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ALCOHOLYSIS OF CANDLENUT OIL INTO BIODIESEL WITH WASTE CATALYST CRACKING PERTAMINA RU III PALEMBANG

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Abstract: Candlenut oil is one type of vegetable oil that has a high content of fatty acids and has the potential to be used as raw material for biodiesel production. Because candlenut seeds contain several fatty acids, namely 0.202% capric acid, 6.32 palmitic acid, 2.31% stearic acid, 26.93% oleic acid, 38.52% linoleic acid, and 25.25% linolenic acid. This study aims to obtain the optimal composition in the manufacture of biodiesel using the transesterification method using waste catalysts from the c racking process of Pertamina Unit II Palembang. Based on the results of the alcoholysis reaction of candlenut oil with operating conditions of pressure above 1 atm, and the catalyst used in the form of a petroleum cracking waste catalyst, in the transesterification process the chemical reaction that occurs is a chemical reaction with pseudo-first order to glycerides, and takes place in the liquid phase. Optimal operating conditions are at a temperature of 383^{o}K and agitation speed of 300 rpm, with an equivalent ratio of oil/methanol 5 mgek/mgek, and the percentage of catalyst as much as 2% by conversion of biodiesel amounted to 92.089%.

Keywords: Alcoholysis, Biodiesel, Catalyst, Candlenut Oil

1. Introduction

Indonesia has a fairly large dependence on oil and coal. On the other hand, for conditions when fossil fuel sources have a very limited amount. Therefore, there is a need for a shift from fossil energy to renewable energy. And for now, the use of vegetable oil as a raw material for the manufacture of renewable energy, can be used as a solution. (Padil, Wahyuningsih, and Awaluddin 2012), Vegetable oil is oil derived from plants or seeds, such as coconut oil, castor seed oil, rubber seed oil, used cooking oil, candlenut oil, and many others. (Octavian 2011)

Candlenut oil is an oil obtained from the extract of candlenut seeds (Aleurites moluccana) which is a plant from the Euphorbiceae family (Yusnita, Erra., Wiyono, B. 2001). Candlenut seeds contain several fatty acids, namely 0.202% capric acid, 6.32 palmitic acid, 2.31% stearic acid, 26.93% oleic acid, 38.52% linoleic acid, and 25.25% linolenic acid. 2006). Due to the high content of fatty acids, candlenut seed oil has the potential to be used as raw material for the manufacture of renewable energy in the form of biodiesel.

Biodiesel is a monoalkyl ester derived from long chain fatty acids. In general, biodiesel is obtained from the synthesis of fatty acid esters on the carbon chain between C_6 - C_{22} (K. A. Roni 2012). Biodiesel production generally uses vegetable oil as raw material due to its renewable availability. In

addition, biodiesel produced from vegetable oils has several advantages, namely non-toxic, biodegradable, has a high cetane number, reduces emissions of carbon monoxide, hydrocarbons, and nitrogen oxides. And has a flash point that is higher than petroleum diesel fuel (Ristianingsih, Hidayah, and Sari 2016). Biodiesel has the same characteristics as conventional diesel fuel, therefore biodiesel can be used as an alternative fuel for conventional diesel fuel (Putri et al. 2013). There are several ways to process vegetable oil and animal oil (fat) into biofuel. namely: mixing with petro-diesel, pyrolysis, microemulsification (cosolvent blending) and transesterification. Among these methods, only the transesterification reaction creates fatty acid methyl esters (FAME) products commonly known as biodiesel (Inggrid et al. 2013). In its use, biodiesel can be used directly in diesel engines without any modification to the engine first (known as B100) or used for diesel fuel mixtures such as B20 (20% biodiesel, 80% conventional diesel) based on the Indonesian National Standard (SNI) for Biodiesel issued by BSN with SNI number 7182:2015 which has revised SNI 04-7182-2006 and SNI 7182:2012 - Biodiesel. (Santoso, Kristianto, and Setyadi 2013)

In this study, a catalyst with a heterogeneous base was used. Heterogeneous base catalyst is a substance that can accelerate the occurrence of a reaction by lowering the activation energy, has basic properties, and the phase of the substance is different from the reactant phase (Aziz, Nurbayti, and Rahman 2012). Heterogeneous base catalysts can accelerate the transesterification reaction of making biodiesel. The transesterification reaction is a reaction between plant oils or animal fats with alcohols to form esters and glycerol. If you use methanol, the ester produced is known as Fatty Acid Methyl Ester (FAME). This reaction is widely used to reduce the viscosity of triglycerides (Kusuma et al. 2011). Heterogeneous catalysts include CaO, MgO.

