CATALYTIC CONVERSION OF RBD PALM OIL TO FUEL : THE EFFECT OF SILICA-ALUMINA RATIO IN ZSM-5

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A report submitted in partial fulfillment of the
requirement for the award of degree the of
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Faculty of Chemical & Natural Resources Engineering
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Date : 20 APRIL 2008

Dedicated, in thankful appreciation for support,
encouragement and understanding to my beloved family,
friends and my supervisor

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ABSTRACT

The refined, bleached and deodorized (RBD) palm oil was converted to Organic Liquid Products (OLP) by passing it's the vapor through ZSM-5 catalyst. The constituents of OLP consist of gasoline, C12-C15, and other type of organic liquid. The equipment that was used to carry out the experiment was modified based on the suitability of the substance used. There are three types of ZSM-5 that were used to investigate the effect of ratio of silica oxide to the alumina oxide (23 SiO2/Al2O3). From recent research has showed that zeolite ZSM-5 with the ratio of 23 SiO2/Al2O3 will produce the highest OLP amount in which are about 96.9%. The alumina oxide in ZSM-5 is the one that influences the strength of the acid site zeolite. Therefore, the relationship between the two is inversely proportional, which when the ratio is lower, the higher the strength of the acid will be. The ratio of 23 SiO3/Al2O3 is the smallest ratio when compared to the other three catalysts than were used. The rate of conversion of palm oil to OLP is influenced by the concentration of acid site. All the OLP was analyzed with Fourier Transform Infrared (FTIR) in order to detect the functional group of alkanes, alkenes and aromatic. The products was analyzed and shown that the functional groups is presence, which showed that all the ratio that was used can convert palm oil to OLP.

ABSTRAK

Minyak kelapa sawit (RBD) ditukarkan kepada Cecair Organik (OLP) dengan melalukan wapnye melalui mangkin ZSM-5. Kandungan OLP adalah terdiri daripada gasoline, C_{12}-C_{15} dan lain-lain cecair organic. Radas yang digunakan telah diubahsuai mengikut kesesuaian bahan yang digunakan. Tiga jenis ZSM-5 digunakan untuk mengkaji pengaruh nisbah silika oksida terhadap alumina oksida (23 SiO_2/Al_2O_3) . Hasil daripada kajian menunjukkan bahawa zeolite ZSM-5 yang bernisbah 23 SiO_2/Al_2O_3 akan menghasilkan OLP yang paling banyak iaitu 96.9%. Kandungan alumina oksida dalam ZSM-5 akan mempengaruhi kekuatan acid site zeolite tersebut. Oleh sebab itu, semakin rendah nisbah SiO_2/Al_2O_3 maka semakin tinggi asid di dalam zeolite ZSM-5. Nisbah 23 SiO_2/Al_2O_3 adalah nisbah yang terkecil di antara ketiga-tiga jenis mangkin yang telah digunakan. Ini menunjukkan kadar penukaran minyak kelapa sawit kepada OLP dipengaruhi oleh asid secara langsung. Ketiga-tiga OLP yang diperolehi telah dianalisa dengan FTIR bagi mengesan kehadiran kumpulan berfungsi iaitu alkana, alkene dan aromatic. Ketiga-tiga hasil ujikaji yang dianalisa menunjukkan kehadiran kumpulan berfungsi tersebut, ini boleh disimpulkan zeolite yang digunakan mampu menghasilkan OLP daripada minyak kelapa sawit.

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LIST OF ABBREVIATIONS

LPG	-	Liquid Petroleum Gas
LNG	-	Liquid Natural Gas
CNG	-	Compressed Natural Gas
RBD	-	Refined, Bleached and Deodorized
SiO_2/Al_2O_3	-	Silica Alumina
CO_2	-	Carbon Dioxide
FTIR	-	Fourier transform Infra Red
WHSV	-	Weight Hour Space Velocity
OOP	-	Other Organic Products
OLP	-	Organic Liquid Products

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CHAPTER 1

INTRODUCTION

1.1 Introduction

In this new era, people around the world is chasing for development, luxury, own benefits and interest without thinking about others. Many hard situation faced by government around the world caused by global problems. As such problem is the increase of global fuel price, which causes for community to seek new methods that are low cost and high efficiency in producing fuel. The main reason for the push for new method of fuel production is due to the depleting petroleum or natural gas resources. The amount of petroleum reserves now is not enough to support today's demand and the future because of many challenges and obstacle faced by the producer countries. Many factor affect the production of petroleum around the world, as such factors are war, natural disaster, political and speculation factor. Hence, many discoveries are made in finding alternative to problems faced such as production of fuel from palm oil. The oil is extracted from the palm seed that can be converted to Organic Liquid products (OLP) by reaction with catalysts ZSM-5 under specific alumina-silica ratio. The components of OLP are gasoline, C_{12}-C_{15} and Other Organic Products (OOP).

The main advantages of using this alternative fuel are its renewability, better quality of exhaust gas emissions, its biodegradability and given that all organic carbon present is photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere and consequently to the greenhouse effect. One of the disadvantages of using this alternative is the higher cost of production result from the high price of raw material compare to fossil fuel.

The fast depletion of fossil fuels coupled with the increasing awareness of environmental issue, concern for increasing green house gas emissions and escalating petroleum price, have led Malaysia to concerted efforts in the search for renewable and environmentally friendly alternative energy source. The Malaysian government is refocusing the use of palm oil to cater to the huge demand from European countries, it has encouraged the building of biofuel plants. Palm oil is a form of edible vegetable oil obtained from the extraction of the palm fruit. Over the past two decades, Malaysia's total oil palm planted area increased from 640 000 hectares in 1975 to 4.17 million hectares in 2006. The total oil palm planted area driven mainly in Sabah and Sarawak with a combined of 4.5% versus Peninsular Malaysia's 1.6%.

1.2 Palm Oil

The Malaysian palm oil industry has grown rapidly over the years to become the world's largest producer and exporter of palm oil and it products. In 2003 more than 3.79 million hectares of land were under oil palm cultivation, occupying more than one-third of the total cultivated area in Malaysia and 11% of the total land area. In the same year production of palm oil in Malaysia had reached 13.35 million tonnes of crude palm oil and 1.64 million tonnes of crude palm kernel oil which was an increase of app. 12% over that of the previous year.

Malaysia's production of palm oil in 2003 contributed to about 49 percent of world palm oil output and 8.9% of world output of the 17 major oils and fats. The world demand for palm oil is expected to increase with respect to the competitive prices and energy efficient production of palm oil along with the growing markets globally especially in big country like China and India.

Being involved in three sectors, namely agriculture, transport and industry the production of palm oil faces a triple environmental challenge which must be monitored and dealt with. With a vast use of fertilizer in the plantations, poorly maintained transportation trucks exhausting black clouds as the go and emissions from the mill, the industry has both environmental responsibilities to live up to and money to save by making the right technological investments and incorporating environmental management.

During the last few years, environmental issues are increasingly becoming more important in Malaysia and the world over. The palm oil industry is aware of the environmental pollution and is striving towards quality and environmental conservation through 'sustainable development and cleaner technology approach. Thus, to remain competitive the oil palm industry must be prepared for new challenges ahead. Self regulated environmental management tools like the ISO 14000, EMAS and Life cycle assessment could be adopted by the palm oil industries to structure their environmental efforts to the benefits of themselves and the environment.

1.3 Gasoline

Gasoline was not being invented but it is a natural by-product of the petroleum industry and kerosene being the principal product. Gasoline is produced by distillation, the separating of the volatile, more valuable fractions of crude petroleum. However, what was invented were the numerous processes and agents needed to improve the quality of gasoline making it a better commodity.

Gasoline is one of the petroleum-based fuels that have an essential function in the industrial economy of a developing country and used for transport of industrial and agricultural goods and operation of gasoline tractor and pump sets in agricultural sector. The price of gasoline is soaring in these last years and it will be exhausted some day. A lot of efforts have been carried out to develop on alternative fuel for the current energy and transportation vehicle system such as methanol, ethanol, compressed natural gas (CNG), liquefied petroleum gas (LPG), liquefied natural gas (LNG), vegetable oils, reformulated diesel and reformulated gasoline fuel have all been considered as alternative fuels.

Gasoline is a mixture of fuel that has been produced from petroleum consisting mostly of aliphatic hydrocarbons, enhanced with iso-octane or the aromatic hydrocarbons toluene and benzene to increase its octane rating and is primarily used as fuel in internal combustion engines. The mixture of hydrocarbons, although some may contain significant quantities of ethanol and some may contain small quantities of additives such as methyl tert-butyl ether as anti-knock agents to increase the octane rating. The hydrocarbons consist of a mixture of n-paraffins, naphthenes, olefins and aromatics. Naphthenes, olefins and aromatics increase the octane rating of the gasoline whereas the n-paraffins have the opposite effect.

1.3.1 Cracking

There was a need for improvement in the refining process for fuels that would prevent engine knocking and increase engine efficiency. Especially for the new high compression automobile engines that were being designed. The processes that were invented to improve the yield of gasoline from crude oil were known as cracking. In petroleum refining, cracking is a process by which heavy hydrocarbon molecules are broken up into lighter molecules by means of heat, pressure, and sometimes catalysts.

1.3.2 Catalytic Cracking

Eventually, catalytic cracking replaced thermal cracking in gasoline production. Catalytic cracking is the application of catalysts that create chemical reactions, producing more gasoline. The catalytic cracking process was invented by Eugene Houdry in 1937.

1.3.3 Others Processes

Other methods used to improve the quality of gasoline and increase its supply including:

- Polymerization - converting gaseous olefins, such as propyl butylene, into larger molecules in the gasoline range.
- Alkylation - a process combining an olefin and a paraffin such as isobutene.
- Isomerization - the conversion of straight-chain hydrocarbons to branched-chain hydrocarbons.
- Reforming - using either heat or a catalyst to rearrange a molecular structure.

1.4 Crude Oil

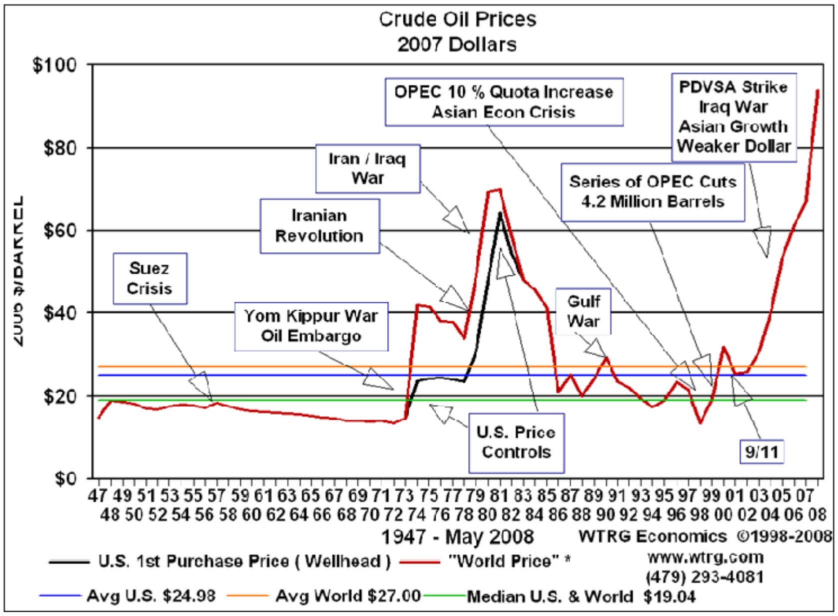


Figure 1.1: Crude Oil Prices 1947

Oil companies won't be building more refineries, because there won't be enough oil left to refine by the time new refineries could pay for themselves. There hasn't been a new refinery built in the US since 1976. In 1982, there were 301 operable refineries in the U.S and they produced about 17.9 million barrels of oil per day. Today there are only 149 refineries, and they're producing 17.4 million barrels. This increase in efficiency is impressive but not a miracle. As with everything these outputs are carefully calculated to optimize profitability.

The world at large consumes 30 billion barrels of oil per year, and the top oil consumers largely consist of developed nations. In fact, 24% of the oil consumed in 2004 went to the United States alone. The production, distribution, refining, and retailing of petroleum taken as a whole represent the single largest industry in terms of dollar value on earth.

1.5 Problem Statement

Nowadays, fuel is most valuable source in the world because this source are become decrease follow the year. It is because, fuel is a very important sources to generate the energy that widely used in commercial, industrial and transportation. Natural gas one of the alternative to produce gasoline, but the problem of transportation and safe handling of the gas makes it difficult to distribute the gas to rural areas. Coal investment in liquid fuel production had almost ceased after exploration of the petroleum around a half-century ago.

Bio-fuel appears as a promising alternative for petroleum. The reasons of using bio-fuel because it comes from renewable sources, is environmental friendly due to low sulfur and nitrogen content, do not contain any toxin or poison, full of energy, easy on handling and transportation, as it appears in liquid form and can be operate at winter time that has a temperature of -20°C and above.

As viscosity of palm oil is very high, a suitable method to crack the triglycerides is essential. Low in selectivity of organic liquid products is the main problem in this research and it seems that it is not commercially viable. The research palm oil catalytic cracking has a bright prospect in the future. More studied have to be done to make sure this process is economically viable. The ultimate challenge still lies in catalyst development. A stable, shape selective and high acidic catalyst is needed in order to achieve high conversion and selectivity in this process.

The researchers in this field also agree that the process of converting palm oil to OLP depend on the acidity of the catalysts, especially Bronsted acid. Therefore, this research will try to find the suitable for the catalytic cracking of palm oil to organic liquid products (OLP). ZSM-5 catalyst follow specific silica-alumina ratio in order to achieve higher percentage of organic liquid production. ZSM-5 is chosen as catalyst in this process because it has better characteristic and properties than other type of catalyst.

1.6 Objective

The objective of this study is to determine the catalytic conversion of refined, bleached and deodorized (RBD) palm oil to organic liquid products (OLP) by using silica-alumina ratio in ZSM-5 as catalyst with help of fixed-batch reactor.

1.7 Scope of Research Works

i) To study the effect of ratio silica-alumina in catalyst HZSM-5 in producing organic liquid products (OLP) from palm oil.
ii) To study the selectivity OLP that produced by catalytic conversion of palm oil.

1.8 Rational Significant

Nowadays the price fuel is rapidly increased due to limited source because this fossil fuel is non-renewable energy. Therefore, strong needs to find the alternative fuel source of petroleum. This research is about to find the alternative fuel to replace fossil fuel as primary source of energy. The palm oil had been study the potential to produce alternative fuel because the raw material is abundant. Besides that, this fuel has many advantages such as environmental friendly due to low sulfur and nitrogen content and easy on handling and transportation, as it appears in liquid form.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The majority of the world’s energy is supplied by petroleum derived fuels and petroleum based distillates are used in a wide range of industrial applications. Petrochemicals serve as raw materials for the chemical industry in the production of solvents, lubricants, paints, and lacquers. The spectacular growth in consumption of crude petroleum during the middle and late twentieth century can be attributed to the ease with which petroleum can be discovered, produced, transported, processed, and utilized. The oil crisis in the 1970s, depleting reserves, national scarcity issues, price uncertainty, and growing environmental concern over the combustion of fossil fuels highlight major issues associated with the extensive use of petroleum in our society.

