Bioavtur Synthesis from Palm Fatty Acid Distillate through Hydrotreating and Hydrocracking Processes

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Abstract. Increasing concern in fossil fuel depletion and CO_2 emissions create an urgent need for biofuel substitution. Bio-jet fuel is a possible alternative for conventional jet fuels which currently accounts for 2% of the world's CO_2 emission. Palm Fatty Acid Distillate (PFAD) is the byproduct of palm oil refinery process, which has a potential to become a promising raw material for the synthesis of bioavtur due to its high free fatty acid content. The oil-to-jet pathway is a possible route to produce bioavtur from PFAD, which includes hydrotreating, hydrocracking, and hydroisomerization processes. This research aims to investigate the hydrotreating and hydrocracking processes. The parameters that were investigated are temperature, solvent to PFAD ratio, catalyst loading, and pressure. The parameters variations were as follows: the temperature at 350ºC and 400ºC, the pressure at 40 bar and 32.5 bar, the solvent to PFAD ratio at 2:1 and 1:1, and the catalyst loading (%wt) at 1%, 2%, and 3%. Presulfided NiMo/γ-Al$_2$O$_3$ PIDO 120 1.3 was used for one-step hydrotreating and hydrocracking processes. Results indicated that the 400ºC provided better free fatty acid (FFA) conversion. FFA is also almost completely removed when the catalyst used is 3% weight. Solvent to PFAD ratio affected the FFA conversion marginally, while higher catalyst loading (3%) improved the FFA conversion. Gas chromatography results show that the hydrocarbon chains are successfully hydrocracked into C_9-C_{17}. The best selectivity of the product to bioavtur range was calculated at 68.99%. Solvent ratio affects the hydrocracking more significantly than the catalyst loading. One sample with temperature operation 400ºC and solvent to PFAD ratio 1:1 was in the range of conventional avtur density. With the method used in this study, it can be concluded that PFAD is a promising raw material for bioavtur.

Keywords: Palm Fatty Acid Distillate (PFAD), hydrotreating, hydrocracking, bioavtur

1. Introduction

Indonesia is currently the highest palm oil producer in the world. Palm oil is produced by treating crude palm oil (CPO) in palm oil refineries. From the physical refinery, a non-edible by-product is produced, which is called palm fatty acid distillate (PFAD). PFAD accounts for 6% of CPO physically refined, and more than one million ton per year of PFAD is produced (Blesvid, Yelmida, & Zultinar, 2013). PFAD consists of the free fatty acid, which is separated from the CPO to create RBDPO (refined, bleached, and deodorized palm oil).

PFAD is utilized mainly as raw materials in soap and cosmetic industries. Despite the abundance of PFAD in Indonesia, PFAD is exported as a raw material that causes economic disadvantages, where PFAD could be utilized or exported as a more valuable product. One of the alternatives of PFAD utilization is producing bio-aviation fuel known as bioavtur. It is suitable as a bio-aviation fuel raw material due to its high free fatty acid (FFA) content. Moreover, it is a non-edible, refuse-derived substance that answers the recent concerns on the sustainability of biofuels derived from food resources. The development of bio-aviation fuel is crucial due to the increasing demand for aviation sector globally. The total worldwide aviation turbine fuel consumption in 2016 is recorded at more than 292

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million tonnes (International Energy Association, 2016) whereas the consumption in Indonesia was at 2.6 million tonnes in 2015. The increasing number of flight passengers every year could cause increased CO_2 emission problems where currently aviation sector has already covered 2% of the world's CO_2 emission.

Aviation turbine fuel, known as avtur, derived from fossil crude oil is imported with an increasing amount every year. This is caused by the depletion of petroleum oil reserves and the increase of fossil fuel demand in Indonesia. In 2017, imported fuel accounted for 52% of the total fuel demand (PERTAMINA, 2017). Not only in Indonesia, but fossil fuel reserve depletion is also happening globally, where oil reserves will only last for another 50 years with the current rate of consumption.

There are a lot of pathways to produce bio-aviation fuel from various sources, namely alcohol-to-jet (ATJ) fuel, oil-to-jet (OTJ) fuel, gas-to-jet (GTJ) fuel, and sugar-to-jet (STJ) fuel. Currently, the only pathway that has gained significant commercial interest is OTJ. There have been successful flight tests using bio-synthetic paraffinic kerosene or known as Bio-SPK derived from this pathway. OTJ pathway involves a series of reaction: hydrogenation, propane cleave, hydrotreating, hydrocracking, and hydroisomerization (Wang et al., 2016). Moreover, bio-jet fuel from OTJ pathway has cleaner combustion properties due to its high cetane number and low sulfur content.

