

**BIOGASOLINE SYNTHESIS THROUGH FLUID CATALYTIC CRACKING
OF RUBBER SEED OIL– EFFECTS OF CRACKING TEMPERATURE**

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UNIVERSITI MALAYSIA PAHANG**

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OF RUBBER SEED OIL– EFFECTS OF CRACKING TEMPERATURE**

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Thesis 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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Dedicated to my family, and my friends.

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ABSTRACT

Biogasoline generally can be produced from the fluid catalytic cracking process of vegetable oils, including rubber seed oil which is the alternative of gasolines sources that overcome the depletion of fossil fuel. Rubber seed oil has been converted into biodiesel in the previous research. However, biodiesel is only limited to diesel engines. Therefore, this research aims to focus on the effects of cracking temperature of the rubber seed oil in the biogasoline production via fluid catalytic cracking process to fulfil the biogasoline demand. The experiment in this research is being conducted by using laboratory-scaled set-up fluid catalytic cracking method. Through this method, the rubber seed oil is vaporized, condensed and collected in the attached Dean Stark trap. This method provides an easy-handling and easy-monitoring experiment as well as producing yield at sufficient amount. Zeolite ZSM-5 is selected as the catalyst used in this method due to its thermal stability and good shape-selective properties. The optimum cracking temperature of the fluid catalytic cracking of rubber seed oil was investigated by varying the temperature within 250°C to 400 °C with fixed masses of catalyst and rubber seed oil. Also, the reaction time of the experiment are varied in the range of 1 to 10 minutes. The liquid product of the experiment will then be analysed by using the gas chromatography analysis which provides information regarding the gasoline fraction in the liquid product. From these results, optimization of the temperature and reaction time of fluid catalytic cracking of rubber seed oil in biogasoline synthesis is determined. The yield of the biogasoline is expected to increase as the temperature goes higher due to quantity of molecules being cracked increases as heat is supplied. The heating energy supplied will crack the chain of the rubber seed oil. However, the temperature limit is set to be at 400°C as it is expected that the reaction rate will decrease beyond this temperature due to changes of the catalyst structure caused by the breaking link within the catalyst. Therefore, the optimization of cracking temperature can be determined based on biogasoline yield obtained. The optimized temperature will provide optimum biogasoline yield. Thus, the optimum condition of the fluid catalytic cracking process can be improved. This will contribute in increasing the production capacity of the biogasoline that will allow the substitution of the biogasoline in the gasoline usage to be fulfilled.

ABSTRAK

Biogasolin secara umumnya dihasilkan melalui proses cecair peretakan bermangkin minyak sayur-sayuran. Minyak biji getah telah digunakan untuk penghasilan biodiesel dalam kajian yang lalu. Namun, penggunaan biodiesel hanyalah terhad kepada enjin diesel. Oleh itu, kajian ini bermatlamatkan fokus terhadap suhu peretakan minyak biji getah dalam penghasilan biogasoline melalui process cecair peretakan bermangkin untuk memenuhi permintaan biogasolin dalam penggunaan enjin biogasolin. Minyak biji getah akan melalui proses cecair peretakan bermangkin untuk menghasilkan biogasolin. Eksperimen yang digunakan dalam kajian ini dijalankan menggunakan kaedah cecair peretakan bermangkin berskala makmal. Melalui kaedah ini, minyak biji getah diwapkan, dikondensasikan dan disimpan di dalam perangkap Dean Stark. Kaedah ini meediakan pengendalian dan pengawalan eksperimen yang mudah dan juga menghasilkan hasil pada jumlah yang mencukupi. Zeolite (ZSM-5) dipilih sebagai pemangkin dalam proses peretakan bermangkin ini kerana sifat pengaliran habanya yang stabil dan kemampuannya yang baik dalam pemilihan bentuk. Suhu peretakan cecair bermangkin juga dipelbagaikan dalam kadar 200°C kepada 400 °C dengan jisim pemangkin dan minyak biji getah yang ditetapkan. Produk terhasil akan dianalisa menggunakan analisis gas kromatografi. Keputusan gas kromatografi biogasolin tersebut akan dibandingkan dengan gasolin standar dan komponen gasoline standar sebagai kawalan. Melalui keputusan yang diperolehi, pengoptimuman suhu cecair peretakan bermangkin minyak biji getah dalam penghasilan biogasolin dapat dikenalpasti. Hasil biogasolin dijangka meningkat dengan kenaikan suhu kerana kuantiti peretakan molekul yang turut meningkat disebabkan oleh pembekalan haba. Tenaga pemanasan akan meretakkan rantaian molekul minyak biji getah. Walau bagaimanapun, suhu had yang ditetapkan adalah 400°C kerana dijangka pada suhu melebihi suhu tersebut, kadar reaksi akan berkurang kerana perubahan pada struktur pemangkin yang disebabkan oleh rangkaian pemangkin yang terputus. Justeru pengoptimuman suhu peretakan dapat dikenalpasti berdasarkan hasil biogasolin yang diperolehi. Seterusnya, keadaan optimum untuk proses cecair peretakan bermangkin dapat diperbaiki. Ini akan menyumbang kepada penambahan kapasiti penghasilan biogasolin seterusnya dapat memenuhi pengantian biogasolin dalam penggunaan gasolin.

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LIST OF SYMBOLS

| | |
|-----|-------------------|
| W | weight |
| X | conversion of RSO |
| Y | yield of RSO |

LIST OF ABBREVIATIONS

| | |
|-------|-----------------------------------------------------------|
| CPO | Crude Rubber Palm Oil |
| CRSO | Crude Rubber Seed Oil |
| DHA | Detailed Hydrocarbon Analysis |
| FCC | Fluid Catalytic Cracking |
| PIANO | n-paraffin, isoparaffin, aromatic, naphthalene and olefin |
| REY | Rare Earth-Y catalyst |
| RSO | Rubber Seed Oil |
| USY | Ultrastable- Y catalyst |

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Biogasoline is liquid biofuels that have the potentials for replacing gasoline. Gasoline is the volatile liquid petroleum fraction whose boiling point ranges from around 30 to 200 °C, comprising a mixture of hydrocarbons from C4 to C12 (Tsuchida et al, 2008) . Gasoline is being used as the world's major automotive fuel and source of energy. Currently gasoline is produced from crude oil, therefore the world might encounter its depletion someday. The consumption of this fossil fuel has also discharge a huge amount of carbon dioxide into the atmosphere which lead to global warming.

Biogasoline is the solution for having a sustainable source of energy replacing the gasoline while maintaining its ecofriendly environment. It contains between 6 (hexane) and 12 (dodecane) carbon atoms per molecule and can be used in internal-combustion engines. Its characteristics are intended to match the chemical, kinetic, and combustion characteristics of its petroleum counterpart, but with much higher octane levels (Jujarama et al., 2014). Therefore, pure biogasoline can immediately be used as a drop-in substitute for petroleum gasoline in any conventional gasoline engine, and can be distributed in the same fueling infrastructure, as the properties match traditional gasoline from petroleum. Due to biogasoline's chemical similarities with gasoline, it can also be mixed with regular gasoline.

Biogasoline can be synthesized by fluid catalytic cracking process. Catalytic cracking is the conversion processes used in petroleum refineries and is widely used to

convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable and lighter gasoline, olefinic gases, and other products.

Rubber seed oil (RSO) is a promising feedstock for biogasoline production which is extracted from the rubber seed of the rubber tree. Up to now the rubber seed has no major application and therefore these seeds are regarded as waste. Since Malaysia has an estimated of 1,229,940 hectares of rubber plantation producing an estimated average of more than 1.2 million metric tons of rubber seeds annually (Malaysian Rubber Board, 2009), a sustainable source of renewable energy may be available. The rubber seed consist of about 40% kernel with 20-25% moisture. Approximately 40-50% of oil is found in the dried kernel which may contribute to 20 million liters of oil yearly (J. Gimfun et al., 2012).

Consequently, production of biogasoline from RSO could economically benefit the country and at the same time prevent waste generation. Hence in this paper, the aim is to analyze and characterize the optimum conditions of fluid catalytic cracking process of RSO in terms of cracking temperature and reaction time. The appearance and the purity of the biogasoline produced will be examined. This analysis can potentially help in determining the suitability of the RSO fluid catalytic cracking process for biogasoline production.

