

Effect of Co-solvent Addition on Glycerolysis of Waste Cooking Oil

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ABSTRACT

Glycerolysis can be a useful alternative for lowering free fatty acid (FFA) content present in waste cooking oil. In the present work, the effect of mass ratio of co-solvent hexane to oil on glycerolysis of waste cooking oil was investigated to enhance the miscibility of the oil and glycerol phases. The experimental results showed that the addition of hexane as co-solvent affected the glycerolysis reaction rate. However, a suitable amount of co-solvent must be added to achieve an optimum of FFA conversion. The use of 0.125:1 of mass ratio of co-solvent to oil leads to higher rate constant of approximately two times compared to glycerolysis without a co-solvent. The glycerolysis reduces the FFA content, peroxide and saponification values of oil; however, it does not change the density and kinematic viscosity as well as the fatty acid composition of oil.

Keywords: Co-solvent, free fatty acid, glycerolysis, waste cooking oil

ARTICLE INFO

Article history:

Received: 08 July 2016

Accepted: 23 June 2017

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INTRODUCTION

The glycerolysis process can convert free fatty acid (FFA) content back to its respective glyceride molecules. In glycerolysis, the glycerol reacts with the FFA to form monoglycerides, diglycerides and triglycerides (Anderson, 1962). It can be a good technique for reducing FFA content in the oil compared to other techniques such as acid esterification, which is limited by the requirement of higher purification. The advantage of this approach is

that no alcohol is needed during the process. The process has the potential of using glycerol as a byproduct of the transesterification process, which lowers the cost of the process. However, the drawbacks of this method are that it requires a high temperature, has a relatively slow reaction rate and is limited by equilibrium; in addition it involves two liquid phases, in which the solubility of glycerin is rather limited in triglycerides (Felizardo et al., 2011). These drawbacks have limited the application of glycerolysis in FFA processing to the production of more costly products. Despite its potential for lowering FFA content, the glycerolysis process has been used to produce monoglycerides and diglycerides, which are widely used in many applications such as surfactants and emulsifiers in food, cosmetics and pharmaceutical products (Satriana et al., 2016).

The glycerolysis process can be performed via enzymatic, alkaline and acid catalysed reactions (Sonntag, 1982). Most of the existing literature on glycerolysis reports on the use of high temperatures and low pressures in the process. It also shows that the temperature of reaction, type and amount of catalyst, molar ratio of glycerol to oil, mixing intensity and reaction time are important variables in the glycerolysis reaction (Noureddini et al., 2004; Felizardo et al., 2011; Gole & Gogate, 2014; Cai et al., 2015). Wang et al. (2012) reported a reduction in FFA content of waste cooking oil from 84.4 to 3.4 mg of KOH/g under the optimised conditions of oil to glycerol with a molar ratio of 1:4, solid superacid catalyst concentration of 0.3% w/w, temperature reaction of 200°C and reaction time of 4 hours. Felizardo et al. (2011) also reported that the optimised conditions for the glycerolysis of acidulated soap-stocks of soybean oil were oil to glycerol with a molar ratio of 1:10, with a stirring speed of 300 rpm, catalyst concentration of 0.2% w/w, temperature of 220°C and reaction time of 2 hours. It can be seen that glycerolysis requires considerably severe conditions and longer reaction times, making this process an energy-intensive operation. Recently, Kombe et al. (2013) reported the application of low-temperature glycerolysis for pre-treatment of oil with high FFA content. Based on the optimisation study, the highest glycerolysis efficiency level of 98.67% was found for oil to glycerol with a mass ratio of 1:2.24, temperature of 65°C and reaction time of 73 minutes.

In glycerolysis, immiscibility between oil and glycerol can inhibit the process of mass transfer and reaction rate limit. This condition generally can be overcome using intensive stirring of the reaction mixture. However, this increases the cost of energy in the production process. There is a need to develop an intensification process for the glycerolysis process with an aim of reducing the reaction temperature with high reaction yields as well as lowering the energy requirement and the processing cost. Intensification aspects of glycerolysis have been investigated in the literature (Gole & Gogate, 2014; Moquin et al., 2005). One strategy to overcome the problem of mass transfer limitations is one-phase reaction (Mahajan et al., 2006). It can be formed by adding a co-solvent to increase the solubility of oil and glycerol.

