

Alcoholysis of Kepyar Castor Seed Oil (Ricinus Communis) Using Alumina Silica Catalyst (Used Cracking Process in Pertamina Ru-III Palembang) at 1 Atm Pressure

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Kepyar castor oil has not been widely used. Therefore, this kepyar castor oil needs to be processed, among others by the process of alcoholysis, using catalysts from the Pertamina unit III Palembang oil cracking waste, which is also a waste, so that it can be utilized. Alcoholysis of used cooking oil in more than one atmospheric pressure at the exhaust catalyst for petroleum cracking Pertamina unit III Palembang, run in a three-neck rounded flask, equipped with a thermometer, heater and stirrer. At first, three-neck rounded flask filled with kepyar castor oil, alcohol, and catalyst to a certain amount, then powerstat heater and stirrer is turned on and set. Samples were taken at each interval of 10 minutes and then the lower layers of glycerol levels were analyzed by acetone. In a certain range, an increase in temperature, the percentage of catalyst, stirring rotation, and ethanol-oil ratio, resulting in increased glyceride conversion. Alcoholic analysis of kepyar castor oil follows pseudo first-order reactions to glycerides. The process is relatively good, found in 60 minutes, temperature 110 °C, catalyst percentage 2.5%, stirring speed 320 ppm, and alcohol-oil ratio 6 mg/mg. In that situation the conversion reached 0.7099 parts.

Keywords: Alcohol Sis, Biodiesel, Kepyar Castor Oil, Used Catalyst.

1. INTRODUCTION

Petroleum is a non-renewable energy source. Increased use of fuel, resulting in the depletion of petroleum supplies, so that if new sources are not found, then within a short period of time, petroleum must be imported. Bio energy is being developed in Indonesia, which is an alternative energy source to replace fossil fuels, one of them is biodiesel. Biodiesel is produced from vegetable or animal oils/fats. Biodiesel is used as a substitute for diesel fuel to diesel engine. The advantages of using biodiesel such as: the raw materials are continuously available, ecofriendly, low sulfur content, and reduce exhaust emissions. The right raw materials selection can reduce production costs. Therefore the selected raw materials are cheap and renewable raw materials. Raw materials used in the manufacture of biodiesel are vegetable oils, especially nonfood vegetable oils, low-quality, and has not been widely used.

Kepyar castor oil (ricinus communis) is one of the potential vegetable oils. Kepyar castor oil (ricinus communis) is non-edible so that its use as a fuel does not compete with cooking oil. In some countries, biodiesel from vegetable oil has been produced and consumed in large quantities. In 2008 the United States biodiesel production reached 700 million gallons. The equation for the reaction of vegetable oil can be written as follows:



Where R1, R2, R3, and R' are alkyl groups. In Eq. (1) it appears that 1 mole of glyceride, which has 3 fatty acid groups, reacts with 3 moles of ethanol to produce 1 mole of glycerol and 3 moles of fatty acid esters. In this case

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1 mole of glyceride is equal to 3 equivalents, and 1 mole of ethanol is equal to 1 equivalent, so if it is stated in equivalents, then Eq. (1) can be written as:



In this process, the possible reactions that occur, that is: (1) reagents A and B are both absorbed and activated by the catalyst and then followed by a chemical reaction on the surface of the catalyst, (2) reagent A is only absorbed and activated by the catalyst, then followed by a chemical reaction between A that is absorbed by B which remains in the liquid phase, and (3) Solid catalyst releases hydrogen ions (H^+) from its surface into a liquid containing A and B, then followed by a chemical reaction between A and B. By looking at similar studies, it turns out chemical reactions occur in the liquid phase. Therefore, the reaction of speed equation can be written with:

$$r = k \text{ CAL CBL} \quad (2)$$

If CBL is constant, and then $k\text{CBL}$ is expressed as k' , then:

$$r = -\frac{d\text{CAL}}{dt} = k' \text{ CAL} \quad (3)$$

Then, by entering the x_A conversion, and after it is set and internalized, Eq. (4) changes to:

$$-\ln(1 - x_A) = k't + b \quad (4)$$

If the relationship between $-\ln(1 - x_A)$ the results of the study are drawn against t , and it turns out that a straight line is obtained, then the value of k' is equal to the tangent as same as the direction of the line.

2. RESEARCH METHODS

2.1. Material

Used Cooking Oil is obtained by collecting it from fried food sellers, which mostly are found in South Sumatra, especially in Palembang. After doing the analysis, it turns out that the oil density is 0.8624 g/mL.

Ethanol is obtained from markets around Palembang, South Sumatra and the density is 0.7779 g/cm and a list of 3–109 levels obtained is 95.54%.