1.2 Motivation

The growing concern regarding on the depletion of the fossil fuel and environmental awareness has initiated the thought of preparing a renewable energy source that can replace the use of gasoline from crude petroleum oil. With the technology of biogasoline synthesis from fluid catalytic cracking process, mass crops can be utilized well and help in increasing the production capacity of the biogasoline. Nowadays, the common feedstock of vegetable oils that are widely used in production of biogasoline in Malaysia is palm oil. However, this research is focusing on using the rubber seeds oil as the feedstock of the biogasoline synthesis. The outcome of this research will improve the biogasoline synthesis from rubber seed oil via the process of fluid catalytic cracking. Furthermore, using rubber seeds oil is considered as an advantage as the rubber seeds are being largely available in Malaysia which will ensures

the sustainability of these mass crops for the biogasoline production. From this research, optimum temperature and reaction time of the fluid catalytic cracking process of RSO will be provided and that will help in utilizing well the crude RSO. Therefore, the production capacity of the biogasoline can be increase and RSO will be a promising alternative energy source to fuel vehicles in the future.

1.3 Problem Statement

In order to increase the production capacity of biogasolines, RSO is used as the feedstock in this study so that another type of mass crop can be utilized as well for the biogasoline synthesis. Plus, it is reported that RSO has no major application in the biogasoline production and previous research are more focusing on the RSO conversion to biodiesel. Somehow, it is not yet commercialized. It is ought to know that biodiesel usage is only limited to diesel engines. Therefore, it is important to study the optimum condition of the fluid catalytic cracking process of rubber seed oil in the biogasoline synthesis to contribute to large production capacity of biogasolines and will be able to fulfil the biogasolines demand.

1.4 Objectives

The following are the objectives of this research:

- 1) To synthesis biogasoline from RSO by fluid catalytic cracking
- 2) To optimize the temperature of fluid catalytic cracking process of RSO for biogasoline synthesis with effects of residence time of reaction.
- 3) To determine the yield of biogasoline formed after RSO conversion being completed and correlate the yield and conversion with cracking temperature.

1.5 Scopes of Study

The following are the scopes of this research:

- 1) RSO undergo fluid catalytic cracking process to be converted to biogasoline.
- 2) The cracking temperature of the fluid catalytic process is varied in the range of 250°C - 400° C with fixed masses of catalyst and RSO.
- 3) Analyze cracked RSO using Gas Chromatography (GC) with comparison using commercial gasoline and standard gasoline component as controls.
- 4) Determination on conversion rate affected from the cracking temperature by varying the reaction time.

CHAPTER 2

LITERATURE REVIEW

2.1 Rubber Seed Oil (RSO)

Every year, Malaysia is estimated to produce the average of more than 1.2 million metric tons of rubber seeds (Eka et al., 2010). With an estimated acreage of 1,229,940 hectares of rubber plantation (Malaysia Rubber Board, 2009), Malaysia has the potential in the sustainability of supplying the feedstock of biogasoline production from RSO. So far, the Malaysia economy is only contributed by the natural rubber industry. In terms of the biogasoline production, the rubber industry has not been well utilized yet which mean rubber seed do not have main application (Natural Rubber Statistic, 2016). However, RSO has found to be as non-edible oil which could be the alternative in biogasoline production. RSO is extracted from the from the rubber seeds. Instead of being regarded as waste, the rubber seed can gives about 40% kernel with 20-25% moisture in their content. Generally, about 40-50% of oil is can be obtained from the dried kernel of the rubber seeds. And that will contributes about 20 million litres of oil per year (J. Gimnun et al., 2012).

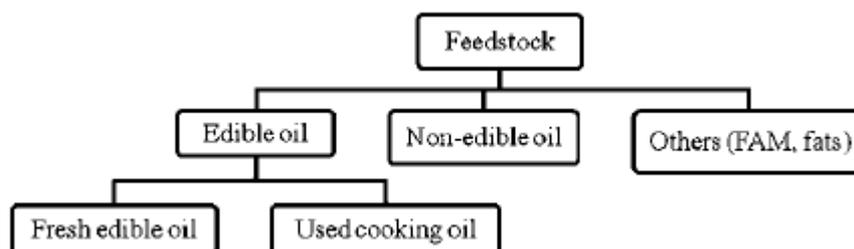


Figure 2.1: Type of feedstock for biofuel production (Niken Taufiqurrahmi et al., 2011).

In the production of biogasoline in Malaysia, the main feed stocks used is palm oil as Malaysia is known as world's largest exporter of palm oil (Malaysian Oil Palm Industry, 2009). Therefore, the properties of RSO has been analyzed in comparison with the properties of crude palm oil (CPO). By this way, the effectiveness of the RSO as the feedstock of the biogasoline can be ensured in parallel with the CPO. Therefore, Malaysia can depend on other resource of feedstock for the biogasoline production instead of CPO.

Table 2.1: Physicochemical properties of CRSO and CPO (Singh et al., 2016).

| Properties | Crude RSO | Crude Palm Oil [17, 18] |
|-----------------------------------------|------------|-------------------------|
| Colour | Dark brown | Orange red |
| State | Liquid | Liquid |
| Viscosity (mm ² /s) | 40.86 | 38.1 |
| Specific gravity | 0.91 | 0.92 |
| Peroxide value (Mg/g) | 3.42 | 5.97 |
| Moisture content (wt. %) | 0.37 | 0.1 |
| High heating value, HHV (MJ/kg) | 39.71 | 40.8 |
| Acid value (mg KOH/g) | 83.76 | 18.5 |
| Free fatty acids, FFA (wt. %) | 41.64 | 7.23 |
| Iodine value (mg/I ₂ /g oil) | 118.8 | 50.6 |
| Sulphur content (wt. %) | None | None |

Form the above Table 2.1, it can be observed that at room temperature, the colour of RSO is dark brown. This type of colour is not really desirable for the biogasoline production. A gasoline liquid should be yellow in colour. CPO is orange-red for which it changes into clear light yellow oil when undergoes refining. However, the colour of RSO can be improved by refining the RSO (Singh et al., 2016). Therefore, there should not be any concern regarding the colour of the RSO since it could be overcome by the refining method.

For biogasoline production, the feedstock should be in liquid form. RSO has the potential as the feedstock in biogasoline production since it exists in the form of liquid at room temperature (Ishak et al., 2013). This state will allow easy process and provides stability to the process as well. The viscosity of the RSO were studied as well. It is reported that the viscosity of the RSO influences the gasoline standard. In the table 2.1 below, it is observed that the viscosity of the oil is high. High viscosity of the RSO might cause problems especially on the long term durability test. Therefore, it is not encouraged to run the oil as alternative fuel in compression-ignition engines even though with slight modification and maintenance (Singh et al., 2016).

Viscosity will increase as the temperature decreases. This property will affect the fluidity of fuel. When viscosity increases, fuel operation equipment might encounter disturbance in the injection. Due to this, during fuel atomization, soot formation and deposition on the engines might occur as well (Atabani et al., 2013). Increase in viscosity will also cause the degree of saturation in oils and hydrocarbon chain length increase (S.Yusup & M. Khan, 2010). However, there is the bright side of the high viscosity property whereby it is found that high viscosity promotes lubrication of the injector and avoids leakage and exhaustion generated by fuel injection pumps. High viscosity in RSO is considered as a limitation. This limitation is somehow can be reduced by using the catalytic cracking method (Singh et al., 2016).

Based on Table 2.1, in terms of specific gravity, RSO gives the value of 0.91. Only a small difference is noticed between the CPO specific gravity. This value shows that the oils are less dense than water. Besides that, specific gravity also indicates the presence of heavy elements in the oils (Nik et al., 2007). From the specific gravity, the specific energy can be determined. The specific energy will influence the size of the storage space needed. For fuel with higher energy contained in a specific volume, only a small space of storage is required in a vehicle (Singh et al., 2016).

The peroxide value of CRSO is reported to be 3.42 which is considered low. Peroxide value is the measure of the extent to which an oil sample has undergone primary oxidation (Delgado et al., 2016). Peroxide value shows the tendency of the oil to deteriorate during storage. Unsaturated oil tends to deteriorate as it absorbs more oxygen molecules. As a result, it gives a high value of peroxides reading. RSO is a potential biogasoline production feedstock since it has a low peroxide value. High peroxide number will eventually affect the structure of the biogasolines whereby it can change from a soluble structure to insoluble. Thus, in order to overcome these changes of structure, biogasoline fuels that are having the peroxide in olefin should undergo oxidative degradation. However, the gums or sticky resin form from the oxidative degradation will precipitate out of the gasoline fuel. This will give effects on the gasoline stability and the filter will be blocked as well. Engine efficiency will start decreasing too as there are deposits in the engine (Singh et al., 2016).