Currently, many industries use heterogeneous catalysts which have many advantages and are environmentally friendly, namely non-corrosive, easily separated from the product by filtration and can be used repeatedly over a long period of time. (K. ahmad Roni, Agra, and Sulistyo 1998)

In the cracking process, the catalyst serves to help break down carbon compounds, with the help of a crude oil catalyst, it can be processed so that variations of crude oil derivatives such as premium, kerosene, diesel and other products are obtained depending on the degree of cracking of the carbon chain (Savitri, Nugraha, and Aziz 2016). Petroleum cracking effluent catalyst (Spent Catalyst) PT. Pertamina RU III Palembang consists of elements of silica, alumina and iron. Catalysts that have been used in the petroleum cracking process still have activation energy that can still be utilized and are generally heterogeneous or solid catalysts with high surface and acidity and considerable thermal stability. The solid materials include alumina, alumina oxide, silica alumina, zeolite and clay. (Santoso, Kristianto, and Setyadi 2013)

Based on this explanation, this study aims to obtain the optimal composition with variable temperature and stirring speed in the manufacture of biodiesel using the transesterification method using a waste catalyst from the cracking process of Pertamina Unit II Palembang.

2. Research Methods

This research was conducted at the Process Laboratory in the Department of Chemical Engineering, Faculty of Engineering, University of Muhammadiyah Palembang. The equipment used in this research are laboratory glassware, magnetic stirrer, hotplate, thermometer, stopwatch, analytical

balance, and a set of qualitative analysis tools. The materials used in the form of candlenut oil, ethanol, and a catalyst in the form of solid catalyst waste from the petroleum cracking process at PT. Pertamina RU III Palembang.

This research was carried out in several stages, namely the preparation of candlenut oil ingredients, Candlenut seed oil obtained by pressing the candlenut seeds After being dried, skinned, and mashed, the candlenut seed oil was taken by pressing using a hydraulic press (Arlene, Kristanto, and Suharto 2010) . The second stage is the hydrolysis process, which is mixing candlenut oil with ethanol with temperature variations of 353oK, 363oK, 373oK, 383oK 393oK because the boiling point of ethanol is 351oK, with temperature variations above the yield obtained, it is considered no longer mixed with ethanol. The next variable was to mix candlenut oil with ethanol with a variation of the reagent ratio of 3:1, 4:1, 5:1, 6:1, 7:1, and 8:1 with an operating temperature of 383oK, the percentage variation of the catalyst used was 0% , 0.5%, 1%, 1.25%, 1.5%, and 2%. While the stirring variations used were 260rpm, 280rpm, 300rpm, 320rpm, 340rpm and 360rpm, 2% catalyst and 1 atm pressure. The mixture is then reacted in a three neck flask, the mixture is stirred using a stirrer coupled to a motor. The mixture is reacted by heating and adding a catalyst for the cracking process of Pertamina Unit III Palembang (which has been removed carbon by heating). Samples are taken every 10 minutes which will then be analyzed for the conversion of glycerol and biodiesel as well as the physical properties of the ester itself.

3. Results And Discussion

3.1 Effect of reaction temperature

Based on Table 1, it is known that the glyceride conversion tends to increase with the higher the reaction temperature, this is due to the greater movement of the reactant molecules. Further explanation can be seen in Figures 1 and 2.

