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PENELITIAN &  
PENGEMBANGAN  
INDUSTRI  
KELAPA SAWIT  
YANG BERKELANJUTAN

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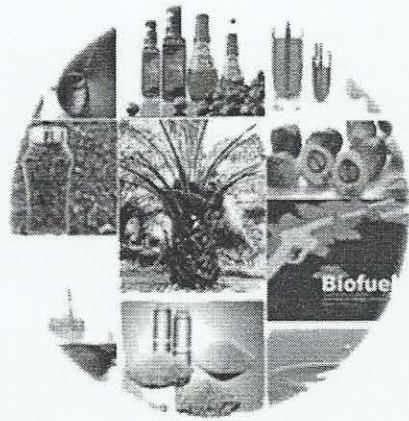
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**PROSIDING SEMINAR TAHUNAN MAKSI 2013**  
**PENGUATAN PENELITIAN DAN PENGEMBANGAN INDUSTRI**  
**KELAPA SAWIT YANG BERKELANJUTAN**



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**Jono M. Munandar**  
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**PT DAMI MAS SEJAHTERA**  
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**2013**

**PENGUATAN PENELITIAN DAN PENGEMBANGAN INDUSTRI  
KELAPA SAWIT YANG BERKELANJUTAN**

**Prosiding Seminar Tahunan MAKSI  
Bogor, 25 September 2013, IICC**

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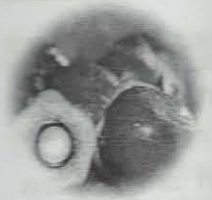
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## BIOAVTUR PRODUCTION PROCESS FROM PALM OIL BASED THROUGH HYDROGENATION AND CATALYTIC CRACKING

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### ABSTRAK

Avtur (aviation turbine) merupakan bahan bakar pesawat komersial yang memiliki komponen utama berupa hidrokarbon paraffin ( $C_{10}$ - $C_{14}$ ). Riset mengenai bioavtur dilakukan untuk mengatasi peningkatan konsumsi avtur dan kewajiban penurunan emisi karbon dari sektor penerbangan. Minyak sawit (CPO) digunakan karena Indonesia merupakan produsen CPO terbesar di dunia, sementara pemanfaatannya di dalam negeri baru mencapai 45%. Konversi CPO menjadi bioavtur melalui tahap proses hidrolisis trigliserida, hidrogenasi ikatan tidak jenuh rantai karbon, dekarboksilasi dan catalytic cracking, sehingga dihasilkan fraksi bioalkanes yang karakteristiknya menyerupai avtur. Tujuan dari penelitian ini adalah untuk mengetahui kondisi proses konversi CPO menjadi bioavtur dan karakteristik produknya. Fraksi gas dan cair bioalkanes hasil reaksi dikoleksi setiap 30-60 menit selama 5 jam pada suhu 300, 400 dan 450°C. Analisis kualitatif fraksi meliputi bau, warna, viskositas dan kejernihan pada suhu ruang. Reaksi sintesis bioavtur diduga optimum pada suhu 450°C, ditandai dengan adanya aroma paraffin yang menyengat, viskositas menurun dan berbentuk cair pada suhu ruang dan suhu 0°C. Sementara itu pada perlakuan suhu 300°C dan 400°C, produk yang dihasilkan berbentuk padat di suhu ruang disebabkan adanya proses hidrolisis dan hidrogenasi trigliserida. Peningkatan suhu sampai 450°C pada tekanan 50 atm dalam atmosfer gas hidrogen selama 1-3,5 jam menghasilkan fraksi yang memiliki densitas 750-850 kg/cm<sup>3</sup>. Fraksi ini sesuai dengan spesifikasi bahan bakar avtur. Densitas tertinggi diperoleh dari produk dengan perlakuan lama waktu proses 3,5 jam yaitu 854 kg/cm<sup>3</sup>. Dari hasil pengamatan terhadap ketahanan suhu, produk bioavtur dengan perlakuan lama proses 3-3,5 jam berbentuk cair pada penyimpanan -55°C.