The moisture content of RSO is 0.37 wt. % which is higher than CPO which is 0.1 wt. %. However, it is still in the acceptable range. Low moisture content of oil is preferable because the shelf life of an oil can be prolonged. High moisture is not desirable as it will decrease the heat of combustion of the fuel and might lead to corrosion of the fuel system parts (Singh et al., 2016).

The standard measure of the energy content of a fuel is its heating value. The heating value is obtained by the complete combustion of a unit quantity of fuel in an oxygen-bomb calorimeter under carefully defined conditions (Demirbas, 2009). It is calculated based on the energy release per mass. From the definition itself, it is known that high heating value generate more energy per time. Based on Table 2.1, the heating value of the RSO and CPO are approximately the same.

RSO has higher acid value than CPO. This indicates that RSO is rich in carboxylic acid groups. The example of carboxylic acid groups are fatty acids which is produced by oil degradation and combustion. The information that can be obtained from acid value are such as the age, quality and degree of purity during storage and processing. Also, from the acid value, the extent of oxidative oil deterioration which caused by chemical or enzymatic activity can be monitored. It is also reported that feedstock storage period influence the acid value of an oil. Therefore, it is important to control this property as highly acidic oil can cause the fuel supply system and the internal combustion engine to corrode severely (Singh et al., 2016).

In terms of free fatty acid content, RSO has high value than CPO which are 41.64 and 7.23 respectively. This is expected as high fatty acid content give higher acid value. However, the acid value can be lowered by catalytic cracking. RSO is found to have higher iodine value 118.8 whereas CPO iodine value is only 50.6. High iodine value indicates the good cold flow properties (S. Yusup & M. Khan, 2010). However, as RSO is highly unsaturated, there is more tendency of oxidation and humidity to occur resulting in poor oxidation stability. The solution to this condition is by adding antioxidants to enhance the stability of the oil (Singh et al., 2016).

RSO is considered as environmental friendly as RSO are free of sulphur in its oil composition. Generally, for a gasoline combustion, converted sulphur compounds like

gaseous sulphur dioxide which is harmful for the environment is emitted. These sulphur dioxide compounds even reacts with vapor forming acidic and corrosive that can corrode and damage the combustion engine and its exhaust system. Therefore, low sulphur content is highly recommended in purpose of environmental and engine performance (Singh et al., 2016).

2.2 Fluid Catalytic Cracking (FCC)

Fluid catalytic cracking (FCC) is the term which is widely being used in a chemical or refineries plant. FCC is a process which involve the usage of catalysts to convert large molecule to a new small molecule of gasoline fuels or to convert heavy into lighter distillates. It is usually applied when involved conversion of high boiling point and high molecular weight gas oil into gasoline (Taufiqurrahmi et al, 2011).

There are many types of catalysts that can be used in cracking process. Those were Rare earth-Y (REY) and, finally, to the Ultrastable-Y (USY) and multi-zeolite catalysts (L. Li et al., 2014). However, during early times of catalytic cracking, it is reported that clays and amorphous silica alumina were used as catalyst (Miliken et al., n.d). The process of catalytic cracking of vegetable oil into biogasoline or generally known as liquid hydrocarbon production is not something new. Not only has been carried out on vegetable oils, the process has also taken place by using animal fats, and recycled cooking greases producing biofuels. This biofuels are found suitable for gasoline engines. And their contents are cyclic paraffins, olefins, aldehydes, ketones and carboxylic acids (Taufiqurrahmi et al., 2011).

Products obtained from the FCC process are not only gas. Organic liquid product, water and coke are obtained as well. Organic liquid product means the composition of hydrocarbons such as gasoline, kerosene, and diesel with respective to the boiling point ranges. As there are many catalysts available for the process, many research and studies have been conducted over various catalyst including the mesoporous one. The type of catalyst used in the FCC process influences the type of fuel and the yield. Therefore, concern are also given to the catalyst properties such as acidity, pore shape and size when choosing the suitable one. In terms of laboratory scale, there are three types of catalytic reactor are used for the laboratory evaluation of

cracking catalysts. Those reactors are fixed bed, fluidized bed and entrained flow reactors. (Taufiqurrahmi et al., 2011).

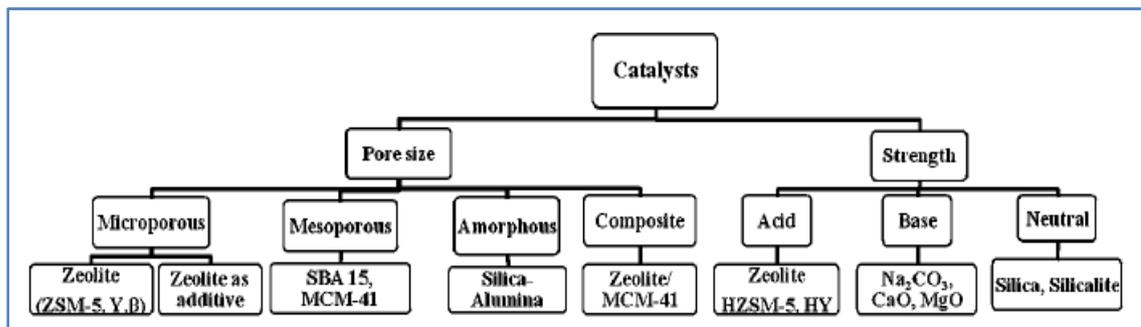


Figure 2.2: Catalysts for biofuel production through catalytic cracking. (Taufiqurrahmi et al., 2011).

2.3 Biogasoline

Biogasoline has been considered as an environmental friendly renewable energy source. It has chemical similarities with gasoline which allow the biogasoline to be the substitute of gasoline. In fact, both of gasoline and biogasoline can be mixed and found to be suitable for gasoline engine. Driven by this factor, studies on biogasoline production by various routes is not something new and are still being made for its improvement. Biogasoline are one category of biofuels produced by a living matter called biomass. In other words, it is can be produced via biomass synthesis such as algae or vegetables oil. Biogasoline consist 4 to 9 carbon number per molecule. (Rengga et al., 2014).

Biogasoline are from the composition of hydrocarbon which makes it different in chemical properties from biobutanol and bioethanol. During combustion of biogasoline, less carbon dioxide is emitted to the environment compared to combustion of gasoline from the petroleum crude oil. This might be because of plants use carbon dioxide, the major greenhouse gas of concern, to grow and produce food. So, plants are able to reduce the amount of carbon dioxide in the atmosphere and thus decrease global warming. Therefore, when grown from plants, can thus offset their CO₂ admissions

because they take up the gas during growth that is produced when the fuel is burned (Koltuniewicz, 2014).

In late March 2010, biogasoline is produced in plant size whereby it is noted as the world's first biogasoline demonstration plant. The plant was started in Madison by Virent Energy Systems, Inc. Virent. This company has discovered and developed a production technique called Aqueous Phase Reforming (APR) in 2001. The stated process involves reforming process of generating hydrogen, alcohols dehydrogenation, carbonyls hydrogenation, deoxygenation reactions, hydrogen lysis and cyclization. The APR process focused on the carbohydrate material as the feedstocks, and producing the mixture of chemical and oxygenated hydrocarbons as product. Further conventional chemical processing were carried out in order to gain the final product (R. D. Cortright, 2006). This factor has made the biogasoline suitable for the gasoline car engine therefore no adjustment or alteration need to be made on the engine of the vehicles while using the biogasoline. This is considered as cost effective way of utilizing the biogasoline and attention has been given to biogasoline development (J. E. Jacquot, 2008).

According to J. E. Jacquot, biogasoline is a hydrocarbon alternatives which would take advantage of the gas infrastructure. Therefore, it is said that the biogasoline do not need specialized infrastructure, blending technologies or new engine design is for its usage. Biogasoline is one the biofuels that does not consume much cost. Unlike the bioethanol production, it requires the plant sugars to be fermented and the distilled which is cost consuming. The company also emphasized that biogasoline has a higher energy content than ethanol and therefore it would deliver superior fuel efficiency.