Hydrotreating refers to a reaction process where the free fatty acid is saturated through hydrogenation reactions, countinued with removal of carboxylic acid groups through three main reaction pathway: decarboxylation, hydrodeoxygenation, and decarbonylation. The decarboxylation process is the preffered reaction pathway as it does not require hydrogen gas (Wiethoff, 2018). Tiwari and team (Tiwari et al., 2011) reported that decarboxylation and decarbonylation pathway is more common when $CoMo/Al_2O_3$ catalyst is used while $NiMo/Al_2O_3$ catalyst promotes a mixture of decarboxylation and decarbonylation hydrocarbons. (Krár, Kovács, Kalló, & Hancsók, 2010)

The general definition of hydrocracking is: a reaction where hydrocarbons are converted into other hydrocarbons with lighter molecular weight, under hydrogenation conditions. Hydrocracking reactions are exothermic and slow reactions. Over-cracking will result in low yields of alkanes in the jet fuel range and high yields of light species in range of C_1 to C_4, naphtha from C_5 to C_8.

A study of special hydrocracking of technical grade coconut oil was performed, where the yield was at 58.75% (Zoltán Eller, Varga, & Hancsók, 2016). A similar hydrocracking process was conduted with Calophyllum Inophyllum Linn Oil using $NiMo/Al_2O_3$ catalyst that produced a sample with 9% FFA left in the product (Ruliana, 2017). In order to complete the synthesis of bioavtur, another step of hydroisomerization is needed where catalysts Pt/SAPO-11, Pt/Zeolite, Pd/Zeolite are commonly used (Dhar, Vekariya, & Sharma, 2017; Liu, Zhu, Guan, He, & Li, 2015).

In this research, sulfided $NiMo/\gamma-Al_2O_3$ was used as the catalyst. Nickel and Molybdenum are fitting metals as they have a high melting point and suitable for very exothermic reactions, which is the case with hydrocracking reactions (Wiratama & Hudaya, 2014). Gamma alumina was used as the catalyst support in this research due to its high thermal stability and large pores that enable reactions of large molecules (Dwiratna & Soebagjo, 2015). The aim of this study work is to investigate the optimum condition for hydrotreating and hydrocracking reaction with $NiMo/\gamma-Al_2O_3$ bifunctional catalyst to convert the FFA in the PFAD into alkanes in the avtur range C_9-C_{16} that is ready for hydroisomerization process and eventually be ready for blending with conventional jet fuel for commercial purposes.

2. Experimental

In order to obtain the research objectives, the effect of temperature, pressure, solvent to PFAD ratio, and catalyst loading were studied. Before the hydroprocessing, the catalyst was presulfided with Dimethyl Disulfide (DMDS). Several reasons for using DMDS are: low-cost, and high sulfur content

(68%) that is much easier to control, as the reaction is exothermic. In presulfiding processes, diesel fuel is needed as a wetting agent to avoid the occurrence of dry areas in the catalyst bed.

PFAD was then processed with the presulfided catalysts. The treatment was in a batch configuration with a batch reactor done in 4 hours, with different temperatures, pressures, solvent ratios, and catalyst loadings. Most of the experiments utilized n-heptane solvent (C_7H_{16}) to improve the hydrotreating process to remove the carboxylic acid group. After the process, the products were evaluated by their FFA content. As the FFA from the PFAD was initially analyzed, the conversion of the FFA could be determined. The density of the products was also measured, where the density of conventional aviation turbine fuel ranges from 0.77 to 0.85 kg/l.

Hydrocracking performance was investigated using GC-FID (gas chromatography-flame ionization detector) result, where the desired chains are between C_9 and C_{16}. Therefore, the percentage of hydrocracked free fatty acid into bioavtur range could be determined.

2.1 Experimental Apparatus

The catalytic hydrotreating and hydrocracking experiments were carried out in a batch autoclave reactor R-201 Series Autoclave Reactor by Reaction Engineering, South Korea. All of the presulfidation, hydrotreating, and hydrocracking processes utilized this autoclave reactor. The reactor can withstand pressure up to 1,500 psig, temperature up to 500˚C, with a 1-liter liquid capacity. The compositional analysis and selectivity to bioavtur analysis of the sample was done with GC-FID. FFA conversion was analyzed with free fatty acid determination through titration. Density of the samples were measured with Metler Toledo Densito 30 PX Density Meter at 15ºC. The weighing of all raw materials were measured with Metler Toledo ME-TE analytical balance.