In this study, low-temperature glycerolysis was applied for lowering FFA in waste cooking oil via a homogeneous base catalyst. It can be an important processing step in the biodiesel production for reducing the initial FFA content in waste cooking oil. The effect of a co-solvent hexane addition was investigated. The kinetic of glycerolysis was also studied.

MATERIALS AND METHODS

Materials

Waste cooking oil was collected from restaurants around Banda Aceh, Indonesia. Oil was filtered to remove impurities (traces of particles and mud) before it was used in the experiments. The initial FFA content of the waste cooking oil was observed to be 5.72%. Additionally, glycerol used in the experiments was of technical grade, and NaOH (99%) in pellet form was of analytical grade. All the chemicals were used as received from the supplier.

Glycerolysis

The glycerolysis reaction was conducted in a glass batch reactor equipped with an IKA RW20 (Germany) mechanical digital stirrer. The molar ratio of oil to glycerol at 1:1 and the NaOH catalyst concentration of 0.875% w/w of oil were kept constant in all the experimental runs. Initially, waste cooking oil was heated at a temperature of 50°C. Catalyst and co-solvent were dissolved in glycerol before mixing with oil. Then, the reaction mixture was mixed and heated at a reaction temperature of 65°C. The stirring rate was kept constant at 600 rpm. Samples were taken at specific intervals of time. The sample was cooled to room temperature and then poured into a separating funnel. The glycerolysis reaction yielded two immiscible phases (layers) due to the differences in the density of the components. The upper layer consisted of oil, whereas the lower layer contained glycerol, dissolved catalyst, water and other minor components from the oil. The upper layer was further analysed for its FFA content to monitor the progress of the glycerolysis reaction.

Method of Analysis

The glycerolysis was monitored for FFA content using the acid-base titration technique. In this method, a known quantity of oil was dissolved in ethanol and heated for 5 to 10 minutes. It was then titrated against KOH using phenolphthalein as an indicator. The conversion of FFA (X) can be determined by Equation (1) as given below.

$$X(\%) = \frac{[\text{FFA}]_0 - [\text{FFA}]_t}{[\text{FFA}]_0} \times 100 \quad (1)$$

where $[\text{FFA}]_t$ is the concentration of FFA at time t (moles.L⁻¹), $[\text{FFA}]_0$ is the initial concentration of FFA (moles.L⁻¹). Further, the characteristics of the glycerolysis product, such as density, viscosity, peroxide and saponification value were determined according to the Indonesian National Standard (No. 04-7182-2006). The fatty acid composition was analysed using gas chromatography-mass spectrometry (GC-MS).

Kinetic Study

A kinetic study of waste cooking oil glycerolysis was conducted using FFA content data. This was performed using a second-order kinetic model (Gole & Gogate, 2014). The kinetic model was based on the following assumptions: (a) the effect of mass transfer was negligible; and (b)

the effects of reverse reaction and other reactions were ignored. The second-order rate constant (k) was predicted to quantify the extent of intensification due to the use of a co-solvent.

RESULTS AND DISCUSSION

Effect of Co-Solvent

In a glycerolysis system, the mass transfer between the two phases of oil and glycerol becomes a significant factor that affects the reaction rate due to the immiscibility of the oil and glycerol phases. Hexane as a co-solvent can be added to enhance the miscibility of the phases and to speed up the reaction rate such as in transesterification and glycerolysis (Qian et al., 2010; Supardan et al., 2017). The effect of a co-solvent of hexane on the rate of glycerolysis was studied by varying the co-solvent to oil mass ratio. Figure 1 shows the progress of the reaction in terms of the change in FFA conversion at different co-solvent to oil mass ratios.

The experiment showed that FFA conversion generally increases as reaction time increases. The final FFA conversions were in the range of 67-93%. Similar trends were reported in the literature for various types of system. Gerpen et al. (2004) reported that the FFA conversion of animal fat was about 92% for an oil-to-glycerol molar ratio of 1:2 and reaction time of 150 minutes. The FFA conversion of acidulated soap-stocks was achieved at 90% for 180 minutes of reaction time (Felizardo et al., 2011). Meanwhile, Kombe et al. (2013) reported that the FFA conversion of crude jatropha oil was about 98% for a reaction time of 73 minutes.

