

PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING BENTONITE CATALYSTS

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Abstract

Demand for diesel continues to increase due to rapid population growth, which could contribute to fossil fuel exhaustion. Biodiesel has been widely developed as a replacement for conventional diesel to resolve the issue. Biodiesel production from waste cooking oil (WCO) was carried out via the transesterification process using two types of bentonite catalysts, which are raw bentonite and NaOH/bentonite. By using the impregnation method, the NaOH/bentonite catalyst was synthesized at 60°C for 12 hours. The transesterification was conducted with 0.5wt% of catalyst, at 15:1 (methanol-to-oil), for 2 hours at different reaction temperatures. The characterization of both raw bentonite and NaOH/bentonite was done using X-ray Diffraction (XRD) and Brunauer, Emmett, Teller (BET) surface characterization. A high yield of FAMES (72%) was found to be obtained in continuous stirring at 55°C for 2 hours and 15:1 methanol/oil molar ratio with 0.5wt.% (0.15g) of NaOH/bentonite catalyst.

Keywords: WCO, biodiesel, bentonite, NaOH, reaction temperature

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Introduction

The growing market for fossil fuels today has contributed to the depletion of fossil fuels available worldwide due to rapid population growth. It has been found that biodiesel can act as the fossil fuels substitute. Biodiesel as a fossil fuel substitute has many significant environmental benefits, such as biodegradability, sustainable nature, low sulphur content, low toxicity, and atmospheric carbon dioxide concentration (Bhuiya *et al.*, 2015).

The main problem in producing biodiesel is the cost of production. Recent use of feedstock which is edible oil (e.g. corn oil, rapeseed oil) is highly cost and has a limited amount due to the high demand and competition with food sources. To counter back the problem, usage of inedible oil (e.g. jatropha, rubber seed) and waste product (e.g. WCO) as feedstock can help in reducing the production cost to 60-70% (Raqeeb and Bhargavi, 2015). Next, biodiesel can be produced through the transesterification process. One of the main points in the process is the presence of a catalyst. Currently, the catalyst used is homogeneous (e.g. NaOH, KOH) which which is easily obtained. Unfortunately, homogeneous catalysts are difficult to recover and can contribute to saponification. Thus, the heterogeneous catalyst can be used to replace homogeneous catalyst (e.g. CaO) (Soetaedjo *et al.*, 2011). Inedible oils and waste materials have also been shown to contain high FFAs content, requiring an acid catalyst in the process of transesterification. However, the acid catalyst is very sensitive as the particles can be easily aggregated (Gardy *et al.*, 2018). A base catalyst will be used to solve the problem because it has good performance under normal reaction conditions (Farooq *et al.*, 2019), and non-corrosive (Khan *et al.*, 2019).

Supported catalysts are always introduced since they are intercropping distribution (active surface volume) with a high catalytic element thermo-stability (Liu & Corma, 2018). Bentonite clay had been

chosen as a supported catalyst due to its widely available and low price. Bentonite is an aluminium phyllosilicate adsorbent resulting from the modification of volcanic activity in an acid's presence. The particle sizes of bentonite were not standardized, adding to its porosity (Gbarakoro *et al.*, 2016). Due to the montmorillonite's high composition in the bentonite clay, the clay contains a large specific surface area with a net specific charge and an extensive exchange capacity (Fosso-Kankeu *et al.*, 2017). As a result, when bentonite was used as a supported catalyst, a micro catalytic site or channel was offered. Another chemical solution, such as potassium hydroxide, sodium hydroxide, and sodium carbonate, was impregnated with bentonite clay to improve its performance.

The use of non-edible oil as a feedstock, such as WCO, can cut biodiesel production price because WCO is more economical and easily obtainable (Das & Jha, 2017). According to the research conducted by Lai (2014), since biodiesel contains unburned hydrocarbons, carbon monoxide, and particulate matter that is reduced in the exhaust fumes, biodiesel is 75% cleaner than common petrol-diesel. This paper focused on the biodiesel formed from WCO produced from palm oil. Palm oil was obtained from the palm oil fruit flesh, which is a bright orange-red. To produce cooking oil, margarine, special fats, and oleochemicals, 40% of Malaysian palm oil was used (Sebayang *et al.*, 2010). As in the food industry itself, it has been estimated that a single branch serving fast foods such as burgers, fried chicken, and French fries could produce as much as 15 litres of used cooking oil every day (Sebayang *et al.*, 2010).