2.2 Materials

The materials used in this experiment include: fresh PFAD from a local palm oil refinery, n-heptane as a solvent (Merck, pro analysis), NaOH flakes for outlet gas trap solution and titrant for free fatty acid titration analysis, hydrogen and nitrogen gas from SII Specialty Gases, isopropanol for free fatty acid titration analysis (Merck, pro analysis), and phenolphthalein solution as an indicator for free fatty acid titration analysis. NiMo/γ-Al$_2$O$_3$ PIDO 120 1.3 commercial catalyst is obtained from ITB. DMDS is used as a presulfiding agent (Merck, pro analysis). The wetting agent used for the presulfiding process is diesel fuel acquired from a local fuel station.

NiMo/γ-Al$_2$O$_3$ catalyst is a bifunctional catalyst that has the two main roles: metallic function and acidic function. The metallic function refers to an ability of the NiMo/γ-Al$_2$O$_3$ catalyst to conduct hydrotreating function in active sites of the activated catalyst by supplying hydrogen and exchanging electrons with the reactant (Weitkamp, 2012). The acidic function refers to the acidic sites in γ-Al$_2$O$_3$ which is mainly lewis acidic sites (Scherzer & Gruia, 1996).

2.3 Experimental Design

To find the optimum condition for bioavtur production, these set experiments were done. All of the experiments were done for 4 hours of reaction time and this parameter remains unchanged. Table 1 describes the experimental design of this research.

<div align="center">**Table 1.** Experimental Design.</div>

No	Catalyst	Temperature (ºC)	Pressure (bar)	Solvent Ratio	Catalyst loading
1	NiMo/γ-Al$_2$O$_3$	350	35	-	1%
2	NiMo/γ-Al$_2$O$_3$	350	40	2:1	3%
3	NiMo/γ-Al$_2$O$_3$	350	40	1:1	2%
4	NiMo/γ-Al$_2$O$_3$	400	40	2:1	3%
5	NiMo/γ-Al$_2$O$_3$	400	40	2:1	2%
6	NiMo/γ-Al$_2$O$_3$	400	40	1:1	3%
7	NiMo/γ-Al$_2$O$_3$	400	40	1:1	2%
8	NiMo/γ-Al$_2$O$_3$	400	32.5	2:1	3%

2.3.1 Temperature variation

Temperature variation of the research can be analyzed through a comparison of experiment no. 2 & 4 results and experiment no. 3 & 6. The different results could decide which temperature would yield a better sample. A previous report by Yang and team has shown that temperature is the most influential parameter to the sample. (Yang, Wang, Zhang, Wang, & Li, 2013). Higher temperature tends to promote more decarboxylation and decarbonylation processes that do not require a lot of hydrogen gas and promotes hydrocracking processes to form shorter-chain hydrocarbons.

2.3.2 Pressure variation

Pressure variation of the research can be analyzed through samples from experiment no. 4 & 7, where all of the other parameters are equal. A variation of pressure was done due to the high cost of hydrogen that could be reduced by lower-pressure operations. Higher pressures tend to promote the hydrodeoxygenation pathway from the hydrotreating process due to the increase of hydrogen solubility in the liquid state sample.

2.3.3 Solvent variation

The variation of solvent include experiments without or with solvent in various concentrations (2:1 or 67% and 1:1 or 50%). Experiments no. 4 & 6, and no. 5 & 7 was used to determine the effect of solvent ratio on the product sample. Heptane was used in this research, similar to the previous research by Wiethoff (Wiethoff, 2018). A reported study showed the usage of solvent for fatty acid hydrotreating and hydrocracking (Yang et al., 2013). The presence of solvent in the hydroprocessing could improve decarboxylation activities, desorption of product, heat transfer in the reactor, fluidity, stability of composition, and interphase mass transfer. Reaction with PFAD also requires a solvent presence as the substrate is very concentrated with more than 90% FFA content. Adding solvent would dilute the FFA content and enable the catalyst to work more effectively.

2.3.4 Catalyst to Sample Ratio

Catalyst loading was varied to find the minimum catalyst loading amount to have an efficient process. A research by Ruliana (Ruliana, 2017) reported that the optimum catalyst loading is at 2% wt%, with calorific value as the determining parameter. Experiment no. 4 & 5 and 6 & 7 results would determine which catalyst loading is the preferred one. Nickel and Molybdenum part in the catalyst has the hydrotreating function, where γ-Al$_2$O$_3$ part acts as the support for hydrocracking functions in the bifunctional NiMo/γ-Al$_2$O$_3$ catalyst.

2.4 Characterization of Palm Fatty Acid Distillate and Product Sample

Three main parameters were used to characterize the PFAD such as FFA profile of PFAD, FFA% titrimetry analysis, and Iodine Value. The parameters used to characterize the product sample were FFA% titrimetric analysis, density, and selectivity through GC-FID analysis.

