalytic reaction by gave protons from the structure surface to long chain hydrocarbon [32, 33]. At the temperature 450°C initial hydrogen pressure of 1 bars and reaction time of 60 minute, gave the yield of liquid, gaseous, and solid of 66.92, 28.48, and 4.60 wt%, respectively.

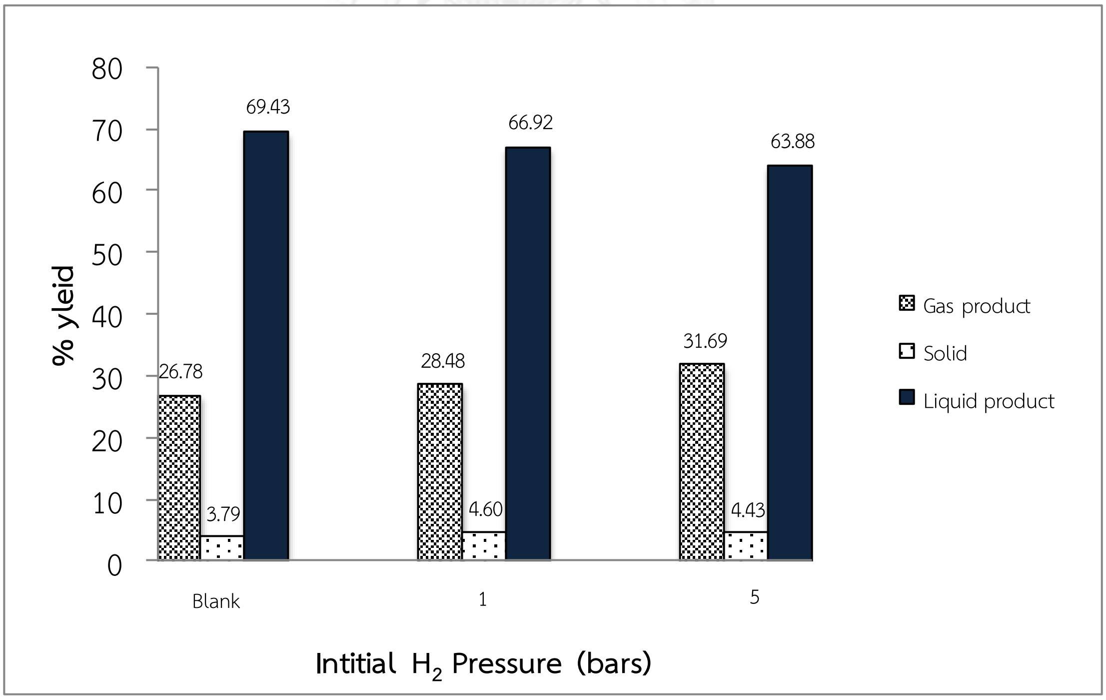


Figure 4. 11 Effect of initial hydrogen pressure on product composition at 450°C of reaction temperature 5.0 wt% of spent FCC catalyst and 60 minutes of reaction time

Normally the initial pressure of hydrogen gas at constant temperature promotes the hydrocracking heavier to smaller hydrocarbon molecule and including promotes hydrogenation reaction lead to become the smaller saturated hydrocarbon product structure[10, 26]. But the effect of initial hydrogen pressure was insignificant for the product distribution. Figure 4.14 shows the effect of initial hydrogen pressure on product composition at 450°C of reaction temperature 5.0 wt% of FCC catalyst and 60 minutes of reaction time but in this study the effects of initial hydrogen pressure was insignificant on product component distribution. As the result, the naphtha fraction stays constant 26.98 wt% at 0 bar and 26.83 wt% at 5 bars, the same as kerosene, whereas diesel was slightly increased from 20.56 wt% at 0 bars to 22.99 wt% at 5 bar.

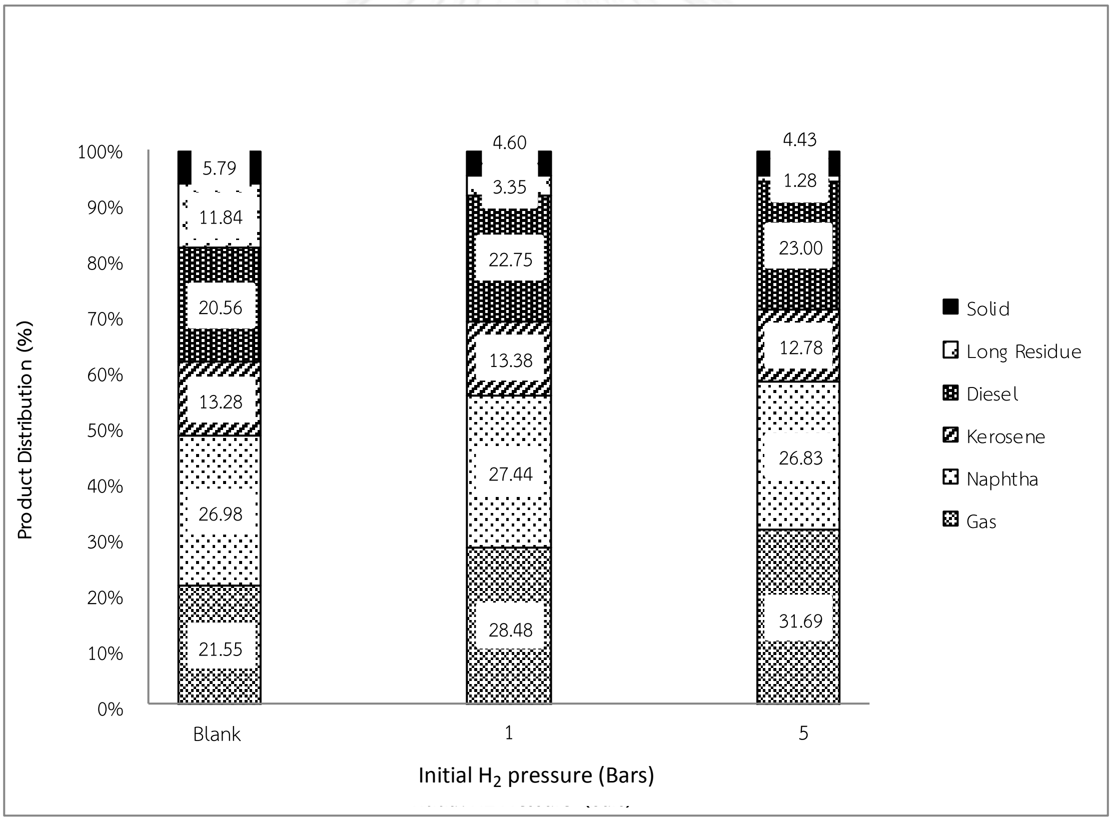


Figure 4.12 Effect of initial hydrogen pressure range of blank-5 bar on product distribution at 450°C of reaction temperature 5.0 wt% of spent FCC catalyst and 60 minutes of reaction time

The results shown in Figure 4.12 showed that the initial hydrogen pressure affects the distribution of product. It was noticed the different between using and without initial hydrogen pressure. But the product distribution by using initial hydrogen pressure between 1-5 bar was not significantly different. It seemed that pressure of 1 bar was enough to provided naphtha yield fraction of 27.44 wt% while kerosene 13.38 wt%, diesel 22.75 wt% and long residue 3.35 wt% were obtained.

4.3 Influence of different variables affecting the percentage of oil yield, naphtha and diesel product from cracking used vegetable oil over spent FCC catalyst.

4.3.1 Influence of variables affecting the percentage of oil yield

The influence of variables for cracking of the used vegetable oil over spent FCC catalyst by factorial bordered with 2^4 factorial and repeatedly experimentation was examined. Table 4.6 showed different condition giving the percentage of oil products in the range from 63.88 to 80.10 percent by weight. Figure 4.13 shows the Half Normal probability plot of the effects which shows the effect of temperature (A), the amount of catalyst (B), reaction time(C), initial pressure(D) and catalyst-pressure of reaction interaction (BC) are significant to cracking of used vegetable oil to oil yield product.

The ANOVA (Analysis of variance) display for model, Prob>F value indicates significance of the model and variable. The variables with Prob>F value less than 0.05 and their inherent are included in mathematical expression. Lack of Fit is not significant indicating a good data modeling. The analysis of variance as shown in Table 4.7 found that the temperature in the reaction. the temperature, the amount of catalyst, reaction time, initial pressure, catalyst-pressure of reaction interaction and pressure-time of reaction interaction have a value Prob> F less than 0.05 percent (calculated with the program Design-Expert 6.0.10), and implies that these variables affect the yield of oil products.

In conclusion, this confirms that the temperature, the amount of catalyst, reaction time, initial pressure, catalyst-pressure of reaction interaction and pressure-time of reaction interaction are significantly a key factor in the occurrence oil products yield. The correlation between the variables and % yield of liquid calculated with the program Design-Expert 6.0.10 is expressed as below.

$$\%\ \text{yield of liquid} = 130.73532 - 0.13442A + 0.58008B + 0.52820C - 0.089146D - 0.27289BC$$

Table 4.6 The percentage yield of oil product from the factorial experimental design 2^4 factorial designs

treatment	**Factor**				**%yield of Liquid**		**Factor Level**	
	A	B	C	D			**Low (-)**	**High (+)**
1	-	-	-	-	77.97	**A($^{\circ}$C)**	380	450
1R	-	-	-	-	78.97	**B(wt%)**	1	5
2	+	-	-	-	68.83	**C(bar)**	1	5
2R	+	-	-	-	69.43	**D(min)**	30	60
3	-	+	-	-	79.01			
3R	-	+	-	-	77.12			
4	+	+	-	-	68.72			
4R	+	+	-	-	70.10			
5	-	-	+	-	79.01			
5R	-	-	+	-	77.12			
6	+	-	+	-	67.28			
6R	+	-	+	-	69.66			
7	-	+	+	-	76.56			
7R	-	+	+	-	74.28			
8	+	+	+	-	66.23			
8R	+	+	+	-	67.12			
9	-	-	-	+	73.94			
9R	-	-	-	+	75.04			
10	+	-	-	+	65.08			
10R	+	-	-	+	64.94			

treatment	Factor				%yield of Liquid		Factor Level	
	A	B	C	D			Low (-)	High (+)
11	-	+	-	+	75.99	A(°C)	380	450
11R	-	+	-	+	78.18	B(wt%)	1	5
12	+	+	-	+	66.92	C(bar)	1	5
12R	+	+	-	+	65.11	D(min)	30	60
13	-	-	+	+	76.18			
13R	-	-	+	+	77.92			
14	+	-	+	+	67.97			
14R	+	-	+	+	67.23			
15	-	+	+	+	71.87			
15R	-	+	+	+	72.17			
16	+	+	+	+	63.88			
16R	+	+	+	+	65.12			

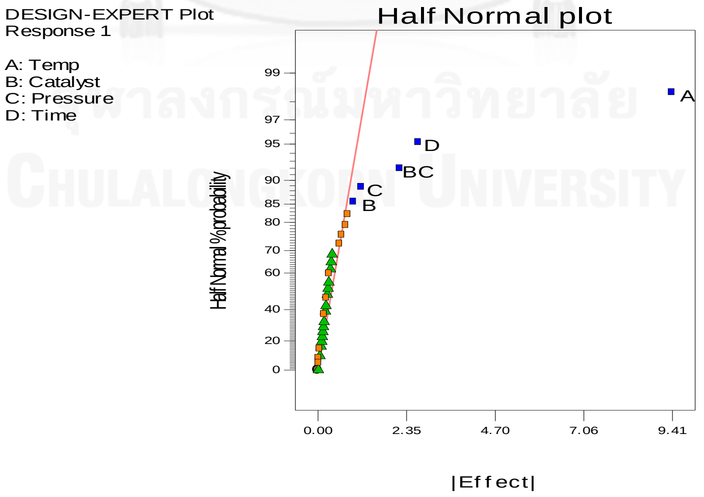


Figure 4.13 Normal Probability Plot of the percentages yield of oil products from the cracking of the used vegetable oil over spent FCC catalyst

Table 4.7 The analysis of variance of the percentages yield of oil products from the cracking of the used vegetable oil over spent FCC catalyst

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob>F Value
Model	821.72	5	164.34	123.94	< 0.0001
A	708.29	1	708.29	534.14	< 0.0001
B	7.29	1	7.29	5.50	0.0270
C	10.80	1	10.80	8.14	0.0084
D	57.22	1	57.22	43.15	< 0.0001
BC	38.13	1	38.13	28.75	< 0.0001
Residual	34.48	26	1.33		
Lack of Fit	17.23	10	1.72	1.60	0.1941
Pure Error	17.24	16	1.08		
Total	856.20	31			

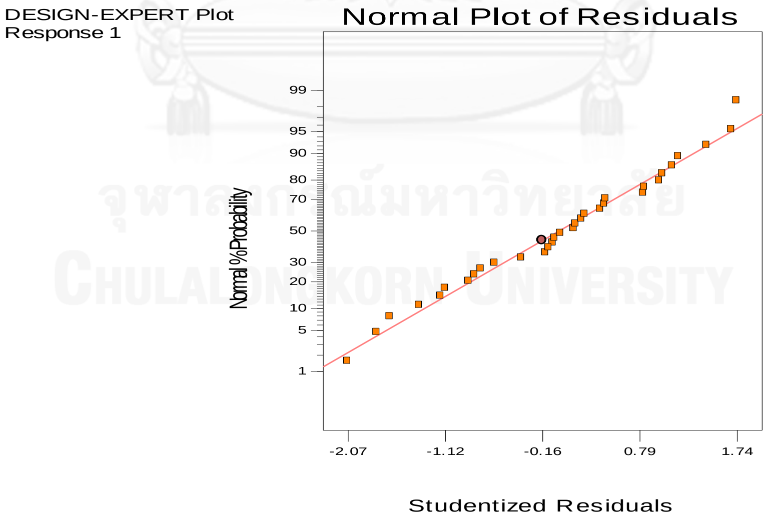


Figure 4.14 Normal Probability Plot of Residuals of oil yield products from the cracking of the used vegetable oil over spent FCC catalyst

Figure 4.14 Normal plot of residues show the percentage of Residuals for yield of oil products is likely a straight line with R^2 = 0.9597. The data on oil yield product fits the normal distribution and contains no outliers.

