

**BIOGASOLINE SYNTHESIS THROUGH FLUID CATALYTIC CRACKING OF
RUBBER SEED OIL - EFFECT OF CATALYST**

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RUBBER SEED OIL - EFFECT OF CATALYST**

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Thesis is submitted in partial fulfilment of the requirements
For the award of the degree of
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

MAY 2017

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DEDICATION

By the name of Allah, the most Gracious and the most Merciful

I humbly dedicate my thesis to both of my beloved parents,
Rosli Bin Taha & Misbah Binti Mokhtar

To my supportive supervisor,
En. Syaiful Nizam Bin Hassan

To every each of my siblings,

To my fellow friends,
Especially the very best friends of mine,
Esamudin Bin Musa,
Norazuwen Binti Rusli,
Jessy Lynn Jaspin,

To all FKKSA's Staffs and lecturers,

Thank you for all your prayers and encouragements all the way.

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LIST OF SYMBOLS

W_1	Weight of RSO in gram
W_2	Weight of catalyst in gram
W_3	Weight of liquid product in gram
W_4	Weight of residue in gram
$^{\circ}\text{C}$	Celcius
%	Percentage

LIST OF ABBREVIATIONS

RSO	Rubber Seed Oil
GCMS	Gas Chromatography Mass Spectrometry
ZSM-5	Zeolite Socony Mobil-5

ABSTRAK

Biogasolin adalah satu penyelesaian alternatif untuk mengurangkan penggunaan bahan api fosil global. Kini, terdapat banyak penyelidikan yang menumpukan penggunaan bahan mentah yang berbeza daripada minyak sayuran untuk menghasilkan biodiesel, akan tetapi, kurang memfokuskan penghasilan Biogasoline. Oleh itu, pendekatan baru untuk menghasilkan Biogasoline diperkenalkan dalam kajian ini dimana minyak biji getah (RSO) digunakan sebagai bahan mentah untuk menghasilkan Biogasoline melalui proses keretakan pemangkin cecair yang menggunakan ZSM-5 sebagai pemangkin. Kaedah ini sesuai dilaksanakan untuk menghasilkan biofuel yang kaya dengan pecahan yang berbeza seperti petrol, minyak tanah dan diesel melalui teknik keretakan pemangkin daripada minyak yang boleh dimakan dan tidak boleh dimakan dan juga ekstrak tumbuhan. Dalam kajian ini, kaedah Dean Stark digunakan sebagai set eksperimen. Kuantiti ZSM-5 dipelbagaikan bermula daripada 0.5 gram hingga 2.0 gram dan dijalankan pada suhu 250 °C. Eksperimen ini dijalankan selama 1 minit, 5 minit dan 10 minit dan sampel yang diperolehi akan dianalisa menggunakan Gas Chromatography. Formula molekul hidrokarbon yang diperolehi daripada analisa sampel akan dibandingkan dengan formula molekul di dalam gasolin standard iaitu di antara C_6 ke C_9 . Justeru itu, sampel yang diperolehi daripada proses ini dijangkakan mengandungi sejumlah besar hidrokarbon (% berat) dengan kandungan C_6 ke C_9 . Berdasarkan daripada hasil analisis sampel yang diperolehi melalui eksperimen yang telah dijalankan, keadaan optima untuk mendapatkan hasil biogasolin yang tinggi adalah dengan menggunakan 1.5 gram pemangkin dan 10 gram minyak biji getah dan dijalankan dalam masa lima minit.

ABSTRACT

Biogasoline is an alternative solution towards reducing global fossil fuel consumptions. Currently, there are numerous researches focusing on different feedstock of vegetable oils used to synthesis biodiesel is performed but less is focusing on biogasoline production. Therefore, the new approach to synthesis biogasoline is implemented in this study. Rubber seed oil (RSO) is studied as a feedstock to synthesis biogasoline through fluid catalytic cracking process using ZSM-5 as a catalyst. It is feasible to produce biofuels rich in different fractions such as gasoline, kerosene and diesel via catalytic cracking technique from edible and inedible oils and also plant extracts. In this study, Dean Stark method is applied as experimental set up. The amount of ZSM-5 is varied from 0.5 grams to 2.0 grams at 250°C. The experiment is run at 1 minute, 5 minute and 10 minute and the sample collected will be analyzed using Gas Chromatography Mass Spectrometry. The molecular formula of hydrocarbon obtained from the analysis of sample will be compared with standard gasoline range which is C_6 to C_9 . Thus, the large the amount of hydrocarbon (wt%) with range of C_6 to C_9 is expected from the sample of product obtained from the fluid catalytic cracking of RSO. Therefore, based from the experiment and analysis of the sample obtained, the optimum condition to obtain the highest yield (58.15%) of biogasoline is using 1.5 g of catalyst and 10 g of RSO at five minutes reaction time.

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Biofuels have become a promising alternative fuel because of their possible environmental benefits and the current concern over the depletion of fossil fuel sources. Biofuels include gaseous fuels and liquid fuels, and usually produced from renewable resources (Ong and Bhatia, 2010). Gaseous biofuels such as methane and hydrogen, as well as liquid biofuels such as biogasoline and biodiesel are primarily used by vehicles. In addition, they are also used for the production of electricity (Ong and Bhatia, 2010). Biofuels can be produced from plant oil based feed stock (vegetable oils and palm oil), waste materials (agriculture, wood, and crop residue), aquatic biomass (algae, and water weed), energy crops (sugar, barley, wheat, etc., containing starch) and forest products (trees, shrubs and wood) (Ong and Bhatia, 2010; Taufiqurrahmi and Bhatia, 2011; Twaiq et al, 2004; Venderbosch and Prins, 2010; Wang et al., 2015).

Besides, biofuels produced from vegetable oils is considered “ CO_2 neutral” since they are from plant sources which remove CO_2 from the atmosphere, and release the same amount when it burnt. Vegetable oils are the most common feed stocks and are converted into liquid fuels due to their high energy capacity, natural liquid-phase material and availability as a renewable feedstock (Taufiqurrahmi and Bhatia, 2011). The use of non-edible plant oils is very important due to the tremendous demand for edible oils as food source. Furthermore, edible oils’ feedstock costs are far expensive to be used as fuel (Atabani et al., 2012).

The composition of oil determines the properties of the biofuel obtained. Several types of edible vegetable oils, as well as nonedible oil with a different composition in fatty acids, are consumed for the production of biofuel. However, the direct conversion of edible oil to fuel may not be economically feasible, even though the results have shown its potential

in obtaining liquid hydrocarbons. This is because, continuous and large-scale production of biofuel from edible oil without appropriate planning could cause negative impact on the food supply chain, causing further economic problems. A potential solution to overcome this problem is to utilize waste used cooking oil or non-edible oil (Gui et al., 2008).

