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2 Preparation of Palm Fatty Acid Distillate (PFAD) As Raw Material for Bio Aviation Fuel Production

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Abstract: Nowadays, aviation sector became one of the most important transportation in the world. The demand in this sector has increased rapidly over the last 10 years. Unfortunately, the increase of the demand leads to an increase of fuel consumption and CO₂ emission in the aviation's sector. Bio-based aviation fuel is believed to be one of the solution for the reduction of CO₂ emission in the aviation's sector. Palm Fatty Acid Distillate (PFAD) which is a by-product of palm oil refinery, contains a high amount of free fatty acids. The free fatty acids contained in the PFAD are able to be converted into straight hydrocarbon chain through decarboxylation process. This thesis conducted 3 different experiments to find out the best decarboxylation reaction's condition to convert the FFA into straight chain hydrocarbons over an activated carbon catalyst. The experiments compared the results between the experiment with different reaction's conditions and the presence of solvent in the reaction. The results have shown that the third experiment, which used heptane as solvent and hydrogen in argon gas as reaction's environment, has the best reaction's condition among others. Experiment 3 has converted 77.07% of the FFA, while experiment 2 and 1 only converted 58.37% and 16.30% respectively.

Keywords: Bio aviation fuel, Palm Fatty Acid Distillate, Decarboxylation, Activated Carbon, Free Fatty Acid.

1. Introduction

Air transportation is now one of the most important transportation modes, since it can transport a lot of passengers and it only takes a relatively short time to travel thousands of kilometre around the globe. In 2016 there were 3.696 billion passengers that travelled by air (The Worldbank 2017). Like any other transportation modes, air transportation needs energy to power the engines. Petroleum based jet fuel is used to power the engines of the aircraft. In 2015, the world aviation sector consumed around 278,894 tonnes of fuel (International Energy Agency 2017). This lead to a serious problem, since the availability of fossil fuel is depleting.

The consumption of fossil fuels also leads to a high amount of carbon dioxide emissions. Worldwide, the aviation sector produced around 781 million tonnes of carbon dioxide emissions in 2015. In order to reduce the emissions, the air transport industry developed a set of environmental targets, which is to reduce the net emission from aviation by 50% by 2050, compared to the emission level in 2005 (Commission et al. 2015). One of the ways to reduce the emission is by blending the aviation's fuel with bio based aviation fuel.

Until now there are several bio-based aviation fuel sources that are already used as a blending for the aviation fuel. The available bio based aviation fuel source are Jatropa, algae, and waste cooking oil. Palm oil may also possible to be one of the alternative bio fuel sources that can be converted into bio- aviation fuel. Fuel generation from palm oil, which is mainly used in biodiesel production, palm oil is refined to remove the fatty acids content. The physical refinery process of palm oil produces Palm Fatty

Acid Distillate (PFAD) as a by-product. Nowadays, PFAD is utilized as a raw material for detergent and soap due to the high Free Fatty Acid (FFA) content.

Since there are several environmental problems being faced by the world today, in the case of the generation of carbon dioxide emission and the depletion of the fossil fuels, the utilization of PFAD as a raw material for the bio aviation fuel production may be one of the alternative solutions to solve the problems.

2. Research Method

The decarboxylation process of the PFAD was done using catatest reactor, which shown in figure 1 and figure 2. The reactor has a capacity of 1000 ml with dimension of 94 mm x 150 mm, temperature up to 500°C, pressure up to 1500 psig, and agitator rotation up to 1750 rpm. The reactor is a jacketed reactor, which is used for the heating, it also has water coolant inlet and outlet for the cooling process, and gas inlet and outlet for gas injection. As shown in figure 3, the system was controlled by a computer, which can control the process temperature, as shown in figure 4 and the agitator rotation speed. The process pressure was controlled manually by adjusting the gas outlet valve.



Figure 1. R-201 Series Reactor System



Figure 2. Catatest Reactor

The purpose of this process is to convert the free fatty acids to fuel range hydrocarbons. To get the desired hydrocarbon range, the experiment was done with 3 different reaction's conditions which are summarized in table 1:

Table 1: Decarboxylation experiment's condition summary

Experiment	Catalyst	Reaction's Environment	Solvent (ratio)	Pressure (bar)	Temperature (°C)	Reaction Time (hour)
1	Activated Carbon	Nitrogen	-	6.89	350	4
2	Activated Carbon	5% Hydrogen, 95% Argon	Heptane (4:1)	16	350	6
3	Activated Carbon	5% Hydrogen, 95% Argon	Heptane (2:1)	16	350	6

