Novel approach of esterification process using heterogeneous catalyst in biodiesel synthesis from waste cooking oil

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Abstract. Esterification process using heterogeneous catalyst in biodiesel synthesis from waste cooking oil (WCO) was investigated. In this study, heterogeneous catalyst TiO\(_2\)P25 was used to replace homogeneous acid catalyst in esterification process. Ultrasonic stirring was also used in esterification process to increase reaction rate with low energy. WCO was purified through filtration and bleaching to remove impurities and recover the colour of oil. After purification, esterification was conducted with photo-reactor that consisted of ultrasonic bath and ultraviolet lamp, which were installed around reaction mixture in order to activate TiO\(_2\) P25, instead of using acid catalyst and mechanical stirring. Esterification process were carried out at different TiO\(_2\)P25 loading, reaction time and ratio molar of oil and methanol. The samples were examined with titration method to obtained FFA content before and after esterification. Esterification process was followed with trans-esterification process to produce fatty acid methyl ester (FAME) or biodiesel. The maximum conversion of FFA was found at 45.2% with following operation condition: 0.25 wt% TiO\(_2\), 2 hours’ reaction time, and 1:24 molar ratio of oil and methanol. Esterification process with heterogeneous catalyst TiO\(_2\)P25 and ultrasonic stirring has been proved to be successfully reduce FFA content of WCO so it can produce high quality of biodiesel which in accordance with the SNI Biodiesel 7182:2015

Keywords: Biodiesel, Esterification, Heterogeneous Catalyst, TiO\(_2\)P25, Waste Cooking Oil

1. Introduction

Waste cooking oil (WCO) is a vegetable oil that has been used for cooking process repeatedly. A WCO collectors stated that in 2013, one family in Bogor, West Java, Indonesia, at least produce 36 L of WCO every year [1]. WCO disposal without further process might be harmful for ocean or river animals. In the attempt to solve the problem, WCO can be used as raw material of biodiesel production. In Indonesia, WCO has been utilized as a raw material for several purposes, such as methyl ester surfactant [2] and biodiesel [3]. WCO has the potential of cheaper raw material for biodiesel production. Because WCO usually contains high level of free fatty acid (FFA) that will lead to saponification in trans-esterification process, it is necessary to do an esterification process to reduce FFA content. Conventional process of the esterification used homogeneous acid catalyst which has excessive drawbacks, such as the complexity of removing acid catalyst from oil after esterification, require high methanol to oil molar ratio, and high acid catalyst concentration [4]. It is said by Zang et al. in Di Serio et al. [4] that disadvantages of using homogeneous acid catalyst in esterification process are concludes of corrosive, produce more by product, and require massive amount of CaSO\(_4\) for the neutralization of H\(_2\)SO\(_4\) (approximately 2,000 ton/year of CaSO\(_4\) for producing 10,000 ton/year of biodiesel. In order to overcome the drawbacks, homogeneous acid catalyst is proposed to be replaced with heterogeneous catalyst, such as photo-catalyst TiO\(_2\). Photo-catalyst TiO\(_2\) is a promising photo-catalyst as it is non-toxic,
inexpensive, and stable [5]. Photo-catalyst TiO$_2$ is chosen since the use and performance in biodiesel production have not been widely studied.

In this study, the novel approach of esterification process using photo-catalyst TiO$_2$ is conducted. The optimum conditions of esterification conditions consist of loading TiO$_2$, reaction time, and methanol to oil molar ratio are investigated. The specification of density, viscosity, iodine value, and methyl ester content for the biodiesel product will also be evaluated to confirm if it is corresponding to SNI Biodiesel 7182:2015 [6].

2. Method and Material

2.1. Waste Cooking Oil (WCO)

WCO was obtained from fried food street vendors in the roadside of Depok City, West Java, Indonesia. WCO was going through a pre-treatment that consist of filtration and bleaching process to remove solid impurities and recover the colour of oil. Filtration process was conducted using filter paper BIPMED 125 mm. Bleaching process is conducted with adsorption method using activated carbon from coconut shell (20 wt.% of WCO) at a temperature 75º C for 40 minutes. After the adsorption is complete, then followed by filtration to remove the activated carbon.

2.2. Biodiesel Production from Waste Cooking Oil

Biodiesel is produced by esterification of WCO and then continued with trans-esterification in order to produce methyl ester. In this study, the esterification conducted by novel approach by heterogeneous photo-catalysis, meanwhile the trans-esterification process is conducted based on another research of ours [7].

2.2.1. Esterification Process Using TiO$_2$ Photo-catalyst. Esterification process is conducted using a newly designed photo-reactor that was created in our laboratory. The schematic drawing of the experimental set up is shown in Fig 1. There are 7 pieces of ultraviolet (UV) lamp @10 Watt from Sanyo Denki as the source of UV radiation (A). The lamp was placed on the top of beaker glass (B) which contains a mixture of methanol, WCO, and TiO$_2$ P25. The reflector (F) is used to maximize the photon to the mixture. Ultrasonic stirring (C, D, E) is used to replace mechanical stirring to enhance reaction rate. FFA’s oil analysis are conducted before and after esterification with acid-base titration according to SNI Cooking Oil 3741:2013 for every variable. FFA content in oil should not exceed 2% to be continued to trans-esterification process in order to avoid saponification that will reduce biodiesel’s yield [8]. The equation for FFA content of WCO is determined according to Eq. (1):

\[
FFA (\%) = \frac{Mr_{FFA} (282) \times V_{NaOH} \times N_{NaOH} \times 10 \times M_{sample}}{100}
\]  

(1)

