Optimization of Biodiesel Washing by Water Extraction

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Abstract—**Castor oil methanolysis produces biodiesel and glycerol. The reaction catalyzed by potassium hydroxide with excess methanol. It forms a homogeneous reaction mixture. Due to the limited solubility of the glycerol in the biodiesel, after the residual methanol been removed, the glycerol then be separated from the biodiesel. To confirm the alternative diesel fuel standards, the biodiesel be washed to remove the residual catalyst and glycerol. On washing, a certain amount of distilled water poured to the flask while stirring. When the stirring has stopped, the water will eventually separate and slowly sink taking with it any soluble material, mainly the remaining glycerol, while the biodiesel will remain on the top. Experiments have been performed in order to determine the optimum conditions of the washing and to find a correlation of the extraction variables. As crude biodiesel, it was quite caustic with a pH more than 9 with glycerol content 0.93 %. Washing the crude biodiesel was sufficient to washout all remaining catalyst and glycerol, bringing the pH down to near neutral and the glycerol content down to 0.05 % or less. As the biodiesel to water volume ratio and temperature are increased, the glycerol mass transfer rates from diluent (biodiesel) to solvent (water) increase, respectively. A correlation to show the effect of biodiesel to water volume ratio on mass transfer coefficient was developed in the form of a dimensionless equation.**

***Keywords*— biodiesel, extraction, methanolysis, washing**

I. INTRODUCTION

The conversion of vegetable oil into esters for the use of biodiesel fuel involves transesterification process of the oil with alcohols. The process is to chemically break the molecule of the raw renewable oil into esters or biodiesel with glycerol as by-product. The reaction proceeds essentially by adding acid or base catalyst. The catalyst used has a determinant effect on the reaction. The base catalyst, such as potassium hydroxide, is preferred to acid catalyst due to the possibility to conduct the reaction completely in shorter times (30-60 min), even at room temperature. While acid catalyst, such as sulphuric acid, require higher temperature (373 K) and longer reaction times (3-4 h). Alcohols more frequently employed are short chain alcohols, such as methanol, ethanol and butanol. Methanol is the one most often used for commercial and process reasons due to methanol is the shortest chain alcohol and it is a polar. The type of the catalyst and alcohol, the reaction conditions, the presence and concentration of impurities in a transesterification reaction determine the path that the reaction follows. For example, for base catalyzed transesterification, water and free fatty acids are not favourable because they give rise to the production of soaps [1]-[4].

Usually, three steps are needed to convert oil into biodiesel. The fisrt step is pre-treatment to put the oil in the form in which it can be reacted properly in the reactor. The second is transesterification reaction step and the third is purification step for the final desired product to be obtained [5]. Complete transesterification reaction usually give high purity level of the biodiesel, then it will confirm to physical standard values for alternative diesel fuels, like ASTM D6751, EN 14214 or SNI 04-7182-2006, etc. The maximum standard value for free glycerol in the biodiesel is 0.02 %.

Conversion of castor oil into methyl ester for use as biodiesel fuel is treated at room temperature in the presence of potassium hydroxide as a catalyst. In performing the reaction, there are no significant problems, but in performing the purification some technical difficulties are usually obtained, especially if the oil contains high level of water and free fatty acid. Therefore the operation cost may increase. The most popular method to purify biodiesel is washing with water. Washing the biodiesel is necessary in order to improve its fuel properties, largely by removing residual free glycerol and small amount of the catalyst. In this work the experiments were conducted to study the effect of temperature and the amount of water on the rate of biodiesel washing by water extraction. A correlation of the extraction variables based on the rate data is proposed.