Since the rise of gasoline in the world market, a lot of efforts have been carried out to develop an alternative fuel for the current energy and transportation vehicle system, i.e.: fuel cell, electric power, hydrogen, biodiesel , bioalcohol, vegetable oil, natural gas for internal combustion engines and other biomass source.

The alternative gasoline fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. There are some advantages that justify biofuel development. It not only provides a market for excess production of vegetable oils but also can decreases although will not eliminate, the country's dependence on imported petroleum. Biofuel is renewable and does not contribute to global warning due to its closed carbon cycle. A life cycle analysis of biofuel showed that overall carbon oxide emissions were reduced by 78% compared with petroleum-based gasoline fuel. This fuel is biodegradable and non-toxic. This alternative also given that all organic carbon present in photosynthetic in origin. So, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere if all of the energy input for the biofuel production are non-fossil based and consequently to the green house effect.

Vegetable oils are attracting increased interest in this respect. Many researchers improved the production of hydrocarbons and chemicals from plant oils using catalytic cracking processes. The vegetable oils that have been investigated as alternative fuels are canola oil, tall oil, and jajoba oil. These plant oils were converted to hydrocarbon over many types of catalysts such as ZSM-5, hydrogen-zeolite Y, silica-alumina, H-mordenite, and silica-alumina pillared clay at a temperature range of 300 – 500 °C. Over 95 wt% of the plant oils were converted to liquid hydrocarbons in the gasoline boiling range, light gases, and water.

Palm oil has been converted into a more compatible form of methyl ester known as biodiesel, by the Palm Oil Research Institute Malaysia (PORIM). The biodiesel was developed to substitute the diesel for engines. Rapeseed, sunflower, and soybean oils are examples of oils used in methyl ester production. There is a need for a direct conversion process for converting palm oil to clean premium transportation fuels and chemicals.

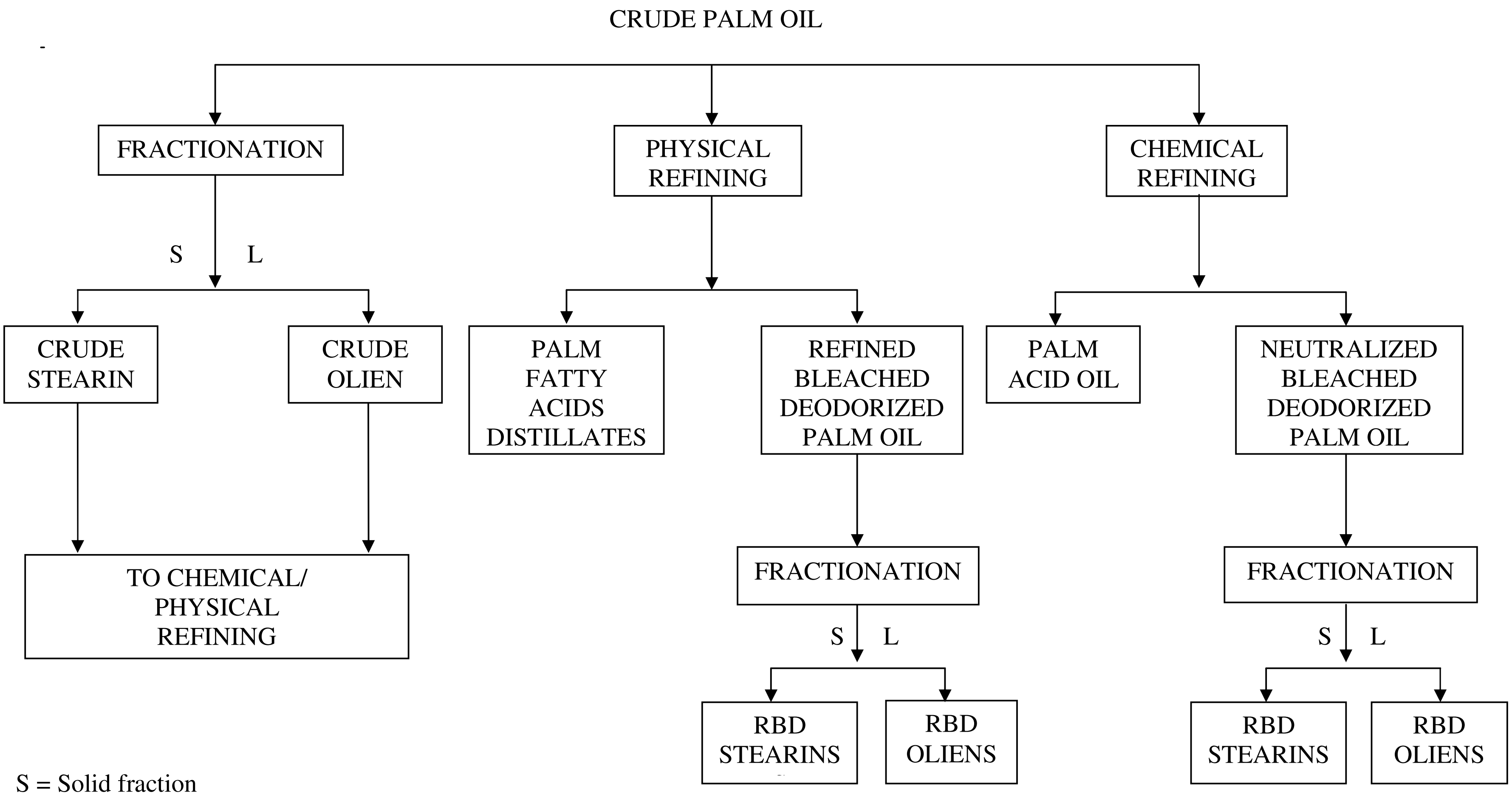
The shape selective zeolite catalysts have been used for catalytic cracking and the medium pore size catalyst such as ZSM-5 was found to be more efficient in the cracking process and in the organic liquid production. Prasad and co-workers reported that ZSM-5catalyst gave mainly aromatic hydrocarbons. The properties of shape selective catalysts control the product distribution in the process, and therefore, the choice of the shape selective zeolite catalyst is an important factor. Activity and selectivity of these catalysts are governed by several factors, such as acidity, pore size and its distribution, and also the shape of the pores.

Hybrid catalysts were used to improve the shape selectivity of the catalyst. Co-worker reported cracking of canola oil over hybrid catalysts using the mixture of ZSM-5 with silica-alumina and H-Y with silica-alumina. The addition of zeolite catalysts to silica-alumina increased the cracking of canola oil and aromatic hydrocarbon contents. Acidity of a catalyst was determined to be one of the important factors in the cracking process. The conversion was found to decrease with a decrease in catalyst acidity. The acidity of the catalyst influences selectivity of the catalyst. Co-workers reported that potassium impregnation of ZSM-5 catalysts affects the aromatization and oligomerization reactions.

2.2 Palm Oil

Palm oil is a form of edible vegetable oil obtained from the fruit of the oil palm tree. It is an important component of washing powders and personal care products. It is also used to treat wounds and has been controversially discovered as a feedstock for biofuel. The other usages of palm oil include cooking oil, margarine and a component of many processed foods. The palm oil source is the palm oil extracted from palm fruit and the fruit seeds. Palm oil is one of the few vegetable oils relatively high in and thus semi-solid at room temperature and can be fractionated into solid and liquid fractions. The solid product is known as stearins while the liquid products are known as oleins. The crude palm oil is can also be processed to yield RBD (refined, bleached, and deodorized) and NBD (neutral, bleached, and deodorized) palm oil, which are used in daily activities. The process can be done through physical or chemical refining treatment respectively. Figure 2.1 shows the three processes that can be done with crude palm oil. Fractionation process is employed to crude palm oil to produce crude stearin in solid form and crude olien in liquid form. The crude olein and stearin then will undergo either physical or chemical refining process to produce refined, bleached, and deodorized (RBD) stearin and olien.

Crude palm oil is also can be directly processed via physical refining. In this type of refining, crude palm oil is separates to palm fatty acids distillates and RBD palm oil. In chemical refining process, crude palm oil is separated to palm acid oil and neutral, bleached, and deodorized (NBD) palm oil. Fractionation process is employed to both RBD palm oil from physical refining and NBD palm oil from chemical refining to obtain RBD stearin and olien.



S = Solid fraction
L = Liquid fraction

Figure 2.1: Three Process Route Available to Process Palm Oil

The differences between physical refining and chemical refining are shown in Figure 2.2. The physical refining of palm oil has two main steps, 1) degumming, and 2) distillation and deodorization with high temperature and high vacuum process. Degumming process includes gum conditioning, bleaching and filtration. The objective of these steps are to reduce the phosphorus level, to reduce trace iron and contents and also to reduce the content of pigment decomposition products which are not heat decomposable and steam volatile (Young, 1981). Ortho-phosphoric acid, activated bleaching earth and calcium carbonate were used in the processes.

The ortho-phosphoric acid decomposes the calcium and magnesium compounds. The iron and copper complexes are attacked in the same reaction and are removed together with phosphatides, pigments and a part of oxidation products through adsorption process on the activated bleaching earth. The calcium carbonate acts as neutralizer to neutralize residual phosphoric acid (Young, 1981).

The second step is the deodorization process. This process involves steam distillation under vacuum condition. The purpose of this process is to remove residual free fatty acids, aldehydes and ketones that are responsible for unacceptable oil odors and flavors. This process is also responsible to decolorize the oil by heat decomposition of the pigments (Young, 1981).

In chemical refining, chemical, usually caustic soda (NaOH) is added to neutralize the fatty acid in the oil. Caustic soda reacts with fatty acids to produce soap, which is soluble in water. Using the difference in specific gravity, the waste phase containing the soap is separated from the oil.

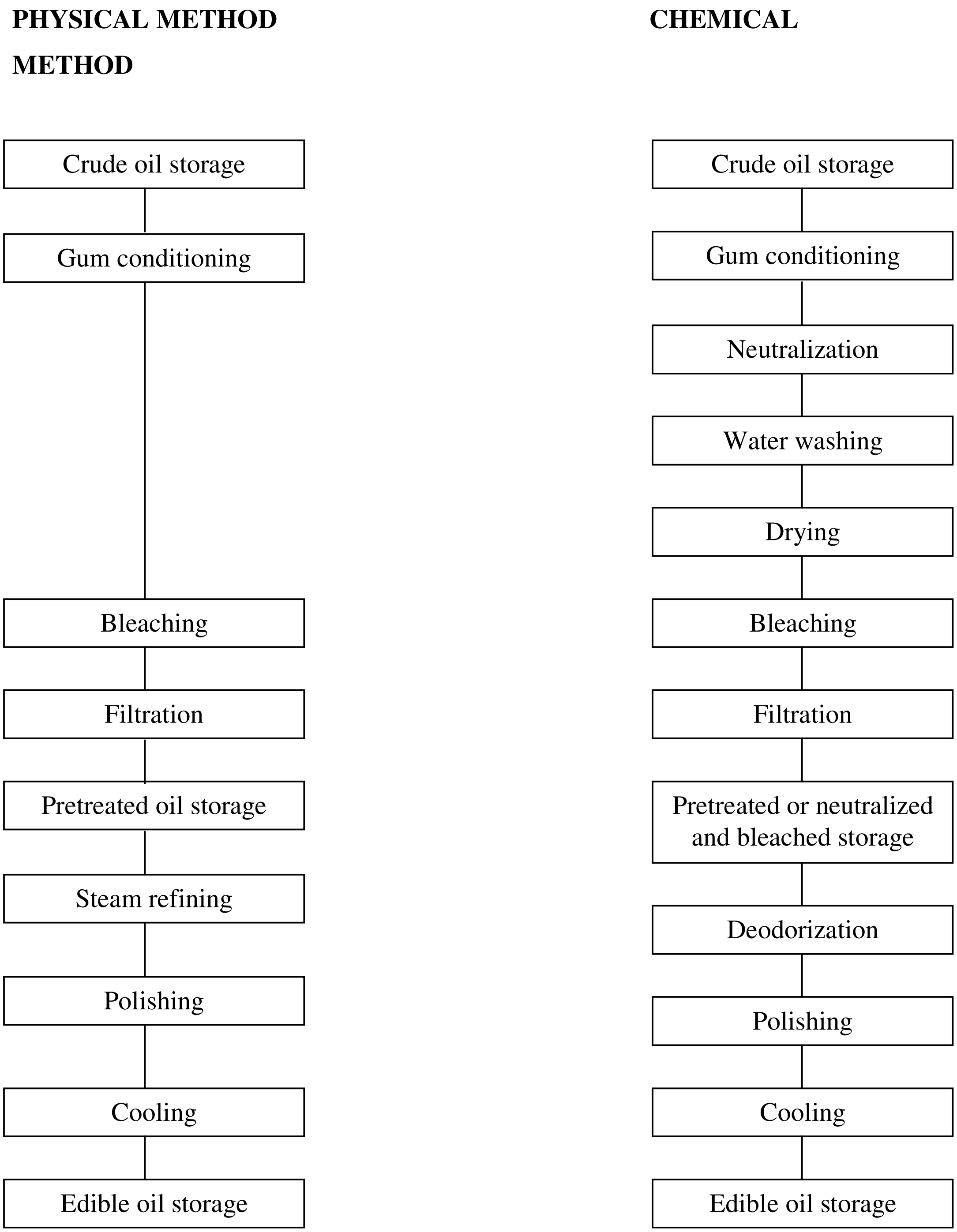
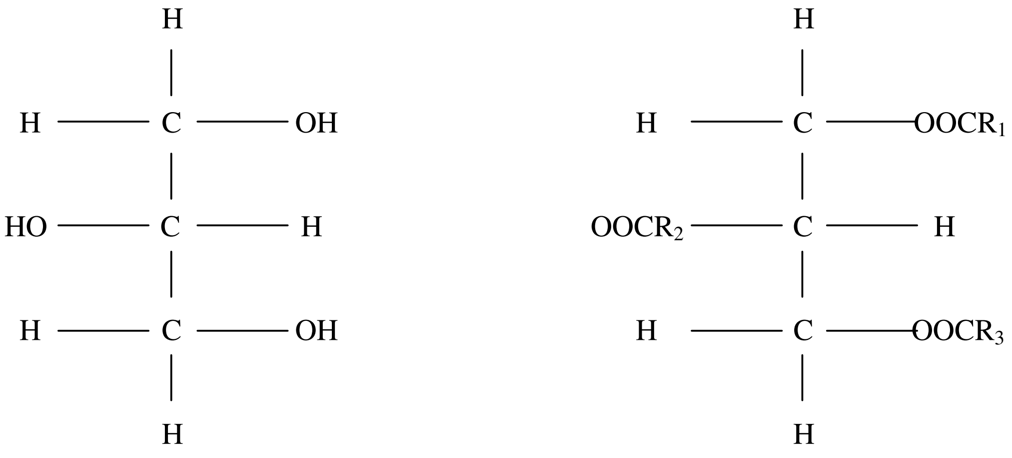


Figure 2.2: Physical and Chemical Palm Oil Refining Stages (Young, 1981)

2.2.1 Chemical Properties of Palm Oil

Triglycerides form the major component in palm oil. Triglycerides are esters formed from glycerol and fatty acids with the hydrogen in all the hydroxyl groups in the glycerol molecules replaced by fatty acid chain via the acid carboxylic ends as shown in Figure 2.3. Figure 2.3(a) shows a single glycerol molecule while Figure 2.3(b) shows the molecule after hydroxyl groups are replaced with fatty acids groups.

