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To cite this article: Indah Thuraya Herman *et al* 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **765** 012077

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A Single Step Transesterification Process to Produce Biodiesel from The Spent Cooking Oil

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Abstract. A direct process of transesterification has been carried out to produce high yields of biodiesel. Conversion of waste cooking oil to methyl esters was performed using potassium hydroxide-glycerol (KOH-Gly) as a catalyst. KOH-Gly was produced by mixing KOH and glycerol at a mass ratio of 1:20 at a temperature of 80 °C for 120 minutes. The process of transesterification was performed at a reaction temperature of 60 °C, a molar ratio of oil to methanol of 1:6, 2% wt KOH-Gly catalytic loading for 30 minutes. This process resulted in a waste cooking oil conversion yield of about 97-98% to biodiesel using KOH-Gly as a catalyst. The two layers of the product were produced without the formation of soap, which facilitated the separation and purification process. Gas chromatography-mass spectrometry was used to analyse the chemical content of biodiesel.

1. Introduction

In recent times, the rapid depletion of fossil fuel has made biodiesel an attractive alternative fuel due to its similar characteristics to fossil diesel fuel. Biodiesel is described as mono-alkyl esters with a long chain of fatty acids derived from vegetable oils, animal fats or waste cooking oil [1]. About 95% of world biodiesel production is derived from edible oils, such as palm, canola and rapeseed oils [2]. Consumption of edible oil in the production of biodiesel has contributed to a rise in the price of edible oil and biodiesel to increase to levels 1.5 to 2 times higher than diesel fuel [3]. Recently, low cost feedstocks such as spent cooking oil and animal fats have been utilized to replace refined vegetable oil [4][5][6][7] in order to improve the economic feasibility of biodiesel. Biodiesel produced from waste oil can be a very promising alternative feedstock that could reduce the cost of production and the cost of controlling global emissions by reducing emissions of pollutants. However, based on diesel oil in the world, it may not be able to completely replace diesel fuel, but it may make a significant contribution to reducing dependence on diesel fuel-based petroleum [8].



Malaysia diversifies its biodiesel feedstock towards non- edible oil, such as spent cooking oil derived from palm oil [8] which is considerably cheaper to five times the average lower than refined cooking oil [9]. The amount of spent cooking oil generated by homes and restaurants is rising rapidly due to the massive growth in human population [10]. Disposal of spent cooking oil is a major issue in the world, due to the contamination of rivers, and blockages in water drainage systems that need extra cleaning work. The properties of the spent cooking oils are different from fresh vegetable oils due to physical and chemical changes because of oxidative and hydrolytic reactions that take place during frying [11]. The quality of spent cooking oils is estimated in terms of acidity and saponification values. One downside to the use of spent cooking oils for the production of biodiesel is that it contains several impurities, such as free fatty acid (FFA) and water, which must be processed prior to transesterification due to their potential adverse effects on the process [5].

Transesterification is a catalyzed reaction of oil or animal fats in the presence of alcohol to produce biodiesel and glycerol, and is the most practical and common method of processing biodiesel. Biodiesel is usually produced by transesterification reaction in the presence of alkaline catalysts if the free fatty acid (FFA) content in feedstock oil is less than 2 wt%. Higher FFA content is a major obstruction of the direct conversion of triglycerides to alkyl esters by transesterification process, as FFA can react with alkaline catalyst and results in saponification [2]. Transesterification failure may occur if the FFA content in the oil is more than 1% which will form a difficult emulsion of soap during the separation of biodiesel [12]. Free fatty acids therefore have a significant disadvantage when using a base- catalyzed transesterification process, because free fatty acids react with base catalyst to saponification reaction [13].

In the present work, a direct alkali- catalyzed transesterification of spent cooking oil was carried out for a reaction temperature 60°C. The molar ratio of oil to methanol was 1:6 in the presence of 2% wt KOH- Gly catalyst concentration. The main objectives of this study were to investigate the potential of KOH- Gly in direct alkali- catalyzed transesterification and evaluate the chemical content in biodiesel production in direct alkali- catalyzed transesterification.

2. Methodology

2.1 Synthesis of catalyst

Potassium hydroxide (KOH) and glycerol were used to prepare KOH- Gly catalyst with mass ratio of 1:20. KOH and glycerol were mixed homogenously at 80°C for 120 minutes until transparent colorless mixture was formed. KOH- Gly was placed inside a vacuum desiccator to prevent structural changes and humidity that may affect the physicochemical properties.