Liquid –liquid extraction is the term applied to any operation in which a material dissolved in one liquid phase is transfered to a second liquid phase. In glycerol extraction or biodiesel washing process there are two phases, the water-phase and biodiesel-phase. The solute (glycerol) is transfered from diluent (biodiesel-phase) to solvent (water-phase). The unsteady mass balance of the solute glycerol in the stirred tank batchwise solvent extraction is

$$k_c a\left(C_A * - C_A\right) = \frac{dC_A}{dt} \qquad (1)$$

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where $k_c a$ (1/min) is the volumetric mass transfer coefficient, C_A* (g/cm^3) is the water-phase concentration of glycerol in equilibrium with X (g/cm^3), a biodiesel-phase concentration of glycerol. Correlation between C_a* and X, is expressed by means of Henry's law:

$$C_A* = H_A X \tag{2}$$

where H_A is the Henry's law constant for species A. The amount of X can be evaluated by overall mass balance of glycerol in the system as follows :

Initial amount of glycerol in the diluent = amount of glycerol in the solvent + amount of glycerol in the diluent at t = t

or

$$V_b X_{(t=0)} = V_w C_A + V_b X_{(t=t)} \tag{3}$$

$$X_{(t=t)} = X_{(t=o)} - C_A \left({V_w}\big/{V_b} \right) \tag{4}$$

$$X_{(t=t)} = X_{(t=o)} - C_A S^{-1}$$

where V_b (cm^3) is volume of crude biodiesel, V_w (cm^3) is volume of water and the ratio of V_b and V_w is S (part). By doing experiment to measure C_A at different extraction times and using Matlab calculation program, the Henry's law constant and the volumetric mass transfer coefficient $k_c a$ can be evaluated.

The variables affecting the mass transfer rate on liquid-liquid extraction in a stirred tank are: physical properties of the solvent and diluent, the mixing parameter and the amount of water used. Correlation between the variables can be expressed in a dimensionless equation [6]:

$$\left(\frac{k_c a.\rho_w.dp^2}{\mu_b} \right) = C \left(\frac{V_b}{V_w} \right)^{c1} . \left(\frac{\rho_b}{\rho_w} \right)^{c2} . \left(\frac{\mu_w}{\mu_b} \right)^{c3} . \left(\frac{\rho_w.D_{AB}}{\mu_b} \right)^{c4} . \left(\frac{\rho_w.N.dp^2}{\mu_b} \right)^{c5} \tag{5}$$

or :

$$\left(\frac{k_c a \rho_w dp^2}{\mu_b} \right) = C.S^{c1} \left(\frac{\rho_b}{\rho_w} \right)^{c2} \left(\frac{\mu_w}{\mu_b} \right)^{c3} Sc^{c4}\,\mathrm{Re}^{c5} \tag{6}$$

where Sc is the Schmidt number, Re is the Reynolds number. The density of biodiesel ρ_b (g/cm^3), the density of water ρ_w (g/cm^3), the viscosity of biodiesel μ_b (g/cm·min), the viscosity of water μ_w (g/cm·min), the stirring speed N (rpm), and the stirrer diameter dp (cm) can be measured directly from the experiment. The Wilke-Chang correlation can be used for predicting the diffusivity of solute glycerol in the water phase [7]:

$$D_{AB} = \frac{\left(117{,}3.10^{-18}\right)\left(\Phi M_B\right)^{0.5} T}{\mu_B v_A^{\ 0.6}} \tag{7}$$

where D $_{AB}$ (cm^2 /min) is the diffusivity of solute A in the solvent B, Φ is an association parameter of the solvent (Φ =2.6 for water), M_B is the molecular weight of solvent B, μ_B (g/cm·min) is the viscosity of B, v_A is the solute molar volume at the boiling point and T (K) is the absolute temperature.

The empirical constants c_1, c_2, c_3, c_4 and c_5 can be determined by multi dimension regression method of the experimental data.

II. EXPERIMENTAL PROCEDURE

A. Materials

The castor oil was purchased from Brataco Chemical Store in Yogyakarta, Indonesia. The free fatty acids content in the oil was determined by volumetry analytical method [8] to be 0.1686 wt % and the water content was 0.2199 wt %. The density of the oil at 302 K was 0.9756 g/cm^3 and the saphonification number was 186.99. Anhydrous methanol with purity of 99.95 % and potassium hydroxide KOH pellets were purchased from JT Baker. Distilled water was used as washing agent (solvent).