R_1, R_2 and R_3 in Figure 2.3 are hydrocarbon chains. These could vary in the number of carbons present in the chain (chain length) and in structure (presence of double bond). It is the variations in R_1, R_2 and R_3 that largely define the chemical and physical properties of oils and fats (Chong, 1993).



(a) Glycerol molecule

(b) Triglyceride molecule

Figure 2.3: (a) Glycerol molecule and (b) Triglyceride molecule, the –OH- in the glycerol chain was replaced with –OOCR- to form triglyceride.

Palm oil obtained from Malaysia Tenera usually has the chain lengths of the fatty acids within a narrow range from twelve carbons to twenty. Fatty acids are composed of a carboxyl group and hydrocarbon chains. Individual fatty acids are distinguished from one another by the nature of hydrocarbon chain. Table 2.1 tabulates fatty acids composition of Malaysian palm oil. The table shows that palmitic acid (16:0) and oleic acid (18:1) are the major components in Malaysia Tenera oil, with 44.02% and 39.15% respectively. Table 2.2 and 2.3 meanwhile show some of the chemical and physical properties of Malaysia Tenera palm oil. The 16:0 and 18:1 indicate that palmitic acid has sixteen carbon chains with no double bond and oleic acid has 18 carbon chains with one double bond.

Table 2.1: Fatty Acid Composition of Malaysian Palm Oil

Fatty Acid Chain C Lengths	% of Total	
	Mean	Range Observed
12:0	0.23	0.1 – 1.0
14:0	1.09	0.9 – 1.5
16:0	44.02	41.8 – 46.8
16:1	0.12	0.1 – 0.3
18:0	4.54	4.2 – 5.1
18:1	39.15	37.3 – 40.8
18:2	10.12	9.1 – 11.0
18:3	0.37	<0.05 – 0.6
20:0	0.38	0.2 – 0.7

Source: 1993

Table 2.2: Chemical Properties of Malaysia Tenera Palm Oil

Chemical Characteristic	Mean	Range
Saponification value (mg KOH/g oil)	195.7	190.1 – 201.7
Unsaponifiable matter (5%)	0.51	0.15 – 0.99
Iodine value (Wijs)	52.9	50.6 – 55.1
Slip melting point (°C)	34.2	30.8 – 37.6

Source: Chong, 1993

The saponification value is a number of milligrams of potassium hydroxide require to saponify completely one gram of the oil. It is a measure of the free and combined fatty acids in the oil.

The unsaponifiable matter refers to material present in palm oil. This material is extractable by solvent and remains nonvolatile on drying. Usually, unsaponifiable matter consists of hydrocarbon, alcohols, sterols, and tocopherols.

Iodine value is measure of the total number of unsaturated double bonds present in oil. The determination of iodine value involves the addition of halogen in the presence of potassium iodide and titration with standard sodium thiosulphate using starch solution as the indicator. Of the various procedures available, the most widely used is the Wjis method.

The slip melting point of a fat is defined as the temperature at which a column of fat in an open capillary tube moves up the tube when it is subjected to controlled heating in a waterbath. Because of their polymorphic behavior, the slip point of some fats is dependent on the previous treatment of the sample.

2.2.2 Physical Properties of Palm Oil

Table 2.3 shows some of the physical properties of Malaysian Tenera palm oil. Apparent density also indicates the purity of the palm oil. The solid fat content indicates the amount of solid fat present in the oil at the temperature stated. Under controlled thermal condition, palm oil can be separated into two components, solid (stearin) and liquid (olein) fractions.

Table 2.3 Major Physical Properties of Malaysian Palm Oil

Property	Mean (of 215 samples)	Range
Apparent Density @ 50°C	0.889	0.888 – 0.889
Refractive index @ 50°C	1.455	1.455 – 1.456
5°C	60.5	50.7 – 68.0
10°C	49.6	40.0 – 55.2
15°C	34.7	27.2 – 39.7
20°C	22.5	14.7 – 27.9
25°C	13.5	6.5 – 18.5
30°C	9.2	4.5 – 14.1
35°C	6.6	1.8 – 11.7
40°C	4.0	0.0 – 7.5
45°C	0.7	0.0 – 4.5
Slip Melting Point °C	34.2	31.1 –

2.2.3 Environmental Issue

In 2005 the Malaysian Palm Oil Association, responsible for about half of the world's crop, estimated that they manage about half a billion perennial carbon-sequestering palm trees. Demand for palm oil has been rising and is expected to climb further. This rising demand is resulting in tropical forest being cleared to establish new palm plantations. According to UNEP at the current rate of intrusion into Indonesian national parks, it is likely that many protected rain forests will be severely degraded by 2012 through illegal hunting and trade, logging, and forest fires, including those associated with the rapid spread of palm oil plantations.

There is growing concern that this will be harmful to the environment in several ways:

- Significant greenhouse gas emissions. Deforestation, mainly in tropical areas, account for up to one-third of total anthropogenic CO_2 emissions.
- Habitat destruction of certain endangered species (e.g. the orangutans in Borneo, the Sumatran tiger, and Asian rhinoceros.)
- Potential extinction of some such species.

2.2.4 Healthier Compound in Red Palm Oil

Palm oil is a very common cooking ingredient in the regions where it is produced. Its heavy use in the commercial food industry elsewhere can be explained by its comparatively low price, being one of the cheaper vegetable or cooking oils on the market, and by new markets in the USA, stimulated by a search for alternatives to trans fats after the Food and Drug Administration required food labels to list the amount of trans fat per serving.

Red palm oil is known to be healthier than refined palm oil. This is a result of several mitigating substances found in the red palm oil. These compounds are:

- Betacarotenes
- Co-enzyme Q10
- Squalene
- Vitamin A
- Vitamin E

2.3 Gasoline

Gasoline is produced in oil refineries. Material that is separated from crude oil via distillation, called virgin or straight-run gasoline, does not meet the required specifications for modern engines but will form part of the blend. The bulk of a typical gasoline consists of hydrocarbons with between 5 and 11 carbon atoms per molecule. Gasoline actually contains up to 500 hydrocarbons. The way hydrogen and carbons bond determines the family of the hydrocarbons. Single bond hydrocarbons are called saturated hydrocarbons because they cannot absorb additional hydrogen. Double bond hydrocarbons are called unsaturated hydrocarbons because they can change to reform saturated hydrocarbons by the addition of hydrogen to the double bond.

2.3.1 Saturated Hydrocarbons

Also known as paraffin and alkanes, saturated hydrocarbons are very stable, and form the major component of leaded gasoline. It tends to burn in air with a clean flame and the octane ratings depend on branching and number of carbon atoms. There are three different alkanes, which are normal, iso and cyclic. All the three alkanes have different octane ratings. Normal alkanes are continuous chain of carbon (C_nH_{2n+2}). Normal alkanes have low octane numbers, which decrease with the decrease of the carbon chain length.

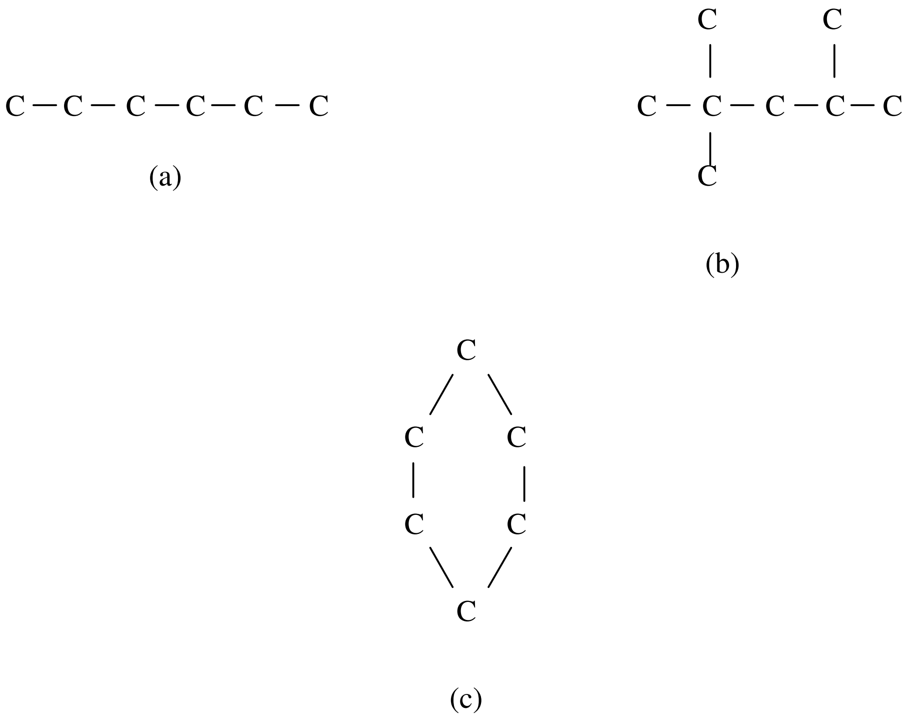
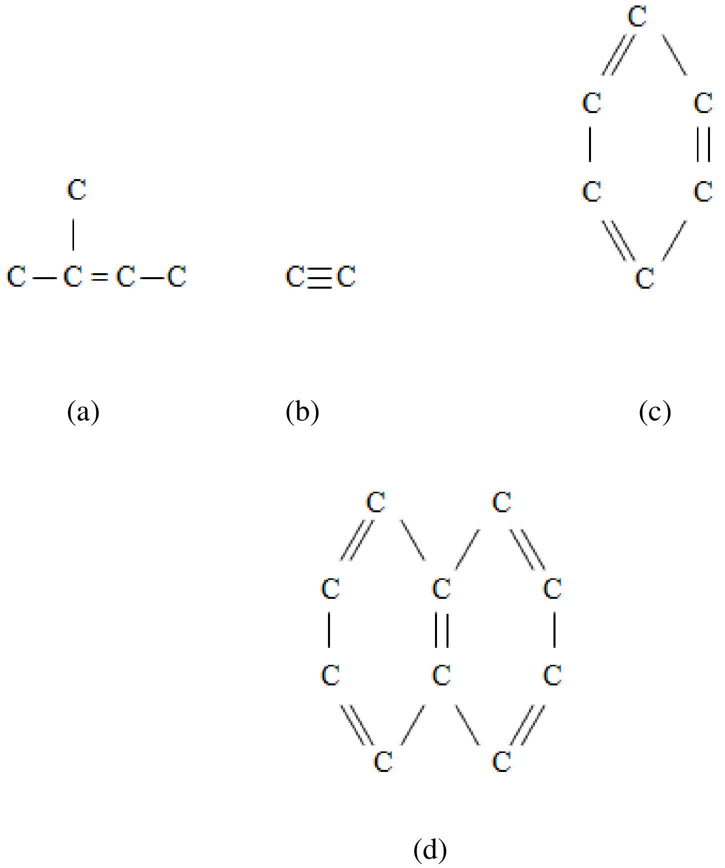


Figure 2.4: Saturated hydrocarbons; (a) heptanes; (b) iso-octane; (c) cyclohexane

Figure 2.4 (a) shows a normal heptanes, normal alkanes with $C_{17}H_{16}$ chemical formula. Iso-alkanes are branched chain of carbons, with the same formula, C_nH_{2n+2}. These chains have higher octing ratings, and it is increasing with carbon chain branching. Figure 2.4 (b) shows the structure of iso-octane, C_8H_{18}. Cyclic hydrocarbons are actually circle of carbons with the chemical formula C_nH_{2n}. Figure 2.4 (c) shows a structure of cyclohexane (C_6H_{12}). The cyclic hydrocarbons have high octane ratings.

2.3.2 Unsaturated Hydrocarbons

Unsaturated hydrocarbons are unstable and tend to burn in air with smoky flame. There are several kinds of unsaturated hydrocarbons, like alkenes, alkynes, arenes and polynuclear aromatics. Also known as olefins, alkenes have carbon-carbon double bond. Alkenes are unstable, tend to be reactive and toxic, but have desirable octane ratings. Figure 2.5 (a) shows 2-methyl-2-butene, one example of alkenes.alkynes, also known as acetylenes, Figure 2.5 (b), have a carbon-carbon triple bond. These are also unstable and only present in some poor-refined gasoline. Arenes or aromatics tend to be more toxic, but have desirable octane ratings. Figure 2.5 (c) indicates two examples of aromatics, which is benzene. The last one is polynuclear aromatics. These are high boiling substance, and are only present in small amounts in gasoline. It contains benzene rings that join together. The simplest is naphthalene, $C_{10}H_8$ as shows Figure 2.5 (d).



(a) (b) (c)

(d)

Figure 2.5: Unsaturated hydrocarbons; (a) 2-methyl-2-butene (b) acetylene (c) Benzene and (d) Naphthalene

2.3.3 Properties of Gasoline

Gasoline has its own fuel properties. These properties can be obtained from several tests in the special laboratory. Table 2.4 shows the fuel properties of commercial gasoline.

Table 2.4: Fuel Properties of Gasoline

Property	Gasoline
Chemical Formula	C_5-C_{11}
Molecular Weight	100 – 105
Specific Gravity, 15 °C/°C	0.72 – 0.78
Density, g/ml	0.730 – 0.805
Boiling Temperature, °C	27 – 225
Research Octane Number	90 – 100
Cetane Number	5 – 20
Freezing Point, °C	-40
Autoignition Temperature, °C	257

Data from Masjuki et al (1993)

2.3.4 Volatility of Gasoline

Gasoline is more volatile than diesel oil, kerosene not only because of the base constituents but because of the additives that are put into it. The final control of volatility is often achieved by blending with butane. The Reid Vapor Pressure test is used to measure the volatility of gasoline. The desired volatility depends on the ambient temperature such as in hotter climates, gasoline components of higher molecular weight and thus lower volatility are used. In cold climates, too little volatility results in cars failing to start. In hot climates, excessive volatility results in what is known as "vapour lock" where combustion fails to occur because the liquid fuel has changed to a gaseous fuel in the fuel lines, rendering the fuel pump ineffective.