2.4.1 Iodine Value Analysis

Iodine value is used to determine the degree of unsaturation of fatty acids in the form of double carbon-carbon bonds that react with iodine compounds. The degree of unsaturation is related to the melting point and oxidative stability. Iodine value normally is express in grams of iodine in 100 grams of sample. The analysis is done by titrimetric methods.

2.4.2 FFA% Analysis

The FFA% analysis was done to evaluate the effectiveness of free fatty acid conversion of FFA with the corresponding reaction condition. (Equation 1 was used to measure the free fatty acid content from titration:

$$FFA\% = \frac{25.6 \times N\ titrant \times vol\ titrant}{mass\ titrant}\ \text{(Equation 1)}$$

Calculating the conversion of FFA is simply by comparing the FFA content of PFAD and the FFA content still left in the sample. However, a multiplier factor of the FFA% of the sample according to their solvent ratio in the feed. The solvent would dilute the FFA% of the sample. As solvent ratio is also a varied parameter in this study, the factor *f* will correspond to the reaction condition's solvent ratio.

2.4.2 Selectivity

The selectivity of the product sample is measured with the mass% in the GC-FID analysis without the solvent mass% to create an adjusted composition of the product. Selectivity of the product sample determines the effectiveness of the hydrocracking process.

$$Selectivity\% = \frac{Mass\%\ C_{9-16}\ of\ Product}{100\% - Mass\%\ C_7\ of\ Product}\ \text{(Equation 2)}$$

3. Results and Discussion

3.1 Characterization of PFAD

The iodine value of the feed PFAD was measured based on titration, with 38.24 gI$_2$/100 g as a result. The result showed a lower than average iodine value of PFAD, which indicated that the free fatty acid content was especially high, in the range of 93.22-95.55% according to a previous report (Chang et al., 2016). This report was confirmed with the titration analysis of the FFA content in the fresh PFAD measured, which was 93.46%. The free fatty acid content in this study is similar to the one reported by Wiethoff (Wiethoff, 2018) at 92.6%. This similarity might suggest that the FFA content in the PFAD is relatively consistent in various palm oil refinery sources. The iodine value result also indicated a low degree of saturation in the free fatty acid that could result in a higher freezing point of the free fatty acids. The gas chromatography FFA composition on PFAD has shown that the predominating free fatty acid that exists in PFAD is palmitic acid, oleic acid, and linoleic acid, as shown in Table 2. This composition is very similar to the PFAD used in the previous research from a different palm oil refinery source, which again, show consistency of FFA composition in PFAD. (Wiethoff, 2018)
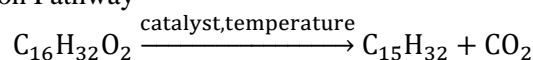
Table 2. Free Fatty Acid in PFAD Composition based on Gas Chromatography Analysis.

Compound	Chemical Formula	Mass%
Myristic Acid	$C_{14}H_{28}O_2$	0.91%
Palmitic Acid	$C_{16}H_{32}O_2$	45.03%
Stearic Acid	$C_{18}H_{36}O_2$	4.65%
Oleic Acid	$C_{18}H_{34}O_2$	35.98%
Linoleic Acid	$C_{18}H_{32}O_2$	8.46%

3.2 Hydrotreating Process

To discuss the result of the hydrotreating process, the pathways of hydrotreating are demonstrated. Hydrotreating reaction pathways of model molecule palmitic acid are shown below.
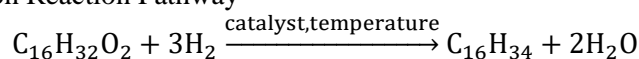
- Decarboxylation Reaction Pathway

$$C_{16}H_{32}O_2 \xrightarrow{\text{catalyst,temperature}} C_{15}H_{32} + CO_2$$

- Decarbonylation Reaction Pathway

$$C_{16}H_{32}O_2 + H_2 \xrightarrow{\text{catalyst,temperature}} C_{15}H_{32} + CO + H_2O$$
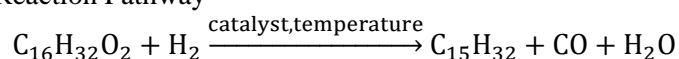
- Hydrodeoxygenation Reaction Pathway

$$C_{16}H_{32}O_2 + 3H_2 \xrightarrow{\text{catalyst,temperature}} C_{16}H_{34} + 2H_2O$$

These reaction pathways show that hydrotreating these carboxylic acid groups would be enough to produce hydrocarbons with a majority of C_{15}-C_{18} chains. The product would mostly lie in the diesel range, where the product is called "green diesel" instead of biodiesel, which refers to a fatty acid methyl ester compounds rather than paraffin blends. The catalyst then hydrocracks these hydrotreating alkanes with bioavtur-range hydrocarbons as the product. Over-cracking would cause in the production of hydrocarbons in biogasoline range, as was reported by Kim et al. when using a highly acidic catalyst, platinum on zeolite catalyst. (Kim, Kim, Lee, Lee, & Choi, 2017)