Time (minute)	**Conversion, x part at temperature**				
	353 ºK	**363 ºK**	**373 ºK**	**383 ºK**	**393 ºK**
10	0.15564	0.21715	0.28203	0.3068	0.2973
20	0.21715	0.25679	0.29785	0.33	0.3181
30	0.35089	0.39577	0.44275	0.4312	0.3949
40	0.46832	0.48979	0.5118	0.7241	0.4413
50	0.50195	0.53694	0.57352	0.8325	0.5465
60	0.62911	0.63785	0.64671	0.9208	0.6493
K(10^2) minute^{-1}	0.0095	0.0087	0.0078	0.0139	0.0071
b	0.0533	0.1186	0.1872	0.1039	0.1921

Table 1. Conversion results of the effect of reaction temperature (2% catalyst percentage, stirring speed 300 rpm, oil/methanol 5 mgek/week)

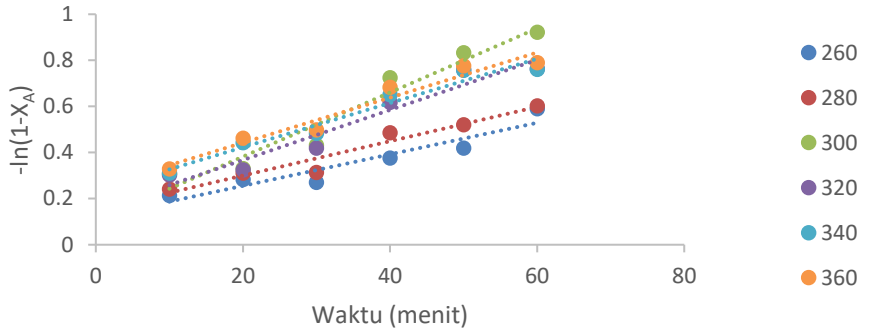

Figure 1. The relationship between –ln (1-xA) with stirring time and speed (rpm)

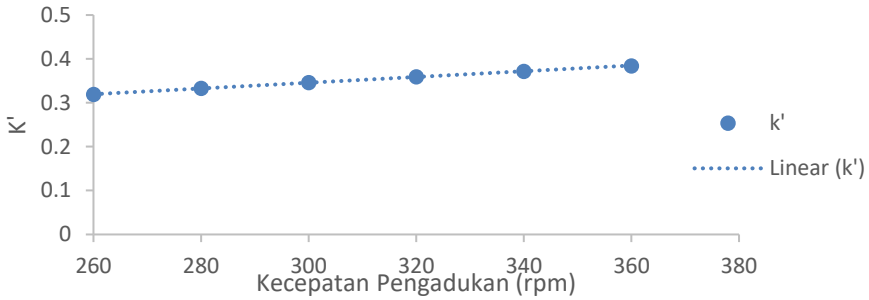

Figure 2. Relationship of k' with stirring speed

Based on Figure 4. is a condition that is supported by the relationship k' with stirring speed (N), which is based on the equation:

$$K' = 1{,}3108\ (10^{-2})\ N^{0{,}574} \qquad (2)$$

(K. ahmad Roni, Agra,and Sulistyo 1998)

The average k' error of the research results is 0.07% and the deviation of x ± 0.14 based on equation (2) is known that the Reynolds refractive index has a value of 0.0574 which is much lower than 0.5. This clearly shows that chemical reactions play a role (Ahmad Roni 2016).

3.2 Effect of catalyst percentage

Based on Table 3, it is known that the conversion of glycerides tends to increase with the greater the percentage of catalyst used, this is because the more active reagents, therefore causing the collisions to occur even greater. Further explanation can be seen in Figures 3 and 4.

Tabel 3. Conversion Result of Percentage Effect catalyst

Time (minutes)	Conversion, x part at temperature					
	0%	**0.5%**	**1%**	**1.25%**	**1.5%**	**2%**
10	0.06270	0.10016	0.14872	0.17881	0.21411	0.3068
20	0.13957	0.17475	0.22653	0.26279	0.28236	0.3300
30	0.15876	0.21692	0.31516	0.39502	0.42169	0.4312
40	0.19154	0.32528	0.49580	0.62812	0.67669	0.7241

50	0.23836	0.39079	0.53960	0.70983	0.79169	0.8325
60	0.27476	0.47894	0.58870	0.80882	0.87076	0.9208
K(10^2) minute^{-1}	0.004	0.0076	0.0095	0.0135	0.0145	0.0139
b	0.0386	0.0161	0.0537	0.0248	0.0362	0.1039

(Temperature 38, stirring speed 200 rpm,oil/methanol 5 mg/week)