Figure 4.15 shows randomly the distribution of residual depending on each run from the data from percentage of oil yield products from the cracking of the used vegetable oil over spent FCC catalyst. It concludes that the experiment data are independent of each other.

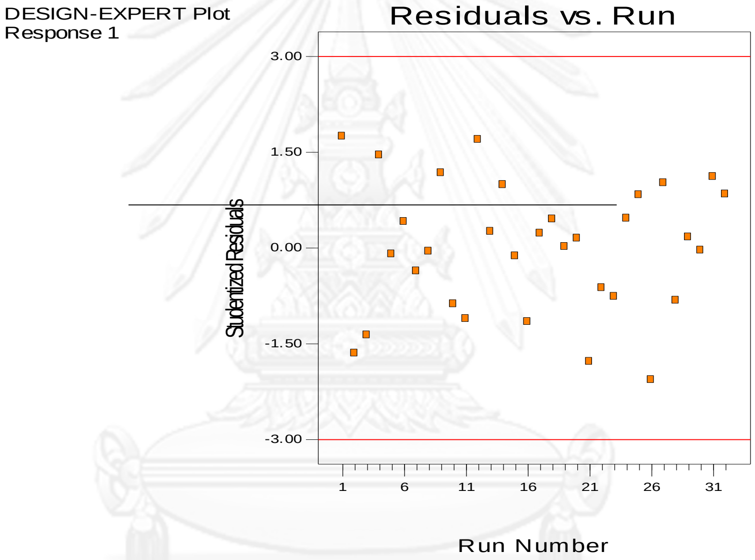


Figure 4.15 Residuals vs. Run of percentage of oil products from the cracking of the used vegetable oil over spent FCC catalyst

4.3.2 Influence of variables affecting the percentage of naphtha

Table 4.8 showed different condition giving the percentages yield of naphtha products in the range from 7.90 to 27.44 percent by weight. Figure 4.16 shows the Half Normal probability plot, which the variables deviate from the straight line are the temperature (A), the amount of catalyst (B) and initial pressure (D). It indicates that these variables are factors that affect the percent yield of naphtha products.

The variance of factors was analyzed by analysis of variance table (ANOVA) as shown in Table 4.9. It presents the individual and joint influence of the factors on the percentage of naphtha product. The factors evaluated are the temperature reaction, the amount of catalyst, initial pressure. Results from the ANOVA test showing factors that have significant individual or joint influence are shown in table 4.9. Factors that have significant effects on the percentage of naphtha product are those with F-value lower than probability value of 0.05.

In conclusion, this confirms that the temperature, the amount of catalyst, initial pressure is significantly a key factor in the occurrence naphtha products yields. The correlation between the variables and % yield of naphtha calculated with the program Design-Expert 6.0.10 is expressed as below.

$$\%\ \text{Yield of naphtha} = -48.38342+0.13797A+1.00047B+0.12498D$$

Table 4.8 The percentage yield of naphtha product from the factorial experimental design 2^4 factorial designs

Treatment	Factor				%yield of Naphtha		Factor Level	
	A	B	C	D			Low (-)	High (+)
1	-	-	-	-	8.58	A(°C)	380	450
1R	-	-	-	-	8.69	B(wt%)	1	5
2	+	-	-	-	13.77	C(bar)	1	5
2R	+	-	-	-	14.58	D(min)	30	60
3	-	+	-	-	18.60			
3R	-	+	-	-	19.87			
4	+	+	-	-	24.05			
4R	+	+	-	-	24.05			
5	-	-	+	-	9.84			
5R	-	-	+	-	8.48			
6	+	-	+	-	19.51			
6R	+	-	+	-	22.99			
7	-	+	+	-	12.25			
7R	-	+	+	-	11.14			
8	+	+	+	-	21.86			
8R	+	+	+	-	23.49			
9	-	-	-	+	13.31			
9R	-	-	-	+	14.26			
10	+	-	-	+	19.52			
10R	+	-	-	+	23.38			

treatment	Factor				%yield of Naphtha		Factor Level	
	A	B	C	D			Low (-)	High (+)
11	-	+	-	+	16.72	A(°C)	380	450
11R	-	+	-	+	16.42	B(wt%)	1	5
12	+	+	-	+	27.44	C(bar)	1	5
12R	+	+	-	+	26.44	D(min)	30	60
13	-	-	+	+	13.71			
13R	-	-	+	+	14.8			
14	+	-	+	+	20.39			
14R	+	-	+	+	22.19			
15	-	+	+	+	14.77			
15R	-	+	+	+	13.53			
16	+	+	+	+	26.83			
16R	+	+	+	+	26.7			

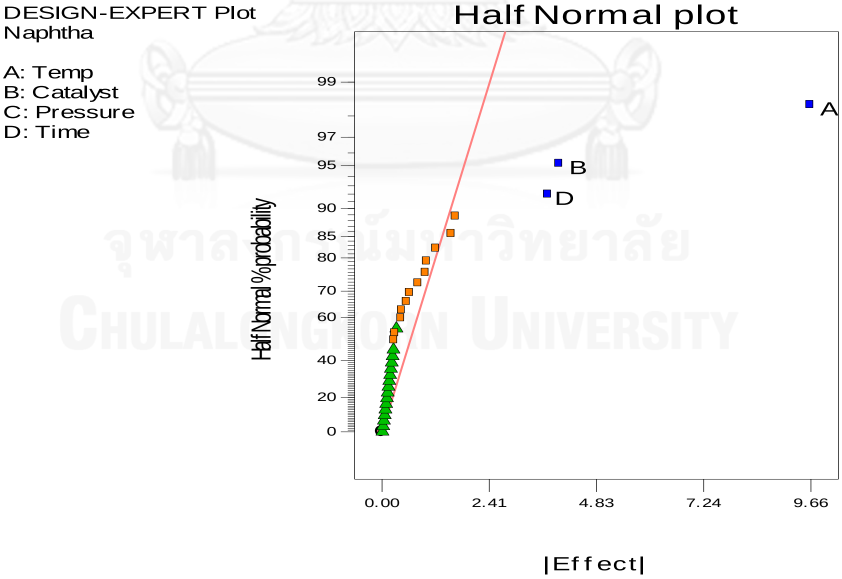


Figure 4.16 Normal Probability Plot of the percentages yield of naphtha products from the cracking of the used vegetable oil over spent FCC catalyst

Table 4.9 The analysis of variance of the percentages of naphtha products from the cracking of the used vegetable oil over spent FCC catalyst

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob>F Value
Model	986.82	3	328.94	85.06	< 0.0001
A	746.24	1	746.24	192.97	< 0.0001
B	128.12	1	128.12	33.13	< 0.0001
D	112.46	1	112.46	29.08	< 0.0001
Residual	108.28	28	3.87		
Lack of Fit	86.5	12	7.21	5.29	0.0013
Pure Error	21.79	16	1.36		
Cor Total	1095.1	31			

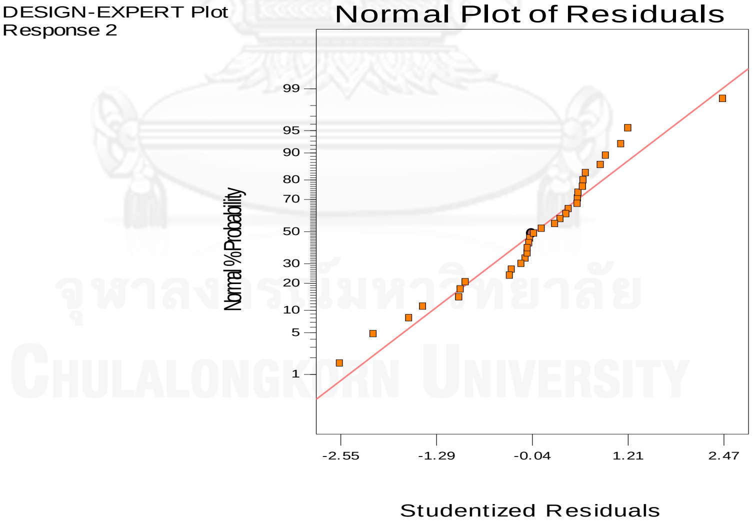


Figure 4.17 Normal Probability Plot of Residuals of naphtha products from the cracking of the used vegetable oil over spent FCC catalyst

Figure 4.17 shows the Residuals Normal plot of residual of naphtha products from the cracking of the used vegetable oil over spent FCC catalyst. The obtained data on naphtha product was then tested for normality. This is to verify if the data obtained from the experiments is suitable for further statistical evaluation. The calculated R-squared value (R^2) of the data is 0.9011. The data on naphtha product fits the normal distribution and contains no outliers.

Figure 4.18 shows randomly the distribution of residual depending on each run from the data of the percentages yield of naphtha products from the cracking of the used vegetable oil over spent FCC catalyst. It concludes that the experiment data are independent of each other.

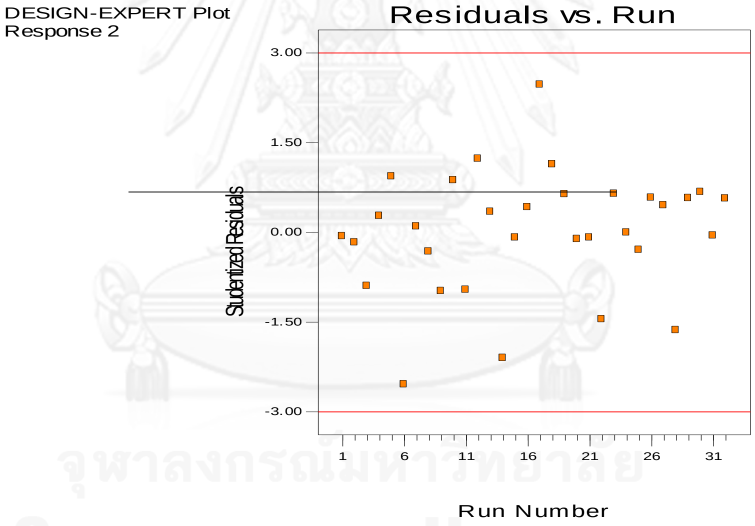


Figure 4.18 Residuals vs. Run of naphtha products from the cracking of the used vegetable oil over spent FCC catalyst

4.3.3 Influence of variables affecting the percentage of diesel

Table 4.10 showed different condition giving the percentages yield of diesel products in the range from 21.48 to 37.40 percent by weight. Figure 4.19 is a Half Normal probability plot of the effect which shows the effect of temperature (A), time of reaction (D) and temperature-time of reaction interaction (AD). It indicates that these variables are factors that affect the percent yield of diesel products. When consider Table 4.11 shows the ANOVA (Analysis of variance). It found that the temperature, initial pressure and temperature-time of reaction interaction have a value Prob> F less than 0.05 percent (calculated with the program Design-Expert 6.0.10), and implies that these variables affect the yield of diesel products.

