International Journal of Engineering &Technology, 7 (4) (2018) 6909-6911

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET
doi: 10.14419/ijet.v7i4.17931
Research paper

Alcoholysis of used cooking oil at high pressure using wasted catalyst obtained from crude oil processing pertamina unit III palembang

Kiagus Ahmad Roni [1] *, Mardwita Mardwita [1]

[1] Chemical Engineering Department, Faculty of Engineering, Universitas Muhammadiyah Palembang, Palembang, 30263
**Corresponding author E-mail: kiagusaroni@gmail.com*

Abstract

One of the possible methods to utilize used cooking oil is alcoholysis. Wasted solid catalyst obtained from Pertamina Unit III located in Palembang was used as catalyst. With this process some benefits might be obtained from these wastes. The alcoholysis of used cooking oil with ethanol and reactivated wasted solid catalyst at high pressure was conducted in an autoclave provided with manometer, thermometer, sampling device, heater, and mixer. The experiment was started by filling the autoclave with used cooking oil, alcohol, and catalyst, then the heater and the mixer were switched on. Samples were taken out at 10 minutes intervals, and after being separated, the bottom layer was analyzed in order to determine its glycerol content using acetin method. By raising the temperature, catalyst concentration, rate of mixing, and ethanol-oil ratio, the glyceride conversion increased. The alcoholysis of used cooking oil followed pseudo first order reaction with respect to the glyceride concentration. The relative favorable process conditions were 60 minutes of reaction time, temperature of 110°C, catalyst concentration of 2 %, mixing velocity of 310 rpm, and alcohol-oil ratio of 6 mgek/mgek. Under this condition the conversion was 70.09.

Keywords: *Alcoholysis; Biodiesel; Used Cooking Oil; Wasted Solid Catalys; Glycerides.*

1. Introduction

Petroleum is a non-renewable energy sources. The sources of petroleum decrease with increasing of petroleum consumption. The petroleum consumption increases with the increasing of population and development of technology. This has huge implications for the availability of energy in the future [1]. Therefore, research on alternative renewable energy and its applications developed rapidly in recent years. Biodiesel is an alternative energy that has been developed extensively to reduce dependence on oil. Biodiesel is a fuel in the form of metal fatty acid ester produced from a chemical process between vegetable oil and alcohol. As a fuel, biodiesel can reduce emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons and nitric solid particles. Besides that, biodiesel is a fuel that is favored due to its environmental friendly [1].

In some countries, biodiesel has been produced and consumed in large quantities. In 2008, US biodiesel production reached 700 million gallons [2]. Most of the raw materials used in the production of biodiesel in these countries are soy oil, canola oil, palm oil, and sunflower seed oil. However, the use of raw materials has become a new obstacle for food needs. Castor oil has been developed and uses to overcome these problems [3,5], however castor oil is economically not feasible on a large scale due to the discontinuity of its supply.

Another way to reduce the viscosity is mixing vegetable oil with petroleum. However, there is a limitation volume of vegetable oil in the mixture, for example, 30% volume of palm oil in diesel oil, on the other hand, biodiesel mixture accuration has no maximal results [6,7]. Therefore, new material for biodiesel is needed.

The use of used cooking oil as a biofuel raw materials is very possible. Used cooking oil has low economic value, it also has carcinogenic properties that is harmful for human body. Therefore, used cooking oil can be use as raw material for biodiesel production. In Indonesia, used cooking oil is still controversial. Until now, most of used cooking oil from large companies was sold to vendors and use to fry food and some of it was dumped into the sewer. The compound of used cooking oil is very dangerous for human body. Innovation to use used cooking oil into biodiesel is needed. The potential of palm oil in Indonesia is very large. The consumption of palm oil in Indonesia in 2006 reached 1.47 million tons and tends to increase as the increase of population. It is assumed that 20% of used cooking oil was obtained from national total consumption of vegetable oil, approximately 294,000 tons of used cooking oil was possible to be processed into biodiesel [8].

Alcoholysis of vegetable oil, such as rubber seed oil, nyampung seed oil, cotton seed oil, used cooking oil, etc, have been done widely. The objective of this research is to investigate the alcoholysis of vegetable oil using used cooking oil, solid catalyst, in an autoclave equipped with a stirrer, at high pressure (more than 1 atm).