**Kata kunci :** bioavtur, CPO, hidrogenasi, catalytic cracking

### ABSTRACT

Aviation fuel is a commercial jet fuel, which has a major component of paraffin hydrocarbons ( $C_{10}$ - $C_{14}$ ). Research on bioavtur conducted to overcome the increasing aviation fuel consumption and carbon emission reduction obligations for the aviation sector. Palm oil (CPO) selected as the biofeedstock because Indonesia is the largest palm oil producer in the world, while its utilization in the country only reached 45%. CPO conversion into bioavtur carried through hydrolysis process of triglycerides, hydrogenated unsaturated bond of carbon chain, decarboxylation and catalytic cracking, so that the bioalkanes product characteristics resemble to jet fuel. The purpose of this study was to determine the condition of bioavtur process and product characteristics. Gas and liquid fractions from bioalkanes

reaction product were collected at 400 and 450°C. Qualitative analysis showed clarity at room temperature and at temperature of 450°C, known as liquid product at 0°C and at 450°C, the product is in a liquid form. The hydrogenation process of triglycerides at 50 atm in a hydrogen gas atmosphere with a density of 750-850 kg/cm<sup>3</sup> specifications. Highest density of 854 kg/cm<sup>3</sup>. From the observation of process is in a liquid form.

**Keywords :** bioavtur, CPO,

Aviation fuel is a fossil fuel, Jet B, JP-4, JP-5, JP-8, JP-14. Indonesian aviation fuel production, except for 2008, reached 20,900 barrels, which is fulfilled by imports, with a research on alternative jet fuel.

Utilization of renewable energy is one of the potential solutions. Beside the 5% reduction of greenhouse gas, Indonesia is the largest palm oil producer in the world, million tonnes in 2011.

CPO conversion into bioavtur is a value-added of oil processing. The sustainability of oil palm is more profitable than biodiesel. The price is lower than other economical price.

Bioavtur produced by a series of biomass conversion treatment (pyrolysis and hydrogenation reaction). Biomass pyrolysis is difficult to control the reaction, such as iso-octane which has been well explored because bioalkanes from syngas require high process costs. Plasma-arc is promising, but still needs further research through hydrolysis process. The characteristics resemble to jet fuel.

If the bioavtur synthesis is through hydrolysis or saponification



reaction product were collected every 30-60 minutes for 5 hours at a temperature of 300, 400 and 450° C. Qualitative product analysis were observed include odor, color, viscosity and clarity at room temperature. The optimum bioavtur synthesis reaction estimated at a temperature of 450°C, known from the strong smell of paraffin, the viscosity decreases and liquid product at 0°C and at room temperature. Meanwhile at the temperature of 300°C and 400°C, the product is in a solid form at room temperature due to the hydrolysis and hydrogenation process of triglycerides. Increase in temperature up to 450°C at a pressure of 5 atm in a hydrogen gas atmosphere for 1-3.5 hours produces fractions which have a density of 750-850 kg/cm<sup>3</sup>. The density of these fractions is suitable with aviation fuel specifications. Highest density obtained from the product after 3.5 hours of process, there is 854 kg/cm<sup>3</sup>. From the observation of temperature resistance, bioavtur product with 3-3.5 hours of process is in a liquid form at temperature -55°C.

**Keywords :** bioavtur, CPO, hydrogenation, catalytic cracking

## INTRODUCTION

Aviation fuel is a fossil fuel for some types of commercial aircraft such as Jet A, Jet A-1, Jet B, JP-4, JP-5, JP-7 or JP-8, which the major component is paraffin hydrocarbons C<sub>10</sub>-C<sub>14</sub>. Indonesian aviation fuel consumption from 2005 to 2011 is always higher than its production, except for 2009 and 2010. In 2011, Indonesian aviation fuel consumption reached 20,900 barrels, while its production was only 18,200 barrels<sup>[1]</sup>. This deficiency then fulfilled by imports, with an import amount in 2011 reached 5,130 barrels. Therefore, research on alternative jet fuels must be pursued.

