Characterization of Combustible Liquid from Thermal Cracking of Crude Palm Oil Using ZSM-5 Derived from Sungai Sayong Pottery Waste

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Demand of fossil fuels is increasing by year as the global consumption of fossil fuels also increase. Both of the problem will lead to depletion of fossil fuels. Hence, many researchers conducting research and development to find an alternative fuels for future needs. The thermal cracking process is cracking process of large organic molecular into a smaller size. There are many studies on thermal cracking of edible and non-edible oils. Hence, thermal cracking of crude palm oil (CPO) using ZSM-5 derived from Sungai Sayong pottery waste in a combustion reactor was conducted. The combustible liquid recovered from the process were characterized using bomb calorimeter, Fourier Transform Infrared Spectroscopy (FTIR) analysis and Gas Chromatography Mass Spectrometry (GCMS) analysis. The results showed that using derived ZSM-5 as a catalyst in the cracking process, producing combustible liquid with an average value of calorific which is 9144 kcal/kg. During the elemental analysis, there are presence of Carbon and hydrogen.

From the GCMS analysis, the highest compound that been identified is estragole followed by hexadecanoic acid methyl ester. These are proven as during the FTIR analysis, there is three type of functional group which alkyl, carboxylic acid and alcohol-phenol group. The derived ZSM-5 is not suitable to the all type of oil as referring to the performance in stearin cracking process.

Crude Palm Oil, Pottery Waste, Thermal Cracking, ZSM-5

I. INTRODUCTION

Over the past several years, non-renewable fossil fuels had been used for source of energy. The demand of this fossil fuels also increase as it becomes feedstock of petrochemical industry, used in transportation, and also generation of electricity. The high consumption of the fossil fuel will leading to depletion of petroleum reserve (Siswanto, Salim, & Wibisono, 2008). As reported by (Taufiqurrahmi & Bhatia, 2011), the world total consumption of the petroleum around 84 million barrels per day in 2005; the petroleum reserves are estimated to be depleted in less than 50 years. It also will leading to fluctuated crude oil prices that can affect the world. Other than that, combustion of the fossil fuels will release greenhouse gases such as carbon dioxide, nitrous oxide and methane. These gases are the primary compound that contributes for greenhouse effect and air pollution (Siswanto et al., 2008). By exploring alternative energy sources by the researchers, it has been proved that greenhouse gas emissions can be reduced by changing the non-renewable fuel into a renewable fuel (Zhao, Wei, Cheng, & Julson, 2015).

Nowadays, there are many renewable sources that can be used such as hydropower, solar power, wind power, geothermal energy and biofuel. Most of the researchers are trying to improve the development of alternative fuels (Mancio et al., 2016). The research are related to the biofuel. Biofuel is defined as a solid, liquid or gases that are produced from combustion of renewable feedstock or the utilization of biomass substrate and can be used to substitute fossil fuels (Taufiqurrahmi & Bhatia, 2011). According to (Mancio et al., 2016), there are a bunch of method in converting animal fats and vegetable oils and one of the most effective is by using pyrolysis or also known as cracking. The catalytic cracking process is the most promising method to produce hydrocarbons (alkanes, alkenes and carbonyl compounds) which is more similarly to conventional fuel (Li et al., 2018). It is supported by (Twaiq, Zabidi, & Bhatia, 1999) as most of the researchers improved the production of hydrocarbon from plant oil using catalytic cracking. They also reported that many of the raw materials have been used in producing biofuel such as carboxylic acid and mixtures of fatty acids, crude vegetable oil such as palm oil, sunflower oil, canola oil, soybean oil, recycled cooking oil and non-edible oils such as camelina oil and jatropha oil. Crude vegetable oil is the most important as their transformation into biofuels does not create competition with other users or having huge impact on the food supply chain.