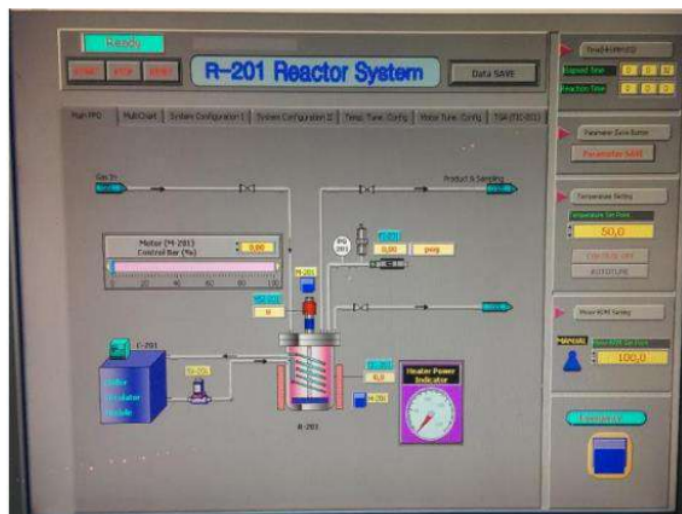


Figure 3. Reaction simulation layout

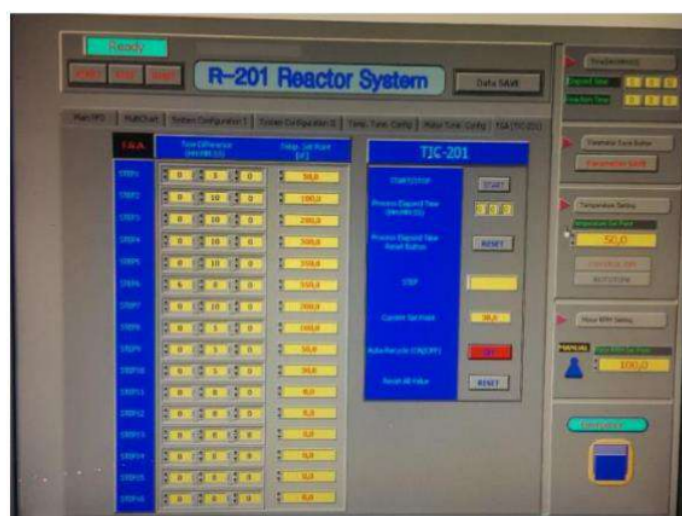


Figure 4. Temperature simulation layout

The first experiment, used activated carbon as the catalyst, Nitrogen gas as the reaction’s environment, and it does not used any solvent to dilute the sample. The second experiment, used activated carbon as the catalyst, 5% Hydrogen in Argon gas as the reaction environment, and Heptane as solvent with a solvent to sample ratio of 4:1. The third experiment, used activated carbon as the catalyst, 5% Hydrogen in Argon gas as the reaction’s environment, and Heptane as solvent with solvent to sample ratio of 2:1.

These experiments used volume basis ratio for the solvent. The usage of Hydrogen as the reaction environment in experiment 2 and 3 is to perform in situ hydrogenation which is to saturate the unsaturated fatty acid presence in the raw material. The solvent which is used in the experiments, is

used to enhance the desorption of alkane that is generated on the surface of the catalyst and also to inhibit the formation of macromolecules.

3. Result and Discussion

Experiment 1. In the first experiment, the reaction takes place using activated carbon catalyst and Nitrogen as the reaction environment with pressure and temperature of 6.89 bars and 350°C respectively. After 4 hours the product of the reaction is analyzed using FTIR and GC-FID. The FTIR result shows a similarity to the FTIR result of the PFAD. The similarity signifies the low conversion of free fatty acid to straight chain hydrocarbons. The assumption is supported by the measurement of the free fatty acid content of the decarboxylation product, which has a value of 76.80%. The free fatty acid value indicated these are only 16.30% conversion compared to the free fatty acid value of the pretreated PFAD which has a value of 93.57 %. This low conversion rate of the decarboxylation product may be caused by the incompatibility of the catalyst with the reaction pressure, reaction's environment, and the absence of solvent in the reaction. The low conversion is also supported with the result from the GC-FID result which shows a low intensity of peaks in the spectrum.

Experiment 2. The second experiment, the reaction takes place using activated carbon as catalyst, 5% Hydrogen in Argon as the reaction environment, and heptane as the solvent with solvent to sample ratio of 4:1. The reaction is done with a pressure and temperature of 16 bars and 350°C respectively. After 6 hours, the product is analyzed and shows a better result than the first experiment. The FTIR result from the second experiment shows no similarity to the result of the PFAD. The result shows that most of the carboxylic acid functional group has been converted, this assumption is supported by the FFA content analysis which shows a result of 58.37% conversion. The GC-FID result of the second experiment also shows a better result than the first experiment, it shows a higher peaks that indicated a higher hydrocarbons presence in the product.