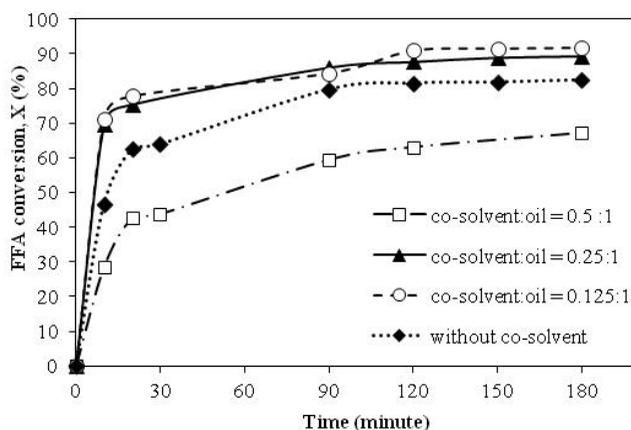


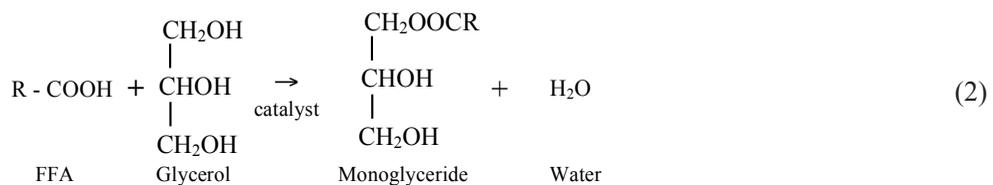
Figure 1. Effect of co-solvent to oil mass ratio on reaction progress

The final FFA conversion obtained at the end of the reaction time of 180 minutes was found to be dependent on the co-solvent to oil mass ratio. As shown in Figure 1, the final FFA conversions of co-solvent to oil mass ratio of 0.125:1 and 0.25:1 were higher than those for the system without co-solvents. Based on the experimental results, it can be concluded that the the addition of a co-solvent improves the reaction; this can be attributed to better homogeneity of the reaction mixture. The role of the co-solvent is to improve the miscibility of the reaction mixture to enhance the reaction rate. The final FFA conversion further decreased at a co-solvent

to oil mass ratio of 0.5:1. Excessive addition of co-solvent into the reaction system can reduce the glycerolysis reaction rate. It might be due to a dilution effect of the reactants (Dabo et al., 2012; Encinar et al., 2010). Therefore, a suitable amount of hexane must be added to achieve an optimum FFA conversion. Experimental results showed that a co-solvent to oil mass ratio of 0.125:1 provided a maximum FFA conversion. Excessive addition of hexane into the reaction system can also increase the operating cost as well as the load on the separation process.

Glycerolysis Kinetic

The glycerolysis reaction scheme and the second-order kinetic model can be written as Equations (2) and (3), respectively, as given below.



$$-\frac{d[\text{FFA}]}{dt} = k[\text{FFA}]^\alpha [\text{Glycerol}]^\beta \quad (3)$$

where $[\text{Glycerol}]$ is the concentration of glycerol (moles.L^{-1}), and k is the second-order rate constant ($\text{L.moles}^{-1}.\text{min}^{-1}$). As presented in Equation (2), 1 mol of FFA reacts with 1 mol of glycerol to produce 1 mol of monoglyceride and 1 mol of water; thus, $\alpha=\beta=1$ and $[\text{FFA}] = [\text{Glycerol}]$. Equation (3) can be written as:

$$-\frac{d[\text{FFA}]}{dt} = k[\text{FFA}]^2 \quad (4)$$

Integration of Equation (4) yields:

$$\frac{1}{[\text{FFA}]_t} - \frac{1}{[\text{FFA}]_0} = k \times t \quad (5)$$

The relationship between FFA conversion and $[\text{FFA}]_t$ is as follows:

$$[\text{FFA}]_t = [\text{FFA}]_0(1 - X) \quad (6)$$

Substituting Equation (6) into Equation (5) gives:

$$\frac{X}{[\text{FFA}]_0(1 - X)} = k \times t \quad (7)$$

By plotting $\left(\frac{X}{[\text{FFA}]_0(1 - X)}\right)$ versus time (t), one can obtain k as the slope. The linearised form of all of the curves corresponding to different levels of co-solvent to oil mass ratio verifies the kinetic model. The kinetic rate constants (k) determined from Equation (7) were calculated

from the experimental data by means of the linear regression method. Equation (7) fitted the experimental data quite well. The coefficient of linear correlation (R^2) was higher than 0.80. The calculated values of the kinetic parameter are presented in Table 1.