2.2 Characterization of spent cooking oil

The quality of oil is expressed in terms of the physicochemical properties such as acid value. The acid value of cooking oil was 1.18 mg KOH/g and spent cooking oil was found to be 8.42 mg KOH/g corresponding to a free fatty acid (FFA) level of 4.21%. It has been reported that transesterification would not occur if FFA concentration in the oil was above 3% [14]. The acid value was determined by a standard titration method and the value was calculated as follows:

$$\text{Acid value} = \frac{\text{volume of titrant} \times \text{normality of KOH} \times 56.1}{\text{mass of sample}} \quad (1)$$

$$\text{FFA \%} = \frac{\text{Acid value}}{2} \quad (2)$$

2.3 Transesterification of spent cooking oil

The transesterification was carried out by using 250 ml conical flask and magnetic hotplate stirrer. Thermometer was used to monitor the increment of temperature during the transesterification [15]. The start of the reaction time was recorded after the temperature reached 60°C. The reaction was kept at a desired temperature for 30 minutes. The molar ratio of spent cooking oil to methanol was 1:6, while the amount of KOH-Gly was 2% of the mixture. The experiment was repeated for baseline data using cooking oil with the same temperature and reaction time, a 1:6 molar ratio of cooking oil to methanol and a 2% wt potassium hydroxide (KOH) catalytic converter.

After some time, the mixture was poured into a separate funnel. The ester layer was separated by gravity and placed in the upper layer. The glycerol, extra methanol and excess catalyst were in the lower layer and decanted. The lower layer was collected, and the ester layer remained to be further processed. The ester layer has been washed several times with a small amount of hot distilled water. Biodiesel obtained has been heated to eliminate excess water. Biodiesel conversion was determined as follows [16]:

$$\text{Conversion (\%)} = \frac{\text{Weight of product}}{\text{Weight of maximum ester}} \times 100 \quad (3)$$

2.4 Analysis

The chemical content in biodiesel sample was analysed by using Varian Instruments CP 3800 gas chromatography interfaced to a 1200 Quadrapole mass spectrometer (ionising energy 70 eV, source temperature 280°C). Chemical compositions will be analysed according to the National Institute of Standards and Technology (NIST) mass spectral library standard reference database.

3. Results and Discussion

3.1 Production of biodiesel

Biodiesel production using spent cooking oil is generally synthesized in two-step reactions, namely esterification and transesterification due to its high free fatty acid content. Esterification is a pretreatment process in which free fatty acids interact with an acid catalyst and form a new ester to reduce the free fatty acid content. Formation of soap may be avoided due to reduction of free fatty acid. In this study, production of biodiesel was carried out at temperature of 60°C for 30 minutes. The molar ratio of oil to methanol was 1:6 with catalyst loading 2 %wt. Reaction of spent cooking oil with KOH-Gly as tested sample (WCO: KOH-Gly) and one repetition sample with same condition of spent cooking oil was used (RWCO: KOH-Gly). Reaction of cooking oil with potassium hydroxide (KOH) was carried out with same condition as baseline data (B-CO). Biodiesel was produced using spent cooking oil by direct transesterification process which esterification process was skipped.

The conversion of spent cooking oil to biodiesel was compared to cooking oil with KOH as baseline data were shown in Figure 1. High conversion of biodiesel from 97 to 98 percent slightly higher than the conversion of baseline data, which is 76.17 percent. The ratio of methanol/oil is one of the most important factors affecting the yield of biodiesel. The 6:1 methanol/oil molar ratio was selected in this study. Previous study reported that the methanol/oil molar ratio <1.5 resulted in the creation of a unique foam layer [17]. Other study proved that optimum condition of methanol/oil molar ratio was 6:1 where the conversion of spent cooking oil to biodiesel was 97% [18]. Although the stoichiometric ratio requires 3:1, transesterification is usually performed with an extra amount of alcohol in order to shift the balance to the methyl ester [16]. The transesterification reaction is a reversible reaction and requires higher concentration of alcohol to shift reaction equilibrium in the forward direction [19].

The temperature of the reaction also affects the parameter for the conversion of biodiesel. In this study, the conversion of spent cooking oil to biodiesel was achieved at a response temperature of 60°C. Previous study indicated that 60°C was the optimum reaction temperature for the production of biodiesel

from spent cooking oil, with a conversion rate of 90%. [13]. The optimum temperature in production biodiesel was from 30 to 50°C and the conversion slightly reduce at temperature 70°C [16]. Increased temperature above 65°C led to a negative effect on the conversion of biodiesel because, at higher temperatures, methanol begins to evaporate, its polarity is changed and the amount of methoxide ions in the reaction is decreased [20]. High temperatures could accelerate the saponification of triglycerides and have had a negative impact on the yield of the product [5]. On the other hand, it could lead to a significant reduction in the viscosity of spent cooking oil, which is beneficial for increasing the solubility of the oil in methanol and improving the interaction between oil and methanol molecules, thus achieving better conversion of triglycerides [5].