Solid catalyst in the form of zeolite powder used as catalyst for cracking of Pertamina Unit III Palembang, which is dark gray to remove the carbon absorbed, the used catalyst is heated in an oven at temperatures over 400 °C so that the color changes to light gray. This solid substance will be used as a catalyst.

2.2. Equipment

The suggested series of tools can be seen in Figure 1. The reactor which will be used is a three-neck round flask equipped with a stirrer, heater, thermometer, and turning cooler.

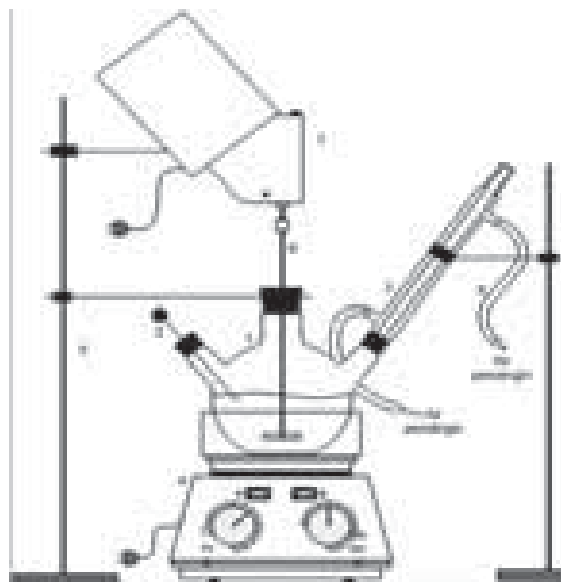


Fig. 1. Series of alcoholysis research tools.

Information: 1. Three neck rounded flask, 2. Thermometer, 3. Condenser, 4. Heater, 5. Stative and Clamps, 6. Stirring rod, 7. Stirring motor, 8. Cooling water hose.

2.3. Methods

Kepyar Seed Oil, ethanol, and a solid catalyst are put into a three-neck flask, then it is tightly closed. The heater and stirrer are turned on. The Stirring temperature and speed are constantly kept by adjusting each powerstat. After a constant temperature has been reached, samples are taken every 10 minutes, then chill and messed up to speed up the separation into two layers.

2.4. Variable

To determine the kinetics of the reaction, studied the amount of catalyst effects, stirring speed, reaction temperature, and the ratio of ethanol-oil equivalent in the period of 10–60 minutes.

2.5. Analysis of the Results

See Figure 1.

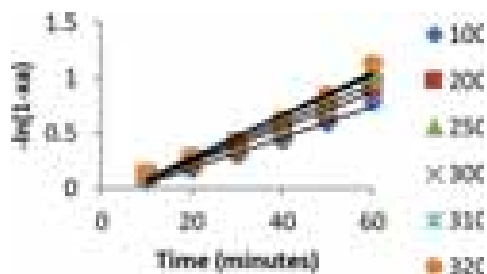
3. RESULTS AND DISCUSSION

3.1. Effect of Reaction Temperature

By looking at Table I and Graph 1, it can be seen that the longer the reaction time, the more the conversion increases, so enlarge the temperature increases the conversion, because the movement of reagent molecules is getting bigger. So, the collisions between them also increase. However, the increase in conversions is not getting large. It could say that chemical reactions determine the overall reaction speed. The graph of $-\ln(1 - x_A)$ with time, t minutes, shows that the points obtained do not deviate

Table I. The effect of stirring speed (temperature 100 °C, catalyst 1% by weight of oil, ethanol/oil = 1 mg/mg).

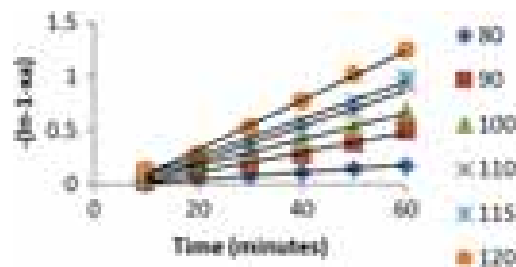
Time in minutes	Conversion, at stirring speed ratio		
	100 rpm	200 rpm	250 rpm
10	0,0667	0,1000	0,1111
20	0,1611	0,2000	0,2194
30	0,2556	0,3000	0,3222
40	0,3500	0,4000	0,4250
50	0,4444	0,5000	0,5278
60	0,5389	0,6000	0,6306
B	0,101	0,0943	0,0972
	300 rpm	310 rpm	320 rpm
10	0,1222	0,1244	0,1267
20	0,2389	0,2428	0,2467
30	0,3444	0,3489	0,3533
40	0,4500	0,4550	0,4600
50	0,5556	0,5611	0,5667
60	0,6611	0,6672	0,6733
$k'(10^2)$	1,87	1,90	1,93
B	0,1021	0,1033	0,1046