2.3.5 Octane Rating

An important characteristic of gasoline is its octane rating, which is a measure of how resistant gasoline is to the abnormal combustion phenomenon known as detonation also known as knocking, pinging and spark knock. Octane rating is measured relative to a mixture of 2, 2, 4-trimethylpentane and n-heptane. There are a number of different conventions for expressing the octane rating. Therefore, the same fuel may be labeled with a different number, depending upon the system used. The octane rating became important in the search for higher output powers from aero engines in the late 1930's and the 1940's as it allowed higher compression ratios to be used.

2.3.6 Energy Content

Gasoline contains about 34.8 MJ/l or 132 MJ/US gallon. actual energy content varies from season to season and from batch to batch, by up to 4% more or less than the average, according to the US EPA. On average, about 19.5 gallons of gasoline are available from a 42 gallon barrel of crude oil (about 46% by volume), varying due to quality of crude and grade of gasoline.

Table 2.5: Volumetric Energy Density of Some Fuels Compared with Gasoline.

Fuel type	MJ/litre	MJ/kg	BTU/Imp gal	BTU/US gal	Research Octane Number
Regular Gasoline	34.8	44.4	150,100	125,000	Min 91
Premium Gasoline	39.5				Min 95
Auto gas (LPG) (60% Propane + 40% Butane)	26.8	46			108
Ethanol	23.5	31.1	101,600	84,600	129
Methanol	17.9	19.9	77,600	64,600	123
Butanol	29.2				91-99
Gasohol (10% ethanol + 90% gasoline)	33.7		145,200	120,900	93/94
Diesel	38.6	45.4	166,600	138,700	25
Aviation gasoline (high octane gasoline, not jet fuel)	33.5	46.8	144,400	120,200	
Jet fuel (kerosene based)	35.1	43.8	151,242	125,935	
Liquefied natural gas	25.3	~55	109,000	90,800	
Hydrogen		121			130

2.4 Vegetable Oil Cracking

Vegetable oils such as palm oil (Masjuki et al, Aziz, 1992, Basiron and Hitam, 1992, Ooi et al, 1986), soybean oil (Schwab et al, 1988, Anjos et al, 1983), canola oil (Craig and Coxworth, 1987, Strayer et al, 1984.) cottonseed oil (Zaher and Taman, 1993), Turkish raisin seed oil (Aksoy et al, 1990) and coconut oil (Arida et al, 1986, Yutiamco et al, 1986, Banzon, 1980) can be used as fuel substitutes in diesel engines. This technology, known as biodiesel technology, has attracted many researchers to carry out numerous experiments, especially in Europe. Manufacture in France and elsewhere in Europe have given their own name to the same substance: diester (France), dieselbi (Italy and France), bio-gazole (France), biodiesel (UK) and oko-diesel (Germany) (Staat and Vallet, 1994).

However, bio-diesel cannot work in gasoline engines. This is due to its relatively higher molecular weight compared to gasoline. Thus, in order to find an alternative for gasoline, the vegetable oils must cracked until they form gasoline range hydrocarbons.

The cracking of vegetable oils is not a new research. In fact, back in the 1920s, there were several attempts to crack the long chain of hydrocarbons. Three methods to crack the vegetable oil chains to smaller chains have been discovered.

The first process is known as hydrocracking, by which hydrogen at suitable temperature and pressure in the presence of catalyst is employed. The second process is known as thermal cracking and the cracking occurs with the aid of heat in the absence of air and catalyst. The third process is conducted in the presence of catalyst only, without the use of hydrogen and is known as catalytic cracking.

2.4.1 Hydrocracking

Hydrocracking is a combination of catalytic cracking and hydrogenation. The process is carried out under substantial pressure (Satterfield, 1991). Hydrocracking development started back at 1930 in Germany and England. Hydrocracking is extensively applied in petroleum refining to produce high quality gasoline, jet fuel, low pour point diesel fuel, high quality lubricants and LPG (Choudhary and Saraf, 1975).

Modern hydrocracking processes were developed then and consequently, the reaction temperature was lower than catalytic cracking, in the range of 200ºC to 400ºC. The hydrogen pressure meanwhile might vary from 1Mpa to 10Mpa, depending on the feedstock and type of reaction (Satterfield, 1991).

Several researches in vegetable oils to gasoline via hydrocraking have been conducted. Anjos et al (1983), report that soybean and babassu oil were completely converted into n-alkanes using presulfided Ni Mo/γ Al_2O_3 catalyst at 360ºC and 20Mpa of total pressure. There was also a study in upgrading canola oil through hydrocracking process. Craig and Coxworth (1987), find that canola oil could be converted in high yields of liquid fuels in the diesel boiling range. Da Rocha Filho et al (1993), test hydrocracking process on unsaturated vegetable oils and the result showed that for unsaturated vegetable oils, hydrocarbon fuels and chemicals are obtained when sulfided Ni Mo/γ Al_2O_3 is used as catalyst.

The hydrocracking catalyst is a dual-functional catalyst. The two functional that it serves; first, cracking of high molecular weight hydrocarbon and second, hydrogenation of the unsaturated formed during the cracking step (Choudhary and Saraf, 1975).

2.4.2 Thermal Cracking

In thermal cracking, the heating of triglyceride, without the use of catalyst, changes the molecular structure. The products obtained from this process however do not have good fuel properties.

In this process, the bonds of long chain triglycerides molecules are cleaved randomly into smaller chain hydrocarbons by free radical mechanism. The bond cleavage cannot be controlled and thus the cleavage approaches near the end of the chain producing appreciable quantities of products that have less carbon atoms. Hence, large quantities of gaseous products are formed.

Many researchers already have investigated the potential of thermal cracking in vegetable to gasoline process. Alencar et al, (1983) for example discovered mostly straight-chain alkenes and 1-alkanes products for the pyrolisis of babassu oil, piqui oil and palm oil.

2.4.3 Catalytic Cracking

When the cracking process involves a catalyst, the process is then called catalytic cracking. The major advantages of catalytic cracking are the process needs less thermal energy requirement and better quality of products obtained.

Different types of vegetable oils are cracked in order to obtained liquid fuels. Canola oil for example has been used extensively as raw material in Canada (Prasad and Bakhshi, 1986a, 1986b, 1986c, Adjaye and Bakhshi, 1995a, and 1995b, Idem et al, 1996). In philippines, Arida et al, (1986) used coconut oil as raw material. Haag et al, (1980) in their work try to crack several kinds of plant material like corn oil, castor oil, jojoba oil, natural rubber latex and copaiba oil. They found out that all these materials produced hydrocarbon products when they used ZSM-5 catalyst in the processed. In Malaysia, researchers tend to use palm oil as raw material since palm oil is found abundantly (Songip ang Mahmud, 1996 Salam 1996, Mahmud 1998, Bhatia et al, 1998, Leng et al 1999, Twaiq et al 1999).

Researchers have used various kinds of catalysts in order to find out the best catalyst for the process. Inorganic catalysts such as NaOH (Arida et al, 1986, Salam 1996), MgO and CaO (Idem et al, 1997) have been used in catalytic cracking process. Idem and co-worker (1997) reported the used of silicate, silica, silica-alumina, and γ-alumina catalyst in their work. Mahmud (1998), used various Y types zeolite such as ultra stable Y (USY), Rare-earth Y (REY) and Na-Y in this study on catalytic cracking of palm oil to liquid fuels.

After ZSM-5 has been invented, the molecular shape selective catalyst is mostly applied to enhance the process. For the past 30 years, medium pore size zeolite ZSM-5 has become the most commonly used catalyst in catalytic cracking of vegetable oils to fuel (Prasad and Bakhshi, 1985, Prasad and Bakhshi, 1986a, 1986b, and 1986c, Adjaye and Bakhshi, 1995a and 1995b, Idem et al, 1996, Bhatia et al, 1998, Leng et al, 1999, Twaiq et al, 1999).

The uniqueness of zeolite, in its uniform size pores and the molecular sieving property makes it popular in the research. The molecular sieving property can discriminate molecules on the size basis. Molecules the smaller than aperture size are admitted to the crystal interior while those larger sizes are not. The high selectivity for C7-C9 aromatics hydrocarbons is due to the shape selective property of zeolite catalysts (Chen et al, 1989).

Bhatia and co-workers (1998, 1999) have consistently reported their works on catalytic conversion of palm oil to gasoline over numerous types of catalysts. They found out that the use of USY in the study obtained highest conversion organic liquid products (OLP). Twaiq et al (1999) also did a study on the effect to reaction condition, acidity and zeolite pore sizes. The reaction temperature and weight hourly space velocity (WHSV) was varied at 350ºC to 450 ºC and 1 to 4 h^{-1} respectively to study the effect of reaction condition.

2. 4. 3.1 Mechanism of Catalytic Cracking

There are two types of catalytic cracking, namely homogeneous catalytic cracking happens when the catalyst and the reactants are both in the same phase, either gas or liquid (Satterfield, 1991). Not much work has been done on homogeneous catalytic cracking.

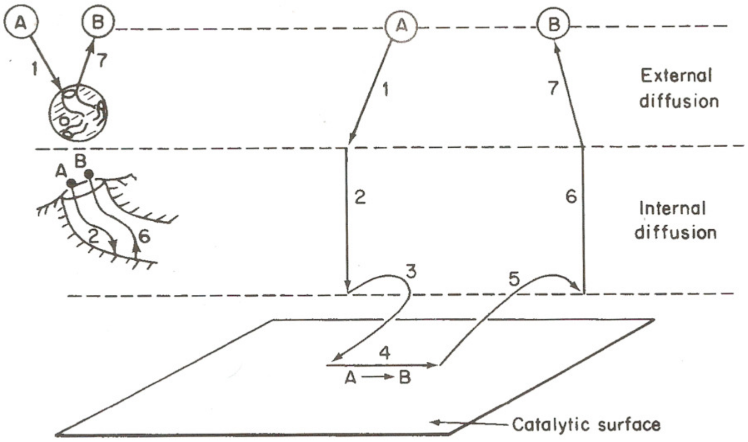


Figure 2.6 : The Reaction Occur in Heterogeneous Catalyst (Fogler, 1999)

Heterogeneous catalytic cracking occurs when the reactants and the catalyst are in different phases. Theoretically, a heterogeneous catalytic reaction consists of five successive steps:

i. Transport of reactants from homogeneous (gas or liquid) phase to the surface of the catalyst.
ii. Balanced sorption of the reactants on specific sites of this surface, to create the intermediate chemisorbed species.
iii. Chemical reactions in the sorbed phase between these intermediate species.
iv. Desorption of the reaction products.
v. Removal of the reactions products into the homogeneous phase.

Almost all the reactions involving heterogeneous catalytic reaction occur at the interface between the solid catalyst and the fluid or gas phase. The reactions are catalyzed in seven stages, as illustrated in Figure 2.6 (Fogler,1999).

i. Diffusion of the reactants to the external surface of the catalyst.
ii. Diffusion of the reactants from the pore mouth through the catalyst pores to the immediate vicinity of internal catalytic surface.
iii. Adsorption of the reactants on the catalyst surface.
iv. Reaction of the adsorbed reactants species in which it is converted to a product molecule.
v. Desorption of the products from the catalyst surface.
vi. Diffusion of the products from the interior of the catalyst to the pore mouth at the external surface.
vii. Mass transfer of the products from the external surface into the bulk of the process stream.

2.5 Zeolites

Swedish mineralogist, Cronstedt, found zeolite back in 1756. He difined zeolites as new materials consisting of hydrated aluminosilicates of alkali and alkaline earths. The word '*zeolite'* was derived when he heated the minerals in blowpipe flames. The crytal exhibited intumescence and therefore it was called zeolite, which is form two Greek words, 'zeo' and 'lithos' meaning 'to boil' and 'stone'.

Zeolites can be obtained either in natural from (natural zeolites) or synthetic zeolites. Natural zeolites are usually located in sediment on volcanic area. There are many types of natural zeolites and some of them are already commercialized like chabazite, erionite and mordenite. Synthetic zeolites were discovered in late 1940's by Barrer (Flanigen, 1991). However, the discovery of zeolites A, X and Y by Milton and Breck between 1949 and 1954 had attracted other researchers to synthesis other zeolites. In 1969, Grace corporation produced the first modified zeolite, known as ultrastable Y. in 1967-1969, Mobil Oil reported the synthesis of the high silica zeolite beta and ZSM-5. After that there were numerous zeolite inventions such as ZSM-11 (Mobil), AIPO, SAPO, MeAPO (Union Carbide) and ECR-1 (Exxon) (Flanigen, 1991).

Zeolites are organic porous materials with a highly regular structure of pores and chambers that allow some molecules to pass through, and cause others to be excluded or broken down. Zeolites are crystalline aluminosilicates with fully cross-linked open framework structures made up of corner sharing SiO_4 and AIO_4 tetrahedra. A representative empirical formula of a zeolite is:

$M_2/nO.AI_2O_3.xSiO_2yH_2O$

where M represents the exchangeable cation. M is generally a Group AI or IIA ion, such as sodium, potassium, magnesium, and calcium. However, other metals, non-metals and organics cations may also balance the negative charge created by the presence of AI in the structure. x is 2 to 10, n is cation valence and y represents the water contained in the voids of zeolite.

There are many types of zeolites. The pores size of these zeolites vary form 0.3 to 0.8 nm (Flanigen, 1991). Chen et al (1989), divided zeolites into three major groups according to their pore system. The first group is 8-membered oxygen ring system zeolites. The members include the earliest shape selective small pore zeolites such as Linde A and others like ZK-5 and ZSM-34. The pore system in these zeolites also contains interconnecting supercages. The supercages are the cause of catalyst deactivation or coking of the acidic catalyst.

The second group is known as 10-membered oxygen ring system. Known as medium pore zeolites, this group consists of varieties of unique crystal structure types like ZSM-5 and ZSM-11. The shape and size of its members vary from on estructural types to another. The other properties of the zeolites in this group, especially ZSM-5 will be discussed hereinafter.

TYPICAL ZEOLITE PORE SIZES

Oxygen Packing

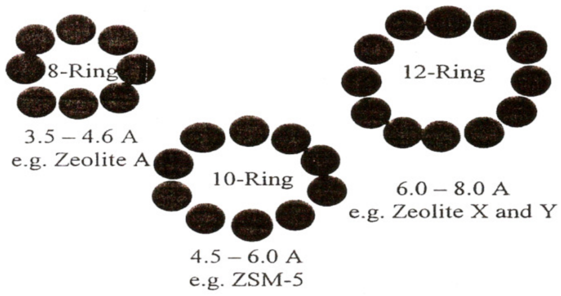


Figure 2.7: Various Sizes of Zeolites; Small Pore Zeolite e.g. Zeolite A, Medium Pore Zeolites e.g. ZSM-5, Large Pore Zeolites e.g. Zeolites X and Y. (Flanigen, 1991)

The last group has dual pore systems. Zeolites in the group have interconnecting channels of either 12- and 8-membered oxygen ring opening or 10- and 8-membered oxygen ring opening. Zeolites in this group are acidic catalysts, and they also coke and deactivate rapidly. The examples of zeolites in this category are mordernite and stilbite. Figure 2.7 illustrates the sizes of 8-ring, 10-ring and 12-ring member zeolites in oxygen packing.