This paper addressed the influence of the reaction temperature on the yield of biodiesel. The oil's viscosity is more significant at a higher temperature, resulting in a higher mixing step and faster isolation of glycerol (Lakshmana *et al.*, 2015). Few other parameters will be affecting the yield of biodiesel, including the type of catalyst, type of solvent, and availability of free fatty acids (FFAs) (Farooq *et al.*, 2019). Heterogeneous catalysts are known to enhance the transesterification process relative to the homogeneous process by removing increased production costs associated with homogeneous catalysis and reducing contaminants' generation. Heterogeneous catalysts help fast recovery, reusability and a cost-effective green operation. These catalysts withstand high levels of FFAs and moisture content (Thangaraj *et al.*, 2018). Methanol as a solvent can facilitate higher reaction rates (Zahan & Kano, 2018) and higher biodiesel's yield than other alcohol due to its high solubility (Lakshmana *et al.*, 2015). The presence of FFAs content also significantly affects biodiesel production through as the formation of gels and foams will hinder the separation of glycerol from biodiesel, causing low yield of biodiesel (Mathiyazhagan & Ganapathi, 2011).

Experimental

Catalyst Preparation

The bentonite was modified by using the impregnation method (Soetaredjo *et al.*, 2011). A mixture of 1.0M sodium hydroxide and bentonite at ratio 1:20 was placed in a three-neck round bottom flask equipped with a condenser, thermometer, and mechanical stirrer. The mixture was then heated at 60°C for 24 hours and the slurry formed was dried in an oven at 70°C for 24 hours. The dried slurry was then calcined in a tabular muffle furnace at 500°C for 5 hours. The final calcination was conducted to remove any volatile substances as a purification process (Britannica, 2016).

Catalyst Characterization

Powder X-ray diffraction (XRD) patterns of bentonite and the catalysts were recorded on PANalytical X'Pert HighScore Plus' device, which operates with Cu K α radiation at a step size of 0.01° and 2 θ range of 10° to 90°. The surface analysis was performed on Micromeritics ASAP 2060 by using N₂ adsorption. Before measuring nitrogen adsorption, the sample was degassed at 150°C under vacuum for 24 hours. The samples' BET surface area was determined using the standard BET equation in the range of relative pressure (p/p₀) from 0.0 to 1.1.

Transesterification of Waste Cooking Oil

An amount of 15g of waste cooking oil (WCO) was placed in the three-neck round bottom flask along with the 0.5wt% bentonite catalysts dissolved in 15:1 methanol to oil molar. The use of only 0.5wt% of catalyst small amount of catalyst had been proven from the previous study. It can produce a high yield of biodiesel, and 15:1 methanol to oil molar ratio was used because it can give optimal result in various

conditions. The flask was then heated up to different temperature (45°C, 50°C, 55°C, 60°C, and 65°C) in a controlled temperature water bath for 2 hours. Later, the catalyst will be separated by centrifugation, and the remaining mixture is allowed to settle into two layers in the separating funnel. The bottom layer's glycerol was removed, and biodiesel at the upper layer was undergoing the purification process. Purification of biodiesel must be carried out using hot water (>70°C) until pH 7. The ratio between the volume of biodiesel and water for washing is 1:1. Biodiesel is then heated at 110°C for 10 minutes using a hot plate to remove moisture (Rahadianti *et al.*, 2018). The yield produced was then calculated using the equation below:

$$\text{yield \%} = \frac{\text{mass of biodiesel}}{\text{mass of WCO}} \times 100$$

