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Preparation of Vegetable Oil as Biodiesel Feedstock Via Re-Esterification: A Suitable Catalyst

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Abstract

A suitable heterogeneous catalyst for reducing 20 wt.% of free fatty acid (FFA) that is contained in vegetable oil to less than 3 wt.% through re-esterification was investigated. There were two groups of heterogeneous catalyst used to reduce FFA: 1) zinc compound: Zn, $ZnCl_2$, ZnO and $ZnSO_4 \cdot 7H_2O$, and 2) stannum compound: $SnCl_4 \cdot 5H_2O$ and $SnCl_2 \cdot 2H_2O$. The reaction was operated at 150°C under ambient pressure, stirred at 600 rpm. with spent retention time of approximately 180 min. Final FFA in re-esterification of products, which were cleaned up with centrifuging and hot wet washing, was monitored. The results after centrifuge indicated that only two catalysts (Zn and ZnO) were capable of promoting the reaction and achieving the requirement. Moreover, final FFA in re-esterification of products, which were cleaned up with hot wet washing, was also monitored. It was found that no significant differences existed in the two purification techniques except for the heterogeneous Zn catalyst in re-esterification product. The results showed that thin layer chromatography with a flame ionization detector (TLC/FID) could not detect all of the compositions in the pre-treatment product using Zn as a catalyst. Therefore, ZnO was the most suitable catalyst for effectively reducing FFA via a re-esterification process.
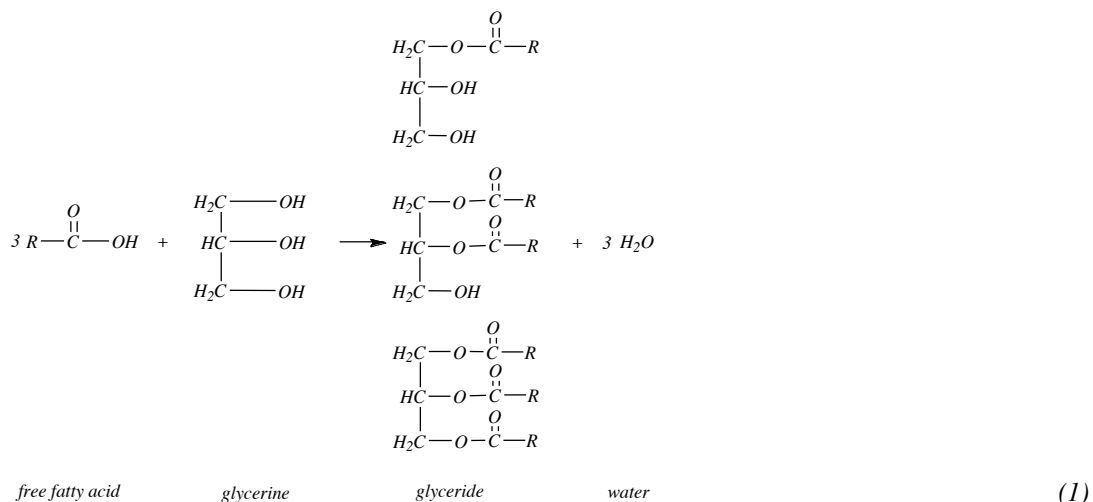
1. Introduction

Due to the high price of vegetable oil and low free fatty acid (FFA) waste cooking oil, low-cost high FFA concentration vegetable oil was used to investigate current production of biodiesel. Trans-esterification is the primary process used to generate biodiesel from high FFA vegetable oil. As a result, low quality biodiesel is obtained because FFA content in oil promotes saponification [1-6]. Therefore,

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high content of free fatty acid oils could be treated via enzyme-catalyzed trans-esterificaton, acid-catalyzed trans-esterifiaction, supercritical and a two-stage process [1,5,7]. The limitations of laboratory experimentation included the production of biodiesel under ambient pressure and in a relatively short time. The two-stage process was considered to produce biodiesel.