Plant oil based feed stock mainly contains triglycerides, which can be easily reformed into liquid biofuels compared to other available biomass containing cellulose and starch (Mushtaq et al., 2016). *Hevea brasiliensis* tree, referred to Rubber tree, belongs to the family Euphorbiaceae (Kumar et al., 2011). It is available mainly in Indonesia, Malaysia, Liberia, India, Sri Lanka, Sarawak, and Thailand. Rubber seed oil is one of the non-edible vegetable oil, which contains 50–60 wt% oil and is considered a promising feedstock for biogasoline production (Ramadhas et al., 2004).

Catalytic cracking is one of the most efficient methods to produce biofuel, especially biogasoline, by cracking of vegetable oil in the presence of suitable catalyst. The catalytic cracking of edible and non-edible oils requires the development of proper cracking catalysts and reactors for the production of biogasoline (Taufiqurrahmi and Bhatia, 2011). The yield of hydrocarbons in catalytic cracking depends on the choice of shape selective catalyst, as well as acidity of the catalyst. In the cracking of vegetable oil, a microporous catalyst is preferred since selectivity of biofuel products such as the gasoline and diesel fractions is produced through the small pores of the catalyst. Besides, zeolites have excellent properties, in terms of high acidity, high thermal stability and excellent selectivity for gasoline production (Taufiqurrahmi and Bhatia, 2011).

1.2 Motivation

In the range of microporous zeolites, the medium pore zeolite catalysts are more effective in the aromatization of the intermediate olefin products compared to those with large pore zeolites. The conversion of canola oil and the overall yield of hydrocarbons decreased as the pore size of catalyst were increased. Also, the medium pore zeolite catalysts are more effective in the aromatization of the intermediate olefin products compared to the large pore zeolites (Katikaneni et al., 1995).

The medium pore size zeolite ZSM-5 gave the best performance among three zeolite catalysts tested in terms of conversion, gasoline and benzene, toluene, and xylene as aromatics yield (Katikaneni et al., 1995). Microporous catalysts such as zeolites, ZSM-5 have shown great potential as cracking catalysts (Taufiqurrahmi and Bhatia, 2011).

1.3 Problem Statement

Based on previous researches, the operating variables affecting cracking activity were feed/catalyst ratio, reaction temperature and weight hour space velocity. A higher reaction temperature and low feed rate gave a higher yield of gaseous product, while at a low reaction temperature and high feed rate deactivated the catalyst faster. The gasoline fraction was one of the desired products, and the optimum operating conditions were determined to maximize its yield (Ooi et al., 2004). This research aims to determine the optimum of feed to catalyst ratio in order to achieve high yield of biogasoline from rubber seed oil.

1.4 Objectives

The following is the objective of this research:

- 1) To determine the optimum amount of catalyst (ZSM-5) in fluid catalytic cracking process of biogasoline synthesis from rubber seed oil.
- 2) To determine the yield of biogasoline and correlate the yield and conversion kinetics with amount of catalyst used.
- 3) To optimize the temperature of fluid catalytic cracking of RSO for biogasoline synthesis with effects of residence time of reaction.

1.5 Scopes of Study

The following are the scope of this research:

- 1) The cracking temperature is fixed while amount of catalyst and oil is varied at 0.5 g to 2.0 g and the reaction time is varied at 1 minute, 5 minute and 10 minute.
- 2) Analyzing cracked RSO using GCMS with comparison using commercial gasoline and standard gasoline components as controls.
- 3) Determination on conversion kinetics (conversion rate) affected from varies amounts of catalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Rubber Seed Oil (RSO)

RSO is a promising feedstock for biogasoline production which is extracted from rubber seed of rubber tree. On 2009 Malaysian Rubber Board has reported that Malaysia has an estimated acreage of 1,229,940 hectares of rubber plantation producing an estimated average of more than 1.2 million metric tons of rubber seeds per year (Eka et al., 2010). Based on an estimated average of 1000 kg seeds per ha/ yr, the projected annual production of rubber seeds in Malaysia would be 1.2 million metric tons. Despite Malaysia being a major rubber growing country, to date, there is a dearth of information on the chemical composition of the Malaysia rubber seed. According to Bressani *et al* (1983), the rubber seed kernel (hull has been removed) contains 29.6% fat and 11.4% protein. Thus, it is estimated that Malaysia wastes about 355,200,000 kg fat and 136,800,000 kg protein per year. The rubber seed consist of about 40% kernel with 20-25% moisture, where approximately 40-50% of oil is found in the dried kernel which contributes to 20 million liters of oil annually (Gimbun et al., 2012).



Figure 1 Rubber Seed (Ramadhas A. S. et al., 2005)

According to research performed by Eka et al., oil extracted from Malaysia's rubber seeds was 68.53%. This value is comparable to those of palm oil which stands at 45-50%, indicating that it can be a promising source of biodiesel production (Jibrail et al., 2008). Based on its fatty acids composition, rubber seed oil is rich in unsaturated fatty acid (oleic acid, linoleic and linolenic)

Table 2.1.1 Composition of fatty acid in RSO (Pan, 2000)

Fatty acid	C _{16:0}	C _{18:0}	C _{20:0}	C _{18:1}	C _{18:2}	C _{18:3}	C _{18:4}	C _{20:2}
Content (%)	8.8	7.7	Trace	24	36.1	20.2	0.8	1.5

Table 2.1.2 Properties of Rubber Seed Oil (Li et al., 2014)

Properties	RSO
Density , kg/m ³ (20°C)	926
Viscosity at 20°C, mm ² /s	58.6
Acid value (mg KOH/g oil)	25.6
Calorific value, MJ/kg	37.5
Cetane number	40
Iodine value, g/100g	135.3
Flash point, °C	242

2.2 Fluid Catalytic Cracking (FCC)

According to Chuaykleang and Ratanawilai (2014), catalytic cracking involves a conversion process which converts high molecular weight oil components to lower molecular weight by using catalyst. This unit is the most widely used process for the conversion of heavy fraction of crude oil into high-value products (e.g. diesel, gasoline). This unit operates under high temperatures (> 400°C) and pressure close to the atmospheric in the absence of hydrogen and the presence of an acid catalyst. Catalytic cracking of plant

oils, animal fats, and recycled cooking greases can be applied to produce biofuels which suitable for gasoline engines that contain linear and cyclic paraffins, olefins, aldehydes, ketones, and carboxylic acids (Huber and Corma, 2007). Besides, catalytic cracking process is favorable to produce biofuel rich in different fractions (gasoline, diesel and kerosene) from edible and non-edible oils (Sharma and Bakhshi, 1991; Chew and Bhatia, 2008). Fluid catalytic cracking (FCC) is one of the major conversion technologies in the oil refinery industry and produces the majority of the world's gasoline. According to Taufiqurrahmi and Bhatia (2011), catalytic cracking is favorable in producing gasoline, and also reduces the yield of heavy fuel oils and light gases at much lower temperatures compared to thermal cracking. So far, several methods to produce biofuels from vegetable oils is available at petroleum refineries, such as pyrolysis (thermal cracking), fluid catalytic cracking, hydrotreating and hydrocracking reaction.