As reported (Siswanto et al., 2008), based on all of the vegetables oil listed, palm oil has the greatest possibility commercialized in biofuel production. Palm oil is the most produced vegetable oil in the world and Malaysia is the second largest palm oil producer which is led by Indonesia which produced 16 million tons on 2006 (Sirajudin, Jusoff, Yani, Ifa, & Roesyadi, 2013). Some of experiments were conducted to convert palm oil into biofuel such as gasoline and diesel fractions and it were obtained from catalytic cracking using different type of catalysts. During the previous research, the cracking of palm oil at 350˚C can produce light products such as benzene, toluene, xylene methane, gasoline, ethane and kerosene (Nasikin, Susanto, Hirsaman, & Wijanarko, 2009).

In the present study, the ZSM-5 catalyst is derived from pottery waste collected from Sungai Sayong. The objective of this research is to identify the combustible liquid from thermal cracking of crude palm oil using ZSM-5 which derived from pottery waste and to characterize the liquid product to their physical and chemical properties.

II. METHODOLOGY

2.1 Material and catalyst preparation

The crude palm oil used is collected from Sime Darby Estate at Labu, Negeri Sembilan. 1000 mL used for each run of the experiment.

The pottery waste collected from clay industry at Sungai Sayong. The pottery waste being grinded by a grinder Restch (Model: SM100) to form a smaller particles. The process continue with sieving process to sieve the size of pottery waste to 500µm. The sieving process followed by impregnation process as the pottery waste is impregnated in the HCl-NaCl solution. After that, the substance was dried at 120˚C for 6 hours. The dried catalysts are ready to use for the research and a sample process without using any catalyst (blank) is used as constant.

2.2 Cracking Reaction

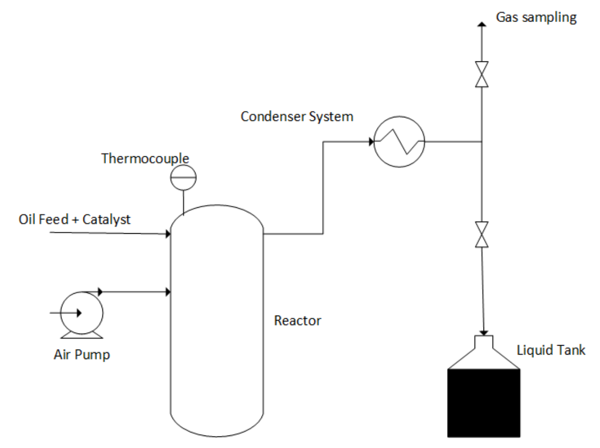

Figure 2.1 Schematic diagram of thermal cracking

The cracking was conducted using a bench-scale combustion reactor. About 1000 mL of crude palm oil was added into the reactor which is a stainless steel vessel. 25 g of the catalyst was added into the reaction chamber. The gas product from the process was cooled down using condenser in order to condense the gas into liquid. Based on (Buzetzki, Sidorova, Cvengrosova, & Cvengros, 2010), it verify that the time taken for obtaining liquid fraction is 20-30 minutes with presence of natural or synthetic zeolite. A 30-min timer was started after the first drop of condensed liquid. The collected liquid also known as combustible liquid is need to be characterized according to its physical and chemical properties.

2.3 Chemical Characterization

The recovery liquids was characterized by testing their calorific value, FT-IR test, elemental analysis and hydrocarbon components analysis. For calorific test, bomb calorimeter (Model IKA Works: 5000 Control) was used at room temperature. The test was run three times in order to get the average reading. For the elemental analysis, the test were conducted using Elemental Analyzer CHNS-O (Model: Thermo Finnigan Flash EA 1112). For the spectrum of the liquid product, FTIR analysis were conducted using Spectrum One, FT-IR Spectrometer (Model: Perkin Elmer). The component of hydrocarbon were determined using gas chromatography-mass spectrometry (GC-MS Varian 450-GC/240 MS) with a RTX-5 column. The sample was injected to the column at temperature 120˚C with oven temperature of 300˚C/30 min. Helium gas was used as a carrier gas with split ratio 1/100.