2.4 Analysis Method

Most methods involve a sample preparation procedure followed by analysis using GC technique. Basically, by using GC, gaseous and liquid mixtures can be analyzed over wide temperature ranges (Lulova, 1974). In order to determine the standard of the biogasoline produced by the catalytic cracking process, a detailed

qualitative and quantitative analysis should be carried out. Examples of information that can be obtained via this analysis are such as their fractional composition, saturated vapor pressure, density and antiknock rating. All of the information regarding the content of n-paraffin, isoparaffin, aromatic, naphthene, and olefin (PIANO) groups of hydrocarbons and its oxyorganic compounds either alcohol or ether can be obtained by knowing the qualitative and quantitative composition of the gasolines (Cherepitsa et al,2001).

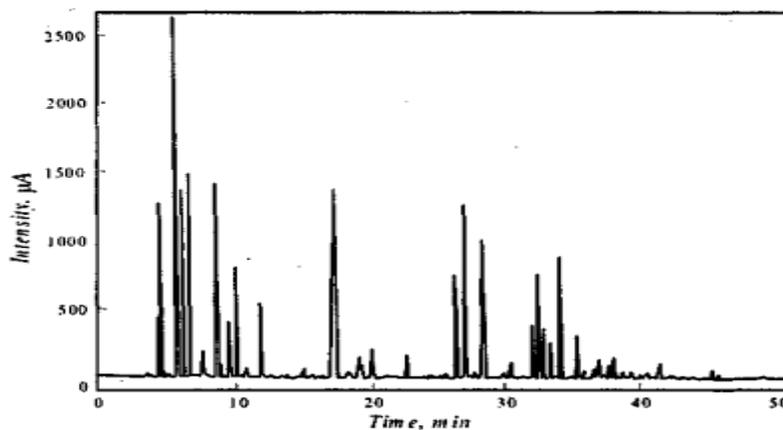


Figure 2.3: Typical chromatogram of automobile gasolines (Cherepitsa et al, 2001).

GC machine consists of a long glass tube packed with a powdered solid material, which is fitted into an oven. The tube is called the column. In analyzing the biogasolines, analysis of gas chromatography is done by using high-resolution capillary columns. High resolution capillary enables complete separation of hydrocarbon components of the product oil (Cherepitsa et al, 2001). A Detailed Hydrocarbon Analysis (DHA) system is install in the GC. Detailed hydrocarbon analysis (DHA) is a separation technique used by a variety of laboratories involved in the petrochemical industry for analysis and identification of individual components as well as for bulk hydrocarbon characterization of a particular sample (E. Connor, 2015). This system are design for data recording and processing systems of chromatographic operation. This technology allows connection of any type of chromatograph to the system.

Table 2.2: Effective octane factors found by linear regression method from the chromatographic data of gasolines samples. (Cherepitsa et al, 2001).

| Sr. No. of chromatographic gasoline group | Chromatographic group | Molecular mass | Saturated vapor pressure, kPa | Octane number | |
|-------------------------------------------|-----------------------------------------------------|----------------|-------------------------------|---------------|--------|
| | | | | MM | RM |
| 1 | Up to n-butane | 47 | 496.1 | 102.57 | 125.44 |
| 2 | n-Butane | 48 | 348.5 | 88.9 | 113.12 |
| 3 | Between n-butane and 2-methylbutane | 47 | 286.9 | 80.34 | 215.66 |
| 4 | 2-Methylbutane | 72 | 141.5 | 89.78 | 96.25 |
| 5 | Between 2-methylbutane and n-pentane | 70 | 123.3 | 115.08 | 180.32 |
| 6 | n-Pentane | 72 | 107.8 | 59.71 | 30.85 |
| 7 | Between n-pentane and 2-methylpentane | 76 | 67.8 | 110.37 | 122.76 |
| 8 | 2- and 3-Methylpentanes and intermediate components | 86 | 44.6 | 74.6 | 108.9 |
| 9 | Between 3-methylpentane and n-hexane | 82 | 36.3 | 77.28 | 104.4 |
| 10 | n-Hexane | 86 | 34.3 | 38.23 | 19.46 |
| 11 | Between n-hexane and benzene | 92 | 30.6 | 58.26 | 124.14 |
| 12 | Benzene | 78 | 22.3 | 87.33 | 111.94 |
| 13 | Between benzene and 2-methylhexane | 95 | 19.3 | 41.48 | 43.47 |
| 14 | 2- and 3-Methylhexanes and intermediate components | 100 | 16.6 | 89.5 | 55.74 |
| 15 | Between 3-methylhexane and n-heptane | 96 | 14.6 | 91.53 | 90.36 |
| 16 | n-Heptane | 100 | 11.2 | 34.38 | 15.04 |
| 17 | Between n-heptane and toluene | 94 | 10.6 | 49.56 | 34.38 |
| 18 | Toluene | 92 | 7.2 | 93.85 | 126.28 |
| 19 | Between toluene and 2-methylheptane | 114 | 5.3 | 70.07 | 188.36 |
| 20 | 2- and 3-Methylpentanes and intermediate components | 114 | 4.8 | 36.83 | 16.15 |
| 21 | Between 3-methylpentane and n-octane | 113 | 4 | 48.48 | 25.18 |
| 22 | n-Octane | 114 | 3.6 | 45.59 | 32.85 |
| 23 | Between n-octane and ethylbenzene | 126 | 2.7 | 49.22 | 39.55 |
| 24 | Ethylbenzene | 106 | 2.5 | 84.27 | 248.76 |
| 25 | Between ethylbenzene and m-xylene | 127 | 2.4 | 36.57 | 14.8 |
| 26 | m- and p-Xylenes and intermediate components | 106 | 2.3 | 109.87 | 62.54 |
| 27 | Between p- and o-xylenes | 127 | 2 | 33.39 | 19.95 |
| 28 | o-Xylene | 106 | 1.8 | 120.04 | 58.62 |
| 29 | After o-xylene and up to n-nonane | 130 | 1.3 | 34.49 | 16.1 |
| 30 | Between n-nonane and n-decane | 134 | 0.9 | 82.23 | 138.58 |
| 31 | n-Decane and components after n-decane. | 141 | 0.4 | 98.65 | 48.49 |

Set of data on the main hydrocarbons contained in gasoline are collected. Then, detailed analysis procedure of the hydrocarbon composition was prepared. Calculations of the complex characteristics of unethyated automobile gasolines were then carried out. The methods of calculation of the complex characteristics of these gasolines is then programmed and developed into software package that has been integrated into the system Unichrom-97 (Cherepitsa et al, 2001). In a simple word, Unichrom-97 is a fully automated Chromatographic Data System dedicated to simplify hard, routine work of chemist, whom deals in a field of gas and liquid chromatography.

During the gasoline analysis, GC will produce a chromatograms. Example of the chromatogram are as shown in Figure 2.3. The recorded chromatograms were then interpreted. The peak of the samples were identified on a spectrometer. There are various peaks ranging from methane to n-hexadecane can be identified. The relative retention indices gives the individual components of the samples. The weight content of each component was then calculated by the internal standardization method. The detector response factor is taken into account as well. Besides that, the concentrations of the hydrocarbon groups were determined by summation of the measured concentrations of individual components. In order to indicate the relative hydrocarbon group to not be more that 3%, comparative analysis is carried out (S.V Cherepitsa et al, 2001).

Another characteristic that can be determined by GC is the saturated vapor pressure. It is a function of molecular composition of the gasoline and can be calculated from the chromatographic data derived by DHA using the equation,

$$P = \sum_{i=1}^{31} C_{gi} P_i^0$$

Where:

P= is the saturated vapor pressure

C_{gi}= mole fraction of the i-th octane group of the gasoline,

p_i⁰ = the effective partial pressure of the components of the i-th group determined from Table 1. (S.V Cherepitsa et al, 2001)

Besides that, the density of the gasoline can be determined as well by using equation below, where

$$D = \sum_{i=1}^n X_i \rho_i$$

Where:

D = density of the gasoline

X_i = volume proportion of the i-th component,

P_i = density of the i-th component

n = the number of peaks on the chromatogram. (S.V Cherepitsa et al, 2001)

It can be concluded that, GC method is a suitable method to determine volumetric, mass, and molar content of individual hydrocarbons and PIANO groups of gasoline oil. Not only that, the oxyorganic compounds can be determined as well. The information about the fractional composition, the saturated vapor pressure and the octane number can also be determined.