B. Biodiesel Preparation

The crude biodiesel was prepared by transesterification as follows: A stirred tank reactor was initially charged with the castor oil. Separately, KOH was dissolved in the methanol and the solution was poured to the reactor. The reaction was conducted for 1.5 hours. After completion of the reaction, the excess methanol was recovered from the mixture by vacuum distillation and the methanol free mixture was transferred to a separatory funnel, allowing the glycerol to separate. The glycerol layer was drained and the biodiesel layer was collected. A liter of castor oil needs 550 cm^3 methanol and 9.6 g KOH. Prior to washing, the glycerol content in the crude biodiesel was analyzed and it was 0.9331 % wt, while the pH was 9.1

C. Biodiesel Washing Conditions

Mechanical mixing is normally applied to increase the mass transfer rate. Therefore for all experiments on biodiesel washing, a maximum rotation of 300 rpm was used. To examine the temperature dependency on mass transfer of glycerol, biodiesel washing at 301 K (room temperature), 308 K, 318 K and 328 K were studied. Four different volume ratios of biodiesel to water were used to investigated the effect of biodiesel to water volume ratio on glycerol mass transfer . The volume ratios were: 2 :1, 1:1, 1:2 and 1:3.

D. Apparatus and Washing Procedures

A 1000 cm^3 three neck flask equipped with stirrer, thermometer and sampling device as an extractor. The extractor was immersed in a constant temperature water bath.

Three necks flask was initially charged with 100 cm^3 of crude biodiesel, then placed in constant temperature bath A certain volume of water was poured while mixing. Ten mililitres of sample was taken every 2 minutes. Then, the sample was tranferred to a sample bottle and allowing the water to separate by gravity. After removing the biodiesel layer, the glycerol concentration in water layer was analyzed.

III. Results and Discussions

A. *Effect of Water Amount on Biodiesel Washing*

The dependency of biodiesel washing on water amount is examined by varying volume ratio of biodiesel to water, while temperature and mixing speed were kept constant at 301 K and 300 rpm, respectively. Fig. 1 shows the changes of glycerol concentration in water phase C_A, when washing was done at different amount of water solvent. At the same washing (contact) time, the more water was used, the more amount of glycerol was extracted.

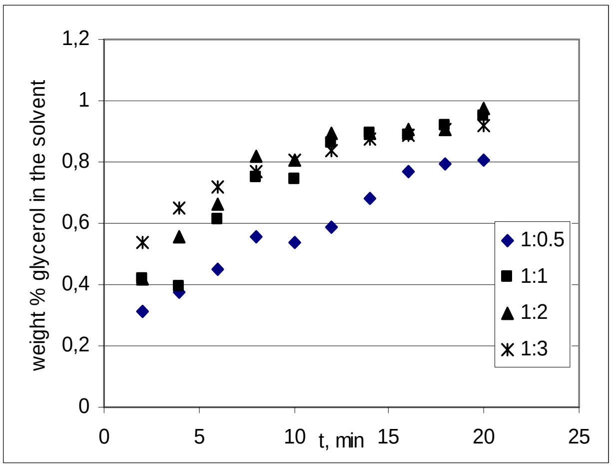

Fig. 1. The effect of washing time on glycerol concentration C_A at various biodiesel to water volume ratio (T= 301 K and N= 300 rpm)

The amount of glycerol extracted was also influenced by washing time. On the early washing, as the glycerol concentration difference in biodiesel and water phases was high, the rate of glycerol mass transfer was high. Then as the concentration difference decreases, the rate decreases as well. The rate reaches an equilibrium condition and the time to reach the equilibrium was about 20 minutes. The glycerol concentration in diluent (biodiesel phase) and in solvent (water phase) at equilibrium condition are presented in Table I.

Table I. Equilibrium Glycerol Concentration at Various Biodiesel to Water Volume Ratio (T= 301 K and N = 300 rpm)

No	Biodiesel to Water Volume Ratio, S	Equilibrium Concentration of Glycerol, 10^2 (g/cm^3)	
		Biodiesel Phase	Water Phase
1	2:1	0.0880	0.8059
2	1:1	0.0574	0.8617
3	1:2	0.0530	0.8801
4	1:3	0.0423	0.9178

As shown from Table I, for more than 20 minutes washing time at room temperature the glycerol content in biodiesel reduced from 0.9331 % to 0.0423 % and the pH down to 7.3 by using biodesel to water volume ratio of 1:3. This value is still higher than the allowable standard value of 0.02 % wt.