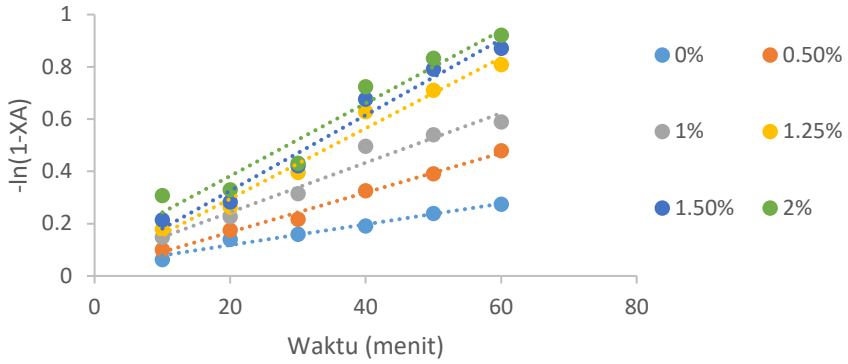

Figure 3. Relationship between $-\ln(1-x_A)$ with time and percentage catalyst

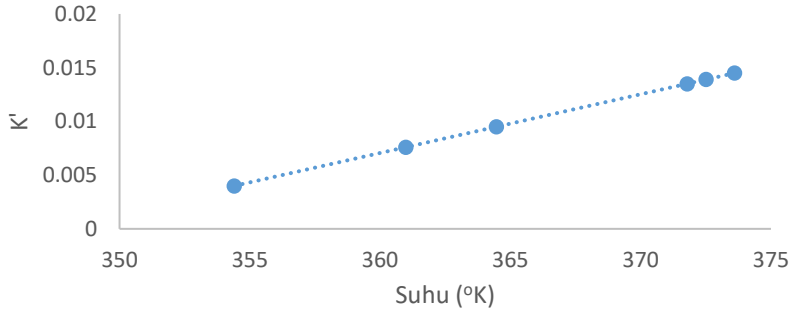

Figure 4. The relationship between temperature and k'

The value of k' is the tangent of the direction of the relationship between $-\ln(1-x_A)$ and time (t) in minutes, and can be seen in Table 3 and Figure 4. The relationship between k' on the percentage of catalyst and the weight of oil (H), was obtained almost straight line and can be seen in Figure 5, with the equation:

$k' = 7{,}4976(10^3) + 5{,}0566(10^3)H$ ……(3)

(K. ahmad Roni, Agra, and Sulistyo 1998)

And for the error k' the average research result is 5% with a deviation of x ± 1%. The value of ko is $7{,}4976(10^{-3})$ which is not much different from the value of k' that does not use a catalyst, which is $7{,}6(10^{-3})$. This condition occurs because it is caused by the nature of the acid possessed by the alcohol used. And from these data it can be proven that chemical reactions occur in the liquid phase with a pseudo-order of glycerides (Putri et al. 2013)

3.3 Effect of the equivalent ratio of candlenut-methanol oil

The equivalent ratio of oil and methanol affects the probability of collisions that will occur, the greater the equivalent ratio between oil and methanol, the greater the possibility of collisions between reactants will also be greater. Based on Table 4, it is known that the higher the conversion value, the higher the equivalent ratio, the value tends to increase.

Based on Figure 5. It is known that the relationship between $-\ln(1-x_A)$ and time (minutes), is a straight line. With the value of k' which is shown in Figure 8. Therefore, it can be concluded that the reaction is pseudo-first order with respect to glycerides.

Table 4. Conversion results of the effect of the speed of the equivalent ratio of candlenut-methanol oil

Time (minute)	**Conversion, x part at temperature**					
	3	**4**	**5**	**6**	**7**	**8**
10	0.287	0.291	0.30687	0.3068	0.288	0.278
20	0.323	0.355	0.33005	0.383	0.378	0.352
30	0.36	0.372	0.43128	0.382	0.383	0.37
40	0.377	0.392	0.72411	0.4224	0.404	0.39
50	0.44	0.449	0.83258	0.4332	0.443	0.435
60	0.478	0.483	0.92089	0.4605	0.478	0.472
K(102) minute^{-1}	0.0038	0.0036	0.0139	0.0027	0.0033	0.0035
b	0.2452	0.2641	0.1039	0.302	0.2791	0.2589