2. Methodology

Used cooking oil was obtained from vendors in South Sumatera, especially in Palembang. Analysis results showed the density was 0.924 g/ml, free acid equivalent 0.0313 mgek/g oil, and total acid equivalent 3.215 mgek/g oil, caloric value 9.98733 cal/g.Ethanol properties density is 0.7779 gr/cm3 [9]. Solid catalyst, zeolite, was

Copyright ©2018 Kiagus Ahmad Roni, Mardwita Mardwita. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

obtained from wasted cracking catalyst Pertamina Unit III Palembang, which was dark grey. Used zeolite was heated in an oven at a temperature higher than 400^0 C to remove the adsorbed carbon. After heating, the used zeolite was light grey. Autoclave equipped with thermal insulation, a stirrer, heater, thermometer, manometer, and faucets trailer makers [10], [12].

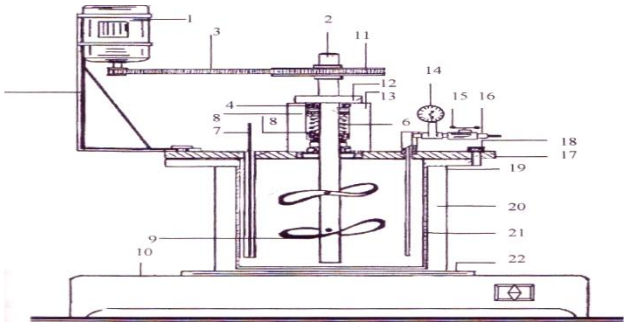


Fig. 1: Ethanolysis Reactor of Used Cooking Oil.

Caption		
1. Stirrer motor	8. Pressure sealing	15. Tap regulator
2.Axis	9. Stirrer	16. Channel
3. holder	10. Electric stove	17. Cylindrical cover
4. Lager	11. Drive wheel	18. bolt hardener
5. Motor placement	12. Retainig shaft	19. Protective tube
6. Pir penahan	13. Pressure sealing box	20.Thermal insultion
7. Thermometer	14. Manometer	21. Main cylinder

Used cooking oil, ethanol, and solid catalyst were fed into an autoclave. Temperature and mixing speed was kept constant by adjusting the powerstat. Sample was taken every 10 min, then cooled, and centrifuged to accelerate separation into two layers. Sample was taken, weighed, and the glycerol level in bottom layer was analyzed using acetin method [13].

Sample was taken and centrifuged to separate top and bottom layer. If the boundary between these layers is already clear, the top layer is taken with a pipette, and the bottom layer weighed again, the residual ethanol was evaporated. 1.3 gr of liquid was taken then inserted into Erlenmeyer, and 3 gr of sodium acetate and 7.5 ml of acetic acid anhydride was added, respectively. The mixture was boiled for 1 hour, then cooled to room temperature (50^0C) then 50 ml of distilled water was added.

The cooled mixture was neutralized with 3 N NaOH fenolptalin until pink color was obtained. 10 ml NaOH 1 N was added after 15 min boiling. Then it was cooled. After cooling, the mixture was titrated with HCl 1 N until the red color disappeared. In addition, blanko titration, which is the same way with the analysis of hash but without sample, was also carried out.

Conversion Calculations using the equation:

$$G = \frac{W_1}{W_2}\frac{W_3}{W_4}(Vb - Vc)N0 \qquad (1)$$

G: amount of glycerol formed, mgek
W_1: mass of process sample, g
W_2: mass of sample, g
W_3: mass of bottom layer, g
W_4: mass of bottom layer that was use to analyze, g
V_b: Volume of HCl for blangko titration, ml
V_c: Volume of HCl for sample titration, ml
No: HCL normality, mgek/ml

Co nversion, x was calculated using equation:

$$x = (G-(A1\ Vm\rho m))/(A2-A1)(Vm\rho m) \qquad (2)$$

A_1: free fatty acid, mgek/g oil
A_2: total of fatty acid, mgek/g oil
Vm: volume of oil to process, ml
ρm: used cooking oil mass density, m/ml

3. Results and discussion

3.1. The influence of reaction temperature

The influence of reaction temperature can be seen in figure 2. The increase of temperature will increase the conversion, this is because molecules movement will be faster.Relation between -ln(1-Xa) with time, resulting linier lines.

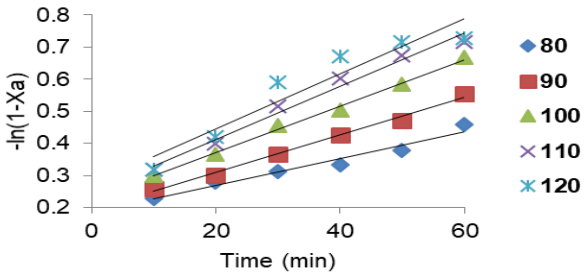


Fig. 2: Relationship between –Ln (1-Xa) with Time and Temperature.