After the hydrotreating and hydrocracking processes, the samples were expected to have a lower free fatty acid content compared to the PFAD after the reaction through hydrotreating mechanisms. The result of FFA left in the sample, and FFA conversion from the experiments is shown in Figure 1. The calculation was based on titration results using (Equation 1 and the conversion of FFA was calculated based on the comparison of FFA left in the sample with the initial FFA amount in the PFAD. These parameters are essential to evaluate the hydrotreating performance of the catalyst in their specific conditions.
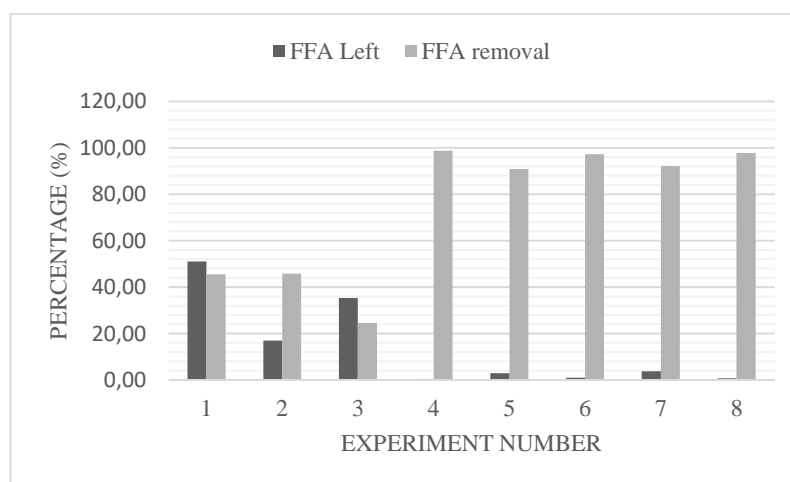

Figure 1. FFA left in product and FFA removal percentage of each experiment.

As can be seen in Figure 1, experiment no. 1, 2, and 3 still had a high amount of FFA left in the sample and had a quite low conversion of FFA, below 50%. The similarity between those experiments is that all of them were conducted at 350°C. The low conversion at 350°C showed us that this temperature was not enough for effective hydrotreating performance for 4 hours under 40 bar of pure hydrogen atmosphere. This result is contradictive with a study by Eller (Zoltán Eller et al., 2016) where it was reported that the optimum hydrocracking temperature was at 350°C. It also contradicted with the research using Calophyllum Lynn oil that is able to produce an optimum hydrotreating process at 350°C (Ruliana, 2017). This contradiction proves that the feed would affect the optimum condition for the hydrotreating process and optimization needs to be done on each specific feedstocks, confirming the study by Vazquez et al. (Vásquez, Silva, & Castillo, 2017). Vazquez et al. showed that some feedstocks has optimum hydrotreating over the 350°C common operation temperature, such as carinata oil (400°C), jatropha oil (450°C), and sunflower oil (450°C).

With higher temperatures than the normal hydrotreating operations, decarboxylation, and decarbonylation pathways can be promoted over hydrodeoxygenation pathway. Decarboxylation and decarbonylation pathways, especially the decarboxylation pathway, are the preferred pathways due to their lower hydrogen consumption. Hydrodeoxygenation, on the other hand, has an advantage where neither carbon dioxides nor carbon monoxides are emitted. However, as the hydrogen production in Indonesia is not produced from a GHG-free lifecycle, using less hydrogen also minimizes the overall emission of the process. Using less H_2 gas could also increase the economic feasibility of the process. Also, the utilization of PFAD as a raw material that has a high FFA content also requires less H_2 for the reaction compared to triglycerides in common vegetable oils.

Experiment no. 1, which did not use any solvent, resulted in a solid product. This result indicated that the sample still had a high free fatty acid content. The predominating free fatty acid in PFAD, palmitic acid ($C_{16}H_{32}O_2$), has the freezing point of 62.9°C, compared to 18°C, the freezing point of n-hexadecane, leading to a sample with a high freezing point when the FFA is not converted, still similar to its feed, PFAD. This result was analogous to a previous report that used pure stearic acid as the feed with a low solvent to PFAD ratio that lead to a sample with waxy precipitates (Yang et al., 2013). Although they remained in a liquid state under room temperatures, experiment 2 & 3 results started to freeze when stored in temperatures below 20°C, due to the high FFA content.