In conclusion, this confirms that the temperature, initial pressure and temperature-time of reaction interaction are significantly a key factor in the occurrence diesel products. The correlation between the variables and % yield of diesel calculated with the program Design-Expert 6.0.10 is expressed as below.

$$\%\ \text{Yield of diesel} = +39.46286 - 0.032429A + 1.00129D - 2.26786E\text{-}003AD$$

Table 4. The percentage yield of diesel product from the factorial experimental design 2^4 factorial designs

Treatment	Factor				%yield of Diesel		Factor Level	
	A	B	C	D			Low (-)	High (+)
1	-	-	-	-	31.19	A(°C)	380	450
1R	-	-	-	-	33.17	B(wt%)	1	5
2	+	-	-	-	25.00	C(bar)	1	5
2R	+	-	-	-	25.03	D(min)	30	60
3	-	+	-	-	30.77			
3R	-	+	-	-	32.04			
4	+	+	-	-	23.02			
4R	+	+	-	-	21.48			
5	-	-	+	-	30.77			
5R	-	-	+	-	32.04			
6	+	-	+	-	23.00			
6R	+	-	+	-	24.00			
7	-	+	+	-	34.20			
7R	-	+	+	-	35.87			
8	+	+	+	-	22.75			
8R	+	+	+	-	22.79			
9	-	-	-	+	30.02			
9R	-	-	-	+	30.08			
10	+	-	-	+	22.78			
10R	+	-	-	+	21.48			

Treatment	Factor				%yield of Diesel		Factor Level	
	A	B	C	D			Low (-)	High (+)
11	-	+	-	+	34.2	A(°C)	380	450
11R	-	+	-	+	35.87	B(wt%)	1	5
12	+	+	-	+	23.79	C(bar)	1	5
12R	+	+	-	+	23.53	D(min)	30	60
13	-	-	+	+	31.39			
13R	-	-	+	+	31.94			
14	+	-	+	+	24.51			
14R	+	-	+	+	24.83			
15	-	+	+	+	33.06			
15R	-	+	+	+	33.2			
16	-	+	+	+	23			
16R	-	+	+	+	29.6			

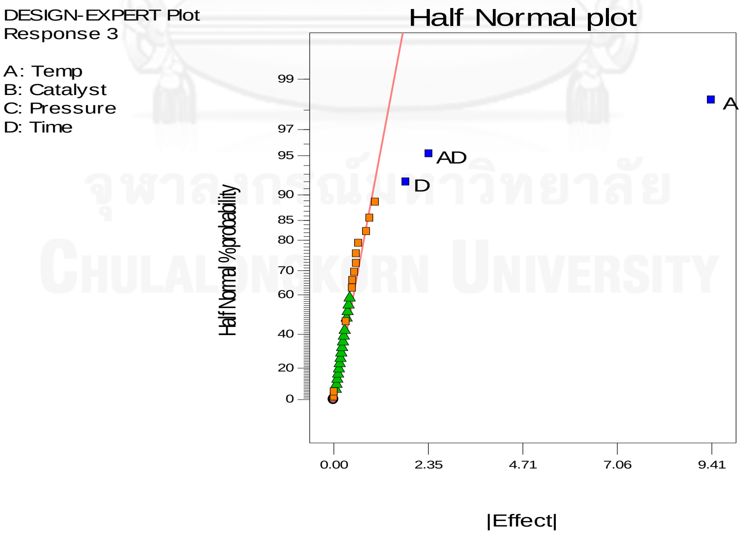


Figure 4.19 Normal Probability Plot of the percentages yield of diesel products from the cracking of the used vegetable oil over spent FCC catalyst

Table 4.11 The analysis of variance of percentages yield of diesel products from the cracking of the used vegetable oil over spent FCC catalyst

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob>F Value
Model	749.56	3	249.85	97.89	< 0.0001
A	687.46	1	687.46	269.35	< 0.0001
D	22.04	1	22.04	8.64	0.0065
AD	40.05	1	40.05	15.69	0.0005
Residual	71.46	28	2.55		
Lack of Fit	43.43	12	3.62	2.07	0.0879
Pure Error	28.04	16	1.75		
Cor Total	821.02	31			

Figure 4.20 shows the Residuals Normal plot of residues. The obtained data on diesel product was then tested for normality. This is to verify if the data obtained from the experiments is suitable for further statistical evaluation. It found that the percentage of diesel is likely a straight line with $R^2 = 0.9030$ and the data on diesel product fit the normal distribution and contain no outliers.

Figure 4.21 shows randomly the distribution of residual depending on each run from the data of the percentages yield of diesel products from the cracking of the used vegetable oil over spent FCC catalyst. It concludes that the experiment data are independent of each other.

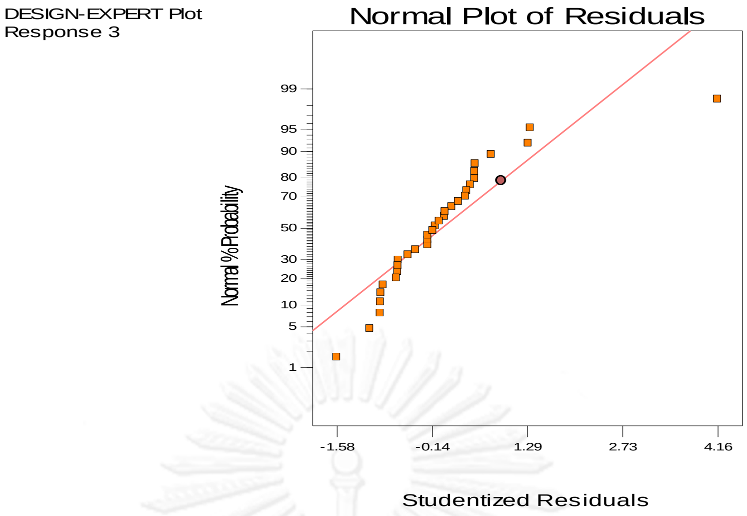


Figure 4.20 Normal Probability Plot of Residuals of diesel products from the cracking of the used vegetable oil over spent FCC catalyst

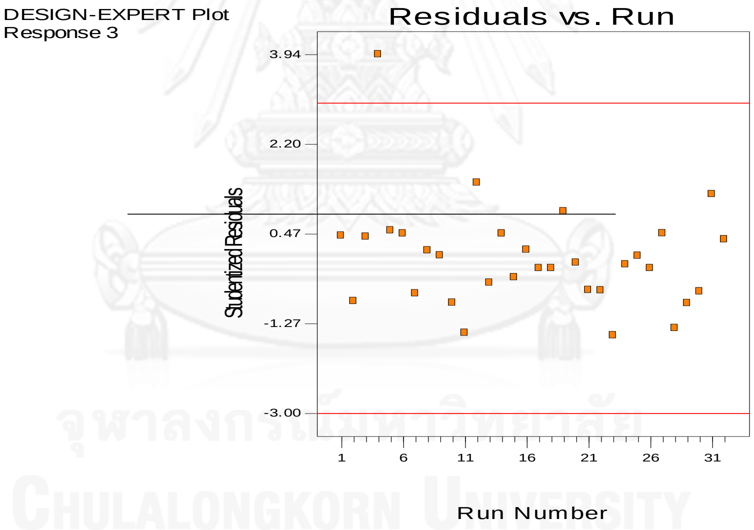


Figure 4.21 Residuals vs. Run of the percentages yield of diesel products from the cracking of the used vegetable oil over spent FCC catalyst

4.4 Determine the optimum condition of the cracking of used vegetable oil over spent FCC catalyst used by the Design-Expert 6.0.10 program

The optimum condition was determined by considering the lower and upper limit of five value response such as percentage of gaseous product, oil yield product, naphtha, kerosene and diesel product as shown in Table 4.10. The Design-Expert 6.0.10 program calculated for minimizing the percentage of gas products and remaining maximize the other values such as the percentage of oil yield products, naphtha, kerosene and diesel product.

Table 4.12 Scope of finding the optimum condition from Design-Expert 6.0.10 program

Name	Goal	Lower Limit	Upper Limit	Unit
Temperature (A)	is in range	380	450	°C
Catalyst (B)	is in range	30	60	%wt
Pressure (C)	is in range	1	5	bar
Time (D)	is in range	1	5	min
Yield of gas	Minimize	8.48	31.69	%wt
Yield of oil product	Maximize	63.88	80.10	%wt
Yield of naphtha	Maximize	7.90	27.44	%wt
Yield of kerosene	Maximize	3.12	18.69	%wt
Yield of diesel	Maximize	21.48	37.40	%wt

In conclusion the optimum condition calculated from the Design-Expert 6.0.10 program as shown Table 4.11 is temperature reaction of 400.49°C, The reaction time of 60 minutes, amount of the spent FCC catalyst is 5 percent by weight and initial hydrogen pressure of 1 bars.

Table 4.13 The optimum condition obtained from the Design-Expert 6.0.10 program

Variation	**The optimum condition calculated from Design Expert program**
Temperature(°C)	400.49
Mass of catalyst (wt%)	5
Initial hydrogen pressure(bar)	1
Time of reaction(minute)	60
Yield of gas (wt%)	20.65
Yield of oil product (wt%)	73.21
Yield of naphtha (wt%)	19.88
Yield of kerosene (wt%)	10.21
Yield of diesel (wt%)	31.02

The condition obtained from Design-Expert 6.0.10 program was set up to run two experiments in order to compare the percent of gas, liquid, naphtha, kerosene and diesel with the ones from program as shown in table 4.11. From Table 4.12 shows the close values of the percent of gas, liquid, naphtha, kerosene and diesel obtained from program and experiment as the same optimum condition.

Table 4.14 The comparison of the value from the Design-Expert 6.0.10 program and the value from the real experiment

Variation	**The optimum condition calculated from Design Expert program**	**Average Value of real experiment**
Temperature (°C)	400.49	401
Mass of catalyst (wt%))	5	5
Initial hydrogen pressure (bar)	1	1
Time of reaction (min)	60	60
Yield of gas (wt%)	20.65	19.74
Yield of oil product (wt%)	73.21	74.56
Yield of naphtha (wt%)	19.88	20.07
Yield of kerosene (wt%)	10.21	12.42
Yield of diesel (wt%)	31.02	32.035

4.5 Characterization of functional group of oil product by Fourier Transform Infrared Spectrophotometer(FT-IR)

The oil yield products form optimum conditions of the cracking of used vegetable oil over spent FCC catalyst analyzed functional group by a Fourier Transform Infrared Spectrophotometer. The oil yield product receive from cracking reaction at temperature 401 °C, 1 bar hydrogen pressure, reaction time 60 minutes using spent FCC catalyst 5 percent by weight analyzed the functional group found structural band of hydrocarbon with carbon 5-6 molecules and aromatic compound as shown in Figure 4.24.

The main absorption bands of oil product showed a strong spectrum presence of both C-H stretching aromatic and C-H stretching aliphatic functional group. The strong peak shows the absorption of stretching aliphatic, C-H stretching aromatic compounds and the carbonyl functional group bands at 2854, 2955 and 1710 cm^{-1}, respectively. Aromatic ring is bending vibrations in the region 670-870 cm^{-1} and C-H bending of CH_3 vibration at 1458 cm^{-1}. The spectrum of oil product has characteristic frequency at 1377 cm^{-1} which is assigned to its C-H bending of CH_2 group [34].

The functional groups of liquid products derived from the cracking of used vegetable oil over spent FCC and the gasoline oil are presented in Figure 4.25. The main functionality groups was similar, indicating that the cracking used vegetable oil can be used as gasoline substitutes.