Zeolites have microporous character with uniform pore dimension. This allows them to let certain hydrocarbons molecules to enter their framework while rejecting the others based on molecular size. Figure 2.8 (a) shows how zeolites rejecting branched molecule of iso-octane while Figure 2.8 (b) shows how straight chain molecule of normal octane passes through 8-ring 5A zeolite. The rejection occurs because the branched molecule iso-octane is too large for the 5A zeolite's pores.

Zeolites have been used various kinds of applications. Natural zeolites like mordernite are used in adsorbent applications including air separation and in drying and purification (Rege et al, 2001, Rege et al, 2000, White and Bussey, 1997). They are also used as fillers in paper (Mumpton, 1999), in fertilizer (Park and Komarneni,

1997) and soil conditioner as well as dietary supplements in animal husbandry industries (Mumpton, 1999)

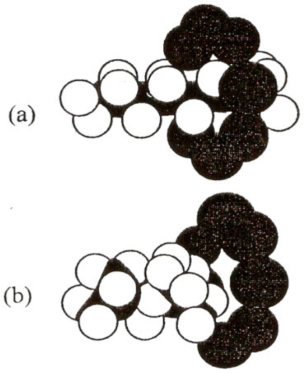


Figure 2.8: Illustration of Molecular Sieve Effect; (a) Reactant Passes through Zeolite, (b) Reactant cannot Passes through Zeolite (Flanigen, 1991).

Synthesis zeolite's earliest applications were the drying of refrigerant gas and natural gas. Zeolites are used in some of the separation processes like separation of n-paraffin from branched paraffin (Oonkhanond and Mullins, 2001, Shendye and Rajadhyaksha, 1992). Some synthesis zeolite are widely used as detergents for the replacement of phosphates (Basaldella and Tara, 1996).

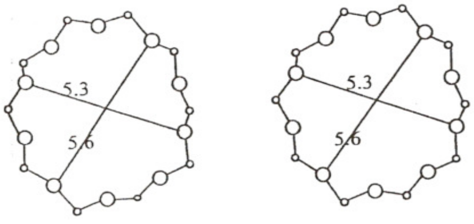
However, zeolites are mainly used as catalyst in catalytic processes. Petroleum refining for example, uses zeolite Y in catalytic cracking of hydrocarbons (Eberly and Winter, 1995, Venuto, 1971). ZSM-5 in the mean time is widely used in fluid catalytic cracking process as octane enhancement additive in order to get high-octane gasoline(Shih, 1996, Adewuyi et al, 1995). ZSM-5 has also attracted several researchers in the development of alternate resources to motor fuels. The Synfuel production (methanol to gasoline) also favors ZSM-5 as catalysts (Lee, 1995, Sardesai, 1995). Zeolites are also reported being used in nuclear waste cleanup (Prikry et al, 2001, Marinin and Brown, 2000).

2.5.1 ZSM-5 Zeolite

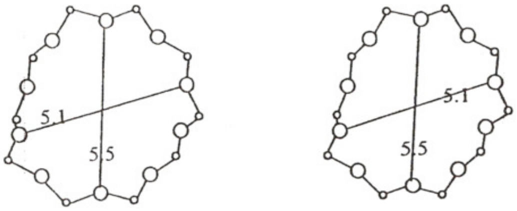
ZSM-5 stands for zeolite Socony Mobil-5, discovered in the early sixties. Also know as MFI, ZSM-5 has been used for commercial applications such as Mobil xylene isomerization, ethylbenze synthesis, Mobil toluene disproportionation, Mobil distillate dewaxing and methanol to gasoline process. ZSM-5's most famous application is as additive in fluid catalytic cracking for propylene production and gasoline octane improvement (Degnan et al, 2000).

In 1965 Landolt and Arguer (Landolt and Arguer, 1972) synthesized the first ZSM-5 in Mobil's laboratory. Since then, ZSM-5 remained a laboratory curiosity until 1967 when it was first evaluated for processing waxy gas oil. The continuous works then found out that ZSM-5 to be a very shape selective material that cracks only normal or slightly branched paraffin (Degnan et al, 2000). After that, the development of ZSM-5 was overshadowed by the successes made by zeolite Y-based as cracking catalyst. However, the elimination of lead from gasoline in the early 1980s, which prompted a search for a means to increase octane from non-traditional sources re-boosted the attraction towards ZSM-5. The need for cleaner gasoline depleted in sulfur, olefins, and aromatics as well as robust market for propylene also helps ZSM-5 making a comeback in catalysts industries (Degnan et al, 2000).

ZSM-5 was first used in cracking processes in the early 1970s. By then, several studies with small quantities of ZSM-5 showed that ZSM-5 did improve gasoline octane. After several year of studies under lab and pilot plant scale, first full-scale commercial trial was conducted in the TCC unit of the Neste Oy refinery in Naantali, Finland (Degnan et al, 2000). As expected the gasoline octane number for the product obtained showed steady increases that paralleled the ZSM-5 addition rate.



10 – ring viewed (circular opening)



10 – ring viewed (elliptical opening)

Figure 2.9 Stereographic View and Channel-cross Section of Zeolite MFI (van Hoffs and Roelofsen, 1990).

ZSM-5 is high silica zeolites. ZSM-5 is built on ten-member ring building unit (Figure 2.7). These building units link together with each other to form a chain. The interconnection of these chains then forms a channel system of the ZSM-5. The ZSM-5framework contains two types of intersecting channels. One type is straight, has near circular (0.53-0.56 nm) openings and runs parallel to the b-axis of the orthorhombic unit cell; the other has elliptical (0.51-0.55 nm) openings, is sinusoidal (zig-zag) and runs parallel to the a-axis of the unit cell (Figure 2.9).

ZSM-5 has been used for numerous applications. Some of the most famous applications are listed below (Flanigen, 1980).

i. The isomerization of C_8 aromatics to produce isomerically pure xylenes for polyester manufacture.
ii. Ethylenebenzene synthesis for styrene production.
iii. Catalytic dewaxing.
iv. A catalyst for new route from coal or synthetic or natural gas to motor fuel.
v. Conversion of oxygenated hydrocarbons compounds in biomass to gasoline.

2.5.1.1 Structure and Properties of ZSM-5

Zeolites, in general are unique because they can discriminate between reactant molecules. This shape selective property is a consequence of the well-defined geometry of zeolite pores, channels and cages. ZSM-5 has a unique shape-selective property, which has important role in enhancing gasoline product in gas oil cracking. Shape selectivity property makes ZSM-5 capable to control the size and shape of molecules diffusing through its pores network.

Figure 2.10 shows a schematic view of channel system in ZSM-5. These two intersecting channels, both formed by 10-membered oxygen rings, are slightly different in their pore sizes. As described before in section 2.5.1, one sinusoidal channel has an elliptical opening (5.1 x 5.5 Å). This channel run parallel to the a-axis of the unit cell. The other channel has a nearly circular opening (5.3 x 5.6 Å) and run the parallel to the b-axis (Figure 2.7). These two types of channels intersect to form a 3-dimensional network of pores.

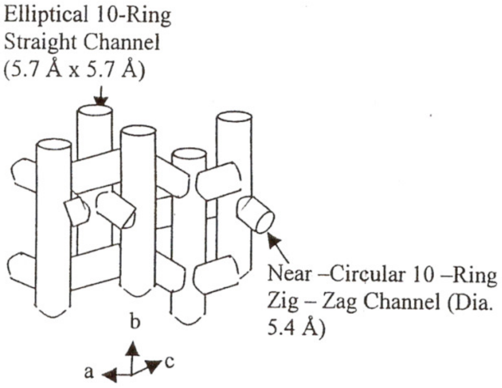


Figure 2.10 Schematic View of the Channel System in ZSM-5 (Scherzer, 1990)

CHAPTER 3

METHODOLOGY

3.1 Introduction

In order produce organic liquid products (OLP), there are five major steps taken place which are the catalysts selection, equipment selection, raw material preparation, experimental procedure and analytical method. In experiment procedure, the catalyst was placed in a stainless-steel tube reactor and supported with glass wool. The experiment was carried out at atmospheric pressure and the operating temperature at 450º C. To analyze OLP products, using Fourier Transform Infrared (FTIR) characterization in order identify the present OLP such as alkanes, alkenes, aromatics and other functional group as OLP.

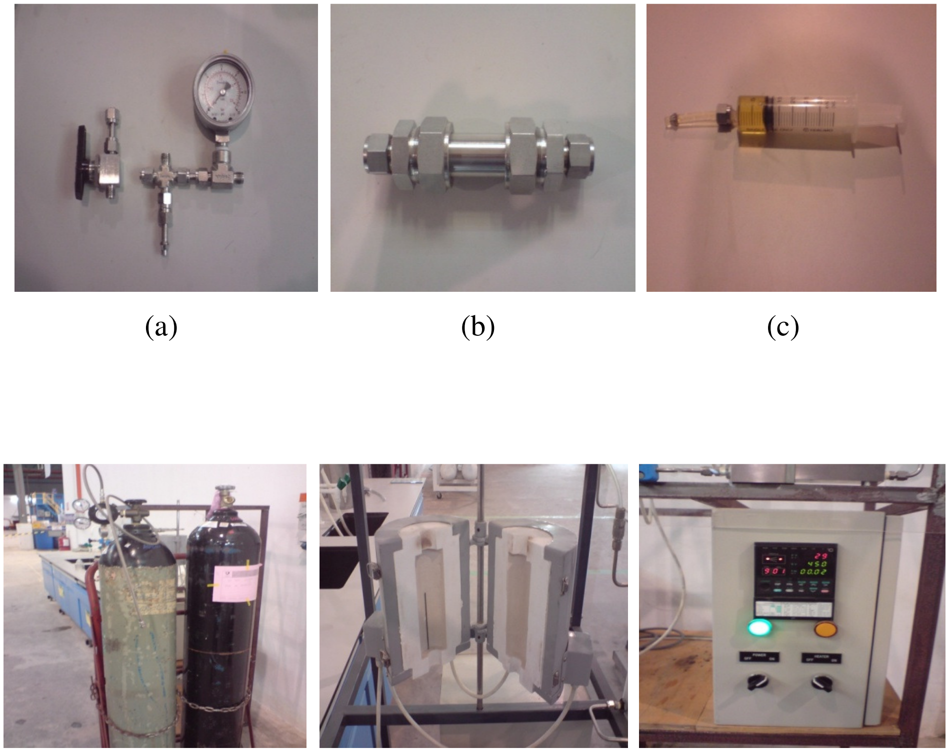
3.2 Catalysts Selection

After get the topic for my research, the catalyst selection is the first step in order to produce OLP. The zeolite ZSM-5 is the best catalyst for the catalytic conversion of palm oil compare others zeolite such as zeolite ZSM-15,zeolite ZSH-5, zeolite A, zeolite 13, zeolite 14, zeolite, zeolite Beta and etc. The selection of zeolite based on three difference ratio of SiO_2/Al_2O_3 in ZSM-5 such as 23 SiO_2/Al_2O_3, 50 SiO_2/Al_2O_3 and 80 SiO_2/Al_2O_3. The ratio of zeolite can be identified by the code as shown at container label. The codes of catalysts are 23 SiO_2/Al_2O_3(CBV 2314), 50 SiO_2/Al_2O_3(CBV 8014) and 80 SiO_2/Al_2O_3(CBV 5524G) the Figure 3.1 below showed the zeolite that have been used in this research.

Figure 3.1: Types of Zeolite that have been Use for the Experiment

3.3 Equipment Selection

The equipment selection needs to be considered before the reaction occurs. It will depend on equipment availability on the UMP (University Malaysia Pahang) lab and their effectiveness of the equipment to the task. The type of equipment that have been selected are valve, pressure gauge, syringe pump, reactor stainless steel, nitrogen tank, tubular furnace and monitor for tubular furnace**.** The Figure 3.1 showed the selected equipments.



(a) (b) (c)

(d) (e) (f)

Figure 3.2: The Equipment Selection; (a) Valve and Pressure Gauge (b) Reactor Stainless Steel (c) Syringe Pump (d) Nitrogen Tank (e) Tubular Furnace and (f) Monitor for Tubular Furnace

3.4 Raw Material Preparation

Refine, bleached and deodorized (RBD) palm oil of the brand 'Vesawit' was purchase from Razak Food Industries Sdn. Bhd. (Pahang, Malaysia). The feedstock was preheated by using hot plate to remove water contents, the temperature used will be around 100 ° C to 110 ° C. Some of the properties of Vesawit were listed in Table 3.1.

Table 3.1: Some of the Properties of Vesawit Brand Palm Oil.

Characteristic	**Descriptions**
Fatty acid contents	Less than 0.1% (as palmatic acid)
Saponification value	194-202 mg KOH
Iodine value	Not less than 56
Melting point	Not more than 24 ° C
Density	0.907 g/cm^3

3.5 Catalytic Activity Testing

The catalyst was carried out in a fixed-bed reactor as shown schematically in figure 3.3. The catalyst was placed in a stainless-steel tube reactor and supported with glass wool. The experiment was carried out at atmospheric pressure with the operating temperature at 450° C.

The reactor was loaded with 1g of the catalyst and heated to the operating temperature in a stream of nitrogen (1L/h). After 2 hours preheating, the N_2 flow was shut off and syringe pump injected palm oil continuously in order to supply the palm oil into the system. The palm oil vapor than went through the axial stainless-steel reactor, which was heated by a programmable furnace.

There were two phases of products obtained which is liquid and gas. The liquid product is Organic Liquid Product (OLP), was collected in a glass trap cooled with ice. The gas however was released to the atmosphere because the gas Fourier Transform Infrared (FTIR) was unable to do the analysis for gas.

The run period was about 4 hours. After the pump was shut off, the reactor was flushed with N_2 at low flow rate for an hour. Because the OLP still contained impurities, which prevented us to analyze the products by the chromatography, the OLP then was distilled at 100 ° C. The distilled products then were injected into the Fourier Transform Infrared (FTIR) to identify the components of the products.