It can be seen from experiment no. 2 & 3, experiments with 350°C and solvent utilization, that solvent and catalyst variation affected the remaining FFA on the sample and the conversion. A higher solvent to PFAD ratio would naturally cause in a lower remaining FFA because the feed had a diluted FFA content. The conversion% of the FFA revealed that 2:1 solvent to PFAD ratio and 3% catalyst loading would lead in a better result. However, it was unclear which parameter affected the product more significantly. Thus, solvent to PFAD ratio and catalyst loading were varied in the next set of experiments. The results in experiment no. 4, 7, and 8 with 400°C were significantly better and showed a better overall conversion of FFA. It indicates that 400°C is necessary to hydrotreat the free fatty acid almost completely. Experiment 4 has the lowest FFA remaining in the sample by using 2:1 solvent ratio and 3% catalyst and 40 bar.

The effect of lower pressure was not nearly as significant, which can be seen in the experiments no. 4 & 8 of Figure 1. The result agreed with a report that showed that pressure is the least affecting parameter to the hydroprocessing reactions (Yang et al., 2013). However, experiment 8 result showed a slight decrease in the FFA conversion. The decreasing diffusivity of hydrogen gas under a lower temperature could be the reason of this decline in conversion, which lead to a slightly lower FFA removal than in higher pressures. However, decreased pressure reaction condition is preferred due to a more efficient hydrogen gas consumption in the process.

The effect of catalyst loading could be seen in experiments 4 & 5 and 6 & 7. It is apparent from a slight glance in Figure 1, that experiments 5 & 7 which utilize a 2% catalyst loading had a decreased FFA conversion than its counterparts, experiments 4 & 6. The result contradicted with a reported 2% as an optimum catalyst loading in a previous research (Ruliana, 2017). More catalyst would allow a better

conversion due to more metallic sites, the sulfided NiMo part of the NiMo/γ-Al$_2$O$_3$ catalyst, which can catalyze the hydrotreating reactions.

The effect of solvent to PFAD ratio variation, similar to pressure variation, did not affect the product significantly. It can be seen in the conversion from experiment 4 at 98.7% and experiment 6 at 97.3% that only has a %difference of 1.5%. This statement is also supported by the experiment 5 & 7 that has a %difference of FFA conversion at 1.3%. The better result was obtained when the solvent concentration was higher. However, as the difference is insignificant, 1:1 solvent ratio is preferred as it allowed for more feed to be reacted in one batch and would increase the efficiency of the process.

It can be concluded that in the hydrotreating process, temperature has the most significant effect to the FFA conversion, followed by catalyst loading, solvent to PFAD ratio, and pressure variation. The best result was obtained with higher temperature (400°C), higher catalyst loading (3%), higher solvent to PFAD ratio (2:1), and higher pressure (40 bar).

3.3 Hydrocracking Process

Gas chromatography analysis was used to analyze the hydrocarbon composition in the sample. It was needed to analyze the hydrocracking reaction and ensure if the hydrocracking results are within the bioavtur hydrocarbon chain-length range. Gas Chromatography analysis was done on samples 4, 6, and 7 to analyze the effect of solvent and catalyst variation on the effectiveness of the hydrocracking process into bio-jet fuel range.
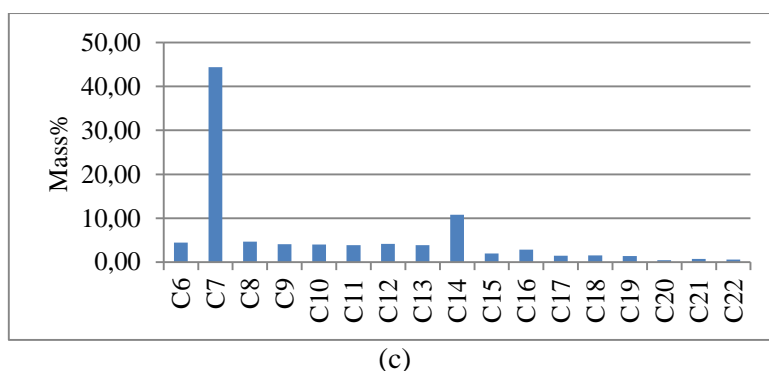

(a)

(b)