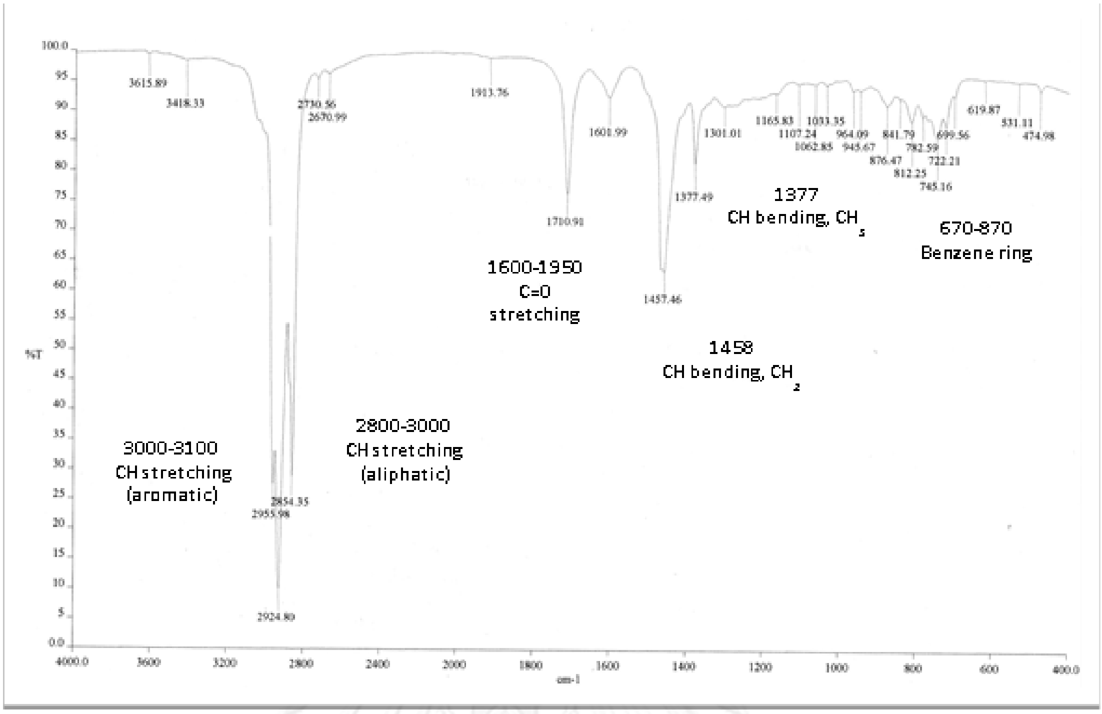


Figure 4.22 FTIR spectrums of oil products from the cracking of used vegetable oil at 401 °C for 60 minutes, hydrogen pressure is 1 bar using a catalyst FCC is 5 percent by weight.

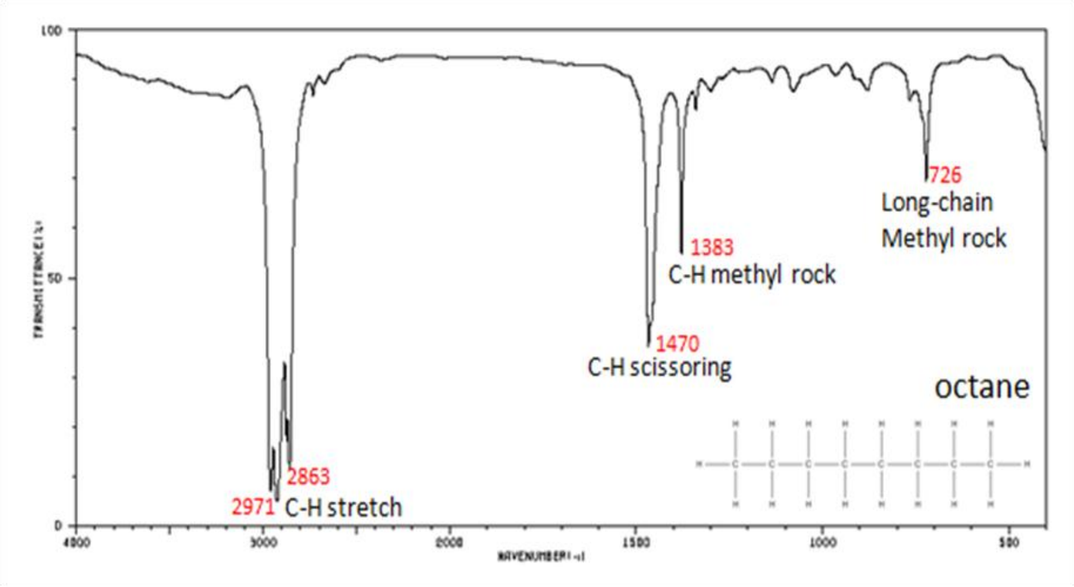


Figure 4.23 FTIR spectrum of the gasoline oil

4.6 Gas Chromatography-Mass Spectrometry

The chemical compound in the oil yield product from optimum conditions of cracking of used vegetable oil over spent FCC catalyst was analyzed by Gas Chromatography Mass Spectrometry is presented in Table 4.13. The oil yield produced consisted of hydrocarbon compounds with the paraffin branches and the aromatic paraffin chain, particularly for toluene, ethyl benzene, methyl benzene and xylene.

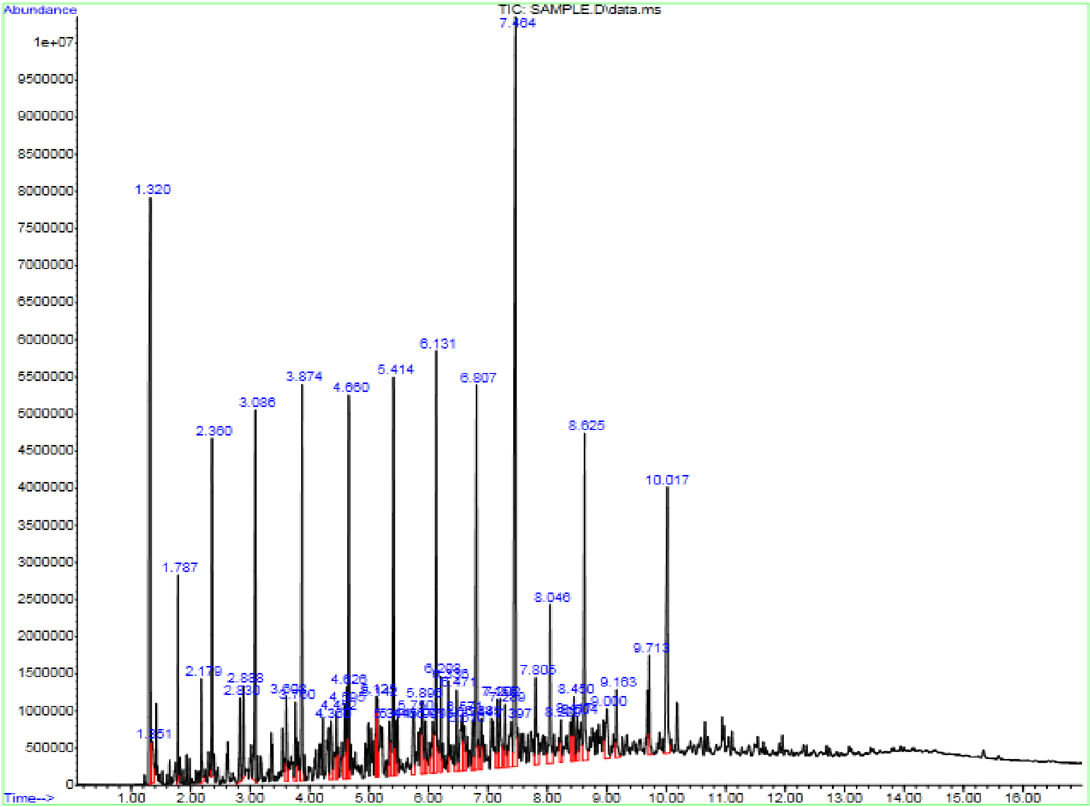


Figure 4.24 Diagram of Gas Chromatography-Mass Spectrometry

Table 4.15 The chemical compound in the oil yield product of cracking of used vegetable oil over spent FCC catalyst

Time R.T. (min)	Compound	Formular	Classification
1.787	Heptane	C_7H_{16}	Alkane C_7
2.181	Toluene	C_7H_8	Alkyl-benzene
2.832	Ethylbenzene	C_8H_{10}	Alkyl-benzene
2.359	n-Octane	C_8H_{18}	Alkane C_8
2.888	P-Xylene	C_8H_{10}	Alkyl-benzene
2.889	1,3-Dimethyl benzene	C_8H_{10}	Alkyl-benzene
3.087	n-Nonane	C_9H_{20}	Alkane C_9
3.608	1-Ethyl-3-methyl benzene	C_9H_{12}	Alkyl-benzene
3.872	n-Decane	$C_{10}H_{22}$	Alkane C_{10}
4.596	4-Ethyl-1,2-dimethyl benzene	$C_{10}H_{14}$	Alkyl-benzene
4.661	n-Undecane	$C_{11}H_{24}$	Alkane C_{11}
5.125	1-Methyl-1-propenyl benzene	$C_{10}H_{12}$	Alkyl-benzene
5.415	Dodecane	$C_{12}H_{26}$	Alkane C_{12}
5.446	1-ethyl-1-propenyl-benzene	$C_{11}H_{16}$	Alkyl-benzene
5.949	1-methyl-2-(1-ethylpropyl)-benzene	$C_{11}H_{16}$	Alkyl-benzene
6.074	1,2,3,4-tetrahydro-1,5-dimethyl-naphthalene	$C_{12}H_{16}$	Naphthalene
6.131	Tridecane	$C_{13}H_{28}$	Alkane C_{13}
6.209	Naphthalene	$C_{10}H_8$	Naphthalene
6.807	Tetradecane	$C_{14}H_{30}$	Alkane C_{14}

Time R.T. (min)	Compound	Formular	Classification
6.885	2-Methyl naphthalene	$C_{11}H_{10}$	Alkyl-naphthalene
7.397	Cyclopentadecane	$C_{15}H_{30}$	Alkane C_{13}
7.466	Pentadecane	$C_{15}H_{32}$	Alkane C_{15}
8.047	Hexadecane	$C_{16}H_{34}$	Alkane C_{16}
8.415	Cyclohexadecane	$C_{15}H_{32}$	Alkane C_{16}
8.623	Heptadecane	$C_{17}H_{36}$	Alkane C_{17}
9.161	Octadecane	$C_{18}H_{38}$	Alkane C_{18}

4.7 Analysis of the gas product

The analysis of the gas components of the oil yield product from the optimum condition of the cracking of used vegetable oil over spent FCC catalyst analyzed by gas chromatography (GC). Hydrocarbon gas was found concluding of methane (CH_4), ethane (C_2H_6) Ethylene (C_2H_4), propane (C_3H_8), butane (C_4H_{10}) and carbon dioxide gas (CO_2).

The 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 Moreover, hydrocarbon gas such as CH_4, C_2H_4, C_3H_8 and C_4H_{10} were obtains with oil product occur from the cracking reactions of long-chain hydrocarbon molecules into shorter chain of hydrocarbon molecules. A possible reason for this behavior is that the higher temperature accelerated the thermal cracking and hence changing the long chain of hydrocarbon molecule from thermal cracking in to middle hydrocarbon and light hydrocarbon molecules [32]. Thereafter light hydrocarbon molecules were thermally and catalytically cracked converting them into gaseous product [20].

4.8 Analysis of the quality of oil products

4.8.1 Analysis the heating value of oil products from cracking of used vegetable oil over spent FCC catalyst.

Table 4.14 shows the heating value of the oil yield product from the cracking of used vegetable oil over spent FCC catalyst comparing with gasoline and diesel. The heating value of oil yield product increase from 39.26 to 44.65 MJ/kg, and close to the heating value of the gasoline and diesel from petroleum.

Table 4.16 Comparison of calorific value from various fuels

Type of oil	Heating value (MJ/kg).
Used vegetable oil	39.26
Oil yield product	44.65
Gasoline	47
Diesel	45

4.8.2 Analysis percent of carbon, hydrogen and oxygen (CHO Analysis)

The analysis of used vegetable oil was found that the element contents as following; carbon, hydrogen and oxygen were 70.07, 11.55 and 16.51%, respectively (Table 4.15), according to the result of oil product of the cracking of used vegetable oil over spent FCC catalyst showed the carbon, hydrogen, nitrogen, and oxygen of 80.56, 11.45 and 7.84, respectively. The percent of oxygen of oil yield product decrease from 16.51% to 7.84 %.

It is clear that the oil yield product derived from cracking process over the spent FCC exhibited a low percent of oxygen of oil yield product compared to initial used vegetable oil. The percent of oxygen of oil yield product decrease from 16.51% to 7.84 %. With the decreasing of the percentage of oxygen, the heating value generally increases.

Table 4.17 Elemental analysis of oil yield products of the cracking of used vegetable oil over spent FCC catalyst

Type of oil	C	H	O
Used vegetable oil	70.07	11.55	16.51
Spent FCC	80.56	11.45	7.84
Without added catalyst	73.23	10.23	13.82

4.8.3 Analysis viscosity of oil products from cracking of used vegetable oil over spent FCC catalyst

Table 4.18 shows the viscosity value of the oil yield product from the cracking of used vegetable oil over spent FCC catalyst comparing to gasoline and diesel. The viscosity value of oil yield product decrease from 31.34 to 4.38 centipoises strokes, closing to the viscosity value of the gasoline and diesel from petroleum

Table 4.18 Comparison of viscosity value from various fuels

Type of oil	Viscosity (centipoises strokes)
Used vegetable oil	31.34
Oil yield product	4.38
Gasoline	1.8-4.1

4.8.4 Analysis total acid value of oil products from cracking of used vegetable oil over spent FCC catalyst

Table 4.19 shows the acid value of the oil yield product from the cracking of used vegetable oil over spent FCC catalyst compare with used vegetable oil. The acid value of oil yield product decrease from 5.90 to 5.18 mg KOH/g.