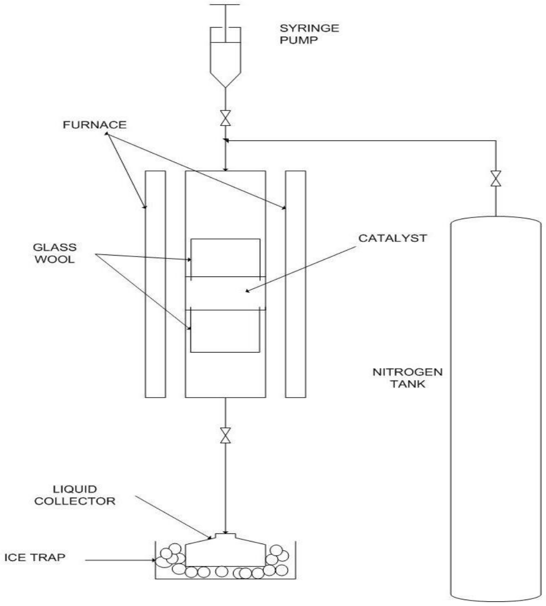


Figure 3.3: Rig Use in Catalytic Conversion of Palm Oil

The conversion was defined based on work by Twaiq et al (1999).

$$To\ convert\ to\ wt(\%) = \frac{\text{residue (g)}}{Palm\ oil\ injected\ (g)}\ \text{x}\ 100\%$$

$$Conversion\ (wt\%) \quad = \frac{\text{P} - \text{R}}{P}\ \text{x}\ 100\%$$

Where P = weight of palm oil injected
R = residue oil

3.6 Analysis of Products

Organic liquid products will be analyzed using Fourier Transform Infrared (FTIR). FTIR result shows that catalytic conversion of palm oil over each ratio SiO_2/Al_2O_3 in this study produce OLP which contain fuel such as gasoline that has functional group like alkanes, alkenes and aromatics. The main absorption will be the C-H stretch at 3000-2800 cm^{-1} for alkanes, there will be a CH stretch band at 3100-3000 cm^{-1} for alkenes and look for the benzene, double bonds which appear as medium to strong absorptions in the region at 1650-1450 cm^{-1} all existed in the samples confirming the presence of gasoline in OLP.

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CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Calculation for Percentage of Conversion

Table 4.1 shows the result for percentage of conversion 23 SiO_2/Al_2O_3 in ZSM-5, table 4.2 for 50 SiO_2/Al_2O_3 in ZSM-5 and table 4.3 for 80 SiO_2/Al_2O_3 in ZSM-5.

Table 4.1 Result of Experiment for 23 SiO_2/Al_2O_3 in ZSM-5

	Weight (g)	(Wt %)
Palm oil injected, A	10.00	-
Catalyst + Glass wool (before exp.), B	2.04	-
Catalyst + Glass wool (after exp.), C	2.35	-
Residue, D (C-B)	0.31	3.1
OLP,E	6.67	66.7
Gas, (A-D-E)	3.02	30.2

Calculation of percentage of Residue in sample 23 SiO_2/Al_2O_3

$$To\ convert\ to\ wt(\%) = \frac{\text{residue (g)}}{Palm\ oil\ injected\ (g)}\ \text{x } 100\%$$

$$= \frac{0.31}{10}\ \text{x } 100\%$$

$$= 3.1\%$$

Calculation of Total Conversion Percentage in sample 23 SiO_2/Al_2O_3

$$Conversion\ (wt\%) \quad = \frac{\mathrm{P - R}}{P}\ \text{x } 100\%$$

$$Where\ P = weight\ of\ palm\ oil\ injected$$

$R\ = residue\ oil$

$$= \frac{10 - 0.31}{10}\ \text{x } 100\%$$

$= 96.9\%$

Table 4.2 Result of Experiment for 50 SiO_2/Al_2O_3 in ZSM-5

	Weight (g)	(Wt %)
Palm oil injected, A	10.00	-
Catalyst + Glass wool (before exp.), B	2.12	-
Catalyst + Glass wool (after exp.), C	2.57	-
Residue, D (C-B)	0.45	4.5
OLP,E	6.00	60.0
Gas, (A-D-E)	3.55	35.5

Table 4.3 Calculation of Experiment for 80 SiO_2/Al_2O_3 in ZSM-5

	Weight (g)	(Wt %)
Palm oil injected, A	10.00	-
Catalyst + Glass wool (before exp.), B	2.07	-
Catalyst + Glass wool (after exp.), C	2.70	-
Residue, D (C-B)	0.63	6.3
OLP,E	5.00	50.0
Gas, (A-D-E)	4.37	43.7

4.2 Influence of Different Ratio of ZSM-5 in Formation of OLP

In Table 4.4 show the first sample 23 SiO_2/Al_2O_3 in commercial ZSM-5 produce highest conversion about 96.9 % and followed by ratio 50 SiO_2/Al_2O_3 and 80 SiO_2/Al_2O_3 are 95.5 % and 93.7 %, respectively. In the metal-free ZSM-5, the decrease in the concentration of Bronsted and Lewis acid sites is proportional to the increase in SiO_2/Al_2O_3 (Ivanov et al, 1999). This phenomenon surely will affect the cracking process because acidity plays such an important role in the process (Groenenboom et al, 1989).

Table 4.4: Percentage of Conversion and OLP

	23 SiO_2/Al_2O_3		50 SiO_2/Al_2O_3		80 SiO_2/Al_2O_3	
Conversion (%)	96.9		95.5		93.7	
OLP	6.67(g)	68.8 (%)	6.00(g)	62.8(%)	5.00(g)	53.36(%)

The increasing of alumina oxide ($Al_2O_{3)}$ in catalyst ZSM-5 is proportional to decreasing of organic liquid products. It is because acid site bronsted and lewis will affect the rate of formation of OLP. Meanwhile the decreasing of acid site will effect the increasing of gas production selectivity. Normally the gas produce contain light hydrocarbon and other gas.The decrease in acid sites is proportional to the increase of SiO_2/Al_2O_3 ratio (Costa et al, 1999). Mean that, Al_2O_3 plays the main role of strange of acid site in zeolite ZSM-5. In the metal-free ZSM-5, the decrease in the concentration of Bonsted and Lewis asid sites is proportional to the increase in SiO_2/Al_2O_3 (Ivanov et al, 1999). This phenomenon surely will affect the cracking process, because acidity plays such an important role in the process (Gronenboom, 1989).

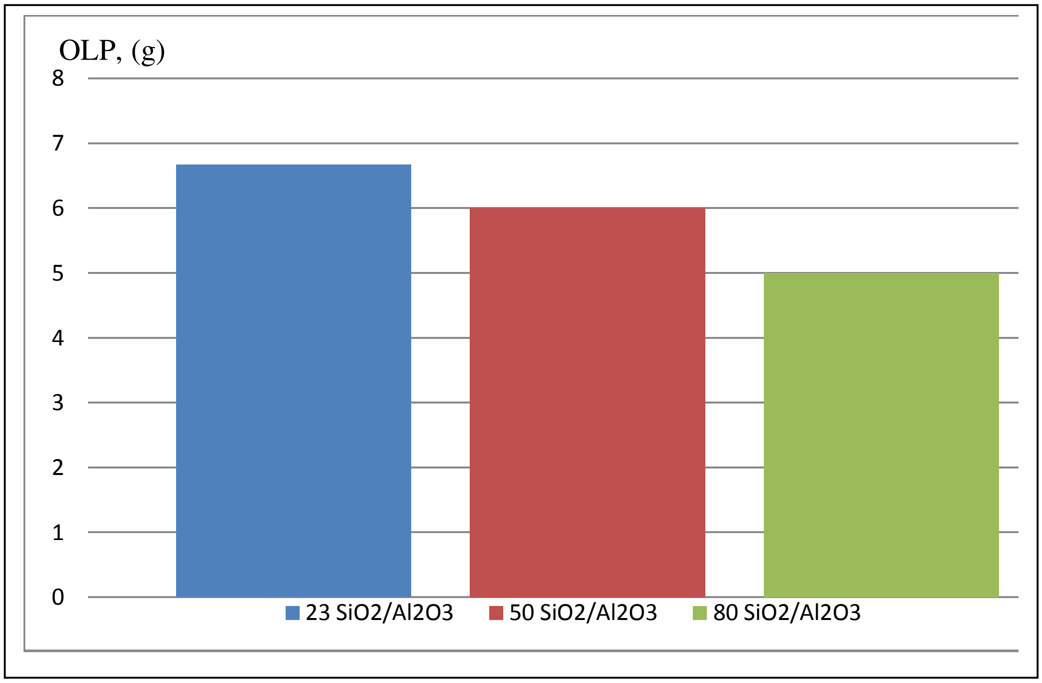

Figure 4.1: The Selectivity of OLP

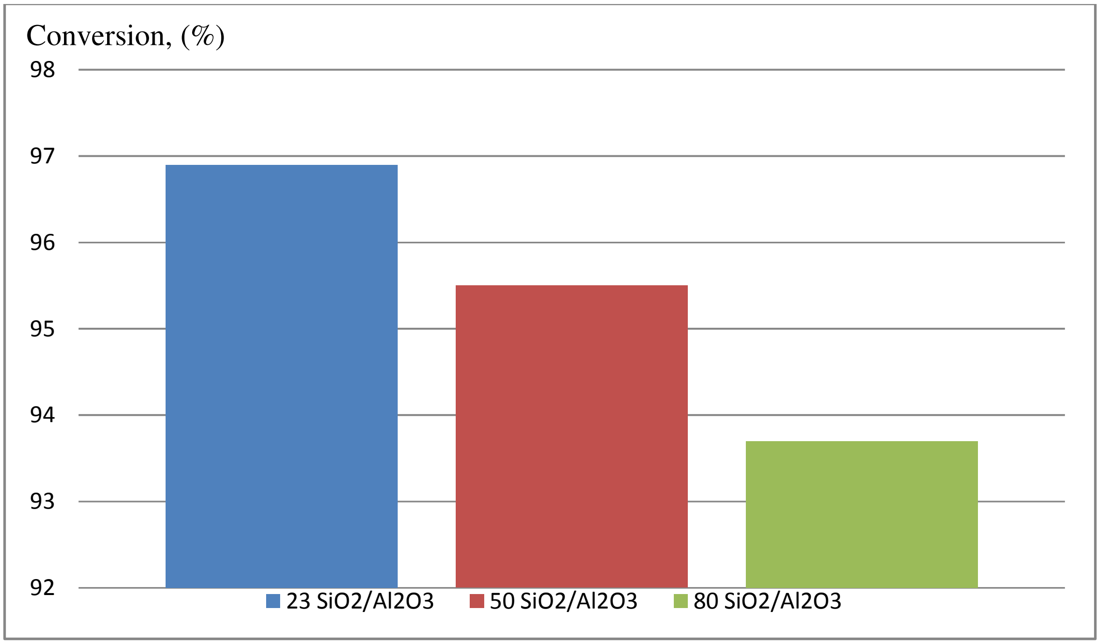

Figure 4.2: Percentage of Total Conversion

It appears that the difference in SiO_2/Al_2O_3 ratio does affect the OLP obtained from the catalytic conversion of palm oil fuels. Figure 4.1 shows that OLP obtained from the experiments using ZSM-5, 23, 50 and 80 SiO_2/Al_2O_3. One assumption was made prior to calculate selectivity. The assumption is the residue oil was assumed as the unreacted fed.

Figure 4.2 tabulates the conversion as well as the result for the experiments. The maximum conversion was 96.9% obtained with the 23 SiO_2/Al_2O_3. The 50 SiO_2/Al_2O_3 obtained the second highest conversion, 95.5% and 80 SiO_2/Al_2O_3 produced 93.7% conversion respectively.

4.3 Effect of SiO_2/Al_2O_3 to the Catalytic Cracking of Palm Oil to OLP

The selectivity organic liquid products for 23 SiO_2/Al_2O_3 and 50 SiO_2/Al_2O_3 and ratios were 68.8% and 62.8% respectively. ZSM-5 with 80 SiO_2/Al_2O_3 ratios produces the lowest organic liquid at 53.36%. The selectivity gas products 23 SiO_2/Al_2O_3 and 50 SiO_2/Al_2O_3 and ratios were 31.2% and 37.2% respectively. ZSM-5 with 80 SiO_2/Al_2O_3 ratios produces the highest gas product at 46.64%.

The acidity of the catalysts played pivotal roles in the process. This was because acidity, acid sites are very important in cracking process (Klyacko et al, 1987, Groenenboom, 1989). Vitolo et al, (2001) indicate that acid sites play dominant roles in catalytic upgrading of pyrolytic oils over ZSM-5 zeolite.

The importance of catalysts acidity in the cracking of vegetable oils is published elsewhere by numerous researchers. Idem et al, (1997) for example ran experiments to test the role of catalysts acidity in catalytic conversion of canola oil to fuels. They observed that the canola oil conversion, yields of various products and composition of OLP fractions obtained increased when acidic catalysts such as ZSM-5 and γ – alumina were used. Furthermore, works by Prasad and Bakhshi (1985) and Prasad et al (1986a) found that the acid sites of ZSM-5 were very important in the catalytic conversion of canola oil and mustard oil. This is probably because secondary reactions such as isomerrization and aromatization take place on the strong acid site. (Prasad et al, 1986a).

4.4 FTIR Analysis Result

By taking 10% error as assumption, the main absorption will be the C-H stretch at 3000-2800 cm^{-1} for alkanes, there will be a CH stretch band at 3100-3000 cm^{-1} for alkenes and look for the benzene, double bonds which appear as medium to strong absorptions in the region at 1650-1450 cm^{-1} all existed in the samples confirming the presence of gasoline in OLP.

Table 4.5: Wavelength of IR for OLP

Sample	Wavenumbers (cm-1)		
	alkanes	alkenes	Aromatic (benzene)
23 SiO_2/Al_2O_3	2853.62	2923.74	1465.25
50 SiO_2/Al_2O_3	2853.37	2923.37	1465.20
80 SiO_2/Al_2O_3	2852.71	2923.31	1464.30

The IR spectrum for benzene, C_6H_6, has only four prominent bands because it is a very symmetric molecule. Every carbon has a single bond to hydrogen. Each carbon is bonded to two other carbons and the carbon-carbon bonds are alike for all six carbons. The molecule is planar. The aromatic CH stretch appears at 3100-3000 cm^{-1} there are aromatic CC stretch bands (for the carbon-carbon bonds in the aromatic ring) at about 1500 cm^{-1}. Two bands are caused by bending motions involving carbon-hydrogen bonds. The bands for CH bends appear at approximately 1000 cm^{-1} for the in-plane bends and at about 675 cm^{-1} for the out-of-plane bend.

Figure 4.3, Figure 4.4 and Figure 4.5 shows the result of FTIR for the sample 23 SiO_2/Al_2O_3, 50 SiO_2/Al_2O_3 and 80 SiO_2/Al_2O_3 in ZSM-5.