FCC is the most favorable among those methods. Firstly, the temperature of catalytic cracking process (450°C) is lower than pyrolysis (500–850°C) (Chew and Bhatia, 2008). In the cracking process, the reaction temperature applied is lower than pyrolysis (Taufiqurrahmi and Bhatia, 2011). According to Huber and Corma (2007), compared to hydrotreating and hydrocracking, the significances of catalytic cracking include that no H_2 is needed, atmospheric processing reduces operating cost, and the temperatures employed are similar to those used in the production of bio-oil. Besides, FCC also considered as a cheaper route in terms of energy consumption, by converting feedstock to lighter fractions that mostly fall in the gasoline boiling range (Zhang et al., 2005).

However, although catalytic cracking is known as a cheaper route, poor yields and quality of hydrocarbons and high yields of coke (8–25 wt %) may be obtained (Taufiqurrahmi and Bhatia, 2011). According to Tamunaidu and Bhatia (2006), in order to increase the gasoline yield and simultaneously reduce the yields of coke, many researchers found that short contact times (SCT) between the catalyst and oil vapors and high temperatures are favorable. The cracking reaction takes place on cracking catalysts with short residence time (~20 s).

Table 2.2 Catalytic performance from different cracking processes (Kimura et al., 2012)

Process	Catalytic cracking	Hydrocracking	Hydrotreating hydrocracking
Conversion (%)	100.0	94.9	89.2
Isopara. selectivity (%)	15.2	34.3	89.7
Olefins selectivity (%)	57.6	25.6	5.0
Aromatic selectivity (%)	26.0	39.6	0
Average number of Carbon cracked	10.1	9.6	10.8

2.3 Cracking catalyst

The activities of different catalysts for the cracking of RSO were studied. However, zeolites remain the best catalysts for the cracking of oils, due to their high thermal stability, good shape-selective properties resulting from their microcrystalline structures, and their ability to concentrate reactants inside their pores (Bhatia, 1990; Emst et al., 1999).

Table 2.3 Catalytic cracking of different feedstock for production of biofuel

Feedstock	Catalyst	Product, Yield (Highest)				
		Biogasoline (wt%)	Kerosene (wt%)	Diesel (wt%)	Gases (wt%)	Coke (wt%)
Palm Oil (Twaiq et al., 2004)	HZSM-5	49.2	26.1	2.6	8.2	1.7
	Composite material	48.4	8.8	7.0	11.4	5.4
Used Palm Oil (Ooi et al., 2004)	MCM-41/zeolite beta	28.9	15.9	12.3	13.4	10.7
Palm Oil based waste fatty acid (Ooi et al., 2004)	SBA-15	20.7	15.5	4.8	9.5	7.2
	Al-SBA	36.0	17.2	4.6	16.2	6.3
	Al-MCM-41	32.6	20.0	6.7	6.7	9.8
Soybean Oil (Tian et al., 2008)	Ultra-Y/ZSM-5	22.9	NR	15.0	6.2	5.2

All the studies related to palm oil is conducted under condition pressure of 1 atm, temperature of 450°C, and WHSV of 2.5 h^{-1} while the soybean oil studies is performed at temperature between 500 °C to 520 °C , residence time of 1.4 s to 1.7 s and 6 to 8 catalyst/feed ratio under continuous mode. Ibanez et al. (2014) stressed the activity for biogasoline production from palm oil in the order: HZSM-5 \approx MCM-41/ZSM-5 > MCM-41. Other than that, HZSM-5 produced the highest yield in cracking of canola oil than aluminum-pillared clay, silicate, silica–alumina H–Y, and H-mordenite catalysts (Katikaneni et al., 1995). Therefore, acidity of HZSM-5 which triggers product distribution during the cracking reaction influenced the activity of HZSM-5 and MCM-41/ZSM-5. Equally, the activity and selectivity of HZSM-5 towards biogasoline fraction formation from crude and used palm oil were higher than microporous Zeolite Beta.

2.4 Analysis Method

Gas chromatography (GC) is one of the most widely used techniques in modern analytical chemistry. In its basic form, GC is used to separate complex mixtures of different molecules based on their physical properties, such as polarity and boiling point. It is an ideal tool to analyse gas and liquid samples containing many hundreds or even thousands of different molecules, allowing the analyst to identify both the types of molecular species present and their concentrations. Gas Chromatography (GC) also offers a precise and efficient method for biofuels analysis. To identify the hydrocarbon content of the biogasoline, GC-MS analysis was performed (Nasikin et al., 2009). Based from the research done by Li et al. (2014), the liquid fuels and gas products resulted from the cracking of RSO were analyzed by Gas chromatography–mass spectrometry (GC–MS) and the results are summarized in table.

Table 2.4 The main component of liquid fuels from RSO (Li et al., 2014)

Catalyst	Liquid fuel		Yield of Liquid Product (%)
	Components	Content (%)	
USY	1,3- Octadiene	14.9	75.6
	1-Octylene	13.6	
	Octane	15.2	
	Nonane	30.1	
Na_2CO_3	Nonane	5.5	73.3
	Decane	5.4	
	Dodecane	10.1	
	1-Tridecylene	16.3	
	Cetane	8.6	