CHAPTER 3

MATERIALS AND METHODS

3.1 Catalytic Cracking Experimental Method

Cracking refers to breaking up large hydrocarbon molecules into smaller and more useful bits. Catalytic cracking process is achieved by using lower temperatures and pressures in the presence of a catalyst. There are many experimental methods of catalytic cracking process stated in literature which can be conducted. One way is by using the method like in Figure 3.1.

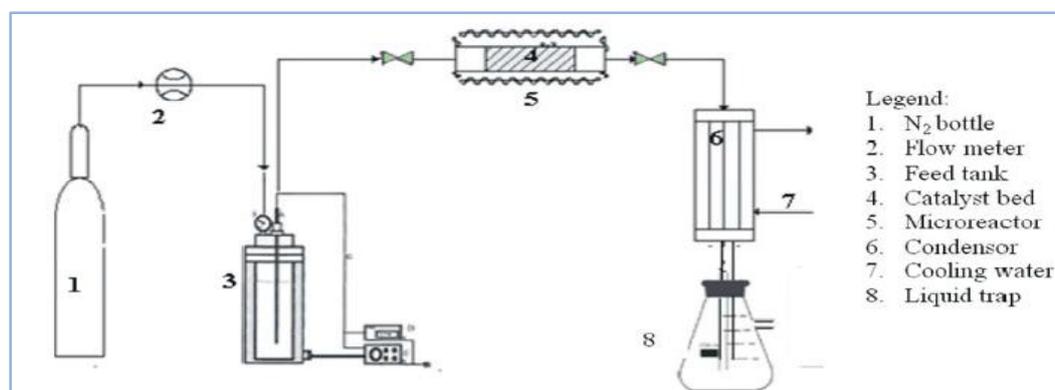


Figure 3.1: Experimental set up of the catalytic cracking of vegetable oils to produce biofuel (Sirajuddin et. al., 2013)

Based on Figure 3.1, the catalytic cracking was carried out in a microreactor filled with approximately 1g of catalyst bed and the reactor was sealed with a heating element. Vegetable oils was feed to the tank at flow rate between 100 – 160 ml.min⁻¹. Oil vapor and N₂ then flown to the fixed bed reactor which was already heated to a desired temperature. The catalytic cracking reaction was conducted for 120min. The products was then analyzed in a gas chromatography (Sirajuddin et. al., 2013).

Besides that, other method that can be used are as Figure 3.2, whereby the catalytic cracking was performed at atmospheric pressure with reaction temperature range of 673-823 K using a fixed-bed reactor. In the experiment, two reactors were used. The first reactor is for feed of refined vegetable oils and second reactor is for catalytic cracking reaction. Refined palm was heated and was evaporated to gas phase and cracking takes place. The product were collected in glass liquid sampled (Chuaykleang & Ratanawilai, 2014).

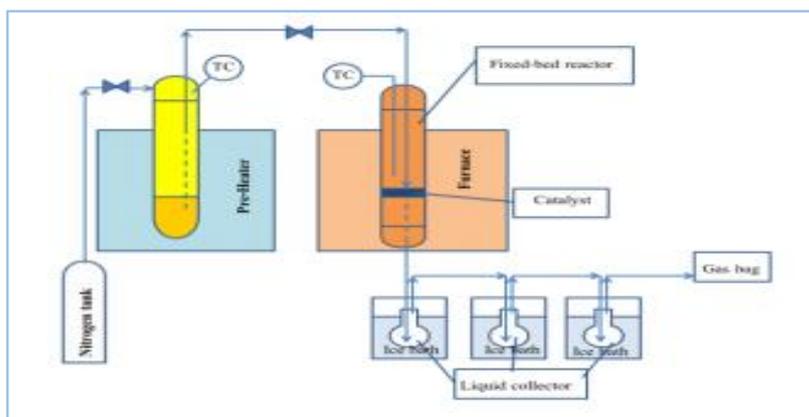


Figure 3.2: Diagram of catalytic cracking process. (Chuaykleang & Ratanawilai, 2014)

Lastly, other method that is commonly used is Dean Stark method. This method is in order to measure the fluid saturation in core sample by distillation extraction. In this method, the feed is vaporized then condensed and collected in the calibrated trap.

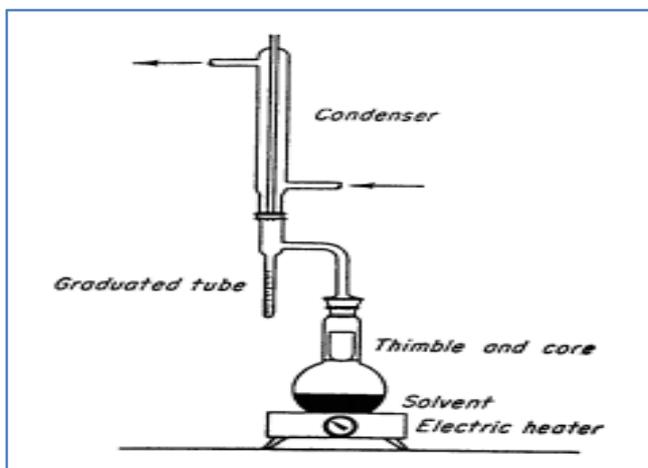


Figure 3.3: Dean Stark experiment set up (O. Torsæter & M. Abtahi, 2000)

Dean Stark method is being used in this study. This is because Dean stark is easier to be set up and handled compared to other analysis method. Dean Stark technique also produce yield at sufficient accuracy. Dean stark method is relatively cheap and officially sanctioned for many applications. The chemical and the equipment used in the experiment of this research are shown in Table 3.1 and Table 3.2.

Table 3.1: Chemical Used in the Experiment

| Material/Chemical | Purpose |
|--------------------------|-------------------------------------------------|
| Rubber Seed Oil | To be cracked to produce biogasoline |
| Catalyst (ZSM-5) | Used as catalyst the catalytic cracking process |
| n-pentane | Used as carrier solvent in GC analysis |
| Cooling water in and out | Receive heat from the condenser |

Table 3.2: Equipment Used in the Experiment

| Equipment | Purpose |
|--------------------------|------------------------------------------------------------------------------------------------------------------------|
| Gas Chromatography | Identify different substances within test samples. |
| Dean stark | Allow vapors from the reaction which contains the reaction solvent travel out of reaction flask up into the condenser. |
| Condenser | Used to condense substance from its gaseous state to liquid state. |
| Heating mantle | Allows adjustable temperature. |
| Stirrer bar | To provide uniform mixing. |
| Spherical reaction flask | To contain RSO and catalyst and allow reactions between those two materials occur. |