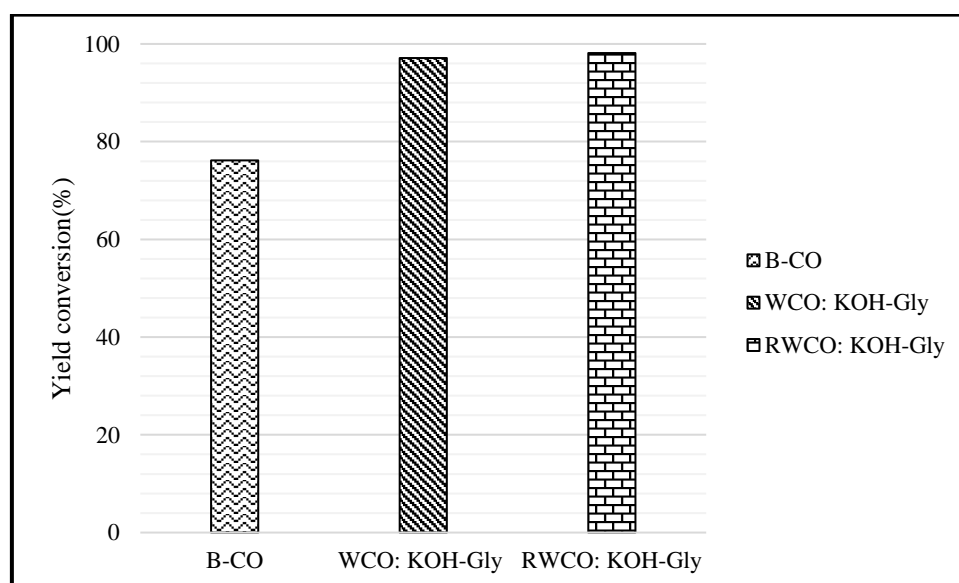


Figure 1. Conversion of biodiesel

Observation in Figures 2 and 3 showed that KOH and KOH-Gly reacted to the spent cooking oil. Soap formation occurred in the reaction of spent cooking oil with KOH, while two layers were clearly produced in the reaction of spent cooking oil with KOH-Gly. The formation of soap produced by the high acid value of the spent cooking oil, which is 8.42 mg KOH/g. In this study, the acid value of spent cooking oil was quite high compared to the other study in which the acid values were 2.5% and 7.25 mg KOH/g respectively [21] [17]. High acid value was derived from the frying process which produced FFA by hydrolysis of triglycerides during the high temperature cooking process. The higher amounts of FFA are present, the large amount of soap will be formed by an alkaline catalyst, which will reduce the conversion rate or even cause a failure of the reaction [22]. Thus, further analysis was carried out by using sample of baseline data and spent cooking oil with KOH- Gly.



Figure 2. Soap formation in conversion of spent cooking oil with KOH



Figure 3. Two layers obtained in conversion of spent cooking oil with KOH-Gly

3.2 Biodiesel characterisation

The esters obtained from transesterification have been characterised and their acid value is shown in Table 1. Chemical compositions of biodiesel are shown in Figure 4 where the highest ester content was obtained from the biodiesel sample from cooking oil. Conversely, the ester content of spent cooking oil samples was relatively low, and the acid content was quite high. Biodiesel ester content followed by EN 14214, which is ≥ 96.5 wt%. The ester contents in biodiesel for all samples shown in Table 2 are relatively low compared to the standard value. Previous study showed that the ester content for the conversion of biodiesel from waste cooking oil and refined cooking oil using KOH as an alkali catalyst at 60 C was 98.2 and 98 wt%, respectively [23].

Table 1. Biodiesel characterization

SAMPLE	ACID VALUE (mg KOH/ g)	ESTER (%)	ACID (%)	KETONE (%)	ALCOHOL (%)	ETHER (%)	PHENOL (%)
B-CO	0.11	89.92	1.37	0.16	0.79	0.5	0.34
WCO: KOH-Gly	1.09	44.1	18.95	0.24	0.56	4.45	-
RWCO: KOH-Gly	1.12	39.64	19.65	0.44	3.4	14.65	-