Generally, 2 techniques are used to produce biodiesel in the two-stage process: 1) saponification followed by trans-esterification [4,7] and 2) esterification followed by trans-esterification [5,7]. Nevertheless, the latter technique (esterification followed by trans-esterification) is preferable for the production of biodiesel from oil containing high FFA because it requires less time and lower production loss than from a process of saponification followed by trans-esterification [7]. Although, the second technique has more advantages than the first does, a large amount of methanol (a high toxicity in humans) is consumed. In order to decrease the methanol consumption rate, re-esterification is used instead of esterification for pre-treatment FFA in oil. In this process, FFA reacts with glycerin to convert into glyceride using or non catalyst [8-10], as shown in Equation 1. Two groups of catalysts (zinc and stannum compounds) [9-12], which were required to achieve the re-esterification under ambient pressure, were not studied comparatively. Therefore, a suitable type of catalyst to reduce FFA in oil by re-esterification under atmospheric pressure was investigated.

$$3\ R-\overset{O}{\underset{\|}{C}}-OH\ +\ \text{glycerine} \longrightarrow \text{glyceride}\ +\ 3\ H_2O \tag{1}$$

free fatty acid   *glycerine*   *glyceride*   *water*

2. Methodology

2.1 Materials

Vegetable oil was prepared by adding 20 wt.% palmitic acid and commercial grade liquid glycerin (98%) (GL) used as raw materials. Two groups of heterogeneous catalysts (AR grade) (cat.): 1) zinc compound: Zn, $ZnCl_2$, ZnO and $ZnSO_4 \cdot 7H_2O$, and 2) stannum compound: $SnCl_4 \cdot 5H_2O$ and $SnCl_2 \cdot 2H_2O$ were also used.

2.2 Apparatus

The pre-treatment of FFA by re-esterification was carried out in a 250 mL. round bottom flask equipped with a 6-blade disc turbine and thermocouple, as shown in Fig. 1. The solution was heated to

150°C using a heating mantle, and the solution was stirred with a fixed stirring speed (600 rpm.) for the entire time.
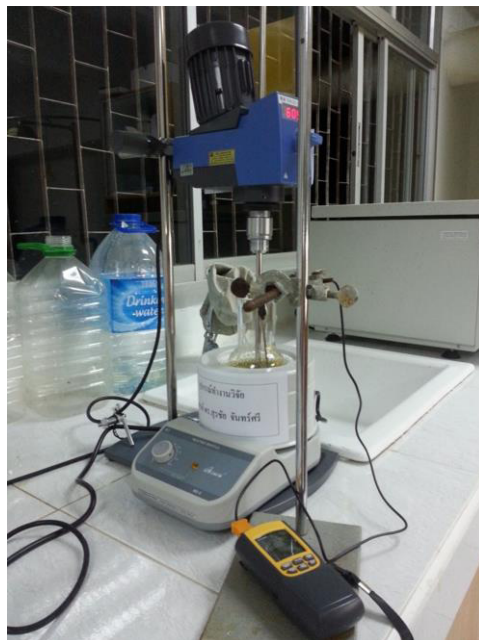

Fig. 1. Experimental apparatus

2.3 Re-esterification in batch process

At the beginning of de-acidified process, the oil added to 20 wt.% palmitic acid was weighed and heated until the temperature reached 60°C. Subsequently, the compositions of oil were analysed by thin layer chromatography with a flame ionization detector (TLC/FID). At the same time, increasing the temperature of the oil to 150°C, 0.6 wt.% of each solid catalyst (Zn, $ZnCl_2$, ZnO and $ZnSO_4 \cdot 7H_2O$, $SnCl_4 \cdot 5H_2O$ and $SnCl_2 \cdot 2H_2O$) [9-12] was dissolved in 50 wt.% of 98% commercial grade liquid GL at 100°C. After that, the solution was added to the heated oil slowly. The solution was heated to 150°C under ambient pressure and stirred with a fixed stirring speed (600 rpm.) for the entire period up to 180 min. One part of the pre-treatment oil was centrifuged at 1500 rpm. for 15 min. Another part had to be cleaned 3 times by hot wet washing (80°C) [7]. Finally, the FFA content contained in the oil was verified.

2.4 Monitoring

The compositions of the cleaned samples were analysed by TLC/FID. Analysis was performed using an Itronscan MK6 with Chromarod type S-III quartz rod (Mitshubishi Kagaku Iatron Inc., Japan). The flame ionization detector used a 160 mL./min. hydrogen flow rate and 2.0 L./min. air flow rate. The samples were diluted in hexane and spotted on each rod, which was coated with an alumina/silica substance (the stationary phase). The rods were developed in the first mobile phase (hexane/diethyl ether/formic acid in the volume ratio of 50/20/0.3) for 20 min. The rods were air-dried for 5 min before developing them in the second mobile phase (hexane/benzene in the volume ratio of 1/1) for 30 min.

After that, the rods were oven-dried at 105°C and the composition of each sample was analysed. The mass ratio of ME, TG, DG, MG and FFA was determined by scanning with 30 sec./rod scan speed [7].