Experiment 3. The third experiment, which used the same reaction condition as the second experiment, except the solvent ratio which in this experiment is 2:1, shows the best result among the other experiments. The GC-FID result shows a much higher peaks than the first and second experiment, which indicates that the product of the third experiment has much higher hydrocarbon content than the others. This is also supported by the FFA content analysis, which shows a result of 77.07% conversion.

9 Bio aviation fuel from PFAD is a new way to produce aviation fuel from a bio based source. Since PFAD is a by-product of palm oil refinery process, this study offers a way to produce aviation fuel that is environmental friendly. There are no previous studies that covers this study, which is producing bio aviation from PFAD, but if compared with other source which also used other method of decarboxylation process, this study shows a promising way to produce bio aviation fuel. Table 2 and table 3 below are the decarboxylation processes which used other source and catalyst as a comparison for the decarboxylation process in this study.

When seen from the third experiment, the result of the decarboxylation process is promising and can go through the next processes which are, hydro-isomerization and hydrocracking process to get the bio aviation fuel. Several developments that can be done to improve the decarboxylation process can be achieve by analyzing the usage of other catalyst, solvent, or reaction's environment and analyzing other reaction's conditions for the reaction.

Table 2: Preparation of hydrocarbons from stearic acid over a palladium catalyst supported on WO₃/ZrO₂ (initial gage pressure, 16 atm; acid, 4 g; dodecane, 16 g; catalyst, 1 g) (Berenblyum, Danyushevsky, Katsman, Podoplelova, & Flid, 2010)

No.	Temperature, °C	Time, h	Atmosphere	Conversion, %
5% palladium				
1	250	6	Hydrogen	89.7
2	300	1.5	Hydrogen	77.4
3	300	6	Hydrogen	~100
4	350	6	Hydrogen	~100
0.5% palladium				
5	350	6	Hydrogen	~100
6*	350	6	Hydrogen	~100
7	350	6	5% H ₂ in He	70.6
8	350	1	Helium	45.3
9	350	6	Helium	50.5

Table 3: Reported results of catalytic decarboxylation of fatty acids over Ni-based catalysts (Wu et al., 2016)

Catalyst	Feed	Gas	Temperature(°C)	Time (h)	Conversion (%)	Selectivity to C ₁₆₋₁₇ (%)	Selectivity to C ₁₇ (%)
20% Ni/C	Stearic acid	N ₂	300	1.5	19	50	26
20% Ni/C	Stearic acid	10% H ₂ /N ₂	300	1.5	64	77	51
20% Ni/C	Stearic acid	H ₂	300	1.5	80	88	81
20% Ni/Al ₂ O ₃	Stearic acid	N ₂	300	1.5	9	48	38
20% Ni/Al ₂ O ₃	Stearic acid	10% H ₂ /N ₂	300	1.5	80	85	67
20% Ni/Al ₂ O ₃	Stearic acid	H ₂	300	1.5	81	84	57
Ni-Al LDH	Stearic acid	N ₂	300	1.5	10	53	13
Ni-Al LDH	Stearic acid	10% H ₂ /N ₂	300	1.5	42	43	30
Ni-Al LDH	Stearic acid	H ₂	300	1.5	73	61	52
20% Ni/C	Tristearin	N ₂	360	6	81	75	30
20% Ni/C	Tristearin	10% H ₂ /N ₂	360	6	88	75	53
20% Ni/C	Tristearin	H ₂	360	6	>99	77	55
20% Ni/Al ₂ O ₃	Tristearin	N ₂	355	6	86	58	31
20% Ni/Al ₂ O ₃	Tristearin	10% H ₂ /N ₂	355	6	96	71	36
20% Ni/Al ₂ O ₃	Tristearin	H ₂	355	6	>99	70	7
Ni-Al LDH	Tristearin	N ₂	355	6	88	70	40
Ni-Al LDH	Tristearin	10% H ₂ /N ₂	355	6	90	72	40
Ni-Al LDH	Tristearin	H ₂	355	6	81	86	69

4. Conclusion

- PFAD is a promising sustainable resource for the bio aviation fuel production, since it has a FFA content of 92.33%.
- The decarboxylation process of palm fatty acid distillate is suitable to convert the fatty acid content in the PFAD into hydrocarbon chain.
- The result of the decarboxylation in this study can produce bio aviation fuel by continue the process to the hydro-isomerization and hydrocracking processes.

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