III. RESULTS AND DISCUSSION

3.1 Characterization of combustible liquid

3.1.1 Calorific analysis

Figure 3.1 shows the calorific value of liquid sample that produced from cracking of crude palm oil using varies types of catalyst. The highest calorific value produced is during the cracking of palm stearin using commercial ZSM-5 which releasing 9361 kcal/kg while the lowest calorific value produced during the cracking of palm stearin using the derived ZSM-5 which is 8979 kcal/kg. A commercialized fuel oil is releasing around 9520 kcal/kg. It shows that the combustible liquid has similarly alike properties to the conventional fuel oil.

The derived ZSM-5 not compatible to the all type of crude palm oil. The derived ZSM-5 is compatible with cooking palm oil and palm olein as these oil produced the third highest of the calorific value which is 9225 kcal/kg and 9229 kcal/kg. However, during the cracking of the palm stearin using derived ZSM-5, the catalyst is not compatible as it produced the lowest value of calorific value which is less value compared to the cracking of palm stearin without using any catalyst.

However, the calorific value for the vegetables oil is valid based on (Demirel, 2012).

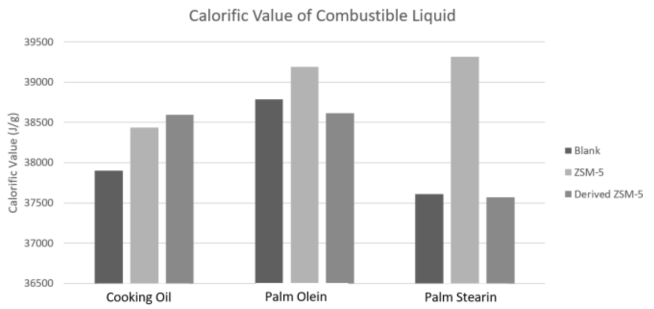

Figure 3.1 Calorific value of combustible liquid

3.1.2 FTIR analysis

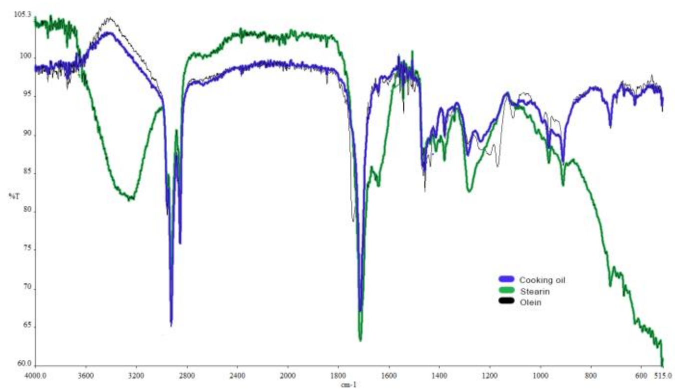

Figure 3.2 Calorific value of combustible liquid

The FTIR spectrum of variety of combustible liquid is given in figure 4.2 until figure 4.4. For overall analysis, it can be shown that there is sharp absorption band at 1714 indicating stretch of carboxylic acid C=O bond. The absorption bands in the region 2950-2850 cm^{-1} showing the stretch of alkyl C-H bond.

However, during the cracking of stearin using derived ZSM-5, there is a broad peak around 3550-3200 cm^{-1} showing that formation of Alcohol/Phenol O-H stretch. It can be satisfy with GCMS analysis where there is high composition of estragole in the combustible liquid. Therefore, it can be concluded that most of the liquid products are containing carboxylic acid and alkyl functional group.

3.1.3 Elemental analysis

Compound	Element Composition (%)		
	Derived ZSM-5 (Blank)	Derived ZSM-5 + Combustible Liquid	Combustible Liquid
Carbon	31.578	58.136	26.558
Hydrogen	4.107	3.266	0.841
Nitrogen	3.973	3.987	0.014

Table 3.3 Elemental composition in the combustible liquid

From the analysis, there are three element that found in the combustible liquid which is carbon and hydrogen. The nitrogen is not identify as one of the elemental compound as the percentage value is too small which indicated the inert gas in the analysis chamber. The percentage element composition in the combustible liquid can be identified by the difference value of composition between the derived ZSM-5 (blank) and derived ZSM-5 + combustible liquid. The percentage of the carbon element in the combustible liquid is 26.558 and for hydrogen the value is 0.841%. Therefore, the elemental compound that exist in the combustible liquid is carbon and hydrogen.