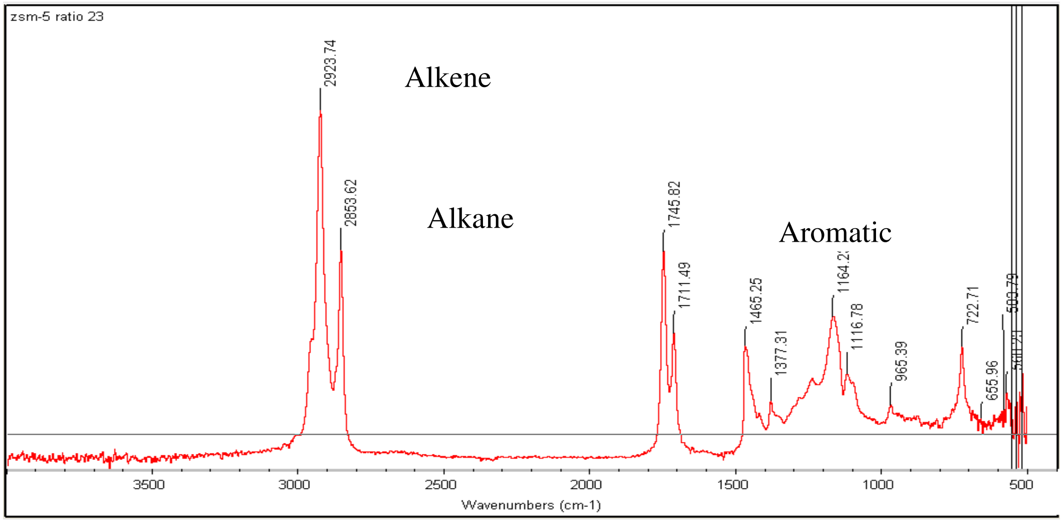

Figure 4.3: IR spectra for formation OLP using 23 SiO_2/Al_2O_3

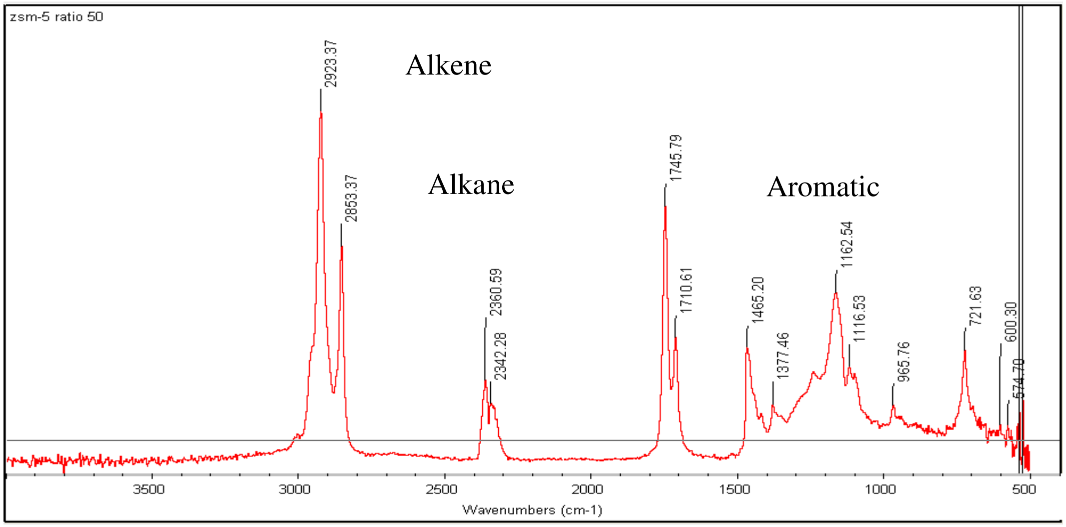

Figure 4.4: IR spectra for formation OLP using 50 SiO_2/Al_2O_3

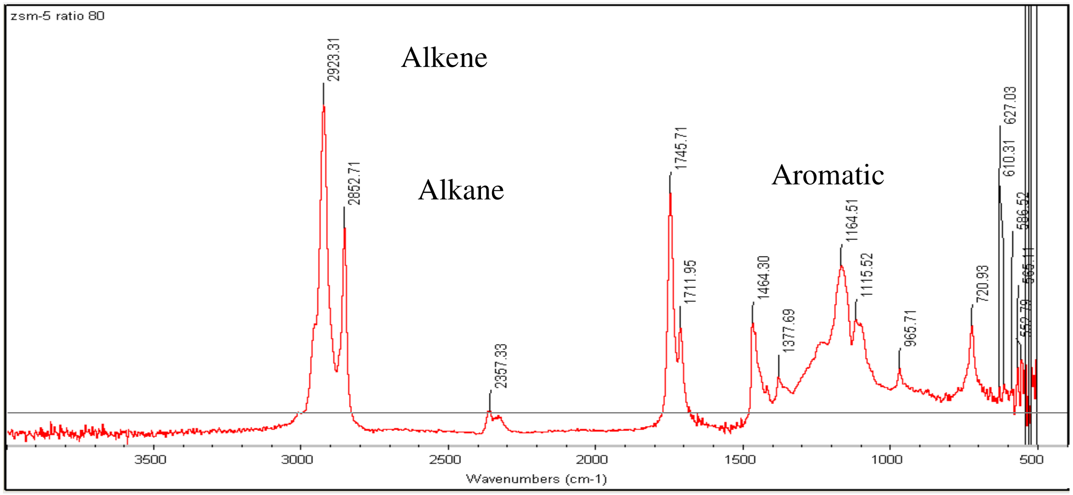

Figure 4.5: IR spectra for formation OLP using 80 SiO_2/Al_2O_3

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The rapid depletion of petroleum-based fuel may cause very serious problem as it is used almost in every aspect of live. Thus, the endeavor to search for renewable alternate fuel sources in essential. Malaysia, abundant with palm oil can overcome this problem by using palm oil as substitute to fuel. Based on my research, the ratio 23 SiO_2/Al_2O_3 in ZSM was found to be the most effective catalyst for the cracking of palm oil to organic liquid products. Its conversion and selectivity was the highest among the catalysts. It was observed that the increase SiO2/Al_2O_3 ratio would decrease the number of Bronsted acid sites. It also appeared that the acidity of the catalysts have a significant effect on OLP selectivity. The ratio 23 SiO_2/Al_2O_3 in ZSM-5 enjoyed the highest number of Bronsted acid sites compared to others catalysts. The objective of my research achieve because each samples produce organic liquid products which contain fuel such as gasoline that have functional group like alkanes, alkenes and aromatic.

5.2 Recommendation

Treated crude palm oil can be used as a feed in expense RBD palm oil. Economically, the price of RBD palm oil is higher than crude palm oil. The deep fry oil or used oil can also be used as a raw material. This will give advantage to this process in term of economy. The accurate way to analyze gaseous products is also important. By analyzing the gaseous products, the possible pathway of the process can be accurately investigated. Furthermore it will help in the mass balance calculation. Using the gas chromatography for analyze organic liquid products (OLP). The stability of the catalysts too can be studied. The modified of ZSM-5 was to be more acid site by doping transition metal such as ferum, cooper, zinc and etc. Besides, perform catalyst characterization using NH_3 TPD for identify acid site in term of bronsted and lewis.

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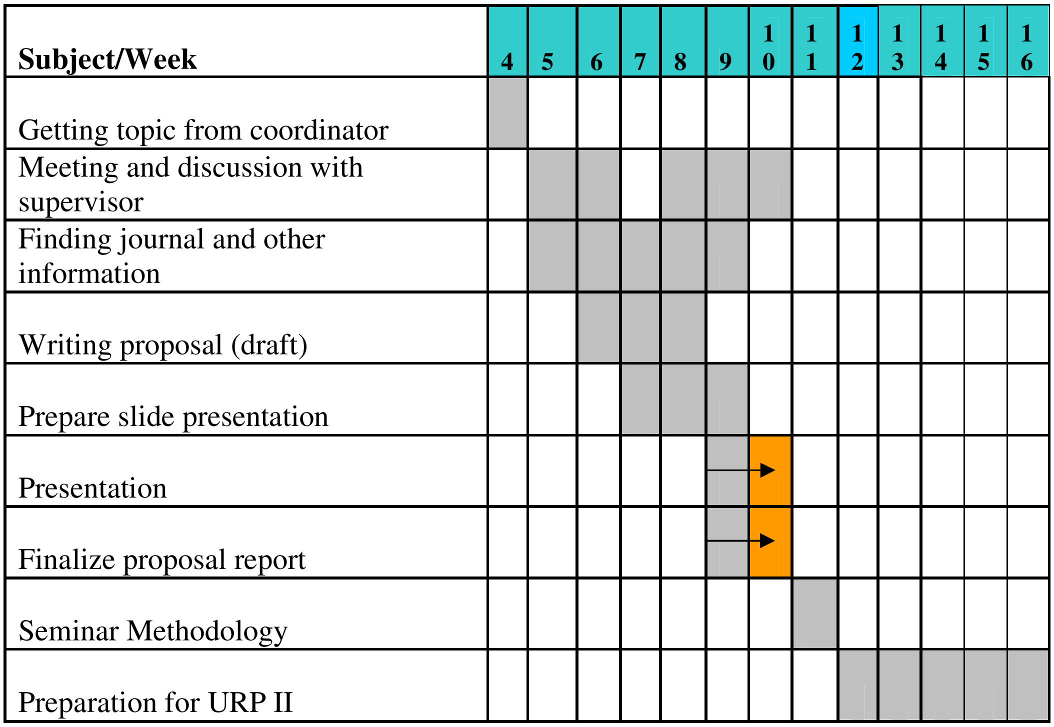
APPENDIX A

Gantt Chart for Undergraduate Research Project I



Subject/Week	4	5	6	7	8	9	10	11	12	13	14	15	16
Getting topic from coordinator	▨												
Meeting and discussion with supervisor		▨	▨		▨	▨	▨						
Finding journal and other information		▨	▨	▨	▨	▨							
Writing proposal (draft)			▨	▨	▨								
Prepare slide presentation				▨	▨	▨							
Presentation						▨ →	🟧						
Finalize proposal report						▨ →	🟧						
Seminar Methodology								▨					
Preparation for URP II									▨	▨	▨	▨	▨

🟧 = Actual progress

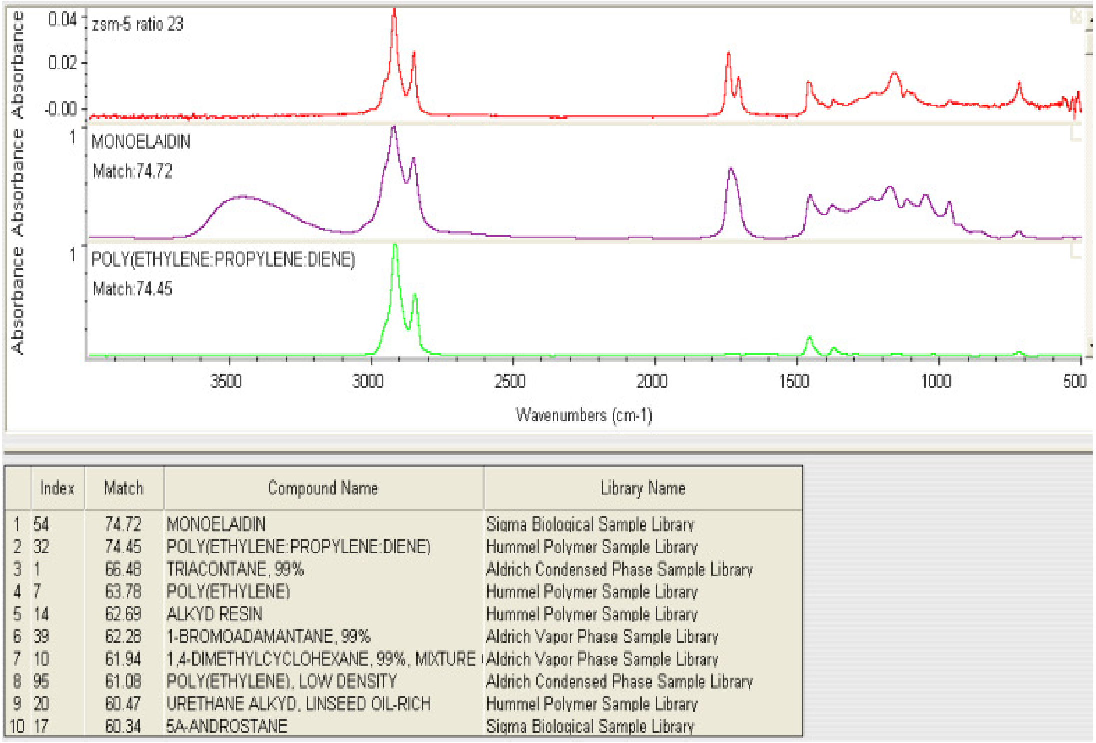
APPENDIX B

Gantt Chart for Undergraduate Research Project II

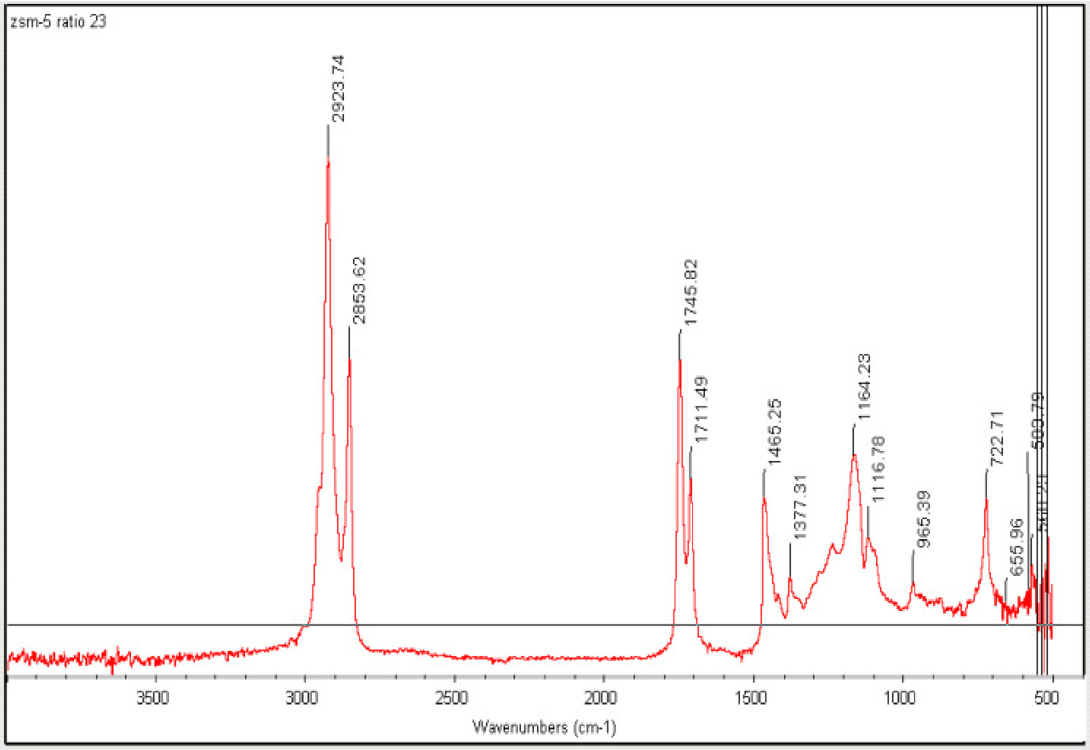
Subject/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
Literature Research	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■		
Experiment Familiarization	■	■															
Equipment Setup	■	■	■														
Experiment Work																	
a) Sample Collection	■	■	■	■	■	■	■	■	■	■							
b)Drying Methods	■	■	■	■	■	■	■	■	■	■							
c) Extraction Methods	■	■	■	■	■	■	■	■	■	■							
d) Separation Methods	■	■	■	■	■	■	■	■	■	■							
e) Analysis Methods	■	■	■	■	■	■	■	■	■	■							
Discussion With Supervisor	■	■	■	■	■		■	■	■	■	■	■	■	■	■	■	
Preparation Of Full Thesis																	
a) Abstract												■					
b) Introduction	■																
c) Literature Review		■	■														
d) Methodology		■	■	■	■												
e) Result And Discussion						■	■	■	■	■	■						
f) Conclusion												■					
g) Reference												■					
h) Appendix												■					
Preparation Of Technical Paper												■					
Submission 1st Draft Thesis													■				
Correction Of 1st Draft Thesis														■			
Submission Of Final Draft Thesis															■		
Submission Of Full Thesis																■	