Table 4.19 Comparison of total acid value from various fuels

Type of oil	Acid value (mg KOH/g)
Used vegetable oil	5.90
Oil yield product	5.18

4.9 Comparison the results to the previous works

In 2003, M. Mongkol [10] studied the catalytic cracking of used vegetable oil to liquid fuels on HZSM-5 and Fe/active carbon in fixed bed microreactor. This research studied at reaction temperature range of 400-430 °C, reaction time 45-60 mins, the amount of Fe/active carbon 0.5-2.0 g with initial hydrogen pressure 10-30 bars and amount of HZSM-5 0.05-0.2 g with 10-20 bars of initial hydrogen pressure.

In 2004, W. Charusiri [20] studied catalytic cracking of the used vegetable oil was used to convert to light oil product by pyrolysis using over HZSM-5, Sulfates Zirconia and hybrid of HZSM-5 and Sulfates Zirconia catalyst in a batch reactor of 70 ml. The process was performed at 400-450°C, reaction time 45-90 min, initial hydrogen pressure 10-30 bars.

In 2011, Niken and co-workers [6] studied the catalytic of waste cooking palm oil to biofuel in fixed bed reactor. This research was studied over different type of nanocrystalline zeolites such as zeolite Y, HZSM-5 and zeolite Beta. The optimum condition determines that maximum conversion as well as maximum yield organic liquid product and gasoline yield by using design expert program following central composite design (CCD). The research study at temperature range 400-500°C, catalyst ratio range 6-14 and catalyst pore size different type of nanocrystalline (zeolite Y, HZSM-5 and zeolite Beta) range 0.54-0.80 nm to studied yield of organic liquid product, the conversion of waste cooking palm oil and yield of gasoline.

. In 2011, N. Wongsawat [29] studied of the cracking of vegetable oil on calcium oxide and magnesium in continuous reactor of 1250 mL was performed operating variable the temperature was varied from 390-440°C, feedstock's flowing rate 2-5 gram/minute and the mass of catalyst ranging from 1-5 wt%. The optimum condition determines that maximum liquid product as well as maximum yield naphtha product while minimum gaseous product by using design expert program.

In 2012, C. Wannawong [30] studied the pyrolysis of used vegetable oil to liquid fuel over spent FCC catalyst in a batch reactor of 70 ml. The process was performed at 380-440°C, reaction time 30-60 min, initial hydrogen pressure 1-5 bars, containing 1-5 wt% of spent FCC catalysts. The optimum condition determines that maximum liquid product as well as maximum yield naphtha, kerosene and diesel product while minimum gaseous product by using design expert program.

Table 4.20 Comparison the result of this study and other research

Experiment	Mongkol 2003	Charusiri 2004	Niken 2011	Wongsawat 2011	Wannawong 2012	This study
Reactant	Used vegetable oil	Used vegetable oil	Used vegetable oil	Used vegetable oil	Jatropha oil	Used vegetable oil
Catalyst	0.5 g of Fe/Active Carbon	0.1 wt% of the ratio 0.3 : 0.7 HZSM-5 : Sulfated Zirconia	Synthesis nano-crystalline zeolite Y	5 wt% of MgO	1 wt% of Spent FCC	5 wt% of Spent FCC
Temperature	430 °C	430 °C	450 °C	422 °C	410 °C	400.5 °C
Initial hydrogen pressure	10 bar	10 bar	-	-	1 bar	1 bar
Time of reaction	60 min	90 min	-	-	30 min	60 min
% wt of oil yield	79.74	79.17	48.1	31.19	88.6	73.21
% wt of Gasoline fraction	28.14	26.75	34.96	12.16	15.62	19.88
% wt of gaseous product	17.78	20.2	-	20.1	9.26	20.65
% wt of Diesel	25.21	29.07	-	11.18	40.15	31.02

CHAPTER V

CONCLUSION

5.1 Conclusion

In this research aims to study the cracking of used vegetable oil to liquid fuel over spent FCC catalyst in microreactor, the temperature was varied from 380-450 °C, 1-5 bars of initial hydrogen pressure, the mass of spent FCC catalyst ranging from 1-5 % by weight and 30-60 minutes of reaction time. Analysis of the products was performed using Simulated Distillation Gas Chromatography. The results are concluded as following:

1. From the experimental results obtained from this study, it may be concluded that, optimum condition for cracking of used vegetable oil are 5 percent by weight of spent FCC catalyst, reaction temperature 400.49°C, initial hydrogen pressure 1 bar, 60 minutes of reaction time. The products from optimum condition were 73.21 wt% of oil product, 20.65 wt% of gaseous product, and 6.14 wt% of solid. The oil products distribution were 19.88 wt% of naphtha, 10.21 wt% of kerosene, 31.02 wt% of diesel and 12.10 wt% of long residue respectively.

2. The variables; temperature(A), the amount of catalyst(B), reaction time(C), initial pressure(D) and catalyst-pressure of reaction interaction (BC) were determined to have significant effect on oil product.

3. Joint effect on naphtha and diesel product can also be observed from the analysis and it was determine that the temperature used in the reaction (A), the amount of catalyst (B) and initial pressure (D) have a significant effect on the naphtha product. The effect of temperature (A), time of reaction (D) and temperature-time of reaction interaction (AD) are factors that affect the percent yield of diesel products.

4. From FT-IR, the oil product was shows strong presence of both C-H stretching aromatic and aliphatic functional group. There were peak of substituted

aromatic groups and the presence of C-H stretching of aromatic which main functionality groups was similar to gasoline oil from petroleum.

5.2 Recommendation

1. Study the cracking of other oil type to liquid fuel over spent FCC catalyst.
2. Study the optimum condition of the cracking of used oil to expand production larger process.
3. Studies to improve the quality of liquid fuels that have to be even better and can be used with virtually any type of engine.
4. Studies the proper cracking of the substrate on the spent FCC catalyst.
5. Study the feasibility and economics of producing liquid fuels or chemicals from the cracking of used oil.

REFERENCES

1. Eduard B., K.S., Effect of oil type on products obtained by cracking oil and fat. Fuel Processing Technology, 2011: p. 2041-2047.
2. Hanna, L., Raimo, A. , Pyrolysis of vegetable oil soaps - Palm, olive, rapeseed and castor oils. Analytical and Applied Pyrolysis, 2011: p. 154-158.
3. Chen, Y., Xiao, B., Chang , J., Fu, Y., Lv, P., Wang, X., Synthesis of biodiesel from waste cooking oil using immobilized lipase in fixed bed reactor. Energy Conversion and Management, 2009. **50**: p. 668–73.
4. Zahira, Y., Masita, M., Mohammad, A., Zahangir, A., Kamaruzaman ,S, Overview of the production of biodiesel from Waste cooking oil. Renewable and Sustainable Energy Reviews, 2013. **18**: p. 184–193.
5. Twaiq, F.A.A., Bhatia,S.,, Catalytic Ccacking of palm oil over zeolite catalysts: statistical approach. IIUM Engineering 2001. **2**(1).
6. Niken, T., Abdul, R.M., Subhash, B., Production of biofuel from waste cooking palm oil using nanocrystalline zeolite as catalyst: Process optimization studies. Bioresource Technology, 2011. **102**: p. 10686-10694.
7. Olazar, M., Lopez,G., Amutio,M., Glordi,G., Elordi, R., Aguado, R., Bilbao,J.,, Influence of FCC catalyst steaming on HDPE pyrolysis product distribution. Analytical and Applied Pyrolysis, 2009. **85**: p. 359-365.
8. Karak, N., Vegetable oil-based polymer. 2012: Woodhead Publishing Limited.
9. Parawat, S., Effect of base catalyst on pyrolysis of soybean oil, in Chemical Engineering, Science Faculty. 2013, Chulalongkorn University.
10. Mongkol, M., Catalytic cracking of used vegetable oil to liquid fuel using Fe/ACTIVE CARBON and HZSM-5, in Chemical Engineering, Science Faculty. 2003, Chulalongkorn University.
11. Yvon, G., et al., Classification of vegetable oils based on their concentration of saturated fatty acids using laser induced breakdown spectroscopy (LIBS). Food Chemistry, 2014. **147**: p. 327–331.
12. Wen, Z., Yu, X., Tu, S.T., Yan, J.,, Biodiesel production from waste cooking oil catalyzed by TiO2–MgO mixed oxides. Bioresource Technology, 2010. **101**: p. 9570–6.
13. Weibing, D., Jing, L., and Laary, L., Anderson., Catalysis and processes for heavy oil conversion. 1997(International Symposium on Advances in Catalysis and Processes for Heavy oil Coversion): p. 428–432.

14.Witchakorn, C., Jintana, U., , Thermal cracking of waste glycerol from esterification process to gasoline and liquid fuels in a continuous, C.U. Conference on Energy Network of Thailand Energy Research Institute, Editor. 2007.

15.Permsubscul, A., Catalytic conversion of waste lubricant oil to liquid fuels over Fe/ACTIVATED CARBON, CoMo/Al2O3 and HZSM-5 catalyst, in Chemical Engineering, Science Faculty. 2004, Chulalongkorn University.

16.Den Hollander, M.A., et al., Gasoline conversion reactivity towards cracking with equilibrated FCC and ZSM-5 catalysts. 2002. **223**(Applied Catalysis A: General): p. 85–102.

17.Foo, K.Y., Hameed, B.H., The environmental applications of activated carbon/zeolite composite materials. 2011. **162**(Advances in Colloid and Interface Science): p. 22–28.

18.Jacobs, P.A., Flanigen, E.M., Jansen, J.C., Herman, V.B.,, Introduction to Zeolite Science and Practice. 2001, Netherlands: Elsevier Science B.V.

19.Szostak, R., Molecular Sieve Principle of Synthesis and Identification. 1989, New York: Norstand Reinhold.

20.Charusiri, W., Catalytic conversion of used vegetable oil to liquid fuels over HZSM-5 and sulfated zirconia, in Chemical Engineering, Science Faculty. 2004, Chulalongkorn University.

21.Taepakdee, P., Catalytic cracking of polypropylene, polystyrene and used-lubricant oil with Fe/ACTIVATED CARBON, in Chemical Engineering, Science Faculty. 2004, Chulalongkorn University.

22.Steele, W.A., Zgrablich, G., Rudzinski, W., , Equilibria and Dynamics of Gas Adsorption on Heterogeneous Solid Surfaces. 1997, Netherlands: Elsevier Science B.V.

23.Saeung, C., Preparation of activation carbon from petrochemical waste sludge by chemical and physical activation., in Petrochemical and Polymer Science. 2009, Chulalongkorn University.

24.James, G.S., The Refinery of the Future. First Edition ed. 2011, United State of America: Elsevier Inc.

25.Promote chaiyavej, N.k., Petroleum technology. 2000, Bangkok: Chulalongkorn University.

26.Pinweha, K., Pyrolysis of used lubricant oil on spent FCC catalyst, in Chemical Engineering, Science Faculty. 2011, Chulalongkorn University.

27.Satterfield, C.N., Schobert, eterogeous Catalysis in Industrial Practice. 1991, NewYork: McGraw-Hill Inc.

28.Eduard, B., Katarína, S., Zuzana, C., Alexander, K., The influence of zeolite catalysts on the products of rapeseed oil cracking. Fuel Processing Technology, 2011(1623-1631).

29.Wongsawat, N., Catalytic cracking of used vegetable oil on calcium oxide and magnesium oxide in continuous reactor, in Chemical Technology. 2011, Chulalongkorn Uiniversity.

30.Wannawong, C., Pyrolysis of jatropha oil to liquid fuel on used FCC in batch reactor in Chemical Technology. 2011, Chulalongkorn University.

31.Sai, P.R.K., et al., Catalytic Conversion of canola oil over Potassium-Impregnated HZSM-5 Catalysts : C_2-C_4 Olefin Production and Model Reaction Studies. Industrial & Engineering Chemical Research, 1996. **35**: p. 3332-3346.

32.John D.A., Sai P.R., and N.N. B., Catalytic Conversion of Biofuel to Hydrocarbon : Effect of Mixture of HZSM-5 and Silica-Alumina Catalyst on Product Distribution. Fuel Processing Technology, 1996. **48**: p. 115-143.

33.Farouq, A., Twaiq,N., Zabidi, A.M., and B. Subhash, Catalytic conversion of Palm oil to hydrocarbon : Performance of various Zeolite catalyst. Industrial & Engineering Chemical Research 1999. **38**: p. 3230-3237.