From the above data, we can obtain a relationship between reaction rate, k1, the reaction temperature, T ° K, shown by the equation:

$k1 = 10103,3222\ e^{-5092,8910/T}$

If this reaction is used to calculate k1 value, , then the average error k1 research results reached 4.69% and the deviation x ± 3.38%, this can prove that chemical reactions controls the process.

3.2. The influence of the percentage of catalyst

From figure 3 it appears that the glycerides conversion increases with increasing percentage of catalyst, because the substances reagent is more activated, so that greater collision occurred.

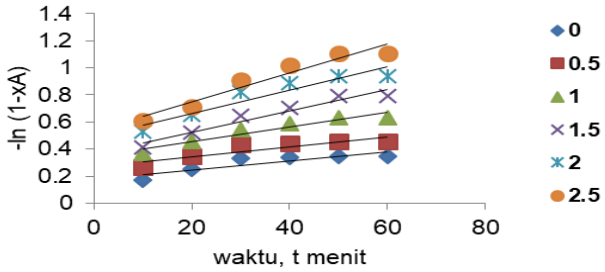


Fig. 3: Relationship -Ln (1-Xa) with Time and The Percentage of Catalyst.

After k" value obtained with catalyst percentage (H) form a straight line that can be expressed by equation:

k" = 7,5044(10-3) + 5,0656 (10-3) H

K0 value was not much different compared to k" that does not use a catalyst. (8, 503(10-3)). This is caused by acidity of alcohol. Therefore, it is proven that the chemical reaction occurs in the liquid phase and the order is pseudo against glycerides.

3.3. Effect of stirring speed

In figure 4, it can be seen that glycerides conversions increase with increasing of stirring speed, because more movement of the reactant molecules occurred, this increase the collosions. However, the increasing of conversions is not high. Thus, it can be said that the chemical reactions control the overall reaction rate.

If a graph of –ln(1-xA) versus time, t min, was made, it appears that the points is not much deviate from straight lines (Fig.4). Thus, it can be concluded that alcoholysis reaction using used cooking oil and solid catalyst was controlled by chemical reaction of pseudo first order against glycerides.

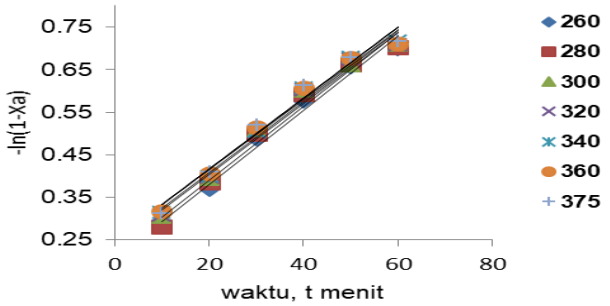


Fig. 4: Relationship -Ln (1-Xa) with Stirring Speed.

An equation between k" and stirring speed (N) was made,

k" = 1,309 (10-2)N 0,0576

From above equation, a Reynolds index was 0.0576 which is much lower than 0.5. this clearly shows that the chemical reaction has important role [12].

3.4. Effect of ethanol-oil ratio equivalent

The collosion of reactant molecules increase with the increasing of ethanol-oil ratio equivalent as shown in figure 5. Relation between –ln(1-xA0 with time, t, was a straight line. This indicates that the pseudo first order against glycerides.

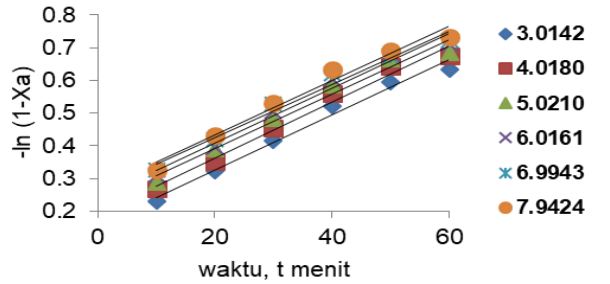


Fig. 5: Relationship -Ln (1-Xa) with Time and the Ratio of Reactants.