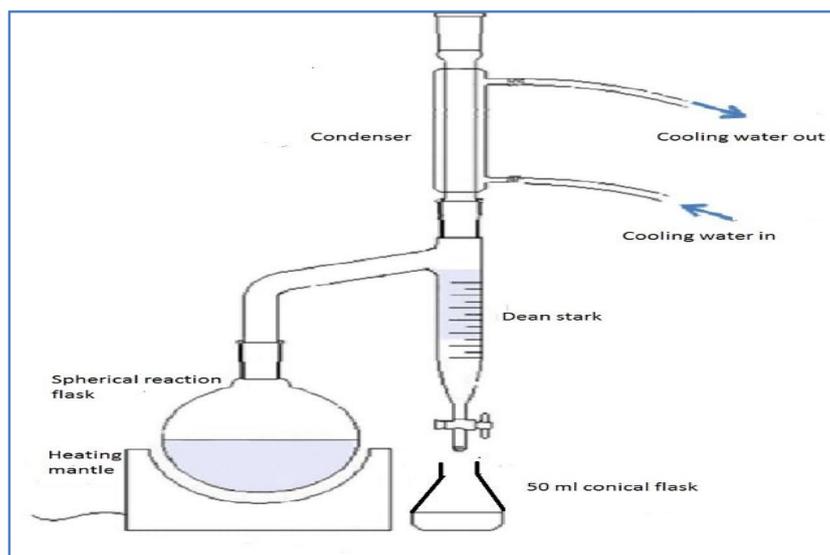


Figure 3.4: Experiment set up of the catalytic cracking of RSO to biogasoline

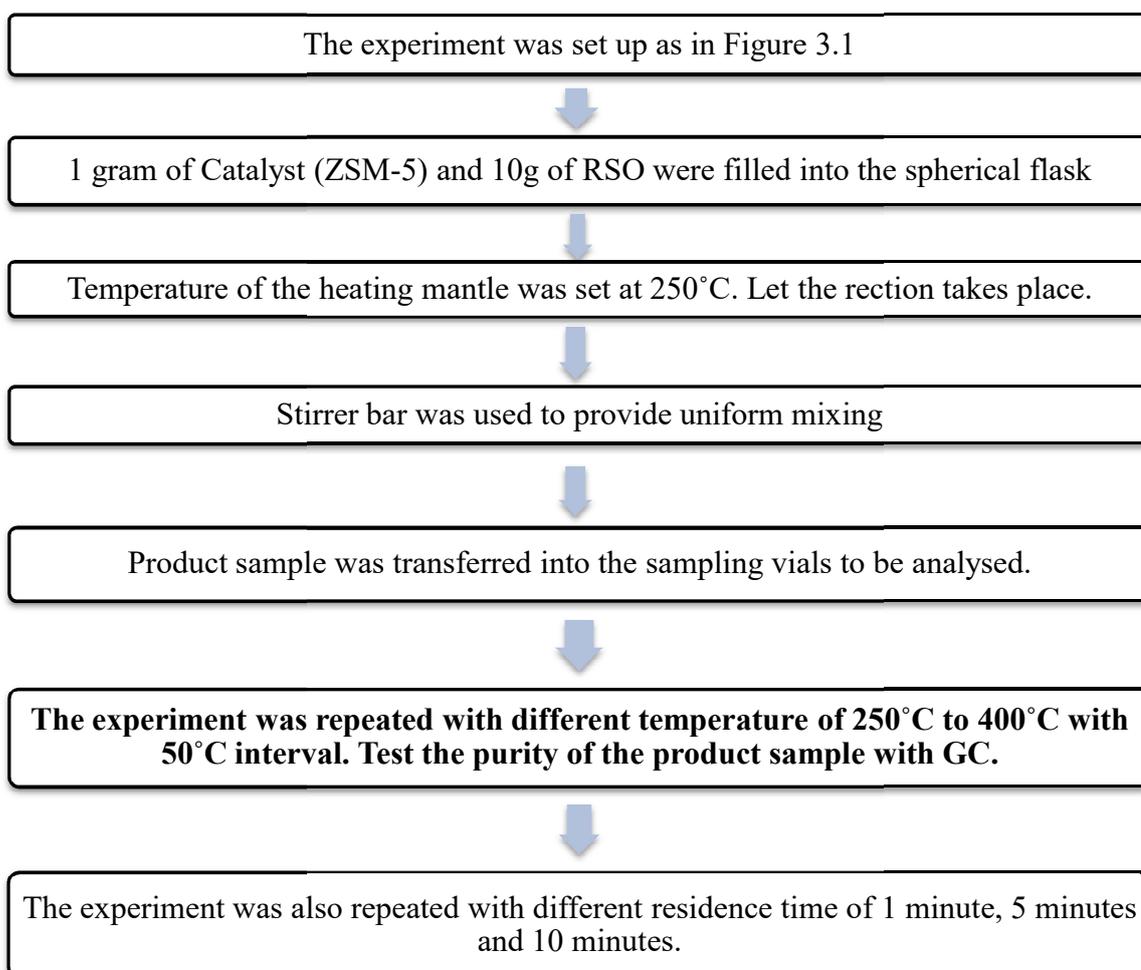


Figure 3.5: The process flow of Fluid Catalytic Cracking of RSO experiment.

Figure 3.4 and Figure 3.5 shows the experimental set up of the experiment of this research and the process flow of FCC of RSO experiment. The RSO and catalysts were mixed inside the spherical reaction flask and then heated by heating mantle. RSO was cracked and vaporized. The vapor entered into the dean stark inlet duct and then into the condenser, which the vapor was then condensed. The condensate entered the dean stark outlet duct with attached pipe, in which the condensate was collected. The weight of residue was the weight of unconverted oil. Zeolite (ZSM-5) is selected as the catalyst to be used in the catalytic cracking process due to its high thermal stability, good shape-selective properties, and ability to concentrate reactants inside the pores (W. Zhiping & Y. Shitao, 2016). Zeolite (ZSM-5) is commercially obtained.

3.2 Temperature differences

With the objective of optimizing the temperature for the catalytic cracking process, the temperature set at the heating mantle is the manipulated variable of this experiment whereby the experiment was repeated with different temperature of 250°C-400°C with 50°C temperature interval. It is expected that as the temperature goes higher, the yield of the biogasoline product will increase. This is because, when the temperature increases, the quantity of molecules being cracked increases due to heat supply (Murzin, 2015). The heating energy will crack the chain of the rubber seed oil. However, the temperature limit for this experiment has been set to 400°C. This is because, it is expected that the reaction rate will decrease. This might be due to the changes of the catalyst structure caused by the breaking link within the catalyst molecule (Murzin, 2015).

3.3 Reaction Time

The effects of the reaction time on oil conversion has been established in previous research. Therefore, under the same experimental condition, the reaction time is studied. It is reported that the reaction time is shortened as the reaction temperature is increased. This is because, high reaction temperature decrease the viscosities of oils. Also, the mass transfer of the reactants to the active site in the catalysts is improved.

This means as more energy is added to the system, the effective number of collisions increased which help to overcome the activation energy barrier.

Thus, reducing the reaction time. To study the effect of the reaction time, the experiment is conducted under the same conditions, however the reaction rate is varied in the range of 10 to 30 minutes with 5 minutes time interval. The reaction time in this study is limited to just half an hour to achieve a satisfactory levels of rubber seed oil conversion.

3.4 Experimental Analysis

Catalytic cracking experiments were carried out at temperatures ranging from 200°C to 400°C using the Dean stark analysis. The RSO and catalysts were introduced into the spherical reaction flask and then heated by heating mantle. RSO was cracked and vaporized. The vapor was then vaporized by the condenser. The weight of residue is which the weight of unconverted or phase that was not distilled is residual oil. The conversion (wt %) for RSO and yields (wt %) for bio-oil were as follows:

$$X, \text{ Conversion (\%)} = \frac{W_1 + W_2 - W_4}{W_1} \times 100\%$$

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

Where:

W1 = weight of RSO (g)

W2 = weight of catalyst (g)

W3 = weight of liquid fraction (g)

W4 = weight of residue (g)

(W. Zhiping & Y. Shitao, 2016)

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

This chapter is about the results and also the discussion for the biogasoline production through fluid catalytic cracking process.

4.2 Visual Observation on Distillate Product



Figure 4.1: Distillate product of RSO by using FCC

Figure 4.1 shows the distillate product of RSO by using FCC. Based on the experiment conducted, the distillate product of RSO catalytic cracking was collected after the condensation in the dean stark. It was observed that the distillate was formed in two or three immiscible layers. The top layer of the product is observed to be brown in colour whereas the bottom layer is observed to be golden translucent colour. The residue of RSO being cracked was observed to be viscous. The brown colour of the top

layer represented the short-chain fatty acids, whereas the clear bottom layer represented the liquid hydrocarbon substance that hypothetically considered as saturated hydrocarbons (Hassan, 2016). This is because during the cracking process, the long-chain triglycerides were broken either one or more places in every single chain.

In this experiment, it is proven that catalytic cracking process occurs from the hydrogenation process that takes place after cracking. This process has resulted the distillates to increase its lighter fraction after the process of fluid catalytic cracking product. The number of hydrocarbon content of the distillate product is identified and compared with the hydrocarbon content in RSO. The result of the analysis are shown in Table 4.1 and 4.2.

Table 4.1: Result of GC analysis of RSO (Ramadhas et al.)

| No. | Hydrocarbon molecule (as fatty acids) | Composition (% weight) |
|-----|---------------------------------------|------------------------|
| 1 | Palmitic acid C16:0 | 10.2 |
| 2 | Stearic acid C18:0 | 8.7 |
| 3 | Oleic acid C18:1 | 24.6 |
| 4 | Linoleic acid C18:2 | 39.6 |
| 5 | Linolenic acid C18:3 | 16.3 |

Table 4.2: Result of GC analysis of Distillate product sample

| No. | Hydrocarbon molecule | Composition (% weight) |
|-----|----------------------|------------------------|
| 1 | C6 | 58.42 |
| 2 | C7 | 3.2 |
| 3 | C8 | 21.64 |
| 4 | C9 | 2.4 |
| 5 | C10 | 6.87 |
| 6 | C12 | 7.39 |

From the above table, it is shown that the hydrocarbon molecules in Table 4.1 are linked to the triglyceride as fatty acids. The molecules are commonly dependent. However, from Table 4.2, it is found that the triglyceride molecules were cracked into

smaller molecules. Table 4.2 shows hydrocarbon of distillate product and the gasoline fractions are the molecules having 4 to 9 carbons atoms with their structure. These molecules were vaporized in the distillation process producing the distillates products which were also composed by the gasoline fraction. It is found that during the catalytic cracking process, the heat from the heating mantle has caused the triglyceride long-chain molecules being broken down into smaller molecules that firstly form in vapor and then partially condensed into liquid form.