B. *Effect of Temperature on Biodiesel Washing*

To study the dependency of biodiesel washing on temperature, experiment was done at various washing temperature, while the mixing speed and biodiesel to water volume ratio were kept constant, at 300 rpm and 2:1, respectively. Fig. 2 shows the changes in glycerol concentration with time at different temperature of washing.

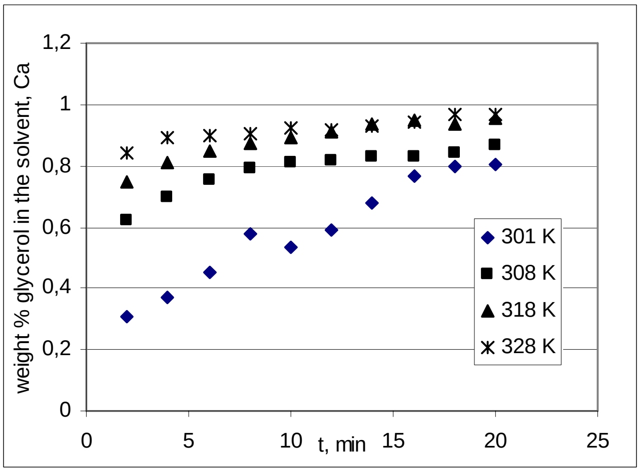

Fig 2. The effect of washing time on glycerol concentration C_A at various washing temperature (S = 2:1 and N = 300 rpm)

For the same washing time, the higher temperature gives more glycerol extraction. The amount of glycerol extracted was also influenced by washing time. At the beginning of the washing, the glycerol concentration difference between the two phases was high, then the rate of glycerol mass transfer was high. As the concentration difference was decrease, the rate was decreasing, before it reached an equilibrium condition. The time to reach equilibrium condition was shorter when washing was conducted at higher temperature. The experimental measurements on equilibrium concentration of glycerol in the two phases is presented in Table II.

Table II. Equilibrium Glycerol Concentration at Various Washing Temperature (S = 2:1 and N= 300 rpm)

No	Washing temperature, T (K)	Equilibrium Concentration of Glycerol, 10^2 (g/cm^3)	
		Biodiesel Phase	Water Phase
1	301	0.0880	0.8059
2	308	0.0838	0.8283
3	318	0.0802	0.9544

4	328	0.0698	0.9678

As shown from the table, that at 328 K the maximum concentration of glycerol in water phase was 0.9678 % in equilibrium with the concentration in the biodiesel phase of 0.0698 %. It meant that the glycerol concentration in biodiesel was reduced from 0.9331 % to 0.0698 % for 20 minutes of washing.

C. Equilibrium Constant and Mass Transfer Coefficient

Evaluating the experimental datas in assosiation with equation (2), (3) and (4) were done to predict the Henry's constant and volumetric mass transfer coefficient, k_ca, by using two variables optimization methode and Matlab program. The predicted Henry's constant and the mass transfer coefficient were presented in Table III and IV.

Table III. Predicted Values of H_A and k_ca at Various Biodiesel to Water Volume Ratio

Biodiesel to Water Volume Ratio, S	Henry's Constant, H_A	k_ca, 1/min
2:1	0.7891	0.1316
1:1	1.0466	0.1746
1:2	1.0505	0.2348
1:3	0.9156	0.3668

The value of Henry's constant H_A is influenced by temperature, but it was not influenced by amount of solvent. The more solvent added, the value of k_ca was higher. This result is due to the more solvent gave larger contacting area. The higher temperature, the mass transfer coefficient was higher. This condition was achieved as higher temperature gave higher diffusivity of glycerol then the mass transfer rate was higher.