34.Ersan, P., Catalytic pyrolysis of biomass : Effects of pyrolysis temperature, sweeping gas flow rate and MgO catalyst. Energy 2010. **35**: p. 2761-2766.

APPENDIX

APPENDIX A

The Product Yield and Product Distribution

Table A-1 the product yield and product distribution of 2^4 factorial design of the cracking of used vegetable oil as a liquid fuel using spent FCC catalyst.

run	Temp. (oC)	Time (min)	Catalyst (%wt)	Pressure (bar)	Liquid (%wt)	Gas (%wt)	Solid (%wt)	Naphtha (%wt)	Kerosene (%wt)	Diesel (%wt)	Long residue (%wt)
1	380	30	1	1	77.97	18.95	3.08	8.58	7.80	31.19	30.41
1R	380	30	1	1	78.97	18.55	2.48	8.69	7.90	33.17	29.22
2	380	30	1	5	79.01	18.60	2.39	9.84	5.53	30.77	33.97
2R	380	30	1	5	77.12	19.87	3.01	8.48	5.40	32.04	33.16
3	380	30	5	1	78.91	19.65	1.44	12.63	11.84	35.46	23.67
3R	380	30	5	1	80.10	19.44	2.46	13.62	10.41	36.02	24.03
4	380	30	5	5	76.56	20.62	2.82	12.25	9.95	34.20	22.97
4R	380	30	5	5	74.28	21.22	4.50	11.14	8.91	35.87	22.28
5	380	60	1	1	73.94	19.67	6.39	13.31	8.87	30.02	16.27
5R	380	60	1	1	75.04	18.98	5.98	14.26	8.25	30.08	16.51
6	380	60	1	5	76.18	20.02	3.86	13.71	3.81	31.39	22.09

run	Temp. (oC)	Time (min)	Catalyst (%wt)	Pressure (bar)	Liquid (%wt)	Gas (%wt)	Solid (%wt)	Naphtha (%wt)	Kerosene (%wt)	Diesel (%wt)	Long residue (%wt)
6R	380	60	1	5	77.92	19.56	2.52	14.80	3.12	31.94	22.60
7	380	60	5	1	75.99	20.02	3.99	16.72	15.20	34.20	9.88
7R	380	60	5	1	78.18	19.45	2.37	16.42	15.64	35.87	10.16
8	380	60	5	5	71.87	23.51	4.62	14.77	3.59	33.06	20.45
8R	380	60	5	5	72.17	22.32	2.51	13.53	3.61	33.20	21.83
9	450	30	1	1	68.83	26.75	4.42	13.77	17.69	25.00	12.39
9R	450	30	1	1	69.43	25.56	5.01	14.58	17.22	25.03	12.50
10	450	30	1	5	67.28	24.21	8.51	19.51	12.25	23.00	11.44
10R	450	30	1	5	69.66	24.56	5.78	22.99	11.84	24.00	10.73
11	450	30	5	1	68.72	27.49	3.79	24.05	15.81	23.02	5.84
11R	450	30	5	1	70.10	27.41	2.49	24.05	16.12	24.00	5.47
12	450	30	5	5	66.23	27.32	6.44	21.86	16.56	22.75	3.31
12R	450	30	5	5	67.12	27.77	5.11	23.49	15.44	22.79	3.36

run	Temp. (oC)	Time (min)	Catalyst (%wt)	Pressure (bar)	Liquid (%wt)	Gas (%wt)	Solid (%wt)	Naphtha (%wt)	Kerosene (%wt)	Diesel (%wt)	Long residue (%wt)
13	450	60	1	1	65.08	30.61	4.31	19.52	13.02	22.78	9.76
13R	450	60	1	1	64.94	30.44	4.62	23.38	11.69	21.48	8.44
14	450	60	1	5	67.97	28.20	3.83	20.39	17.67	24.51	6.12
14R	450	60	1	5	67.23	27.89	4.88	22.19	16.81	24.83	4.71
15	450	60	5	1	66.92	28.48	4.60	27.44	13.38	23.79	3.35
15R	450	60	5	1	65.11	29.88	5.01	26.44	13.02	23.53	3.26
16	450	60	5	5	63.88	31.69	4.43	26.83	12.78	23.00	1.28
16R	450	60	5	5	65.12	30.13	4.75	26.70	13.02	29.60	1.30
17	430	45	3	3	68.35	27.57	4.08	22.56	18.45	20.51	6.84
17R	430	45	3	3	67.75	29.07	3.18	23.71	18.29	23.04	2.71
17R	430	45	3	3	69.23	27.56	3.21	24.23	18.69	21.46	4.85

Table A-2 Study the results of temperature the cracking of used vegetable oil as a liquid fuel using spent FCC catalyst.

run	Temp. (oC)	Time (min)	Catalyst (%wt)	Pressure (bar)	Liquid (%wt)	Gas (%wt)	Solid (%wt)	Naphtha (%wt)	Kerosene (%wt)	Diesel (%wt)	Long residue (%wt)
1	380	60	5	1	75.99	20.02	3.99	16.72	15.20	34.20	9.88
2	430	60	5	1	72.12	24.78	3.10	23.73	16.56	26.48	3.45
3	450	60	5	1	66.92	28.48	4.60	27.44	13.38	23.79	3.35

Table A-3 Study the results of reaction time of the cracking of used vegetable oil as a liquid fuel using spent FCC catalyst.

run	Temp. (oC)	Time (min)	Catalyst (%wt)	Pressure (bar)	Liquid (%wt)	Gas (%wt)	Solid (%wt)	Naphtha (%wt)	Kerosene (%wt)	Diesel (%wt)	Long residue (%wt)
1	450	30	5	1	68.72	27.49	3.79	24.05	15.81	23.02	5.84
2	450	45	5	1	67.89	27.53	4.58	26.33	13.56	23.28	5.95
3	450	60	5	1	66.92	28.48	4.60	27.44	13.38	23.79	3.35

Table A-3 Study the results of mass of catalyst of the cracking of used vegetable oil as a liquid fuel using spent FCC catalyst.

run	Temp. (oC)	Time (min)	Catalyst (%wt)	Pressure (bar)	Liquid (%wt)	Gas (%wt)	Solid (%wt)	Naphtha (%wt)	Kerosene (%wt)	Diesel (%wt)	Long residue (%wt)
1	450	60	0	1	76.90	20.16	2.94	14.54	8.97	34.20	19.19
2	450	60	1	1	65.08	30.61	4.31	19.52	13.02	22.78	9.76
3	450	60	2.5	1	65.65	29.98	4.37	20.12	13.33	22.49	8.78
4	450	60	4	1	65.72	29.83	4.45	20.12	13.58	23.22	7.38
5	450	60	5	1	66.92	28.48	4.60	27.44	13.38	23.79	3.35

Table A-4 Study the results of initial hydrogen pressure of the cracking of used vegetable oil as a liquid fuel using spent FCC catalyst.

run	Temp. (oC)	Time (min)	Catalyst (%wt)	Pressure (bar)	Liquid (%wt)	Gas (%wt)	Solid (%wt)	Naphtha (%wt)	Kerosene (%wt)	Diesel (%wt)	Long residue (%wt)
1	450	60	5	blank	69.43	26.78	3.79	26.98	13.28	20.56	11.84
2	450	60	5	1	66.92	28.48	4.60	27.44	13.38	23.79	3.35
3	450	60	5	5	63.88	31.69	4.43	26.83	12.78	23.00	1.28

APPENDIX B

Statistical analysis and sample calculations

The experimental design was two level factorial statistical analysis. It is under the assumption that the variables and the analysis of the relationship are linear.

1. Symbol of factorial experimental design

1.1 k is the number of variables to be studied.

1.2 n is the number of trials of the same experiment.

1.3 The English alphabet (A, B, C, and D) is the factors such as temperature, time of reaction, amount of catalyst and the initial hydrogen pressure.

1.4 The English alphabet to write combination as AB, AC, and ABC is the interaction of each factor.

1.5 Alphabet letters well written as ab, ac, abc means a trial, which a combination of various factors that influence.

In experiments level of factor represents a low level and high level instead of (-1) to (+1) at low and high levels.

In this research studied the cracking of used vegetable oil as a liquid fuel over spent FCC catalyst. Experimental designs into 2^k factorial and one replication.

Table B-1 the variables and levels of study

	Factor	**Level**		**Unit**
		Low (-)	High (+)	
A	Temperature	380	450	°C
B	% weight of spent FCC	1	5	wt%
C	initial pressure of hydrogen gas	1	5	Bar
D	Time of reaction	30	60	minutes

2. The 2^k factorial experimental design

Factorial design used in real experiments involving several factors. K factors consists of two levels, these result from quantitative data, such as temperature, pressure and time or may be derived from qualitative data such as machinery or workers , etc.

The above is "high" or "low" of one factor. k factors and each factor has only two levels In the first experiment replicated the design like contain a total of 2 × 2 × 2 × ... × 2 = 2k, which is called the 2^k factorial.
The assumption is acceptable for experimentation as following:

2.1 Contrast = Sum of the individual trials Treatment x coefficient.

(-1 Or +1) of the variables or interactions between variables.

2.2 Effect Estimate$_{AB...K}$ (EE)

$$EE = \frac{2\,(\text{Contrast}_{AB...K})}{n\,(2^k)}$$

2.3 Sum of Squares $_{AB...K}$ (SS)

$$SS = \frac{2\,(\text{Contrast}_{AB...K})^2}{n\,(2^k)}$$

2.4 Total of sum of squares (SS_T)

$$\underset{i=1\ j=1\ k=1}{SS_T} = \underset{i=1\ j=1\ k=1}{\sum\sum\sum} y^2_{ijk} - y^2_{...}\ ,\ N = \text{Total number of observations}$$

2.5 Mean of Square Error : (SS_E)

$$SS_E = SST - SS\ \text{of Main Effect}$$

2.6 Mean of Square (MS)

$$MS = SS\ /\ \text{Degree of Freedom}$$

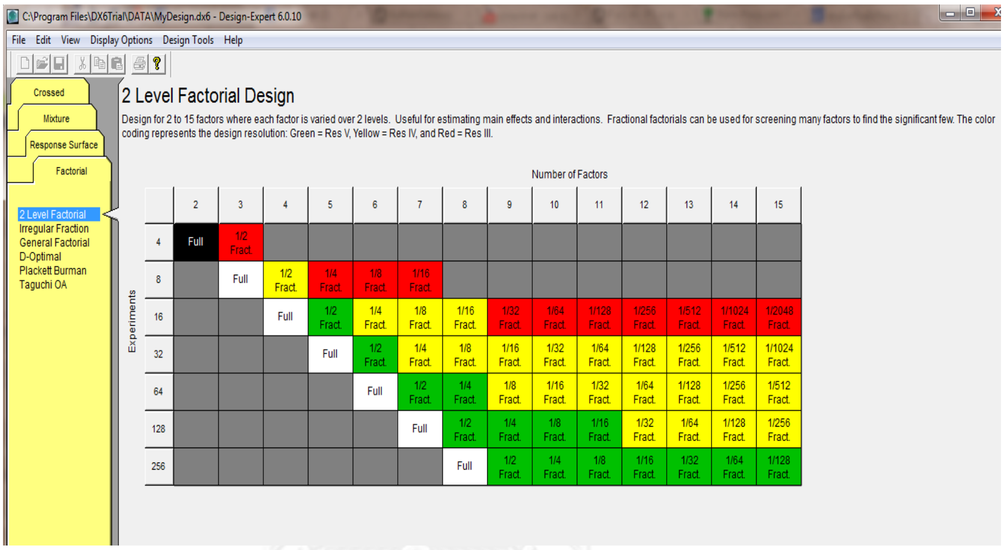
2.7 % Normal probability =

$$\frac{(\text{Cumulative frequency} - 0.5) \times 100}{\text{Total cumulative frequency}}$$

2.8 $F_0 = MS_{effect} / MS_{error}$

3. Procedures of Design-Expert Program

3.1 Enter the program click on the file ----> New Design shown in the Fig B-1



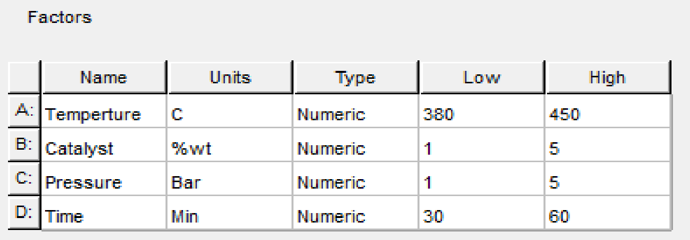
2 Level Factorial Design

Design for 2 to 15 factors where each factor is varied over 2 levels. Useful for estimating main effects and interactions. Fractional factorials can be used for screening many factors to find the significant few. The color coding represents the design resolution: Green = Res V, Yellow = Res IV, and Red = Res III.