4.3 Gas Chromatography Mass Spectroscopy (GC-MS) Analysis

The results of GC- MS analysis of the distillate product of catalytic cracking RSO are used in calculating the yield of the biogasoline. The yields of the biogasoline are determined from the gasoline fraction obtained from the GC-MS analysis. From the GC-MS results, the number of carbon in the product distillate are identified. Based on the quantification of the carbon number, the compound were classified into three classes from which gasoline (C4 to C9), kerosene (C9 to C15) and diesel (C4 to C16). The components with retention time of 1.65 to 7.08 are classified as gasoline (Rengga, 2015).

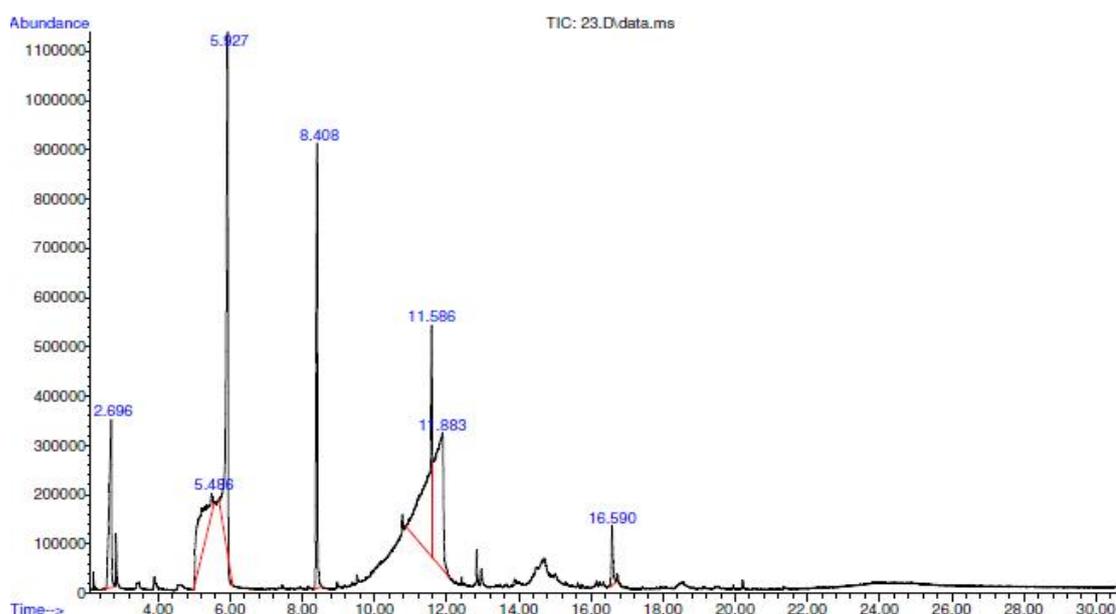


Figure 4.2: GC- MS chromatograms of the Distillate Products (350°C and 5 min)

The analysis of all chromatograms has shown that all samples has the gasoline component. From the peak area value, the gasoline component concentration can be calculated. Previous research reported that for commercial gasoline, there were a total of 25 components of mixture present which paraffin as the major component category, together with olefins, aromatics and oxygenates.

4.4 Effect of Temperature and Reaction Time

RSO was converted to liquid distillate at various cracking temperature and reaction time. Therefore, the effects of temperature and reaction time on the conversion of RSO at 1 gram of zeolite catalyst were investigated by varying the temperature and reaction time from 250 to 400°C and from 1 to 5 minutes respectively. The overall results of the RSO conversion, biogasoline fraction and biogasoline yield in 10 gram of RSO are tabulated Table 4.3.

Table 4.3: Overall results of FCC of RSO

| Experiment Run | | 5 | 6 | 7 | 8 | 23 | 24 | 25 | 26 | 37 | 38 | 39 | 40 |
|---------------------|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Cracking Temp (°C) | | 250 | 300 | 350 | 400 | 250 | 300 | 350 | 400 | 250 | 300 | 350 | 400 |
| Reaction Time (min) | | 1 | 1 | 1 | 1 | 5 | 5 | 5 | 5 | 10 | 10 | 10 | 10 |
| Mass (g) | Converted RSO | 1.7 | 1.7 | 1.8 | 2.7 | 2.8 | 3.2 | 4 | 4 | 3.8 | 4 | 6.3 | 5.4 |
| | Liquid product | 0.4 | 0.6 | 1 | 1 | 4.9 | 5.1 | 6.4 | 5.8 | 6 | 6.7 | 7.2 | 5.7 |
| | Gasoline yield | 0.09 | 0.13 | 0.25 | 0.16 | 2.05 | 1.86 | 2.98 | 2.23 | 4.44 | 4.08 | 5.99 | 3.37 |
| Percent (%) | Converted RSO | 16.67 | 16.83 | 17.65 | 26.72 | 27.72 | 32 | 39.60 | 38.83 | 37.25 | 40 | 63 | 54 |
| | Liquid product | 3.92 | 5.94 | 9.8 | 9.9 | 48.51 | 51 | 63.37 | 56.31 | 58.82 | 67 | 72 | 57 |
| | Gasoline yield | 0.85 | 1.32 | 2.48 | 1.59 | 20.29 | 18.60 | 29.52 | 21.62 | 43.57 | 40.88 | 59.98 | 33.72 |

Table 4.3 shows the effects of both temperature and reaction time set-up for each experimental run on the RSO conversion, liquid product distillates formed and biogasoline yield obtained. Referring to Table 4.4, the product distillate produced at

temperature 350°C is 72% which was the highest. This result occurs at 10 minutes reaction time. At 400°C, RSO converted and the gasoline yield were 54% and 33.72% respectively which were lower from the result obtained at temperature 350°C. It is also observed at 10 minutes reaction time at 400°C, the RSO converted is 54% with biogasoline yield lower than gasoline yield at 300°C. It is found that although the RSO were highly converted at that temperature, it does not mean that it can also produce high yield of gasoline fraction in the distillate. This is might be due to the catalyst limitation at high temperature.

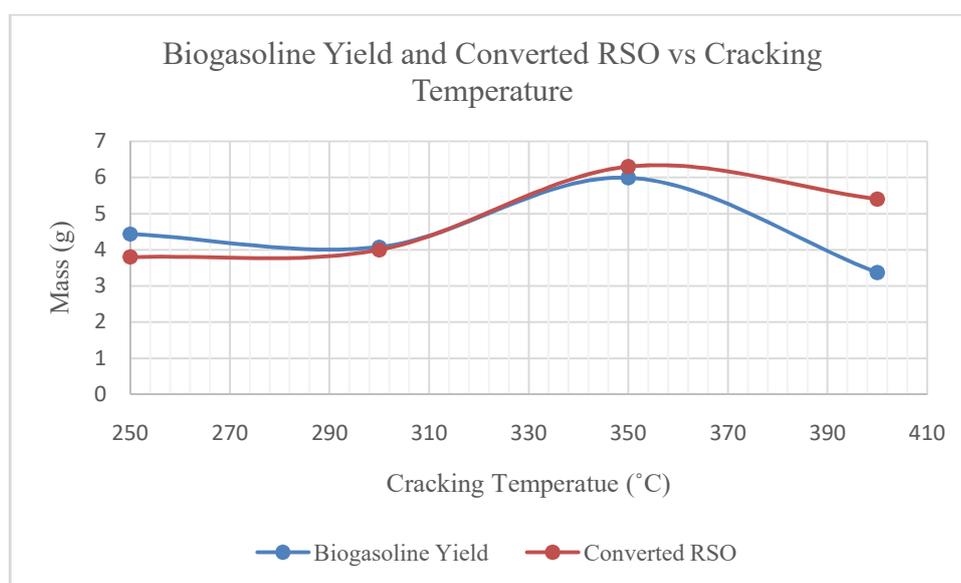


Figure 4.3: Graph of measured biogasoline yield and converted RSO affected by cracking temperature at 10 minutes reaction time.