CHAPTER 3

METHODOLOGY

3.1 Materials and Methods

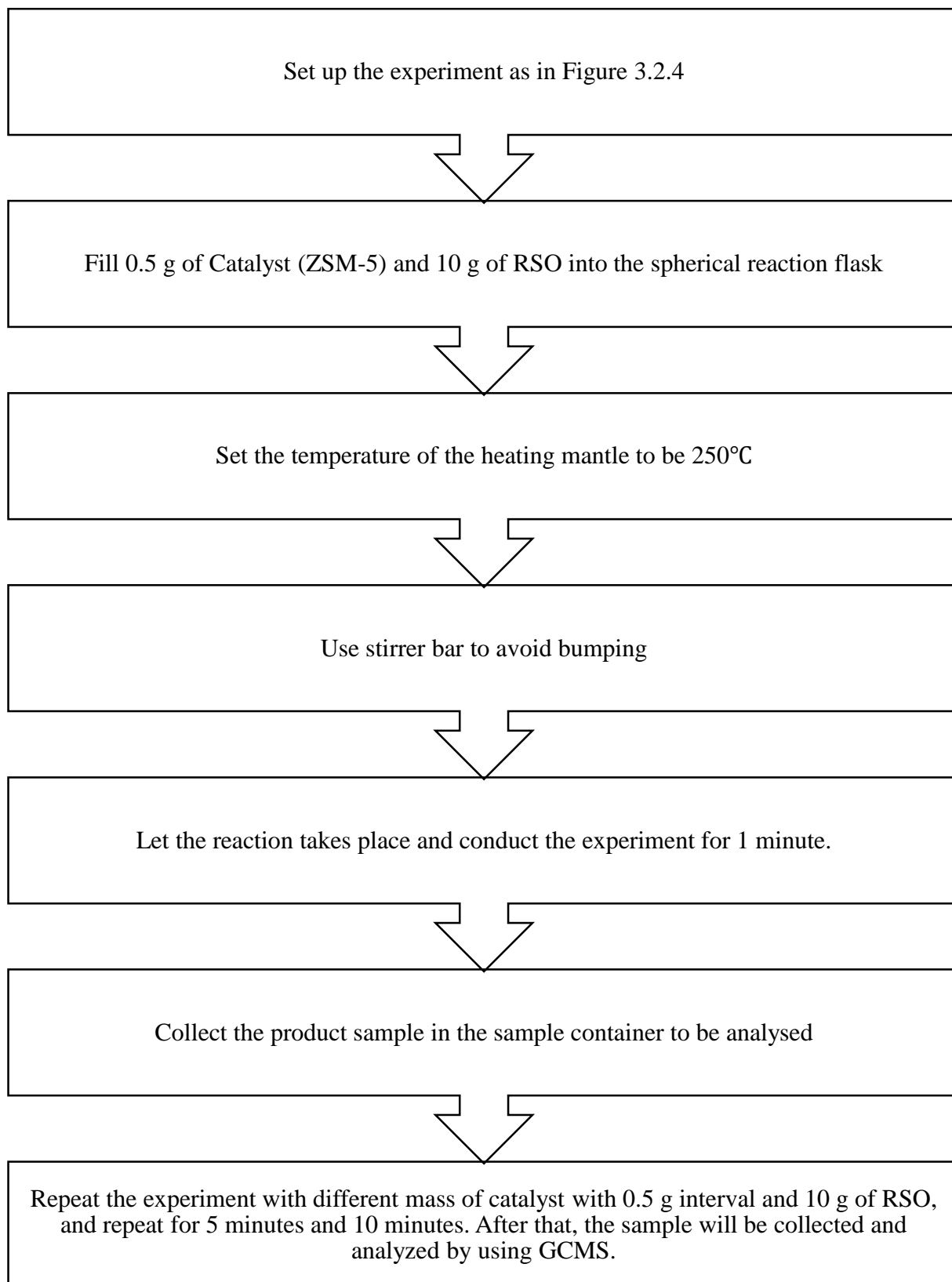
Table 3.1.1 Chemical used in the experiment

Material	Purpose
Rubber Seed Oil	To be cracked during catalytic cracking process
ZSM-5	To be used as catalyst in catalytic cracking process
n-pentane	Used as carrier solvent in GC analysis
Cooling water	Act as a cooling agent

Table 3.1.2 Equipment used in the experiment

Equipment	Purpose
Gas Chromatography	Analyse different substances within the test sample
Dean stark	Allow vapours from the reaction which contains the reaction solvent travel out of reaction flask up into the condenser
Heating mantle	Allow adjustable temperature
Stirrer bar	To ensure perfect mixing
Spherical reaction flask	To contain RSO and catalyst. It also acts as a medium that allow reactions between these two materials occur.
Condenser	Condense substance from gaseous state to liquid state

The experiment will follow the procedure as follows:



3.2 Method for Catalytic Cracking

Currently, there are numerous setup of apparatus or experimental method used by previous researchers for catalytic cracking of vegetable oils to biofuel.

Based on studies conducted by Nurjannah et al. (2013), the catalytic cracking was carried out in a fixed bed microreactor at temperatures between 350 to 500 °C and N_2 flow rates within range of 100 to 160 mL/min for 120 min involving palm oil. From the studies, it was found that at 450°C and N_2 flow rate of 100mL/min resulted in the highest yield of gasoline fraction of 28.87 %, 16.70 % kerosene and 1.20 % diesel oil. The HZSM-5 catalyst is used in the catalytic cracking process.

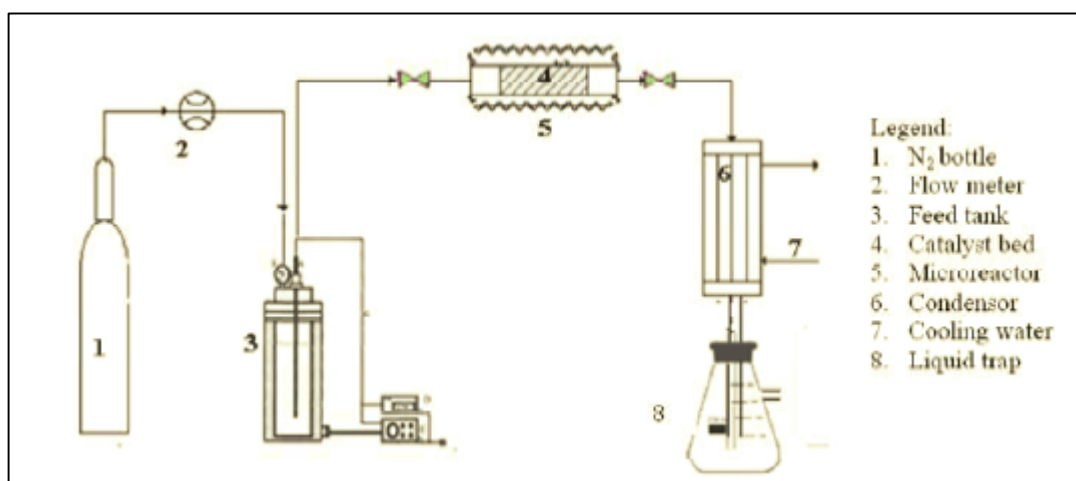


Figure 3.2.1 Catalytic cracking of vegetable oils to produce biofuels
(Nurjannah et al., 2013)

The catalytic cracking was performed in a microreactor filled with approximately 1 g of a catalyst bed and the reactor was sealed with a heating element. Firstly, palm oil was fed to a feed tank which has been heated at 350°C. At the same time, nitrogen was also fed to the feed tank at flow rates between 100 to 160 mL/min. Oil vapour and nitrogen was then flow to the fixed bed reactor which was already heated to a desired temperature within 350°C to 500°C. The products were measured in a GC.