(Temperature Table 4. Conversion results of the effect of the speed of the equivalent ratio of candlenut-methanol oil (Temperature 383^{o}K, stirring speed 300 ppm, percentage catalyst 2%) stirring speed 300 ppm, percentage catalyst 2%)

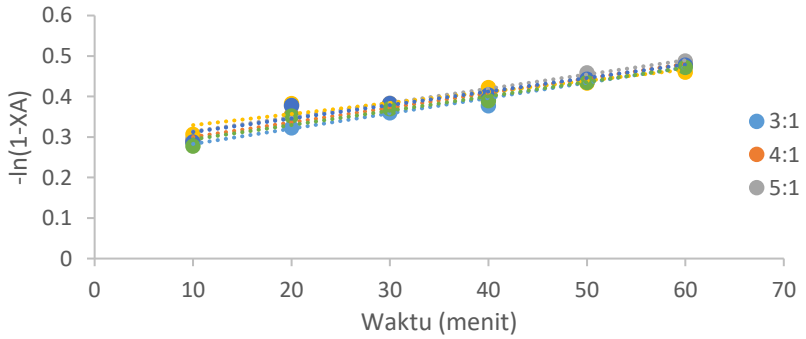

Figure 5. The relationship between –ln(1-XA) with time and the equivalent ratio of candlenut-methanol oil

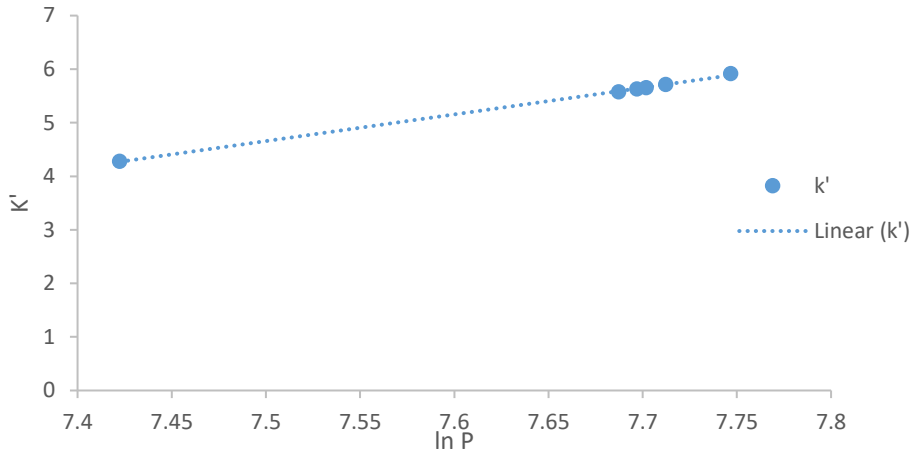

Figure 6. The relationship between temperature and k' ratio of reactants

If –ln k' and temperature are graphed, then a straight line is obtained as in Figure 6, and by least squares the equation is obtained:

$K' = 1{,}2578(10^{-2})\ P^{0{,}2032}$……..(4)

(K. ahmad Roni, Agra, and Sulistyo 1998)

The average error on k' from the results of the study based on equation (2) is 5.7%, with a deviation of x± 0.99%. Based on Figure7. It is known that the relationship between $-\ln(1- x_A)$ with time (minutes), is a straight line. With the value of k' which is shown in Figure 6. Therefore, it can be concluded that the reaction is pseudo-first order with respect to glycerides. (Ahmad Roni 2016)

4. Conclusion

Based on the research that has been done, it can be concluded that, the alcoholysis reaction of candlenut oil with operating conditions of pressure above 1 atm, and the catalyst used in the form of a petroleum cracking exhaust catalyst, in the transesterification process the chemical reaction that occurs is a chemical reaction with pseudo-first order to glycerides, and takes place in the liquid phase.

Optimal operating conditions are at a temperature of 383oK and agitation speed of 300 rpm, with an equivalent ratio of oil/methanol 5 mgek/mgek, and the percentage of catalyst as much as 2% with biodiesel conversion of 92,089%.

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