When graphed between k"with Comparative reagent (P) is obtained by means of a straight line of least squares equation:

-ln k" = 4, 3873 – 02023 ln P

With the average error k" obtained from the research was 1% and deviation x ^{0} 0.78%.
If we compared the research results of this study to other studies [14,16], it can be concluded that all the results have pseudo first order and glycerides conversions do not much different as shown in table 1.

Table 1: Ethanolysis Comparisons (Used Cooking Oil, Nyamplung Seed Oil, Kepuh Seed Oil, Jatropha Oil, Castor Oil, and Rubber Seed Oil)

	Used cooking oil	Nyamplung seed oil	Kepuh seed oil	Jatropha oil	Castor oil	Rubber seed oil
Time, min	60	60	60	60	60	60
Highest temperature,°C	110	120	120	120	100	120
Pressure, atm	2.6	3.6	2.6	5.01	4.3	4.5
Catalyst	Used Solid	Amberlyst-15	Used Solid	NaOH	NaOH	Zeolite Nature
Mass of catalyst	2 % of oil mass	0,1071 g/gminyak	2 % of oil mass	0.7138 %	0.5 %	2%
Ethanol/oil mgek/mg ek	6	10.3317	6	10.4	3.345,16	6
Reaction order	1	1	1	1	1	1
Conversion, %	70.09	70.47	70.91	84.61	64.60	74.47

4. Conclusion

Alcoholysis reaction of used cooking oil at high pressure in liquid phase using wasted cracking catalyst from petroleum plant. The reaction is controlled by chemical reaction of pseudo first order against glycerides. The best condition was achieved at 110 □C, catalyst percentace 2% of oil mass, stirring speed 320 ppm and reactant ratio 6 mgek/mgek, conversion was 70.99. the resulted ester has almost similar properties to diesel oil.

References

[1] T. S. Utami, R. Arbianti, D. Nurhasman. Kinetika reaksi transesterifikasi CPO terhadap produk metal palmitat dalam reactor tumpak. Seminar nasional Fundamental dan Aplikasi Teknik Kimia. (2007) 1-6. https://doi.org/10.15408/jkv.v1i1.209.
[2] N. A. Adeyemi, A. K. M. Mohiuddin, A. T. Jameel. Biodiesel production: a mini review, Intl. Energy Journal 12 (2011) 15-28.
[3] P. L. Pupung, 1985. Beberapa minyak nabati yang memiliki potensi sebagai bahan bakar alternatif untuk motor disel. Lembaran Publikasi Lemigas, 4(1985)34-35.
[4] P. Janulis, E. Sendzikiene, V. Makareviciene, K. Kazancev. Usage of fatty waste for production of biodiesel. 11 (2009).
[5] M. N. Islam M. R. A. Beg. The fuel properties of pyrolysis liquid derived from urban solid wastes in Bangladesh. Bioresources Technology 92 (2004) 181-186. https://doi.org/10.1016/j.biortech.2003.08.009.
[6] D. Wilkis. The impact of blending techniques, feedstock choice, and analytical techniques on biodiesel blend accuracy. 19 (2008) 787.
[7] J. Xue. T. E. Grift. A. C. Hansen. Effect of biodiesel on engine performances and emissions. Renewable and sutainable energy reviews 15 (2011) 1098-1116. https://doi.org/10.1016/j.rser.2010.11.016.
[8] National Stadartritation Unit. Biodiesel. 2006.
[9] J. H. Perry. D. W. Green. Chemical engineer's handbook. 1984.
[10] C. J. Hill Jr. An introduction to chemical engineering kinetics and reactor design. (19970 220-226.
[11] K. R. Westerterp, W. P.M. V. Swaaij,A. A. C. M. Beenackers. Chemical reactor design and operation. (1984) 16.
[12] R. E. Johnstone, M. W. Thring. Pilot plant models and scale up method in chemical engineering. (1957) 66-67.
[13] R. C. Griffin. Technical method of analysis. 2 (1955) 107-110.
[14] A. S. Ramadhas, C. Mulareedharan, S. Jayaraj. Performance and emission evaluation of diesel engine fueled with methyl esters of rubber seed oil. J. Renew. Energy 30 (2005) 1789-1800. https://doi.org/10.1016/j.renene.2005.01.009.
[15] K. A. Roni. I. B. Agra, H. Sulistyo. Alkoholisi minyak biji kepuh (sterculia foeteda) pada tekanan diatas satu atmosfer. BPPS-UGM 11 (1998) 233-245.
[16] F. D. Gustone, J. L. Harword, A. J. Djikstra. The lipid handbook 3 2007.