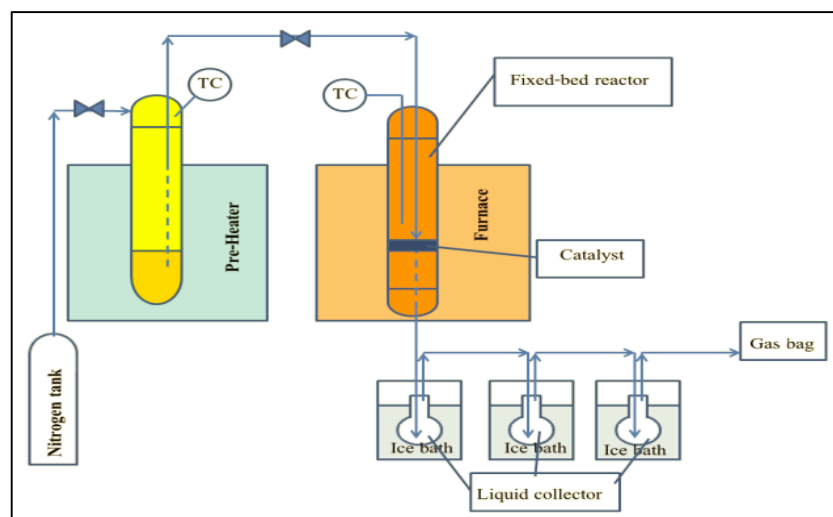


Figure 3.2.2 Catalytic cracking process using Box–Behnken (Chuaykleang & Ratanawilai, 2014)

Based on Figure 3.2, the Box-Behnken design was used in the investigation to study the effect of reaction parameters such as temperature, nitrogen flow rate and weight of catalyst on yield of gasoline-range products involving refined palm oil. This study involves two reactors for catalytic cracking, where the refined palm oil will be feed to the first reactor and the second reactor act as medium for catalytic cracking reaction. Firstly, the refined palm oil is fed to the first reactor for heating process. Next, the oil in liquid phase was allowed to evaporate to gas phase and ready for cracking. The oil in gas phase is carried to second reactor by nitrogen gas and weight of HZSM-5 catalyst was varied within range of one to five gram. When the reaction completed, the gas product leaving the reactor were cooled to 313 K in the condenser system, while the organic liquid product (OLP) were collected in glass liquid sampler at room temperature. Last but not least, OLP was kept while the benzene and isooctane were analysed using GC.

Last but not least, another experimental setup for catalytic cracking is carried out using Dean Stark apparatus. First of all, the right size of heating mantle is used so that it fits snugly around the still pot. A reflux condenser is attached to the top of the Dean Stark apparatus, where the water is going in at the bottom and out at the top of the condenser. Dean Stark enables the determination of fluid saturation in a core sample by virtue of a solvent vaporization and condensation process. This method relies on the miscibility to oil and immiscibility to water of solvents such as toluene. In this experiment, n- pentane is used as a carrier solvent. Initially, the mixture is placed in a still pot connected at the bottom to an

externally heated, solvent-containing flask and to a fluid separation system at the top. By heating the system, the in-situ water vaporizes, condenses in the condenser tube and is collected in a graduated receiver. The vaporized solvent also condenses, soaks the sample, and extracts the oil, which falls into the solvent flask. The experiment continues until the extracted solvent displays its original colour. The sample is then oven dried and weighed again. The weight measurements (saturated core, dry core, produced water) can be inputted into the mass balance equation to deduce the produced oil volume. The apparatus consists of a distillation/extraction glassware unit and a heating mantle with thermostatic controller. Flexible plastic tubing connects the condenser to the water cooling unit.

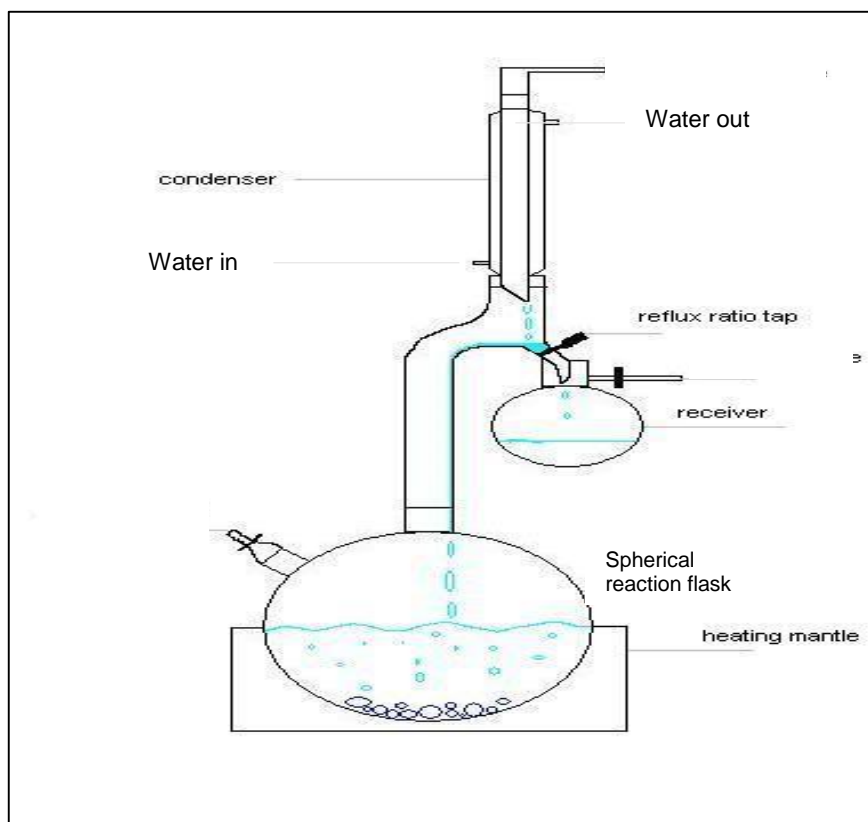


Figure 3.2.3 Dean Stark setup for catalytic cracking process

(www.img.photobucket.com)

In this work, the amount of the heat supplied was well controlled by the temperature of the heating mantle, fitted with the lab scale reactor. At the same time, catalysts were added to lower the activation energy of the cracking process. The presence of catalysts reduced the energy needed to crack long-chain hydrocarbons and thus products were formed in a more energy-efficient way.