Findings

XRD Measurement and Surface Analysis of Bentonite and Catalyst

X-ray diffraction (XRD) is a non-destructive method used to classify crystalline materials. From the XRD pattern in Figure 1, there is clear evidence of sodium present in the NaOH/bentonite sample which reflected at $2\theta = 18^\circ, 19^\circ, 26^\circ, 29^\circ, 35^\circ,$ and 61° . The sodium oxide signal's presence indicated that the sodium hydroxide had been successfully impregnated into the bentonite pores. During impregnation, the bentonite's coating/pillars are not physically damaged but can absorb sodium molecules on the surface (Utubira *et al.*, 2018). The sodium oxide phase plays an essential role in increasing the catalyst's efficiency in biodiesel development (Utubira *et al.*, 2018). As NaOH is loaded into bentonite clay, the catalyst's crystallinity increases (Ali *et al.*, 2016). This can be proved as the XRD pattern's intensity increased in the NaOH/bentonite compared to the raw bentonite (Utubira *et al.*, 2018). Even though there is no correlation between the surface area and the catalytic activity, there is a massive correlation between the cation exchange capacity and catalytic activity (Pushpalettha *et al.*, 2005).

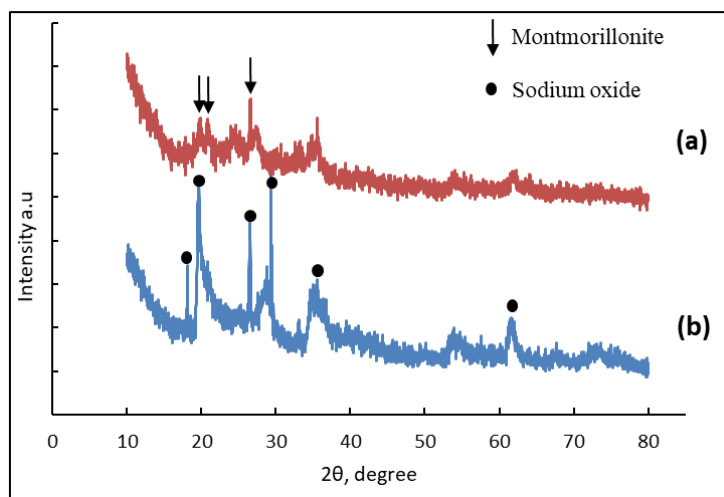


Figure 1. XRD pattern of (a) raw bentonite, and (b) NaOH/bentonite calcined at 500°C.

The most common method of determining powders' surface area and porous materials is using Brunauer, Emmett, Teller (BET). It provides a precise surface area assessment of the materials by N_2 multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. The BET isotherm linear plot of raw bentonite and NaOH/bentonite was shown in Figure 2, and the measured BET surface area, pore size, and pore volume were shown in Table 1. It was found that the surface area is decreasing due to the presence of sodium hydroxide molecules filled in the available bentonite pores. It can be shown that the saturation of bentonite with sodium significantly reduces N_2 absorption. (Ouakouak *et al.*, 2020).

According to the IUPAC classification, the type IV with a hysteresis loop of nitrogen BET isotherms proved that raw bentonite and NaOH/bentonite has a mesoporous structure (Ouakouak *et al.*, 2020). This suggested that NaOH molecules' presence on the surface of the bentonite particles and the surface of the pores inside the bentonite particles and some of the NaOH molecules were possibly converted to Na₂O during the calcination process. The formation of Na₂O can be confirmed when the new phase Na₂O began to appear in the XRD pattern in Figure 1. The narrowing of the hysteresis curve of the adsorption isotherm suggested a transition in the pore structure of bentonite from a mesoporous material to a non-porous structure after loading with NaOH (Soetaredjo *et al.*, 2011).