APPENDIX C

FTIR Analysis for the Sample 23 SiO_2/Al_2O_3

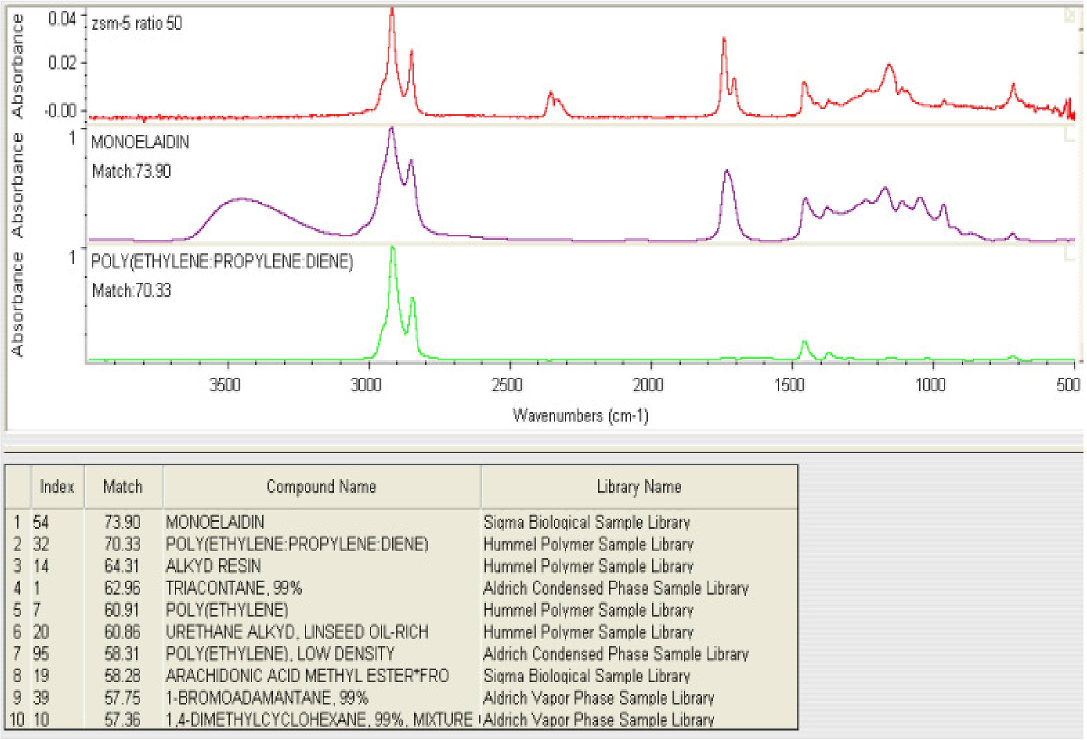


	Index	Match	Compound Name	Library Name
1	54	74.72	MONOELAIDIN	Sigma Biological Sample Library
2	32	74.45	POLY(ETHYLENE:PROPYLENE:DIENE)	Hummel Polymer Sample Library
3	1	66.48	TRIACONTANE, 99%	Aldrich Condensed Phase Sample Library
4	7	63.78	POLY(ETHYLENE)	Hummel Polymer Sample Library
5	14	62.69	ALKYD RESIN	Hummel Polymer Sample Library
6	39	62.28	1-BROMOADAMANTANE, 99%	Aldrich Vapor Phase Sample Library
7	10	61.94	1,4-DIMETHYLCYCLOHEXANE, 99%, MIXTURE	Aldrich Vapor Phase Sample Library
8	95	61.08	POLY(ETHYLENE), LOW DENSITY	Aldrich Condensed Phase Sample Library
9	20	60.47	URETHANE ALKYD, LINSEED OIL-RICH	Hummel Polymer Sample Library
10	17	60.34	5A-ANDROSTANE	Sigma Biological Sample Library

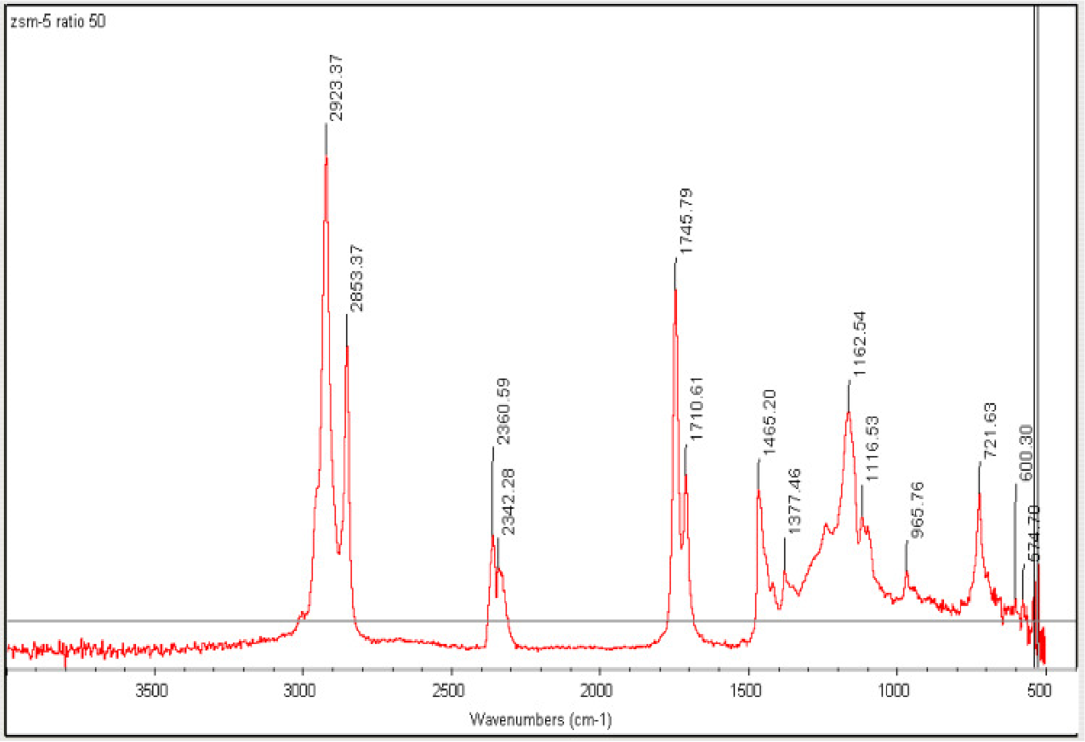

zsm-5 ratio 23
2923.74
2853.62
1745.82
1711.49
1465.25
1377.31
1164.23
1116.78
965.39
722.71
655.96
593.79
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

APPENDIX D

FTIR Analysis for the Sample 50 SiO_2/Al_2O_3

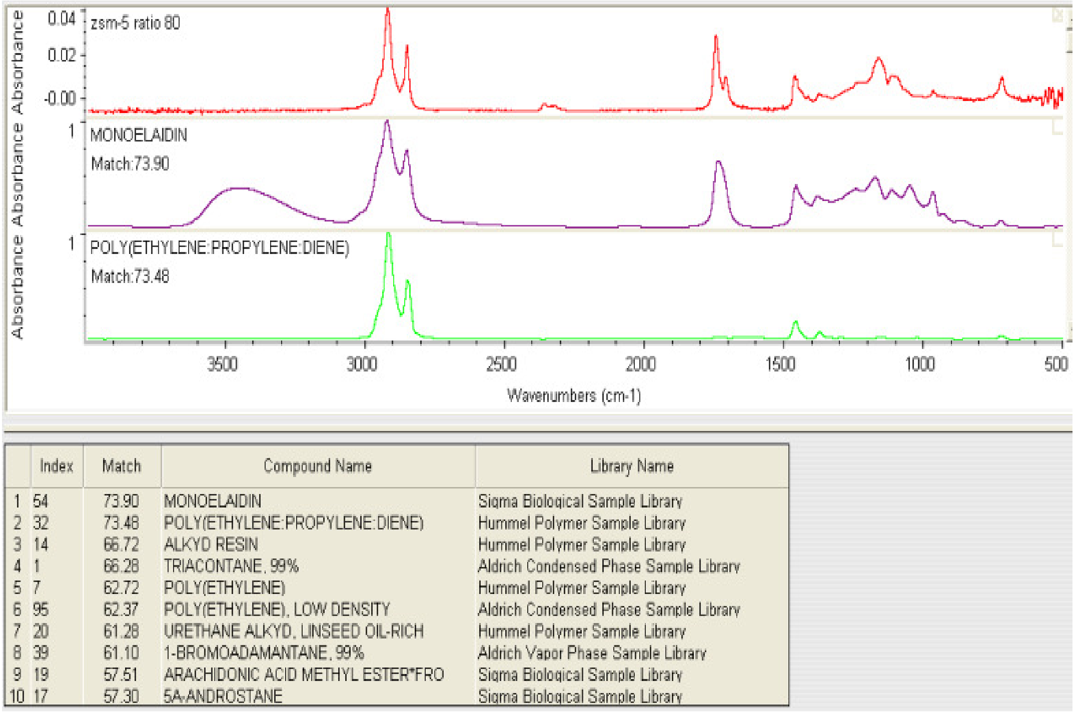


	Index	Match	Compound Name	Library Name
1	54	73.90	MONOELAIDIN	Sigma Biological Sample Library
2	32	70.33	POLY(ETHYLENE:PROPYLENE:DIENE)	Hummel Polymer Sample Library
3	14	64.31	ALKYD RESIN	Hummel Polymer Sample Library
4	1	62.96	TRIACONTANE, 99%	Aldrich Condensed Phase Sample Library
5	7	60.91	POLY(ETHYLENE)	Hummel Polymer Sample Library
6	20	60.86	URETHANE ALKYD, LINSEED OIL-RICH	Hummel Polymer Sample Library
7	95	58.31	POLY(ETHYLENE), LOW DENSITY	Aldrich Condensed Phase Sample Library
8	19	58.28	ARACHIDONIC ACID METHYL ESTER*FRO	Sigma Biological Sample Library
9	39	57.75	1-BROMOADAMANTANE, 99%	Aldrich Vapor Phase Sample Library
10	10	57.36	1,4-DIMETHYLCYCLOHEXANE, 99%, MIXTURE	Aldrich Vapor Phase Sample Library

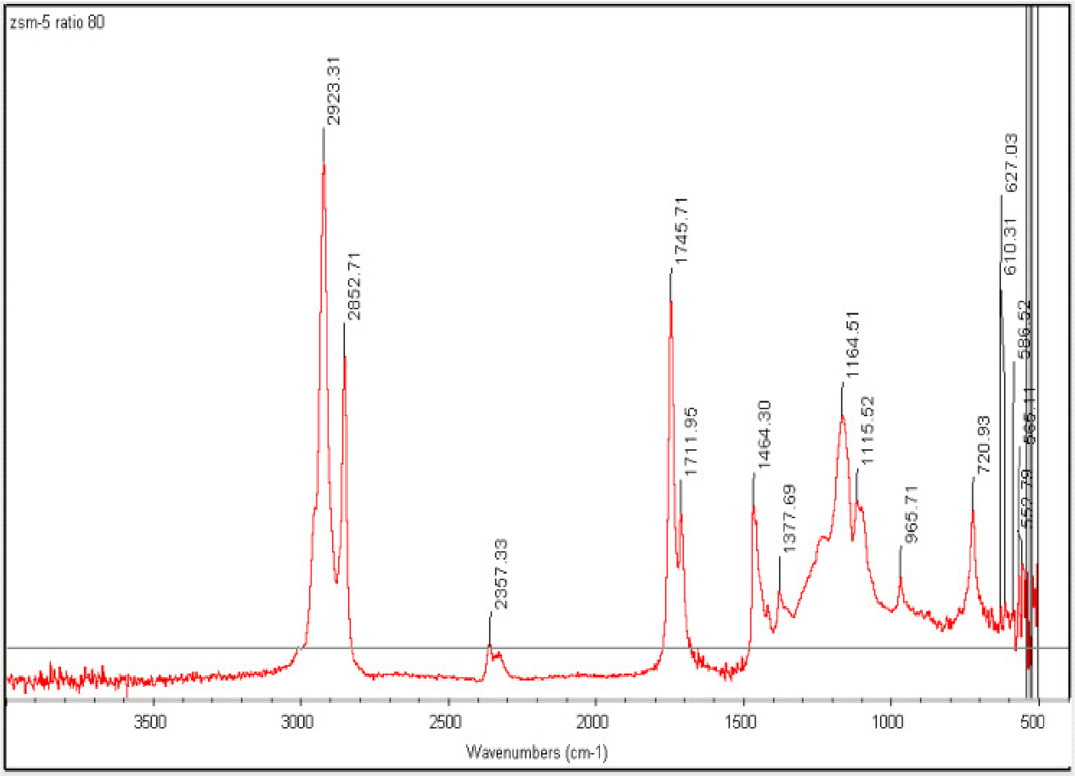

zsm-5 ratio 50
2923.37
2853.37
2360.59
2342.28
1745.79
1710.61
1465.20
1377.46
1162.54
1116.53
965.76
721.63
600.30
574.70
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

APPENDIX E

FTIR Analysis for the Sample 80 SiO_2/Al_2O_3



	Index	Match	Compound Name	Library Name
1	54	73.90	MONOELAIDIN	Sigma Biological Sample Library
2	32	73.48	POLY(ETHYLENE:PROPYLENE:DIENE)	Hummel Polymer Sample Library
3	14	66.72	ALKYD RESIN	Hummel Polymer Sample Library
4	1	66.28	TRIACONTANE, 99%	Aldrich Condensed Phase Sample Library
5	7	62.72	POLY(ETHYLENE)	Hummel Polymer Sample Library
6	95	62.37	POLY(ETHYLENE), LOW DENSITY	Aldrich Condensed Phase Sample Library
7	20	61.28	URETHANE ALKYD, LINSEED OIL-RICH	Hummel Polymer Sample Library
8	39	61.10	1-BROMOADAMANTANE, 99%	Aldrich Vapor Phase Sample Library
9	19	57.51	ARACHIDONIC ACID METHYL ESTER*FRO	Sigma Biological Sample Library
10	17	57.30	5A-ANDROSTANE	Sigma Biological Sample Library


zsm-5 ratio 80
2923.31
2852.71
2357.33
1745.71
1711.95
1464.30
1377.69
1164.51
1115.52
965.71
720.93
627.03
610.31
586.52
565.11
552.79
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)