Therefore, Dean Stark apparatus is chosen as the experimental set up for this study due to its simplicity in term of east to be set up, easy to be handled, besides it provide sufficient accuracy and relatively cheap and officially sactioned for many applications (Torsaeter and Abtahi, 2000).



Figure 3.2.4 Experimental Setup (Dean Stark apparatus)

3.3 Catalyst's Mass Differences

For this experiment, the main focus is to study the effect of catalyst:oil ratio on the yield of product. The reaction is allowed at fixed temperature of 250°C. On the other hand, mass of catalyst is varied at interval of 0.5 g. The purpose is to study the optimum catalyst to oil ratio to obtain highest yield of biogasoline from catalytic cracking of RSO by applying Dean Stark Method.

According to study conducted by Li et al. (2014), the yield of product changes as ratio of catalyst to oil varies. The result of the study is tabulated in a table.

Table 3.3 Effect of catalyst:oil (mass) ratio on yield of product

Catalyst/RSO (mass)	Temperature (°C)	Time (min)	Yield of liquid product (%)
1:30	400	120	66.3
1:40	400	120	70.4
1:50	400	120	71.8
1:60	400	120	61.6
1:70	400	120	58.8

Based on the result, when the ratio $m(\text{cat}):m(\text{RSO})$ is 1:50, the liquid product obtained reaches the highest yield which is 71.8%. However, as the ratio of $m(\text{cat}):m(\text{RSO})$ increases further at 1:60 and 1:70, the yield of product decreases due to occurring of side reactions such as deep cracking of RSO. Thus, according to Li et al. (2014), the optimum ratio $m(\text{cat}):m(\text{RSO})$ is 1:50.

Previous studies conducted by Chuaykleang and Ratanawilai (2014) also concern on the effect of catalyst to oil ratio on the yield of product. The catalytic cracking process is conducted using HZSM-5 as a catalyst. This study is performed under fixed temperature of 475 °C and varies weight of catalyst ranging from one gram to five grams. From the result, as the weight of catalyst introduced to the reaction increases, yield of product increases. However, when further

increase of catalyst weight is applied, the yield of product decreases. Therefore, amount of catalyst is directly affecting catalytic cracking reaction. As the reaction used higher catalyst weight, the long chain hydrocarbon was broken to small hydrocarbon. When the reaction use more amount of catalyst, some hydrocarbon was cracked in smaller hydrocarbon than gasoline range (less than benzene and isooctane range).

3.4 Experimental Analysis

Catalytic cracking of RSO was carried out using Dean Stark method at temperature 250°C, and varies catalyst to oil ratio. The RSO and catalyst were allowed to react in the spherical reaction flask with continuous heating from the heating mantle. RSO was cracked and vaporized. The vapor flow up to the condenser and condensed to liquid phase. Then, the liquid product was weighed and analyzed using GC. The conversion (wt%) of RSO and yield (wt%) for bio-oil is calculated using formula as follows:

$$\text{Conversion (\%)} = [(W_1 + W_2 - W_4) / W_1] \times 100\%$$

$$\text{Yield (bio oil) (\%)} = W_3 \div W_1 \times 100\%$$

Where :

W_1 = Weight of RSO (g) ; W_3 = Weight of liquid product (g)

W_2 = Weight of catalyst (g) ; W_4 = Weight of residue (g)

(Zhiping and Shitao, n.d.)

CHAPTER 4

RESULT AND DISCUSSION

4.1 Visual Observation of Distillate

From all the 12 runs that has been performed, it was observed that the product from the cracked rubber seed oil was formed in two or three immiscible layers after condensation inside the dean stark. Both layers were discarded separately using 2 sample-collecting vials and labelled. The dark brown colour of the top layer represented the short-chain fatty acids, whereas the gold bottom layer represented the liquid hydrocarbon substance that hypothetically considered as saturated hydrocarbons. This is because during the cracking process, the long-chain triglycerides were broken either one or more places in every single chain.

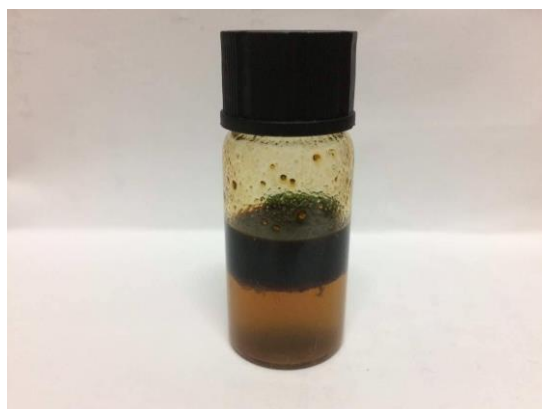


Figure 4.1 Sample Obtained from Fluid Catalytic Cracking of Rubber Seed Oil (RSO)

4.2 Gas Chromatography Mass Spectrometry (GCMS)

The sample collected from FCC of RSO is analysed using GCMS by taking n-pentane as the standard solution. One sample is analysed for 40 minutes. GCMS analysis is conducted to determine the composition of gasoline in the sample obtained. The result or chromatogram obtained from the analysis is interpreted and tabulated in Table 4.2.1.

Table 4.2.1 Gasoline fraction obtained from GCMS Analysis

No. of run	Mass of catalyst (g)	Reaction Time (minute)	Gasoline Fraction (%)
1	0.5	1	84.84
2	1.0	1	21.77
3	1.5	1	12.11
4	2.0	1	55.11
5	0.5	5	69.84
6	1.0	5	67.77
7	1.5	5	83.53
8	2.0	5	55.16
9	0.5	10	60.52
10	1.0	10	74.07
11	1.5	10	74.48
12	2.0	10	78.6

In order to determine the gasoline fraction, the chromatogram is analysed by using the list of average retention time obtained for each component as shown in Table 4.2.2. However, the average retention time stated was only the approximation; the main priority was the retention time range itself. From Table 4.2.2, it could be considered that, all the components between 2.54 until 7.08 minute were considered as biogasoline. Whereas all the components below 2.54 minute were considered as biogasoline and all the components those exceed 7.08 minute were considered as biodiesel.