The kinetic parameter for 0.125:1 of co-solvent to oil mass ratio was larger than for 0.25:1 and 0.5:1 of co-solvent to oil mass ratio as well as without the co-solvent system. The rate of glycerolysis was increased significantly by co-solvent addition, as revealed by the values of the kinetic rate constants. The kinetic rate constant at a co-solvent to oil mass ratio of 0.125:1 was 4.1×10^{-2} L.moles⁻¹.min⁻¹, whereas the kinetic rate constant without the co-solvent system was 1.8×10^{-2} L.moles⁻¹.min⁻¹. Thus, the use of 0.125:1 of co-solvent to oil mass ratio led to a higher rate constant of approximately two times compared to the system without co-solvent.

Table 1
Values of Kinetic Parameter

Co-solvent to oil mass ratio [-]	Kinetic rate constant, k [L.moles ⁻¹ .min ⁻¹]	R^2
Without co-solvent	0.018	0.81
0.125 : 1	0.041	0.81
0.25 : 1	0.030	0.82
0.5 : 1	0.012	0.80

Properties of Oil

The physicochemical properties of the waste cooking oil and the product of glycerolysis are presented in Table 2. Glycerolysis has a significant effect on the FFA content, peroxide and saponification values of waste cooking oil. Glycerolysis reduced the FFA content, peroxide and saponification values of oil. Meanwhile, glycerolysis had no significant effect on density and kinematic viscosity of waste cooking oil.

Table 2
Physical and Chemical Properties of the Oil

Property	Waste cooking oil	After glycerolysis*
Density (kg/m ³ at 20°C)	0.906	0.908
Kinematic viscosity (mm ² /s, 40°C)	39.5	40.3
FFA content (%)	5.7	0.4
Peroxide value (meq/kg)	49.0	24.0
Saponification value	302.1	286.9

* co-solvent to oil mass ratio = 0.125:1

The fatty acid composition of the product of the waste cooking oil and glycerolysis is presented in Table 3. The experiment results showed that the fatty acid composition of the waste cooking oil and the product of glycerolysis was almost similar. In glycerolysis, glycerol

reacts with the free fatty acid to form monoglyceride; thus, it did not change significantly the fatty acid composition of the oil. The composition of oil is similar to the fatty acid composition of palm oil as the source of the oil (Syam et al., 2012).

Table 3
Fatty Acid Composition of the Oil

Property	Waste cooking oil	After glycerolysis*
Palmitic acid	45.7	46.3
Oleic acid	39.4	38.0
Linoleic acid	7.9	8.5
Stearic acid	4.1	3.8
Myristic acid	1.2	1.4

* co-solvent to oil mass ratio = 0.125:1

CONCLUSION

It was observed that the addition of a co-solvent of hexane had a remarkable effect on the FFA content of waste cooking oil. Generally, FFA conversion increased as time of reaction increased. The experiment results showed that a suitable amount of hexane should be added to achieve an optimum level of FFA conversion. The highest final FFA conversion was achieved at a ratio of 0.125:1 of co-solvent to oil mass ratio. The kinetic study also revealed that the kinetic rate constant for 0.125:1 co-solvent to oil mass ratio was about two times higher than for the system without co-solvent. The experiment results also showed that glycerolysis had no significant effect on density, viscosity and the fatty acid composition of oil. The results demonstrated that glycerolysis is a promising technique for lowering FFA of waste cooking oil for use as biodiesel feedstock.

ACKNOWLEDGEMENT

The authors are grateful to Syiah Kuala University and the Ministry of Research, Technology and Higher Education of the Republic of Indonesia for the financial support for this project through the MP3EI 2016 Research Grant. We are also grateful to Universiti Kebangsaan Malaysia for the Zamalah Scholarship awarded to one of the authors.

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