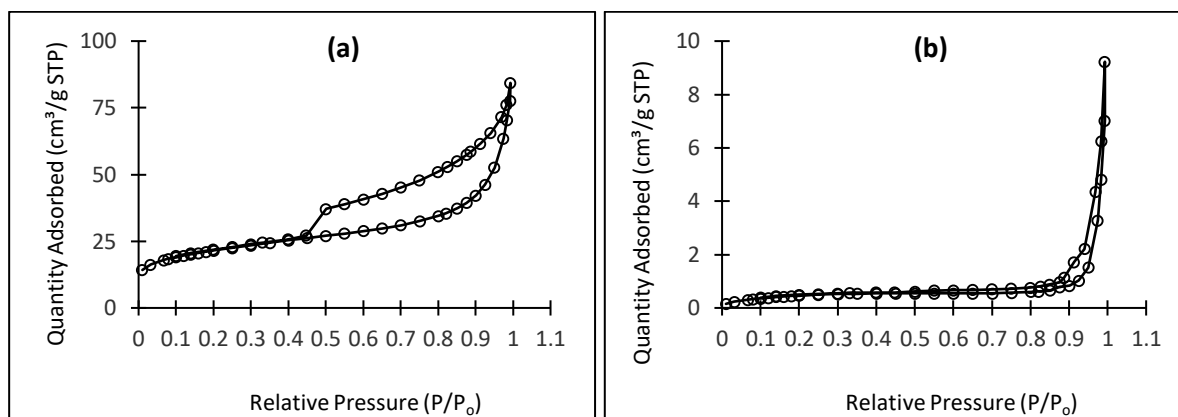


Figure 2. BET isotherm linear plot (a) raw bentonite, and (b) NaOH/bentonite.

Table 1. BET properties for raw bentonite and NaOH/bentonite.

Properties	Raw bentonite	NaOH/bentonite
BET surface area, m ² /g	75.90	1.85
Pore size, nm	10.64	59.34
Pore volume, cm ³ /g	0.10	0.01

Effect of Reaction Temperature

The smaller surface area of NaOH/bentonite and the formation of Na₂O can increase biodiesel production. This is because the smaller surface area has indicated the presence of Na₂O molecules within the bentonite clay. The presence of Na₂O increases electro-negativity and hence increases the fundamental power of the catalyst (Ibrahim *et al.*, 2020). High basicity catalysts can generate high yields of biodiesel (Lee *et al.*, 2014). The activities of the catalysts with distinct fundamental intensity against transesterification have been measured. The transesterification reaction is conducted for 2 hours with 0.5wt.% of catalyst loading, 15:1 methanol to oil molar ratio, and different reaction temperatures.

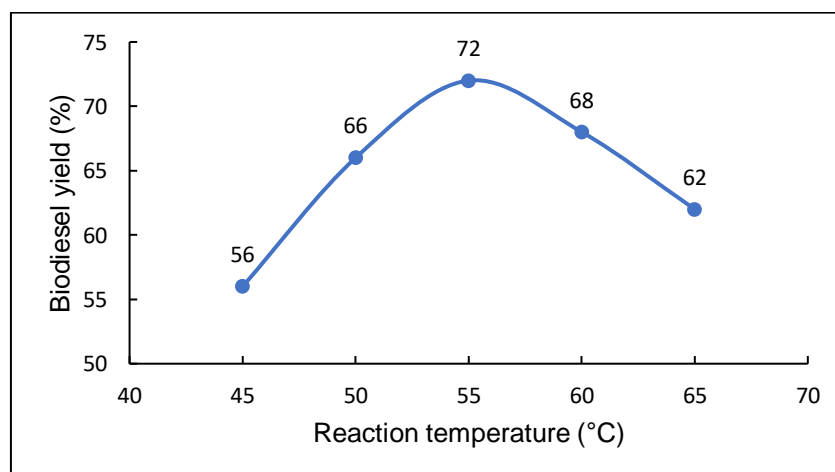


Figure 3. Biodiesel yield at different temperatures.

As the reaction temperature increases, the oil's viscosity will also decrease the reactivity and mass transfer between methanol and oil, thus increasing the biodiesel yield production (Wu *et al.*, 2016). The reaction is conducted at five different temperature, 45°C, 50°C, 55°C, 60°C, and 65°C. Based on the data in Figure 3, the optimum temperature was found to be at 55°C, which produced 72% of biodiesel. This is confirmed by a study carried out before where the reaction temperature must lower than the solvent's boiling point to avoid solvent evaporation (Efthymiopoulou *et al.*, 2018). In this study, the reaction temperature should be lower than the methanol's boiling point, which is 64.7°C.

Conclusion

In conclusion, NaOH/bentonite was prepared successfully and proven by the XRD and BET surface characterization. The impregnation method's succession had been shown in BET resulted where the surface area and pore volume were decreasing upon loading of NaOH onto the bentonite. The optimum reaction temperature obtained was at 55°C. The experiment was able to yield 72% of biodiesel with only 0.5wt% catalyst. Overall, the prepared catalyst could be used as an essential catalyst for biodiesel production. Further optimization of the conditions for transesterification reactions will be required to utilize the catalyst completely. The use of WCO as feedstock can be used as it can be obtained in a massive quantity worldwide.

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