Table 4.2.2 List of retention time for hydrocarbon compound

Compound Name	Compound Formula	Retention time (minute)
1-Hexene	C_6H_{12}	2.54
Hexane	C_6H_{14}	2.62
Cyclopentene,1-methyl-	C_6H_{10}	3.19
1-Heptene	C_7H_{14}	3.66
Heptane	C_7H_{16}	3.79
Cyclohexane,methyl-	C_7H_{14}	4.22
Cyclohexene,1-methyl	C_7H_{12}	4.92
1-octene	C_8H_{16}	5.21
Octane	C_8H_{18}	5.36
Cyclohexane,ethyl-	C_8H_{16}	6.04
Cyclohexene,1,2,-dimethyl-	C_8H_{14}	6.61
1-Nonene	C_9H_{18}	6.93
Nonane	C_9H_{20}	7.08

According to the standard procedure of GC analysis method on fluid organic samples, the quantity of sample taken for GC analysis was very small (5.0 μ l mixed with 1500.0 μ l GC-grade n-pentane), and then followed with 1.0 μ l mixture injected into GC column, the possibilities of the resulting yield differentiation could occur. For example, the 3rd experiment run (10 g RSO, 1.5 g catalyst, 250 $^{\circ}$ C, one minute of cracking) yielded 12.11%, but this yield would change if the same sample was reanalyzed 2nd time onwards with lower yields, either slight lower or far lower than 12.11%. This was because the cracked molecules moved randomly and independently in the “huge space” among n-pentane molecules, so not all the cracked molecules were sipped and injected together. Generally, the yield resulted directly correlated with the amount of sipped and injected cracked molecules during overall GC analysis.

4.3 Effect of Catalyst Mass and on the RSO Conversion and Biogasoline Yield

Table 4.3 Effect of catalyst mass to the RSO conversion and biogasoline yield.

Run	Catalyst mass in gram	Other parameters	Result obtained in %		
			Converted RSO	Liquid product	Gasoline yield in RSO
1	0.5	250 ⁰ C, 1 min	26.47	10.78	9.05
5		250 ⁰ C, 5 min	70.3	38.6	26.96
9		250 ⁰ C, 10 min	98.02	47.52	28.76
2	1.0	250 ⁰ C, 1 min	28.43	3.92	0.85
6		250 ⁰ C, 5 min	37.25	48.04	32.56
10		250 ⁰ C, 10 min	38.83	58.25	43.15
3	1.5	250 ⁰ C, 1 min	45	8	0.97
7		250 ⁰ C, 5 min	94.12	69.61	58.15
11		250 ⁰ C, 10 min	78.21	55.45	41.29
4	2.0	250 ⁰ C, 1 min	50	9	4.96
8		250 ⁰ C, 5 min	96	64	35.3
12		250 ⁰ C, 10 min	69.61	53.92	42.4

Table 4.3 represents the effects of catalyst mass for each run on rubber seed oil conversion, liquid product condensate formed and biogasoline yield obtained. From the table, 1.5 g catalyst used at five minutes reaction time showed the highest yields of biogasoline in RSO, which is 58.15%. The result also showed that RSO conversion was obviously affected by the masses of catalyst used. Based from the result, the reaction time also effect the RSO conversion and biogasoline yield as shown by run 1,2,3 and 4 with the lowest conversion of 26.47%, 28.43%, 45% and 50% respectively at one minute reaction time. For experiments run at catalyst mass of 0.5 g and 1.0 g, the result trend show the increasing conversion is achieved as the reaction time is longer. However, for experiments run at catalyst mass of 1.5 g and 2.0 g, the conversion is decreasing after five minute reaction time.

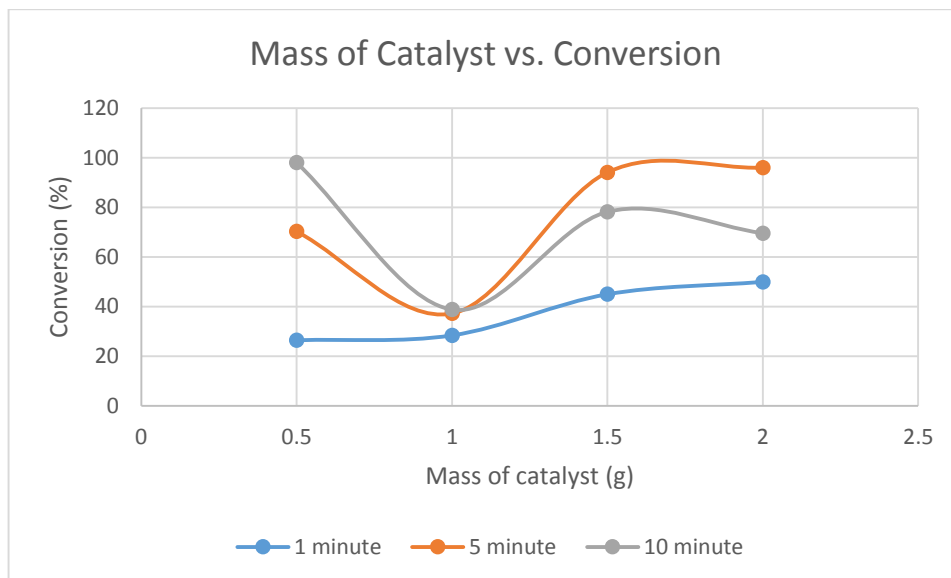


Figure 4.3.1 Mass of Catalyst vs. Conversion

Eventhough highest conversion of 98 % was achieved when the amount of catalyst used is 0.5 g, the yield of biogasoline is lower compared to experiment run using 1.5 g of catalyst. This is because the percentage of liquid product condensed from the experiment using 0.5 g of catalyst is also lower than 1.5 g of catalyst. Low conversion resulted lower biogasoline yield. The yield was affected by the lower percentage of liquid product condensed. This was caused by the opening spaces between the catalyst particles, the reaction surface and voids among the catalyst, and the limitation of heat supply, period and space of recombining and isomerizing cracked molecules.