(c)
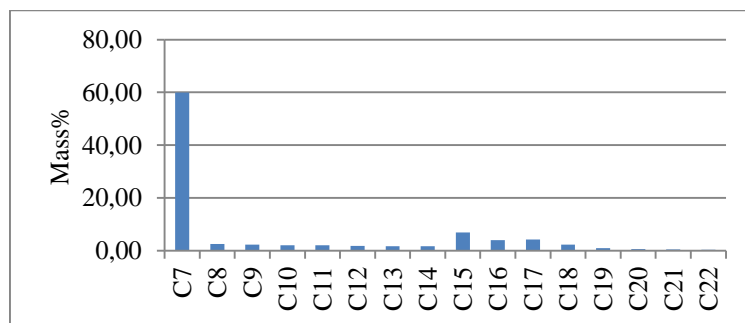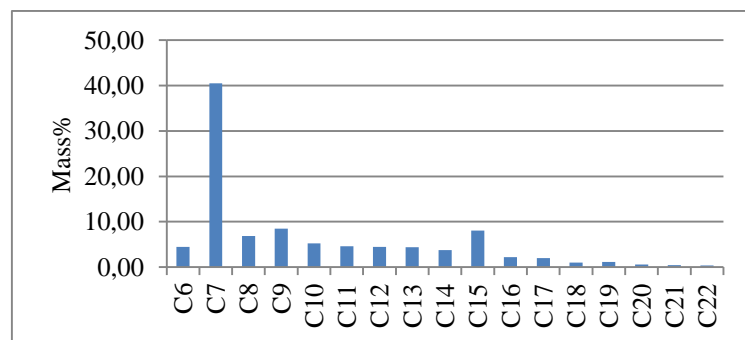
Figure 2. GC-FID result of sample no. 4(a), sample no. 6(b), and sample no. 7(c).

In general, the results in Figure 2(a), (b), and (c) are encouraging. The bifunctional catalyst used in this experiment, $NiMo/\gamma-Al_2O_3$ is currently used commercially for hydrotreating purposes, but not for hydrocracking purposes due to the low acidity of the support. However, this research have shown that the free fatty acid can be converted into hydrocarbons and successfully hydrocracked into smaller chains with $NiMo/\gamma-Al_2O_3$ catalyst, a less acidic catalyst than zeolite-supported catalysts.

It can be seen from Figure 2(a), (b), and (c) that a C_7 peak occurred, which is the solvent peak. This peak is caused by the heptane solvent which reacted in neither hydrotreating nor hydrocracking processes in order to avoid interference of the result in the bioavtur fraction from nonane to hexadecane. Experiment no. 4 GC-FID result shown in Figure 2(a) had the condition of 400^oC, 40 bar, 4 hours, 2:1 solvent ratio, and 3% catalyst. Experiment no. 6 condition differed with a 1:1 solvent ratio and 3% catalyst, and experiment no. 7 with 1:1 solvent ratio and 2% catalyst. As the solvent ratio was higher in experiment 4, the C_7 peak was higher, and the other peaks are lower than experiment no. 6 and 7 results. The selectivities of experiment 4, 6, 7 sample results were calculated at 56.02%, 68.99%, and 64.2911% for bioavtur fraction and 22.03%, 9.13522% and 11.12% respectively for diesel fraction which is heptadecane (C_{17} to C_{22}). This calculation showed us that the hydrocracking process occurred, shown by the significantly smaller diesel fraction compared to the bioavtur fraction. Experiment 4 showed the worst selectivity of the analyzed samples, although it used more catalyst than experiment 7 result. However, experiment no. 6 showed a slightly better result with more catalyst and less solvent than experiment no. 7.

In experiment no. 4 and 6, there existed one peak on the bio-jet fuel range (C_9-C_{16}) at pentadecane (C_{15}). This peak was expected due to the existence of unreacted pentadecane from decarbonylation and decarboxylation of palmitic acid, the predominating component in the PFAD. In experiment 4, although there existed a peak at C_{16}, the difference between C_{15} (6.89%) compared to C_{16} (3.96%) mass was very significant. This difference confirmed arguments that higher temperature conditions promote decarboxylation and decarbonylation pathways that was stated before (Huber, O'Connor, & Corma, 2007; Wiratama & Hudaya, 2014). Another peak appeared in the diesel range at C_{17}, which again confirms the preference of decarboxylation and decarbonylation over hydrodeoxygenation of C_{18} fatty acids. The best hydrocracking activity showed in Figure 2(b) can also be indicated by the low composition of C_{17} and C_{18} at 2% and 0.97%, respectively. These composition suggested that most of the C_{17} and C_{18} alkanes derived from the oleic, stearic, and linoleic acid had been successfully cracked into shorter-chain alkanes.

However, this peak didn't occur in experiment no. 7. Instead, there occurred a high C_{14} peak. It was not expected, as the major constituents of PFAD is C_{16} and C_{18} carboxylic acid that would not produce C_{14} in any of the hydrotreating mechanisms without hydrocracking reaction. The peak in C_{14} in Figure 2 showed us that the condition in experiment no. 7 gave a special selectivity in producing C_{14} which is in the bioavtur fraction. This could be caused by a scission hydrotreating pathway, which emits CH_3COOH instead of CO_2 or CO from the process, as was proposed by Yang et al (Yang et al., 2013).