3.1.4 GCMS analysis

Compound	Molecular Formula	Amount (%)								
		A	B	C	D	E	F	G	H	I
Alcohols										
Estragole	$C_{10}H_{12}O$	0.017	0.015	-	-	-	-	0.005	-	0.027
Esters		**0.107**	**0.107**	**0.024**	**0.011**		**0.021**	**0.08**		**0.277**
Hexadecanoic acid methyl ester	$C_{17}H_{34}O_2$	0.012	-	0.019	0.003	-	0.003	0.007	-	-
9-Hexadecenoic Acid methyl ester	$C_{17}H_{32}O_2$	0.067	0.002	0.003	0.003	-	0.007	0.034	-	0.069
11-Octadecenoic acid methyl ester	$C_{19}H_{36}O_2$	0.015	-	-	0.002	-	0.002	-	-	-
9-Octadecenoic Acid methyl ester	$C_{19}H_{36}O_2$	0.006	-	0.002	0.001	-	0.001	0.004	-	-
Dodecanoic acid methyl ester	$C_{13}H_{26}O_2$	-	0.105		0.001	-	0.001	0.003	-	0.062
Pentadecanoic acid, 14 methyl methyl ester	$C_{17}H_{34}O_2$	0.002	-	-	0.001	-	-	-	-	-
9,12-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$	0.002	-	-	-	-	0.007	0.029	-	0.146
Tridecanoic acid, 12-methyl-, methyl ester	$C_{15}H_{30}O_2$	0.003	-	-	-	-	-	0.003	-	-

Table 3.4 Main components of the combustible liquid

Table 3.4 shows the major components of the combustible liquid produced from different crude palm oil with present of different catalyst; A) cooking oil (no catalyst), B) palm olein (no catalyst), C) palm stearin (no catalyst), D) cooking oil (ZSM-5), E) palm olein (ZSM-5), F) palm stearin (ZSM-5), G) cooking oil (derived ZSM-5), H) palm olein (derived ZSM-5) I) palm stearin (derived ZSM-5). Esters and alcohol were found as the main components of the combustible liquid. The highest production of esters is from cracking of palm stearin using derived ZSM-5 followed by cracking of cooking palm oil without catalyst and cracking of palm olein without catalyst. It shows that the derived ZSM-5 is suitable and compatible with certain of oil such as palm stearin.

In addition, during the cracking reaction, the derived ZSM-5 is more favorably assisting in producing 9-Hexadecenoic acid methyl ester, dodecanoic acid methyl ester and 9, 12-Octadecadienoic acid methyl ester. It can be proven during the cracking of palm stearin using derived ZSM-5, it produces the highest percentage for those chemical compound.

IV. CONCLUSION

The derived ZSM-5 is not fully suitable as catalyst during the cracking of the crude palm oil. Some of the crude palm oil only give a positive feedback on usage of the derived ZSM-5. For calorific value test, the highest calorific value produced was from cracking of palm stearin using ZSM-5 but become the lowest when using derived ZSM-5 catalyst. Some modifications are required towards the derived ZSM-5 to enhance the releasing of the calorific value during the cracking reaction. From the thermal cracking process of crude palm oil using the derived ZSM-5, it mainly contain of esters and alcohol. The highest production of ester and alcohol is during the cracking of palm stearin which is 0.277% and 0.027%. The properties is confirmed by FTIR analysis as the result showing the formation of alkyl, carboxylic acid and alcohol-phenol group. However, there is no production of hydrocarbon at the liquid product which is the most desired compound.

As conclusion, the usage of derived ZSM-5 from pottery waste is not suitable for all type of crude palm oil. Some modification process on the derived ZSM-5 is need to be done to increase the feasibility of the catalyst itself. Hence, it will help in producing more hydrocarbon characteristics in order to substitute the conventional fuel which can help in reducing greenhouse gases and decrease the consumption of fossil fuel.

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