Utilization of renewable resources such as CPO for bioavtur production became the potential solutions. Besides having suitability with the European Union regulations about 5% reduction of greenhouse gas emissions, in terms of the raw material availability, Indonesia is the largest palm oil producer in the world with CPO production reached ± 26.8 million tonnes in 2011.

CPO conversion into bioavtur has several advantages, there are : 1) An increase in value-added of oil processing, 2) Resolve aviation fuel deficiency in the country and 3) Meet the sustainability of oil palm processing. In addition, the CPO conversion into bioavtur be more profitable than biodiesel because aviation fuel is a non-subsidized fuel so it has a better economical price.

Bioavtur produced from various biomass such as fiber, sugar, flour and vegetable oil by a series of biomass conversion processes. It can be through transesterification process, heat treatment (pyrolysis and hydrothermal), enzyme hydrolysis, fermentation, and Fischer-Tropsch reaction. Biomass pyrolysis approach is less preferred because of the low yield and difficult to control the reaction conditions, produces tar and hydrocarbons (HC) that volatiles such as iso-octane which has a flashpoint ~ -40 ° C. Enzymatic synthesis approach has not been well explored because the low reaction rate. Fisher-Tropsch synthesis of long-chain alkanes from syngas requires certain types of raw materials to produce syngas and high process costs. Plasma-assisted approach to achieve the expected reaction conditions is promising, but still needs further development<sup>[2]</sup>. Vegetable oils can be converted into jet fuel through hydrolysis process, decarboxylation, thermal or catalytic cracking so that its characteristics resemble to jet fuel<sup>[3,4,5,6]</sup>.

If the bioavtur synthesis starts with triglyceride, the first step in the process involves either hydrolysis or saponification of the triglyceride to form free fatty acid and glyserol. They



can be done separately before synthesis begins or when bioavtur thermal decarboxylation process. Any acid catalyst that is suitable for performing triglycerides hydrolysis can be used, for example hydrochloric acid, hydrobromic acid, sulfuric acid, nitric acid, and solid catalyst such as Dowex 50<sup>TM</sup>. Free fatty acid then converted to alkanes via thermal decarboxylation of fatty acids. Typically this involves heating the triglycerides and water or free fatty acid to a temperature between 400-600°C. This can be performed in stages, such as a first stage heated to a temperature of 100-300°C, ideally at 150-250°C to perform the hydrolysis step, and the second stage where the temperature are 400-600°C, where thermal decarboxylation and likely some degree of chain shortening occurs. If the decarboxylated fatty acid not include carbon double bond, they can be dehydrogenated before cracking reaction. The dehydrogenation process is typically conducted at temperatures at 260-538°C. The pressure preferably between 0.1-10 atm (1,47-147 psia) at the present of gaseous diluent, preferably hydrogen<sup>[6]</sup>.

Hydrocracking refers to a catalytic process, usually carried out in the presence of free hydrogen, in which the cracking of the longer chain hydrocarbon molecules is primary purpose of the operation. One of the suitable catalyst used in this process is unsulfided group VIIIA and group VIB such as nickel-molybdenum or nickel-tin on an alumina or siliceous matrix<sup>[6]</sup>. The temperature process ranging from 300-500°C, at pressure ranging from vacuum condition to 3000 psia, in the presence of gaseous environment that may contain an inert gas such as hydrogen, and at time from 1 up to 180 minutes<sup>[3]</sup>.

Decarboxylation, include hydrogenation process and catalytic cracking, is an important step in the bioavtur synthesis because it will determine the yield. Decarboxylation plays a role in the formation of long-chain alkanes that will be cut in cracking process. Parameters that most influence the condition of both processes is the catalyst, temperature and processing time. Purpose of this study was to determine the best time and temperature conditions in the hydrogenation and cracking process.