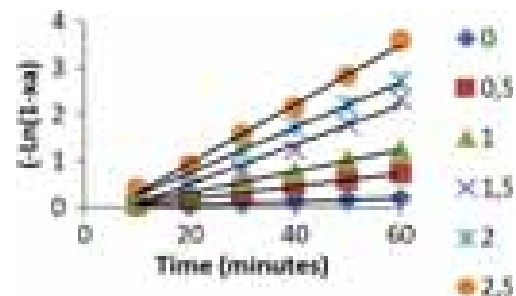
Graph 1. The relation between $-\ln(1 - x_A)$ with the stirring speed.

Table II. The effects of temperature reaction (stirring speed 320 ppm, ethanol/oil = 1 mg/mg, catalyst 1% by weight oil).

Time in conversion, at the temperature minutes variable	Time in conversion, at the temperature minutes variable		
	80 °C	90 °C	100 °C
10	0,0035	0,0261	0,0606
20	0,0530	0,1122	0,1649
30	0,0799	0,1823	0,2470
40	0,1068	0,2432	0,3291
50	0,1337	0,3189	0,4112
60	0,1606	0,3928	0,4933
$k'(10^2)$	0,33	0,92	1,21
B	0,02	0,072	0,0693
	110 °C	115 °C	120 °C
10	0,0828	0,1144	0,1267
20	0,1894	0,2233	0,2417
30	0,2817	0,3333	0,4089
40	0,3944	0,4378	0,5378
50	0,4889	0,5333	0,6400
60	0,6056	0,6278	0,7122
$k'(10^2)$	1,65	1,72	2,29
B	0,1223	0,0856	0,1404



Graph 2. The relation between $-\ln(1 - x_A)$ with the time and temperature.



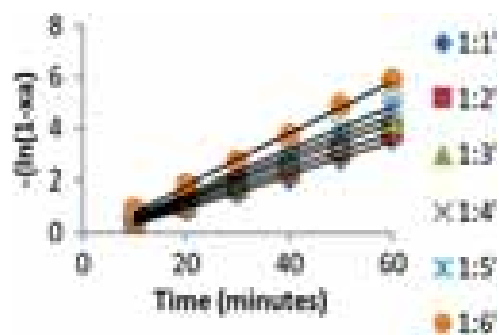
Graph 3. The relation $-\ln(1 - x_A)$.

much from the straight lines formed (Graph 1). It can be concluded that the alcoholysis reaction of keypar castor seed oil with a solid catalyst is controlled by a pseudo-second reaction to glyceride.

By the stirring variations of 100 ppm, 200 ppm, 250 ppm, 300 ppm, 310 ppm, 320 ppm in 10–60 minutes, the highest biodiesel was obtained at 320 ppm stirring in 60 minutes with a conversion of 67.33%. It can be seen

Table III. The effect of percentage catalyst (temperature 120 °C, stirring speed 320 ppm, ethanol/oil = 1 mg/mg).

Time in Conversion at catalyst minutes percentage	Time in Conversion at catalyst minutes percentage		
	0%	0.5%	1%
10	0,0100	0,0606	0,1267
20	0,0439	0,1444	0,2417
30	0,0778	0,2633	0,4089
40	0,1117	0,3628	0,5378
50	0,1456	0,4483	0,6400
60	0,1794	0,5228	0,7122
$k'(10^2)$	0,38	1,39	2,29
B	0,0298	0,0999	0,1404
	1.5%	2%	2.5%
10	0,1928	0,2589	0,3250
20	0,3783	0,5150	0,5961
30	0,5544	0,7000	0,7900
40	0,7128	0,8222	0,8822
50	0,8317	0,8889	0,9406
60	0,9017	0,9333	0,9722
$k'(10^2)$	4,2500	4,8500	6,3700
B	0,3474	0,2220	0,3270



Graph 4. The relation between k' with the comparison of reagent.

Table IV. The effects of comparison of reagents (temperature 120 °C, stirring speed 320 ppm, catalyst 2.5% by weight of oil).