Experiments	Number of Factors													
	2	3	4	5	6	7	8	9	10	11	12	13	14	15
4	Full	1/2 Fract.												
8		Full	1/2 Fract.	1/4 Fract.	1/8 Fract.	1/16 Fract.								
16			Full	1/2 Fract.	1/4 Fract.	1/8 Fract.	1/16 Fract.	1/32 Fract.	1/64 Fract.	1/128 Fract.	1/256 Fract.	1/512 Fract.	1/1024 Fract.	1/2048 Fract.
32				Full	1/2 Fract.	1/4 Fract.	1/8 Fract.	1/16 Fract.	1/32 Fract.	1/64 Fract.	1/128 Fract.	1/256 Fract.	1/512 Fract.	1/1024 Fract.
64					Full	1/2 Fract.	1/4 Fract.	1/8 Fract.	1/16 Fract.	1/32 Fract.	1/64 Fract.	1/128 Fract.	1/256 Fract.	1/512 Fract.
128						Full	1/2 Fract.	1/4 Fract.	1/8 Fract.	1/16 Fract.	1/32 Fract.	1/64 Fract.	1/128 Fract.	1/256 Fract.
256							Full	1/2 Fract.	1/4 Fract.	1/8 Fract.	1/16 Fract.	1/32 Fract.	1/64 Fract.	1/128 Fract.

Fig B-1 Table of 2 Level Factorial Design

3.2 Select the number of variables used in the experiment to study the influence of those variables. In this research consisted of 4 variables is the temperature, amount of catalyst, Initial hydrogen pressure and time as shown in Figure b-2 when variable fill complete, then click on Continue.

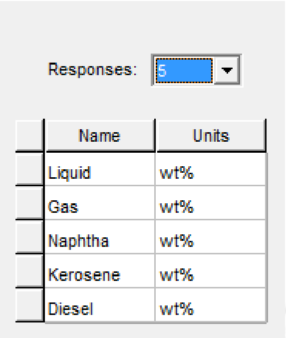


Factors

	Name	Units	Type	Low	High
A:	Temperture	C	Numeric	380	450
B:	Catalyst	%wt	Numeric	1	5
C:	Pressure	Bar	Numeric	1	5
D:	Time	Min	Numeric	30	60

Fig B-2 Variables and units used in the experiments.

3.3 Select the variables used in the experiment and fill in the channel as shown in Fig B-3 then click Continue.

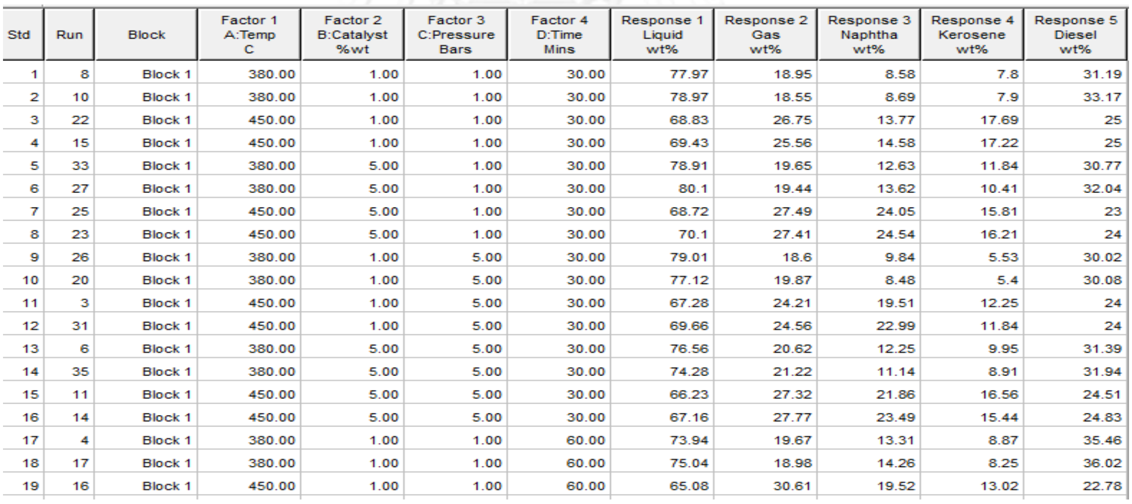


Responses: 5

Name	Units
Liquid	wt%
Gas	wt%
Naphtha	wt%
Kerosene	wt%
Diesel	wt%

Fig B-3 Response and units of the variables tested

3.4 Dominant factor appears 16 trials of the experiments and 3 trials of average of the experiments included trials 19 trials, then fill the data from experiments in channel as shown in Fig B-4



Std	Run	Block	Factor 1 A:Temp C	Factor 2 B:Catalyst %wt	Factor 3 C:Pressure Bars	Factor 4 D:Time Mins	Response 1 Liquid wt%	Response 2 Gas wt%	Response 3 Naphtha wt%	Response 4 Kerosene wt%	Response 5 Diesel wt%
1	8	Block 1	380.00	1.00	1.00	30.00	77.97	18.95	8.58	7.8	31.19
2	10	Block 1	380.00	1.00	1.00	30.00	78.97	18.55	8.69	7.9	33.17
3	22	Block 1	450.00	1.00	1.00	30.00	68.83	26.75	13.77	17.69	25
4	15	Block 1	450.00	1.00	1.00	30.00	69.43	25.56	14.58	17.22	25
5	33	Block 1	380.00	5.00	1.00	30.00	78.91	19.65	12.63	11.84	30.77
6	27	Block 1	380.00	5.00	1.00	30.00	80.1	19.44	13.62	10.41	32.04
7	25	Block 1	450.00	5.00	1.00	30.00	68.72	27.49	24.05	15.81	23
8	23	Block 1	450.00	5.00	1.00	30.00	70.1	27.41	24.54	16.21	24
9	26	Block 1	380.00	1.00	5.00	30.00	79.01	18.6	9.84	5.53	30.02
10	20	Block 1	380.00	1.00	5.00	30.00	77.12	19.87	8.48	5.4	30.08
11	3	Block 1	450.00	1.00	5.00	30.00	67.28	24.21	19.51	12.25	24
12	31	Block 1	450.00	1.00	5.00	30.00	69.66	24.56	22.99	11.84	24
13	6	Block 1	380.00	5.00	5.00	30.00	76.56	20.62	12.25	9.95	31.39
14	35	Block 1	380.00	5.00	5.00	30.00	74.28	21.22	11.14	8.91	31.94
15	11	Block 1	450.00	5.00	5.00	30.00	66.23	27.32	21.86	16.56	24.51
16	14	Block 1	450.00	5.00	5.00	30.00	67.16	27.77	23.49	15.44	24.83
17	4	Block 1	380.00	1.00	1.00	60.00	73.94	19.67	13.31	8.87	35.46
18	17	Block 1	380.00	1.00	1.00	60.00	75.04	18.98	14.26	8.25	36.02
19	16	Block 1	450.00	1.00	1.00	60.00	65.08	30.61	19.52	13.02	22.78

Fig B-4 The data used in all experiments.

3.5 Analysis of the results from the experiment with the program as shown in Table 5, then click Effect.

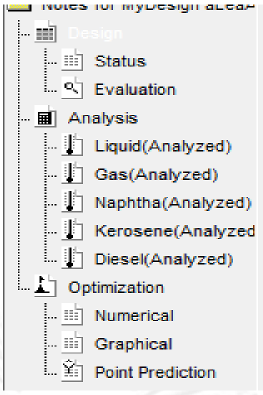


Fig B-5 Tab of the gas liquid kerosene and diesel.

3.6 Based on this plot, all the effects that lie along the line are considered negligible; whereas the significant effects are those far from the line. Select points that far from the line curve trend in Half Normal% Probability graphs as shown in Fig B-6.

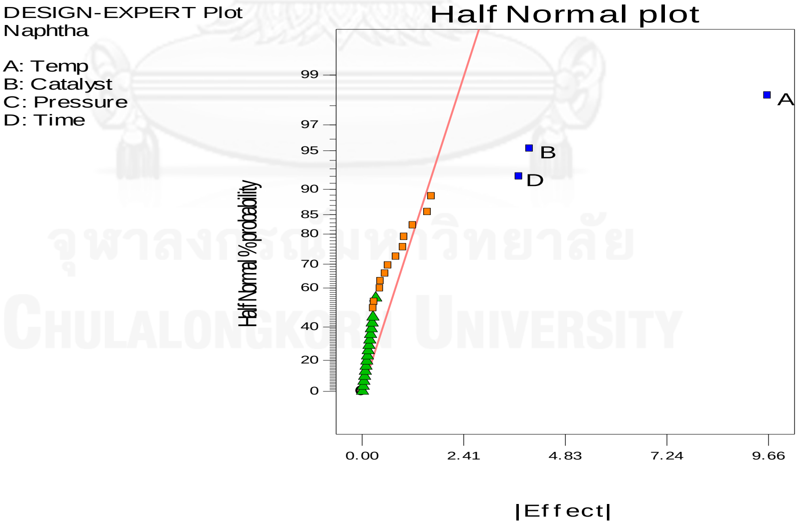
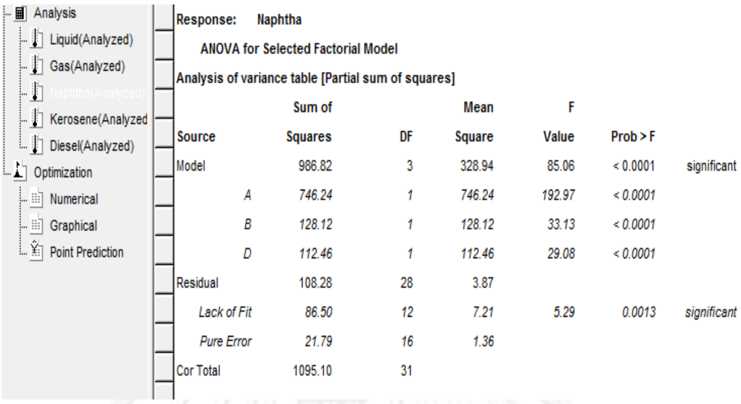


Fig B-6 Half Normal probability plot of the percentage yield of naphtha

The figure B-6 indicates that temperature, the initial hydrogen pressure and reaction time deviation from the straight line that mean those factors are significantly affecting to percentage of naphtha yield product.

3.7 Press the ANOVA as shown in Fig B-7 for the results of the calculations and confirm the results of Normal probability.



Response: Naphtha

ANOVA for Selected Factorial Model

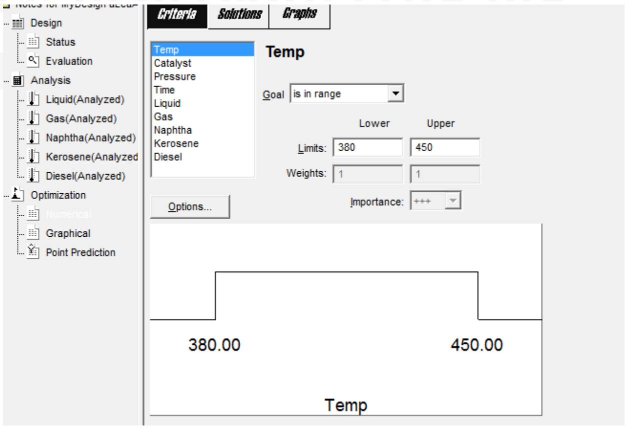
Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	986.82	3	328.94	85.06	< 0.0001	significant
A	*746.24*	*1*	*746.24*	*192.97*	*< 0.0001*	
B	*128.12*	*1*	*128.12*	*33.13*	*< 0.0001*	
D	*112.46*	*1*	*112.46*	*29.08*	*< 0.0001*	
Residual	108.28	28	3.87			
Lack of Fit	*86.50*	*12*	*7.21*	*5.29*	*0.0013*	*significant*
Pure Error	*21.79*	*16*	*1.36*			
Cor Total	1095.10	31				

Fig B-7 Show the calculation results of the ANOVA

3.8 Design-Expert program calculated the factors that Prob> F less than 0.05 of the factors which indicate that factors are significantly affecting to percentage of naphtha.