## MATERIALS AND METHOD

### CPO Refining

CPO (Crude Palm Oil) was refined into RPO (Refined Palm Oil) with 80-85% phosphoric acid at concentration of 0.05-0.2% v/v, homogenized for 30 minutes then neutralized by ±70°C distilled water until pH 6-7. The mixture then poured for settling at separatory funnel to separate oils with water, gum and other impurities. Water was removed by heating the oil at temperature of 90-120°C.

### Bioavtur Synthesis

The method for bioavtur synthesis was hydrogenation followed by catalytic cracking process with NiMo as heterogeneous solid catalyst. Both of the reactions occurred in the same reactor simultaneously. Bioavtur synthesis was divided into two stages. The first stage is to find the best temperature condition, among 300, 400 and 450°C and the second was to find the duration of reaction from 1 up to 5 hours. Fraction of gas and liquid samples were taken every 30-60 min.

A volume of 100 percent of solid catalyst reactor was turned off and gradually, the temperature of gas and oil products were observed. The best temperature to determine the right process optimum temperature was quantitative parameters with temperature.

After the reactions exhausted and leftover in temperature (Table 1). The triglycerides and catalytic hydrogenation saturation of the double bond solid at room temperature.

Table 1. Qualitative analysis of the

Temp	Fraction	Color
300°C	Liquid	Yellow
400°C	Liquid	Brown
450°C	Liquid	Brown
	Gas	Transparent

Reaction condition process has begun. It was the strong smell of paraffin catalyst known to be work well was also activated at a carbon number, because water cold flow properties and cracking n-paraffin into branched.

From the qualitative 450°C and 50 bar pressure, produced because of the strong and at room temperature liquid and gaseous components reaction useful for aviation fuel hydrogen, water and carbon process followed by condensation temperature, mean that it may



A volume of 100-150 ml RPO was heated to 100°C with magnetic stirring. One percent of solid catalyst was added to the reactor. After the mixture was homogenous, the reactor was turned off and hydrogen gas flowed into the reactor with a pressure of 25 bar ( $\pm 372$  psia). Gradually, the temperature then increased up to 300, 400 and 450°C. Sampling of gas and oil products were performed at every 30-60 minutes for 5 hours process. Qualitative parameters were observed include odor, color, viscosity and clarity at room temperature.

The best temperature conditions then used as a reference in the next stage to determine the right processing time. Synthesis process carried out for 3.5 hours after the optimum temperature was reached. Gas and liquid fractions were taken every 30 minutes. The quantitative parameters were observed include density and appearance at -55°C storage temperature.

## RESULT AND DISCUSSION

After the reactions at temperature of 300°C for 2 hours, all the gaseous material was exhausted and leftover liquid fractions. Some of the fractions became solid at room temperature (Table 1). The reactions which occurred at this stage were hydrolysis of palm oil triglycerides and catalytic hydrogenation of its unsaturated fatty acid<sup>[7]</sup> by hydrogen addition. Saturation of the double bonds led to the increase of melting point, so that the oil became solid at room temperature.

Table 1. Qualitative analysis of the product at a temperature of 300, 400 and 450°C

T (°C)	Fraction	Color	Form (at room temperature)	Odor
300°C	Liquid	Yellowish green	Solid, like paraffin	Paraffin
400°C	Liquid	Black	Solid, like paraffin	Strong smells of Paraffin
450°C	Liquid	Black	Liquid	Strong smells of Paraffin
	Gas	Transparent into dark red	Liquid, as well as at 0°C	Gasoline