Time in minutes	Conversion, at comparison of reagents		
	1:1	1:2	1:3
10	0,3250	0,3804	0,4446
20	0,5961	0,6501	0,6943
30	0,7900	0,8288	0,8581
40	0,8822	0,9100	0,9329
50	0,9406	0,9556	0,9668
60	0,9722	0,9788	0,9860
$k'(10^2)$	0,38	1,39	2,29
B	0,02928	0,0999	0,1404
	1:4	1:5	1:6
10	0,4749	0,5226	0,5849
20	0,7450	0,7789	0,8302
30	0,8782	0,8964	0,9332
40	0,9401	0,9544	0,9759
50	0,9727	0,9811	0,9923
60	0,9905	0,9930	0,997
$k'(10^2)$	4,2500	4,8500	6,3700
B	0,3474	0,2220	0,3270

from the Graph 3, that the higher the temperature used, the more biodiesel is produced. Thus, it is known that at 320 ppm stirring is optimal stirring, because the reaction takes place faster and better. So that the conversion value is obtained more. Conversely at 100 ppm stirring the reaction occurs longer and slower so as to produce fewer conversions. It clearly shows that chemical reactions play a role [2].

Table V. The comparison of ethanolysis.

	Kepyar castor oil	Kepuh oil	Used oil	Nyampiung oil	Rubber seed oil
Time in minutes	60	60	60	60	60
Highest temperature	120	120	120	120	120
Catalyst	Used (solid)	Used (solid)	Used (solid)	Amberlyst-15	HCl
Catalyst amount	2.5%	2%	2%	0.1071 g/g oil	2%
Ethanol/oil	6	6	6	10.331	6
Reaction order	1	1	1	1	1
Conversion in percentage (%)	99.71	70.91	70.09	70.47	74.47

3.2. The Effect of Temperature Reaction

It can be seen on Table II and Graph 2 that the longer the reaction time, the more the conversion increases, so the higher temperature increases the conversion, because the movement of reagent molecules is enlarge.

The temperature variation of 809 °C, 900 °C, 1000 °C, 1100 °C and 1200 °C within 1060 minutes proven that the most biodiesel was obtained at 1200 °C at 60 minutes with a conversion of 49.33%. By the graph it can be seen that the higher the temperature used, the more biodiesel produced. Thus it is known that at a temperature of 1200 °C is the optimal temperature, because the reaction takes place faster and better. So we get more conversion value. It also reinforces the opinion that the chemical reaction which controls the process is as stated in Ref. [3].

3.3. The Influence of Catalyst Percentage

From Table III, it shows that the converglyceride increases by the increase in the percentage of the catalyst, because the reactants are activated more and more, so the collisions that occur are getting bigger. The k' value is the tangent of the relationship between $-\ln(1-xA)$ and time, t minutes (Table III and Graph 4).

The percentage of catalyst with variety of 0%, 0.5%, 1%, 1.5%, 2%, 2.5% in 10 minutes–60 minutes with a stirring speed of 320 ppm produced optimal biodiesel on a 2.5% catalyst at 60 minutes with a conversion rate of 97.22%. Based on the graph it can be concluded that the higher the percentage of catalyst the more biodiesel is produced. It is because the higher the catalyst percentage, the conversion obtained will be stronger because the reactants are activated more and more so the collisions that occur are getting bigger. Thus it is known that the catalyst for the best reaction occurs at 2.5% catalyst. It is because the 2.5% catalyst is the optimum catalyst with particles reacting and colliding each other. This might be due to the acidic nature of the alcohol used. Thus, it is proven that chemical reactions occur in the liquid phase and are pseudo-sequential to glycerides [4–6].

3.4. The Effect of Ethanol-Oil Equivalent Ratio

The higher the equivalence of ethanol-oil ratio, the possibility of collisions between the reactants becomes even bigger (see Table IV). The relationship between

$-\ln(1 - xA)$ with time, t , is also a straight line, and the value of k' is shown in Table IV. It shows that the reaction is pseudo one-order against glycerides.

Comparison of reagents with variations of 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, within 10 minutes to 60 minutes with the percentage of catalyst 2.5% produced optimal biodiesel reagents 1:6 on 60 minutes is as same as a conversion of 99.71%. From the graph above it can be concluded that the higher the ratio of reagents, the more biodiesel is produced [7–11]. It is due to the more reagents, the conversion will be increased because the reactants are Moreover, and it is known that reagents for the best reactions occur at 1:6 reagents. It is because at 1:6 reagents are optimum reagents by reacting and colliding particles each other.

3.5. Comparison of Result

The results of this study, when it is compared with the results of other studies, turned out that all of them were of the same order and glyceride conversion did not differ much (Table V).

4. CONCLUSION

The conclusions of this study are:

1. The reaction of castor oil alcoholysis at pressures above 1 atm, with catalysts from petroleum cracking, is controlled by a chemical reaction which is pseudo-sequence to glyceride, and takes place in the liquid phase.
2. A relatively good condition was achieved at 120 °C, percentage of catalyst 2.5% by weight of oil, stirring speed of 320 ppm, and the ratio of reagents was 6 mg/mg, the conversion obtained was 0.9971 parts.
3. The obtained esters have physical properties close to diesel oil specifications.

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