3. Results and discussion

3.1 The characteristics of oil

Prior to discussing the effect of catalysts on FFA reduction, the compositions of oil, both before and after pre-treatment adding only GL, were explained. The concentrations of FFA shown in Table 1 indicated that after adding GL without a catalyst (Sample 1.2) into oil containing high FFA concentration (Sample 1.1), the concentration of FFA and TG (triglyceride) decreased. At the same time, a large amount of diglyceride (DG) and monoglyceride (MG) are observed, according to Bhosle et al. [8]. As previously mentioned, the reaction between the high FFA oil and GL under the catalyst (Sample 1.3) also promotes the reduction of FFA and TG, as well as the increase of DG and MG. The typical description of oil characteristics for re-esterification indicates that besides the re-esterification reaction, TG is also converted to DG and MG by a cracking reaction. Although the cracking reaction promotes the increase of DG and MG more than re-esterification does, only re-esterification is considered and investigated because of FFA forming soap in trans-esterification.

Table 1. The compositions of samples

Sample	Sample composition (wt.%)			
	TG	FFA	DG	MG
1.1	66.483	19.522	5.747	8.248
1.2	51.034	16.081	10.126	22.759
1.3	9.508	1.915	28.135	60.442

3.2 The suitability of catalysts

Normally, FFA contained in oil is the main effect on biodiesel production. While the catalyst promotes trans-esterification, it is captured by FFA forming soap. This causes the amount of catalyst to be insufficient for use in biodiesel reaction. Kombe et al. [13] revealed that the oil should contain FFA in concentrations lower than 3 wt.%. Therefore, this research focuses on FFA reduction by re-esterification. Although both groups of catalyst in the present have been widely used in high pressure re-esterification, no research has been conducted to compare them under ambient pressure. As such, the capability of catalysts to convert FFA into glyceride by re-esterification was investigated. The results after centrifuge (as shown in Table 2) indicated that only two catalysts [Zn (sample 2.1) and ZnO (sample 2.2)] were capable of promoting the reaction and achieving the requirement. Moreover, final FFA in re-esterification of products, which were cleaned up with hot wet washing, was also monitored. It was found that no significant differences existed in the two purification techniques except for the heterogeneous Zn catalyst in re-esterification product.

Table 2. FFA contained in oil by various catalysts

Sample	Catalyst	FFA content	
		Centrifuge (wt.%)	Washing (wt.%)
2.1	Zn	1.240	N/A
2.2	$ZnCl_2$	11.452	11.945
2.3	ZnO	1.416	1.915

2.4	$ZnSO_4 \cdot 7H_2O$	17.503	14.671
2.5	$SnCl_4 \cdot 5H_2O$	9.250	7.486
2.6	$SnCl_2 \cdot 2H_2O$	11.995	12.860

To provide more confidence, the compositions of all products purified by the latter technique were considered, as shown in Table 3. The results showed that TLC/FID could not detect all of the compositions in the pre-treatment product using Zn as a catalyst (sample 3.1). It is possible that saponification is promoted by Zn catalyst during washing of the final product. Therefore, the most suitable and heterogeneous catalyst for reducing FFA by re-esterification under ambient pressure was ZnO.

Table 3. The compositions of each product

Sample	Catalyst	Composition of oil (wt.%)			
		TG	FFA	DG	MG
3.1	Zn	N/A	N/A	N/A	N/A
3.2	$ZnCl_2$	48.555	11.945	16.585	22.915
3.3	ZnO	9.508	1.915	28.135	60.442
3.4	$ZnSO_4 \cdot 7H_2O$	52.156	14.671	12.085	21.089
3.5	$SnCl_4 \cdot 5H_2O$	53.606	7.486	9.944	28.965
3.6	$SnCl_2 \cdot 2H_2O$	67.591	12.860	9.88	9.661

4. Conclusion

A re-esterification process was used for reducing FFA from approximately 20 wt.% to less than 3 wt.% via a re-esterification process under atmospheric pressure by fixing conditions at 150°C for reaction temperature, 600 rpm. for stirring speed and 180 min. for retention time. Final FFA in re-esterification of products, which were cleaned up with centrifuging and hot wet washing, was monitored. Only the heterogeneous ZnO catalyst was capable of promoting the reaction and achieving the requirement and no significant differences existed in the two purification techniques in re-esterification product. Therefore, ZnO was the most suitable catalyst for effectively reducing FFA via a re-esterification process.

Acknowledgements

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