From Figure 4.3, it can be observed clearly that both of the RSO conversion and biogasoline yield are affected by the cracking temperature. From the above figure, it was concluded that lower conversion of RSO gives lower yield of biogasoline. However, not all liquid product follow the trend of RSO conversion since RSO was converted to multiphase components. The optimum conversion of catalytic cracking of RSO is 63% at 350°C from giving a total of 72% of liquid product with total biogasoline yield of 59.98%. From the curve above, the gasoline yield and the converted RSO increase as temperature increase from 250 to 350°C and decrease as the temperature is increase to 400°C. The higher temperature of 350°C accelerates the thermal decomposition and changes the hydrocarbon molecules into light hydrocarbon molecule by catalytic cracking (Rengga, 2015). Also, at high temperature of 350°C, high catalytic

cracking occur as the result of high molecular energy gain from the increase in temperature. The decrease in biogasoline yield and RSO conversion at 400°C is due to the catalyst limitation at high temperature. High temperature can reduce the zeolite's reactivity by lowering its reaction surface, therefore less gasoline can be produce from the fluid catalytic cracking process at high temperature (Hassan, 2016). Also, the amount of catalyst added to the reaction conditions might be not sufficient to catalyze the cracking reaction resulting in the decrease in conversion of the product (Rengga, 2015).

Reaction time represent the interaction time between reactants and reactant-catalyst in the reaction system. The effect reaction time on biogasoline yield and the RSO conversion at temperature 350°C was plotted in Figure 4.4.

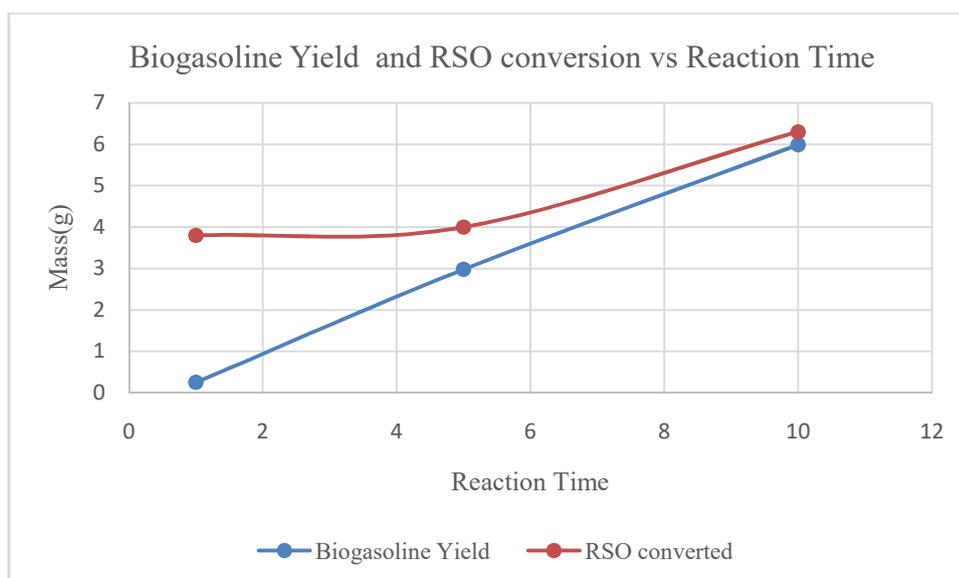


Figure 4.4: Graph of measured biogasoline yield and converted RSO affected by reaction time at temperature 350°C.

From Figure 4.4, it is observed that the highest biogasoline yield and RSO conversion RSO which are 59.98% and 63% respectively were achieved at 10 minutes reaction time. Based on the experimental result, it is found that all the experiment that were conducted at 1 and 5 minutes gives lower biogasoline yield which is at the range of 0.85 to 29.52% and RSO conversion which is in the range of 16.67 to- 39.60% only. Therefore, it is agreed that shorter cracking duration was not enough to crack 10 gram of RSO at maximum amount. From the figure obtained, it is agreed that the gasoline

yield and the RSO conversion increase with increasing reaction time. The longer the reaction time, the longer the interaction, and the greater the probability for the reaction (Rengga, 2015).

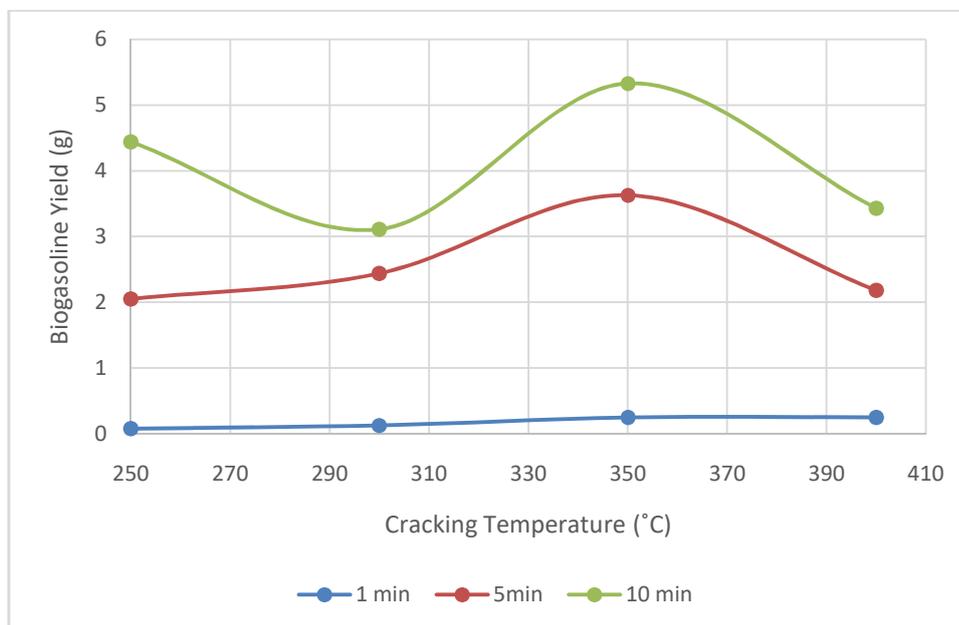


Figure 4.5: Graph of the effects of cracking temperature on the biogasoline yield at different reaction time.

The overall results of the experiment were plotted in Figure 3.4. From the figure, it was concluded that the highest biogasoline yield from rubber seed oil through fluid catalytic cracking was 59.98% at 350 °C, 1.0 g zeolite ZSM-5 catalyst used for 10 minutes processing for 10 gram rubber seed oil. From this research, the fluid catalytic cracking method is the best method of producing biogasoline compared to other reactions such as fermentation and pyrolysis method. Fermentation process requires the plant sugar to be fermented and distilled which is cost consuming (J. E. Jacquot, 2008). For the pyrolysis process, the process of producing biogasoline involves the high temperature of 551°C to achieve 48% of bio oil conversion (Hanif, 2016).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the overall study, it was concluded that the optimum condition of biogasoline synthesis from RSO was at 350°C and 10 minutes reaction time for 1.0 g zeolite ZSM-5 catalyst and 10 g rubber seed oil. The result obtained fitted the stated biogasoline yield results in the literature. Also, it was concluded that the fluid catalytic cracking is the best method of producing biogasoline as it does not involve the use of bacteria and higher temperatures to achieve high RSO conversion. Lastly, the objectives of this research study were successfully achieved which therefore proved that the RSO can be the resource of biogasoline by using the fluid catalytic cracking process.

5.2 Recommendation

For further recommendation, experimental study on Fluid Catalytic Cracking of RSO can be done by varying the reaction time for more than 10 minutes, with increase of RSO mass. By this way, the limitation of reaction time at which the gasoline production from RSO through FCC could be identified. From there, the performance of RSO within wide range of reaction time could be observed as well. Besides, in FCC study of biogasoline synthesis from RSO, different parameters can be used which can give the different percentage of biogasoline yield and RSO conversion. Parameters such as amount of catalyst used, type of catalyst used and ratio of catalyst and RSO can be applied too. In addition, the RSO possibly can be commercialized as the feedstock for biogasoline production that could make the rubber seeds in Malaysia are utilized well.

Further investigation and research is required from enhancing the biogasoline production from RSO feedstock.

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APPENDIX



Figure A.1: Experimental set-up of RSO FCC.