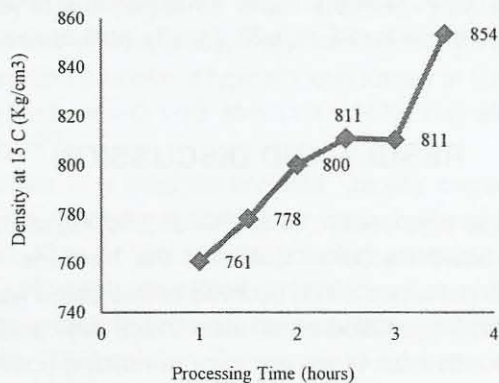
Reaction condition at 400°C temperature and 50 bar vessel pressure, the cracking process has begun. It was characterized by the viscosity and melting point decrease and the strong smell of paraffin or alkanes products in a liquid form at room temperature. The catalyst known to work well at that temperature. Catalyst for deoxygenation of vegetable oils was also activated at a temperature of 400°C and 1 hour heating time. This liquid portion presumably comprised of hydrocarbon fractions containing n-paraffins, mostly 15 to 18 carbon number, because they had poor cold flow properties. Aviation fuel must have better cold flow properties and so the products need further reactions for isomerization and cracking n-paraffin into branched paraffin with C<sub>9</sub>-C<sub>15</sub> carbon number range<sup>[4]</sup>.

From the qualitative evaluation of liquid samples synthesized at a temperature of 450°C and 50 bar pressure, it can be concluded that the short-chain alkanes may have been produced because of the strong smell of paraffin, the viscosity decreased and liquid form at 0°C and at room temperature. The final effluent stream of cracking process comprised both liquid and gaseous component. The separated liquid component comprised the hydrocarbon fraction useful for aviation fuel. While the separated gaseous component comprised mostly hydrogen, water and carbon-dioxide from the decarboxylation reaction<sup>[4]</sup>. The cracking process followed by condensation, resulted in a liquid fraction which had two layers at room temperature, mean that it may consist of lighter and heavier fraction with different polarity.



The fraction which was similar to aviation fuel was the light fraction or upper layer. Further separation of the two fractions were important to characterize it.

The temperature setting of 450°C was used to determine the reaction time. Increase of temperature up to 450°C at a pressure of 50 atm in a hydrogen gas atmosphere for 1-3.5 hours produces fractions which had density of 750-850 Kg/cm<sup>3</sup> (Fig. 1). Density of the fractions were in accordance with the specifications of aviation fuel (775-840 kg/m<sup>3</sup>). The density was increased along with the longer reaction time, with the highest density generated after 3.5 hours was 853 kg/m<sup>3</sup>.



Pic 1 Density of the product at 450°C

Evaluation of freezing resistance of the fractions was done by stored in two temperature conditions, i.e. 0°C and -55°C (Table 2). From these observations, it was known that the product which produced at 450°C after 3-3.5 hours was still in a liquid form when stored at -55°C. Therefore the product met the aviation fuel specification for freezing point, which should be maximum at -47 °C. Freezing point is very important because it determines the fuel resistance to low temperature condition. Fuel specifications have to consider flexibility for application in a variety of climatic conditions during flight. For example, military specifications require that aviation turbine fuel be completely resistant to the formation of solid crystals at temperatures as low as -47°C, which correspond to an altitude of 9500 meters<sup>[3]</sup>. Freezing point is also related to jet fuel pumpability from the fuel tank to the engine. In general, Jet fuel typically remains pumpable approximately 4°C to 15°C (25 to 27°F) below its freezing point.

Table 2. Product resistance at low temperature storage

T (°C)	Processing time (hour)					
	1	1,5	2	2,5	3	3,5
0	-	-	-	-	-	-
-55	-	√	√	√	-	-

Note : - liquid, √ frozen

### CONCLUSION

Bioavtur from palm oil can be obtained through the hydrogenation followed by cracking with Ni-Mo catalyst. The best synthesis reaction occurred at 450°C, 50 bar vessel pressure.

under hydrogen atmosphere  
freezing resistance similar

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under hydrogen atmosphere for 3-3.5 hours. This liquid fraction had density ( $854 \text{ kg/m}^3$ ) and freezing resistance similar with the avtur.

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