Table IV. Predicted Values of H_A and k_ca at Various Washing Temperature

Washing temperature, T (K)	Henry's Constant H_A	k_ca, 1/min
301	0.7891	0.1316
308	0.8197	0.6046
318	0.9993	0.7719
328	1.0341	1.1582

D. Effect of Biodiesel to Water Volume Ratio on Mass Transfer Coefficient

The dependency of mass transfer coefficient on biodiesel to water volume ratio was evaluated by equation (5) or (6). While the stirrer diameter, mixing speed, physical properties and temperature were kept constant, the dimensionless equation of (6) was reduced to be

$$\left(\frac{k_c a.\rho_w.dp^2}{\mu_b}\right) = C'.S^{c1} \tag{8}$$

By introducing $\rho_w = 0.9962$ g/mL, $dp = 3.5$ cm and $\mu_b =$ 12,7027 g/cm·min, the constant c_1 and C' was evaluated by linear regression of ln $\left(\frac{k_c a.\rho_a.dp^2}{\mu_b}\right)$ versus ln S, with intercept was ln C and the slope was c_1. Then the mass transfer coefficient at certain value of biodiesel to water volume ratio can be predicted by using equation

$$\left(\frac{k_c a.\rho_a.dp^2}{\mu_b}\right) = 0.1747 S^{-0.5408} \tag{9}$$

The average error was 1.945%.

E. Effect of Temperature on Mass Transfer Coefficient

The dependency of mass transfer coefficient on temperature was evaluated by equation (5). While the stirrer diameter dp =3,5 cm, mixing speed N = 300 rpm, and volume ratio 2:1 were kept constant, while density, viscosity and diffusivity were influenced by temperature. The diffusivity of glycerol was predicted by equation (7), with $\Phi = 2.26$, $M_b = 18$ and ν_A = 73.0293 cm^3/mole [9]. The physical properties of biodiesel and water at various temperature were presented in Table Va and Table Vb.

Table Va. The Physical Properties of Biodiesel and Water

Temperature,T (K)	D_{AB}, (cm^2/min)	ρ_b (g/cm^3)	ρ_w (g/cm^3)
301	1.35E-15	0.9306	0.996233
308	1.80E-15	0.9285	0.994032
318	1.88E-15	0.9254	0.990213
328	1.95E-15	0.9196	0.985696

Table Vb. The Physical Properties of Biodiesel and Water

Temperature, T (K)	μ_b (g /cm min)	μ_w (g /cm min)
301	12.70269	0.51
308	9.7322148	0.48
318	9.6484608	0.39
328	9.6093756	0.33

By multidimension regression method the values of the empirical constants C, c_2, c_3, c_4 and c_5 were determined. Then the relation of the variables was to be

$$\left(\frac{k_{ca}.\rho_a.dp^2}{\mu_b}\right) = 2537.688(S)^{-0.5408}\left(\frac{\rho_b}{\rho_a}\right)^{150.8912}\left(\frac{\mu_a}{\mu_b}\right)^{1.8213} \left(\frac{\rho_a.D_{AB}}{\mu_b}\right)^{3.3778}\left(\frac{\rho_a.N.dp^2}{\mu_b}\right)^{0.3405} \tag{10}$$

The average relative error was 0.06 %

IV. CONCLUSIONS

These experiments showed that washing the castor oil biodiesel by water extraction in a single stage stirred tank was reduced the glycerol content from 0.9331 % to at least 0.09 % for 20 minutes washing time by adding water at 50 % of biodiesel volume. When the water was 300 % of biodiesel volume the glycerol content was less than 0.05 % and the pH was 7.3. To achieve the standard requirement of glycerol content in biodiesel to be less than 0.02 %, the washing should be done in multistage process.

The rate of mass transfer of glycerol from the (crude) biodiesel into water is affected by the temperature of extraction and the volume ratio of solvent to biodiesel. Higher mass transfer rate is achieved on higher biodiesel to water volume ratio as well as higher temperature.The more water added gives larger mass transfer area, so the volumetric mass transfer coefficient is higher. The higher washing temperature gives higher diffusivity of glycerol from biodiesel to water phase, then the mass transfer coefficient is higher.

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