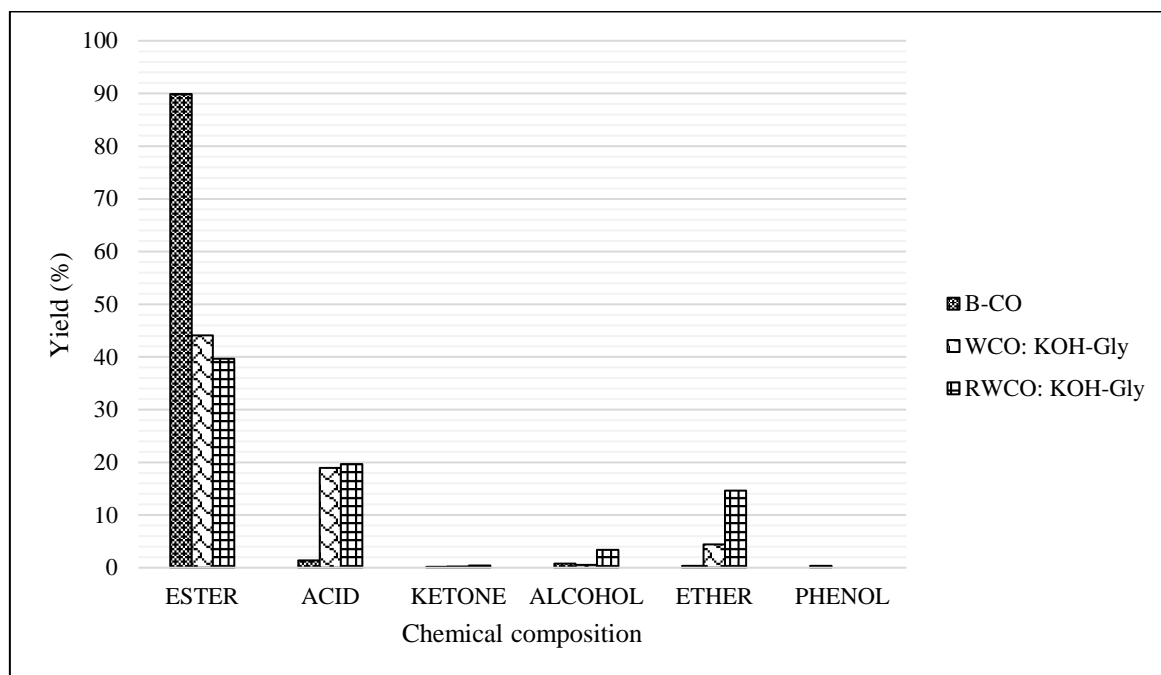


Figure 4. Chemical composition of biodiesel

The acid biodiesel value allowed by ASTM D664 is 0.8 mg KOH/g (maximum). Biodiesel from cooking oil had an acid value of 0.11 mg KOH/g, which met the ASTM standard. The acid value of spent cooking oil with KOH-Gly, on the other hand, was high at 1.09 and 1.12 mg KOH/g and did not meet the ASTM standard, respectively. However, the number of acids spent in cooking oil was reduced by 7.3 mg KOH/g from the initial amount. This could be due to the unresponsive FFA in spent cooking oil. Consequently, if the feedstock contains a large percentage of FFA (>3 wt. percent), as a result of an undesirable side reaction in which the catalyst reacts with FFA to form soap and water (or methanol in the case of potassium methoxide), the standard homogeneous base catalyst would not be efficient, thereby irreversibly extinguishing the catalyst and resulting in an undesirable mixture of FFA [24].

Table 2. Comparison ester content and acid value of biodiesel with standard value

Property	Standard Value	B-CO	WCO: KOH-Gly	RWCO: KOH-Gly
Ester content	≥96.5 wt.% (EN 14214)	89.92%	44.1%	39.64%
Acid value	0.8 mg KOH/g (ASTM D664)	0.11 mg KOH/g	1.09 mg KOH/g	1.12 mg KOH/g

4. Conclusion

Spent cooking oil is an economic feedstock for the production of biodiesel. However, the production process using this feedstock is usually more complicated than using fresh oil feedstock. In this study, the production of biodiesel from spent cooking oil was carried out using direct transesterification with the presence of KOH-Gly as an alkali catalyst. The separation process was easier because two clearly obtained layers and the purification of biodiesel could be done within two times of washing. However, the ester content of spent cooking oil was relatively low compared to other studies. The present study showed that direct transesterification is not effective for KOH-Gly as a catalyst to produce high ester content.

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Acknowledgement

The study was supported by Fundamental Research Grant Scheme (FRGS) of 9003- 00764. The authors gratefully acknowledge the facility and experimental work support provided by the Faculty of Civil Engineering and Technology, Universiti Malaysia Perlis.