3.9 The optimum condition calculated by pressing the “numerical” ---> and set the scope to the channel as shown in Fig B-8



Temp

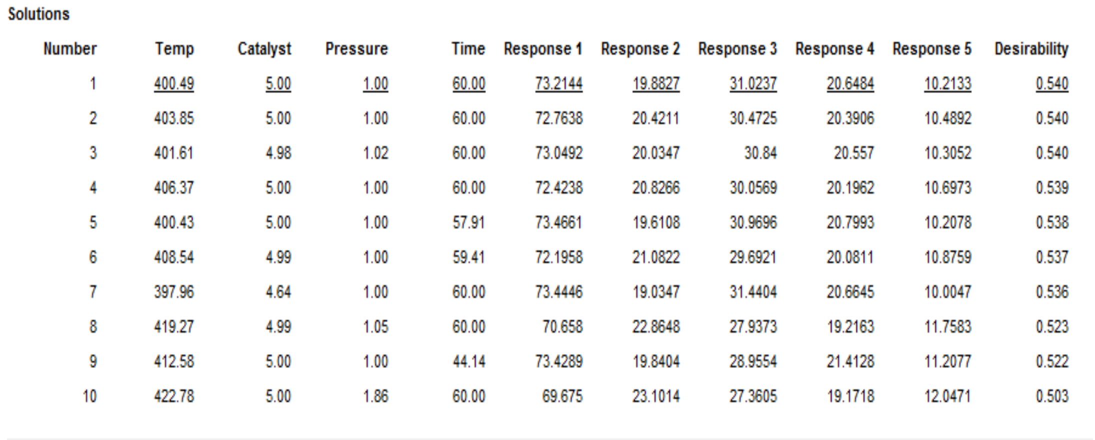
Goal: is in range

	Lower	Upper
Limits:	380	450
Weights:	1	1

Importance: +++

Fig B-8 Scope of the experiment.

3.10. The optimum conditions find by press the “Solution” as shown in Fig B-9.



Solutions

Number	Temp	Catalyst	Pressure	Time	Response 1	Response 2	Response 3	Response 4	Response 5	Desirability
1	400.49	5.00	1.00	60.00	73.2144	19.8827	31.0237	20.6484	10.2133	0.540
2	403.85	5.00	1.00	60.00	72.7638	20.4211	30.4725	20.3906	10.4892	0.540
3	401.61	4.98	1.02	60.00	73.0492	20.0347	30.84	20.557	10.3052	0.540
4	406.37	5.00	1.00	60.00	72.4238	20.8266	30.0569	20.1962	10.6973	0.539
5	400.43	5.00	1.00	57.91	73.4661	19.6108	30.9696	20.7993	10.2078	0.538
6	408.54	4.99	1.00	59.41	72.1958	21.0822	29.6921	20.0811	10.8759	0.537
7	397.96	4.64	1.00	60.00	73.4446	19.0347	31.4404	20.6645	10.0047	0.536
8	419.27	4.99	1.05	60.00	70.658	22.8648	27.9373	19.2163	11.7583	0.523
9	412.58	5.00	1.00	44.14	73.4289	19.8404	28.9554	21.4128	11.2077	0.522
10	422.78	5.00	1.86	60.00	69.675	23.1014	27.3605	19.1718	12.0471	0.503

Fig B-9 The optimum conditions and the scope of the experiment

APPENDIX C

Analysis the production distribution in the boiling range

The product distribution was determined by Simulated Distillation Gas Chromatography (DGC) followed by using ASTM D2887 standard method to classified the product distribution in petroleum boiling range are following:

IBP–200 ^{O}C = Naphtha

200 ^{O}C – 250 ^{O}C = Kerosene

250 ^{O}C – 350 ^{O}C = Light Gas Oil

350 ^{O}C – 370 ^{O}C = Gas Oil

370 ^{O}C – FBP = Long residue

The sample of liquid product was prepared by dissolved 1 µL of liquid product in Carbon disulfide CS_2 to the volume of 100 ml. In this research using Simulated Distillation Gas Chromatography (Agilent Technologies Model GC7890A) by the specification and condition to analyzed the liquid fuel products as shown in Table C-1.

Condition	Value
Open Tubular column capillary column (stationary phase)	CP-SIL 5CB
Internal diameter of capillary column	0.25 mm
Length of capillary column	15 m
Film thickness	0.25 micron
Injector Temperature	298°C
Column Temperature or Oven Temperature	40 - 350°C
Detector Temperature	375°C
Carrier gas	helium
Carrier gas flow rate	1.5µL/min
Temperature Program Rate	20°C/min
Final Temperature	320°C

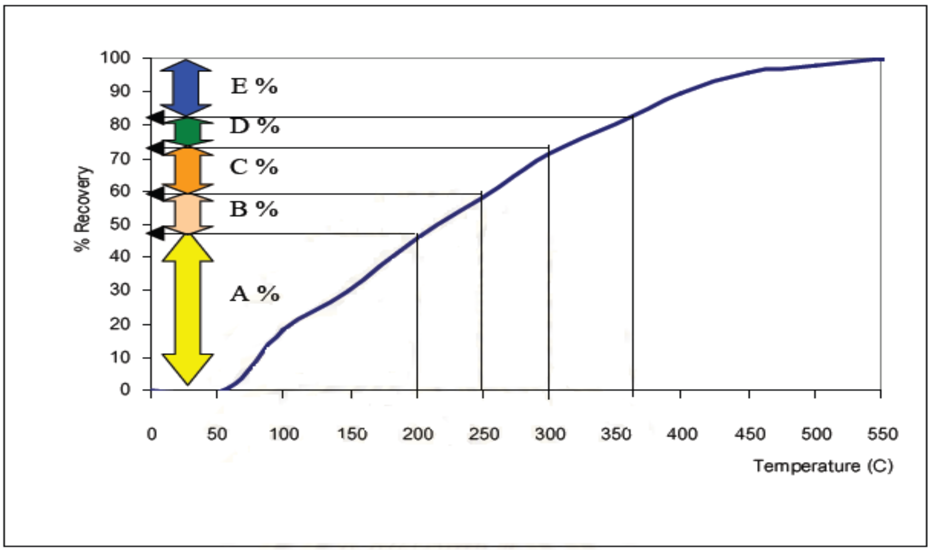


Fig C-1 Determine product boiling range from simulated distillation gas chromatograph

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

The % recovery of Naphtha in chromatograph A%.

So % Naphtha fraction in the liquid products W gram = (A × W) / 100.

The % recovery of Kerosene in chromatograph B%.

So % Kerosene fraction in the liquid products W gram = (B × W) / 100.

The % recovery of Light gas oil in chromatograph C%.

So % Light gas oil fraction in the liquid products W gram = (C × W) / 100.

The % recovery of Gas oil in chromatograph D%.

So % Gas oil fraction in the liquid products W gram = (D × W) / 100.

The % recovery of Long residue in chromatograph E%.

So % Long residue fraction in the liquid products W gram = (E × W) / 100.

APPENDIX D

Liquid product analysis by FT - IR

An important observation made by early researchers is that many functional groups absorb infrared radiation at about the same wavenumber, regardless of the structure of the rest of the molecule.

For example, C-H stretching vibrations usually appear between 3200 and 2800cm^{-1} and carbonyl(C=O) stretching vibrations usually appear between 1800 and 1600cm^{-1}. This makes these bands diagnostic markers for the presence of a functional group in a sample. These types of infrared bands are called group frequencies because they tell us about the presence or absence of specific functional groups in a sample.

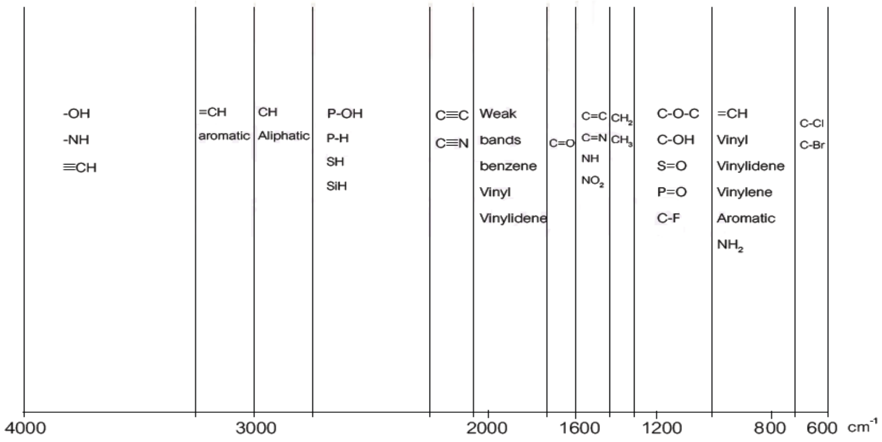


Figure D-1 Group frequency and fingerprint regions of the mid-infrared spectrum

The region of the infrared spectrum from 1200 to 700 cm^{-1} is called the fingerprint region. This region is notable for the large number of infrared bands that are found there. Many different vibrations, including C-O, C-C and C-N single bond stretches, C-H bending vibrations, and some bands due to benzene rings are found in this region. The fingerprint region is often the most complex and confusing region to interpret, and is usually the last section of a spectrum to be interpreted.

APPENDIX E

Liquid product analysis by GC-MS

The composition of liquid product compositions was determined by Gas Chromatography-Mass Spectrometry by comparing fingerprint of mass number (Mass number) of the element. The information contained in Library as shown in the Figure E-1 and Figure E-2.

In this research using Gas Chromatography-Mass Spectrometry (Agilent Technologies model GC7890A) by the specification and condition to analyzed the liquid fuel products as shown in Table E-1.

Table E-1 the specification and condition of GC-MS in this research

Condition	**Value**
Carrier gas (He) Flow rate	1.0 ml/min
Interface Temperature	230°C
Ion source Temperature	40°C
Split ratio	1:500
Molecular Weight Scan Range (m/z)	50-700
Solvent cut time	4 min
Injection Temperature	300°C
Inject volume	0.02µL
Column Initial Temperature	90°C
Temperature Program Rate	40°C/15min
Column Final Temperature	280°C

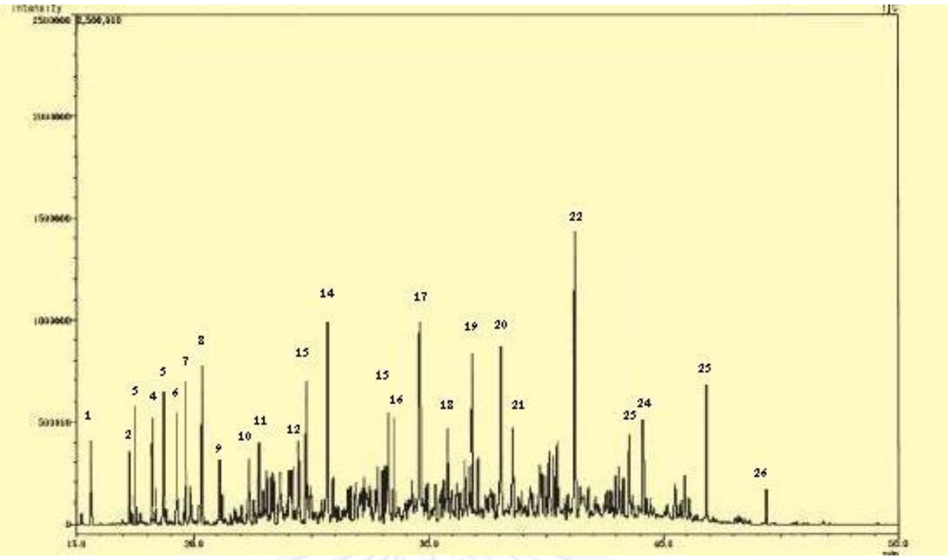


Figure E-1 Interpreting spectra from GC-MS

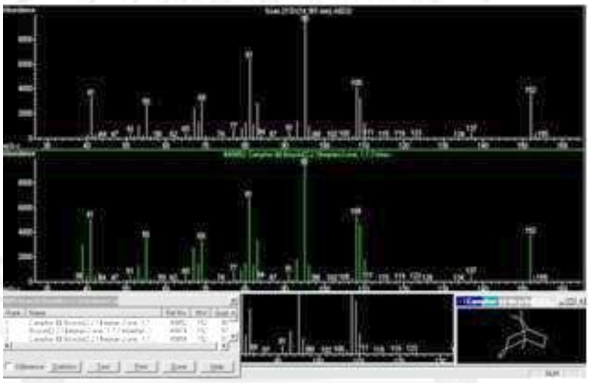


Figure E-2 Library search result

VITA

Ms.Ratiwan Padpibool was born on October 25, 1989 in Bangkok, Thailand. She graduated with a Bachelor's degree of Science, majoring in chemical engineering, Chulalongkorn University in 2011. She has continued her study in Master's degree, majoring in Petrochemical and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok since 2011 and finished her study in 2013.

Presentation experience, Poster presentation from International Graduate Research Conference 2013 (iGRC 2013) organized by Chiang Mai University in the topic of "CRACKING OF USED VEGETABLE OIL TO LIQUID FUEL USING OVER SPENT FCC CATALYST". A merit award for poster presentation: Science and technology.