Where Mr$_{FFA}$ = mass fraction of FFA (usually oleate acid), V$_{NaOH}$ = Volume of NaOH that is used to neutralize the mixture until pink color occurred, N$_{NaOH}$ = normality of NaOH, and M$_{sample}$ is the weight of the sample for this reaction. Meanwhile, the conversion of FFA is able to be calculated according to the Eq. (2):

\[
Conversion (\%) = \frac{FFA_b - FFA_a}{FFA_b} \times 100
\]  

(2)

Where FFA$_b$ is FFA content of WCO before esterification and FFA$_a$ is FFA content of WCO after esterification.
2.2.2. Trans-esterification Process. Transesterification was conducted using heterogeneous base catalyst CaO at temperature 60°C for 4 hours under stirring speed of 500 rpm with mechanical stirring. Biodiesel produced was going through yield calculation. Transesterification product was settled overnight to separate it into two layers. The upper layer was fatty acid methyl ester (FAME) and the lower layer was glycerol. FAME is the main product or biodiesel, meanwhile glycerol is the by-product of this experiment. FAME was then washed with hot water and heated at 100°C for 1 hour. At the end of trans-esterification process, the characterization of FAME was conducted to know density, kinematic viscosity, iodine value, and methyl ester content (using GC-MS). These characterizations are important to know the accordance to SNI Biodiesel 7182:2015.

3. Results and Discussion

3.1. Esterification Process Using TiO$_2$ Photo-catalyst.
The impact of different TiO$_2$ loading to FFA’s content and conversion are shown in Fig 2. As the loading of TiO$_2$ increased, FFA’s conversion increase as well until 0.25 wt% before decreasing significantly. The sudden decrease is caused by shading effect by photo-catalyst TiO$_2$, the similar phenomenon was happened in research by Janczarek and Kowalska [9], Christoforidis and Fornasiero [10] and Cohen et al. [11]. Esterification with TiO$_2$ loading of 0.25 wt%, 60 minutes’ reaction time, and 1:6 methanol to oil ratio has an outcome of 35.9% conversion and 2.8% FFA.
FFA’s content still above 2%, so the reaction time need to be investigated to decrease more FFA’s content. The impact of reaction time to FFA’s content and conversion are shown in Fig 3. Longer reaction time leads to higher rate of FFA’s decreasing, however in the 240 minutes’ reaction time, FFA’s content is increasing. It is caused by the domination of esterification process’ back reaction.

The best esterification reaction time is 120 minutes where FFA’s content of 1.7% and conversion of 28.7% are obtained. Reaction time of 120 minutes seems to be the best reaction time for esterification process, it’s also used for esterification process in biodiesel industry [12].

FFA’s content in WCO after 120 minutes’ reaction with TiO₂ loading is below 2% but the conversion is still low. To increase FFA conversion, different methanol to oil ratio has been investigated. Methanol to oil ratio add a significant role to FFA conversion if the reaction conducted in a longer reaction time, low temperature (50-55°C), and low catalyst loading [13]. The impact of methanol to oil ratio to FFA’s content and conversion are shown in Fig 4. The increasing methanol to oil ratio leads to higher conversion because higher methanol to oil ratio means higher amount of methanol that reacts with FFA to produce methyl ester.

The highest conversion which is 45.2 % achieved at 1:24 methanol to oil ratio. FFA content after esterification of WCO at 0.25 wt% TiO₂ loading, and 1:24 methanol to oil ratio for 4 hours is 1.7%. FFA
content is low enough to be continued to trans-esterification. However, the conversion is still low for it is still under 50%. It’s probably caused by the uneven mixing of methanol, WCO, and TiO$_2$ loading with ultrasonic bath that resulted a mixture that not homogeneous. It’s turned out that ultrasonic bath has low energy and resulted an uneven distribution of ultrasonic within the tank [14].

![Figure 4. Effect of Methanol to Oil Ratio to (a) FFA’s Content and (b) FFA’s Conversion.](image)

Trans-esterification process of WCO with FFA content 1.7% resulted a biodiesel with specification as shown in Table 1. Biodiesel produced from this research are named Biodiesel VAR500. From the comparison, it is appeared that the specifications are in accordance to the allowed range of SNI Biodiesel 7182:2015.

**Table 1. Comparison of Biodiesel VAR500 with Specification of Biodiesel from SNI Biodiesel 7182:2015.**

|                          | Biodiesel VAR500 | Specification as Stated in SNI Biodiesel 7182:2015 |
|--------------------------|------------------|-----------------------------------------------------|
| Density on Temperature 40°C (kg/m$^3$) | 855              | 850 – 890                                           |
| Kinematic Viscosity on Temperature 40°C (cSt) | 4.7              | 233 – 6                                             |
| Iodine Value (g iodine/ 100 g) | 58               | Max. 115                                            |
| Methyl Ester Content (%) | 98.9             | Min. 96.5                                           |

**4. Conclusion**

Novel approach of esterification process using photo-catalyst TiO$_2$ has been successfully used to decrease the level of FFA in WCO to under 2% so it can be continued to trans-esterification process without saponification. Through this process, the FFA conversion is able to reach 45.2% with operation condition as follow: 0.25 wt% photo-catalyst TiO$_2$, 1:24 methanol to oil, and 2 hours’ reaction. Esterification process with TiO$_2$ that was followed by trans-esterification with CaO has been successfully produced biodiesel with specification which is in accordance to SNI Biodiesel 7182:2015 as follows: density 855 kg/m$^3$, kinematic viscosity 4.7 cSt, iodine value 58 g iodine/100 g, and methyl ester content 98.9%.

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