In the hydrocracking process, the temperature variation was not investigated, due to the poor hydrotreating performance at 350ºC. From the results of the catalyst loading and the solvent to PFAD ratio variations, it can be concluded that solvent to PFAD ratio effect was more significant than the catalyst loading effect. It should be noted that the solvent effect in hydrocracking contradicts the effect in hydrotreating.

3.4 Density of Samples

From the density results in Figure 3, only experiment 7 is in the range of conventional avtur at 0.77-0.85 kg/liter. The density of the majority of the experiment samples were rather low, probably due to the involvement of heptane solvent that has a lower density than aviation turbine fuel. It might be the reason that experiment 7 has the highest and required density of conventional avtur due to the lower solvent used. Although the heptane causes distortions to the product's densities, this research still chose heptane as it lies outside of the bioavtur range (C_9-C_{16}). Thus, heptane would not cause any distortions from the result, and all of the bioavtur compositions in the sample was derived from the PFAD, not the solvent.
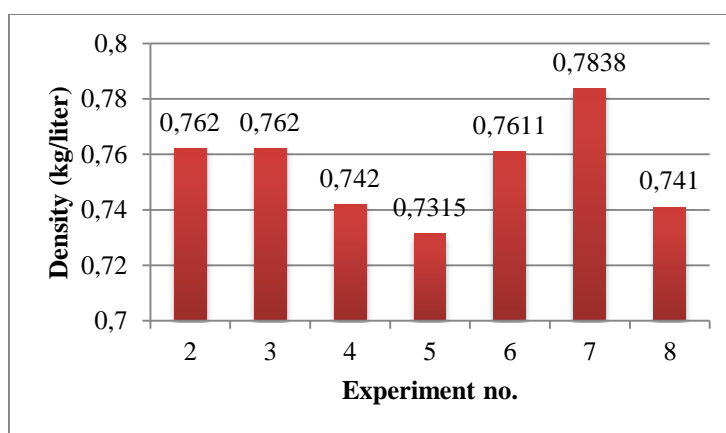

Figure 3. Density of Samples Measurement Data.

Pressure difference did not seem to affect the density, as can be seen in the comparison of experiment no 4 and 8. The experiment sample densities were measured in 15ºC according to ASTM1655-04, a standard for bio-jet fuels, except for sample experiment no. 2 & 3, where the density was taken at 21ºC due to freezing problems below that temperature.

4. Conclusion

Palm fatty acid distillate (PFAD) can be used as a suitable feed for bioavtur due to its high free fatty acid content and ability to be converted into aviation biofuel. In this study, the free fatty acid content was measured at 93.46% through titration. PFAD can be converted into bioavtur-chain hydrocarbons through hydrotreating and hydrocracking processes with NiMo/γ-Al_2O_3 acting as a catalyst for both reactions, as was shown in the results. With 400ºC temperature, all of the samples successfully converted more than 90% of the FFA, with the peak at 98.6% conversion in the experiment no. 4 (400˚C, 40 bar, 2:1 solvent ratio, 3% catalyst loading) , whereas with 350ºC, the conversion of FFA in the samples was lower than 50%. Catalyst loading at 3% converts the FFA significantly better than 2%. On the other hand, pressure and solvent ratio variation didn't have a significant effect on the samples. The density of the product, which is similar to conventional avtur can be found in experiment no. 7 sample, ran at 400ºC, 40 bar, 1:1 solvent to feed ratio, and 2% catalyst loading, at 0.7815 kg/L.

Gas Chromatography results from experiment no. 4, 6, and 7 all showed that the long-chained alkanes were successfully converted into shorter alkanes. Experiment no. 4 and 6 showed the bioavtur range hydrocarbons has a high peak in C_{15} where Experiment 7 showed that the bioavtur range hydrocarbons have a high peak at tetradecane (C_{14}). The best selectivity of bioavtur from the hydrocracking process

was performed in experiment no. 6 with the reaction (400°C, 40 bar, 1:1 solvent ratio, 3% catalyst loading) where the selectivity was 68.99%, and the diesel fraction was small at only 9.13%. This result shows that not only the NiMo/γ-Al$_2$O$_3$ has a decent hydrotreating performance, it could also have a high selectivity for the hydrocracking with bioavtur-range hydrocarbons as the target. Therefore, it can be concluded that PFAD, an underutilized residue, can be converted into bioavtur, a more valuable substance that is in high demand due to the depletion of fossil fuels and a possible solution to concerns regarding carbon dioxide emissions.

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