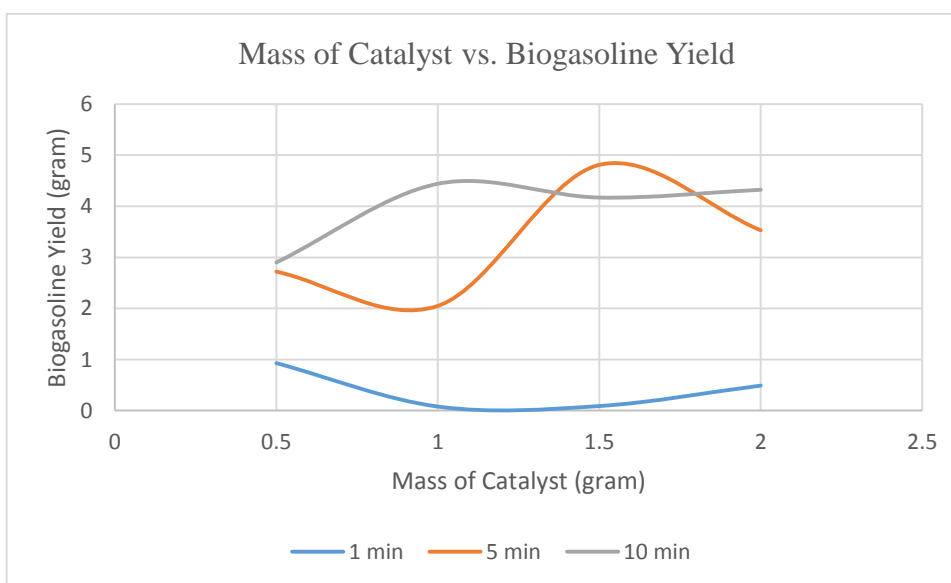


Figure 4.3.2 Mass of Catalyst vs. Biogasoline Yield

Figure 4.3.2 shows that three line are plotted represents the biogasoline yield (g) at different catalyst mass (g) at different reaction times (minute). The highest peak shows the highest yield of biogasoline. From Figure 4.3.1, the experiment run using 1.5 g of catalyst at five minutes reaction time gave the highest peak represent the highest yield of biogasoline. When the amount of catalyst used are 0.5 g, 1.0 g, 1.5 g and 2.0 g, the average biogasoline yield are 2.18 g, 2.19 g, 3.02 g and 2.78 g respectively. This shows that the highest yield was achieved when the mass of catalyst used is 1.5 g.

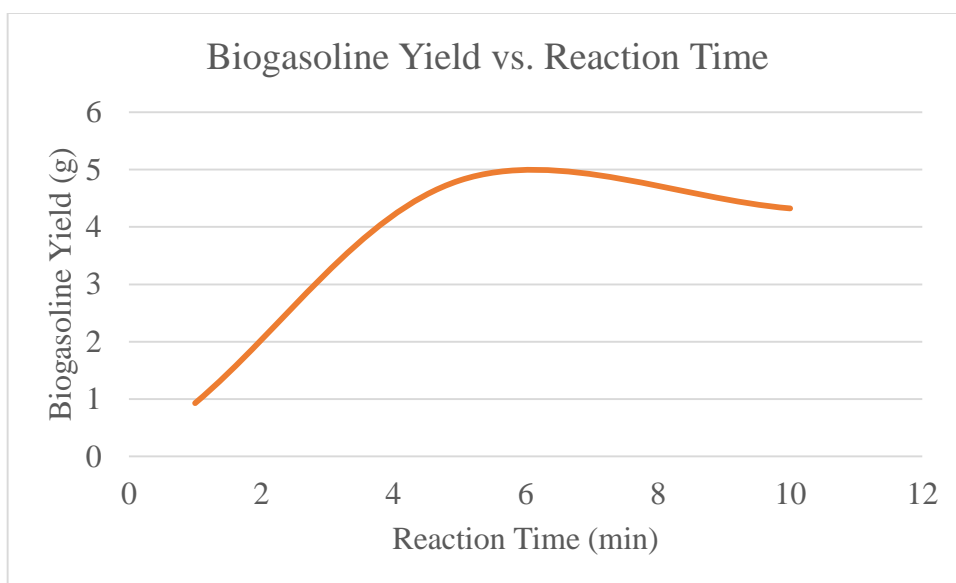


Figure 4.3.3 Biogasoline Yield vs. Reaction Time

Figure 4.3.3 represents the relationship between the reaction time and biogasoline yield. It was shown that the shorter reaction time was not enough to crack RSO at maximum amount, but the longer duration would also increase the gaseous products of that conversion. This was because both liquid product and biogasoline yield obtained were lower for ten minutes cracking than for five minutes cracking. In overall, all those parameters affected the overall results obtained, thus the overall results obtained were parallel.

From the result shown in Table 4.3, the liquid product obtained did not fully follow the RSO conversion because the conversion itself produced various multi-phase products. However, it was agreed that low conversion resulted lower yields, for example, for 1.0 g catalyst used at one minute reaction time. This situation occurred due to opening spaces between the catalyst particles, the reaction surface and voids among the catalyst, and the limitation of heat supply, period and space of recombining and isomerizing cracked molecules.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conclusion, the mass of catalyst and reaction time affect the conversion of RSO and biogasoline yield through fluid catalytic cracking (FCC) process. The reason why FCC is selected for this experiment is due to the temperature of catalytic cracking process (450°C) is lower than pyrolysis (500–850°C) (Chew and Bhatia, 2008) which later supported by Taufiqurrahmi and Bhatia, 2011 whom stated that in the cracking process, the reaction temperature applied is lower than pyrolysis. According to Huber and Corma (2007), compared to hydrotreating and hydrocracking, the significances of catalytic cracking include that no H₂ is needed, atmospheric processing reduces operating cost, and the temperatures employed are similar to those used in the production of bio-oil. Besides, FCC also considered as a cheaper route in terms of energy consumption, by converting feedstock to lighter fractions that mostly fall in the gasoline boiling range (Zhang et al., 2005). Then, Dean Stark apparatus is chosen as the experimental set up for this study due to its simplicity in term of easy to be set up, easy to be handled, besides it provide sufficient accuracy and relatively cheap and officially sanctioned for many applications (Torsaeter and Abtahi, 2000).

Experimentally, it is proven that the mass of catalyst at 1.5 g shows the highest yield of biogasoline whereas the highest conversion of RSO is achieved at catalyst mass of 0.5 g. Eventhough the highest conversion is achieved, however the gasoline yield is lower. Thus, in this study, the optimum condition to achieve the highest yield of biogasoline is using 1.5 g of catalyst and 10 g of RSO at 250 °C for duration of five minutes. According to the previous study, there are a lot of sources and catalyst used to synthesis biogasoline. However, there is none of the research done yet to study the effect of catalyst, ZSM-05 on biogasoline synthesis. Thus, this research is considered worth to be studied.

5.2 Recommendation

There are a few recommendations have to be taken into consideration in order to improve this research. The parameters of this study should be widen so it will provides clearer view about this research. Secondly, the use of heating mantle in this research should be replaced with oven to improve the extraction process and also the catalytic cracking process. This is because, when using the heating mantle, the heat supplied to the process is difficult to be maintained at desired temperature. Thus, it will affect the result of the process as temperature is one of significant parameter in order to obtain a high yield of biogasoline

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