Biodiesel production from soybean oil catalyzed by $NaBiO_3$ and $NaVO_3$

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Abstract

Using biodiesel to replace petrodiesel has become the most popular issue in recent years. The purpose of bioresource development is to ease petroleum exhaustion problem. In this study, we use $NaBiO_3$ and $NaVO_3$ as the solid base catalysts for the transesterification of soybean oil with methanol on biodiesel production. Two heating methods, traditional heating and microwave irradiating are used to transesterificate soybean oil. When using $NaBiO_3$ as the catalyst, under the optimal reaction conditions of a methanol/oil molar ratio of 24:1, a 0.5 wt % catalyst amount, and a reaction temperature of 65℃ for 1 h under microwave irradiation (2.45 GHz 50 W), this approach achieves 95.0% conversion to biodiesel. When using $NaVO_3$ as the catalyst, under the optimal reaction conditions of a methanol/oil molar ratio of 24:1, a 6 wt % catalyst amount, and a reaction temperature of 65℃ for 0.75 h under microwave irradiation (2.45 GHz 50 W), this approach achieves 97.1% conversion to biodiesel. Moreover, different vegetable oil (olive oil, coconut oil) and waste edible oil are used as the raw materials for biodiesel production. The catalysts are characterized by Scanning electron-microscopy (SEM-EDS), Thermogravimetric analysis (TGA), BET surface area measurements and Hammett indicator method.

Keywords: Biodiesel, Solid base, Transesterification, $NaBiO_3$, $NaVO_3$.

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1 Introduction

Owing to human needs, main energy was tremendously increased the consumption in the last century [1], including petrochemical sources, coal and natural gases. Therefore, fast depleting fuel reserves has led to a proactive search for environmental protection fuels, such as biodiesel [2].

Biodiesel is a renewable energy, nontoxic, with low emission profiles and biodegradable. Biodiesel can be obtained from renewable resources, such as vegetable oil and animal fat. Lots of vegetable oil was used to the transesterfication for producing biodiesel, including palm oil [3], sunflower oil [4], rapeseed oil [5], canola oil [6], cottonseed oil [7] and soybean oil [8].

Two kinds of catalysts can synthesize biodiesel, base catalyst [9] and acid catalyst [10]. In many biodiesel production technologies [11], using microwave is potential to perform reactions quickly, efficiently, and safely [12]. In this study, the solid base $NaBiO_3$ and $NaVO_3$ are used as effective catalysts for biodiesel production. Effects of different vegetable oil on biodiesel production are studied. Moreover, the transesterification reaction by microwave radiation is also studied.

2 Methods

2.1 Chemicals

Soybean oil (cooking grade) was purchased from Great Wall Enterprise Co., Taiwan. The other different oil was purchased from Chung Shing Chemicals Co., Taiwan. Methanol (ACS grade) was purchased from ECHO Chemical Co., Taiwan. Sodium bismuthate (A.C.S. reagent) and methyl heptadecanoate were purchased from Sigma-Aldrich, USA. Sodium metavanadate was purchased from Aldrich, USA.

2.2 Experimental procedure

The transesterification reaction was carried out in a 250 ml flat bottom flask equipped with a circulating water bath and a magnetic stirrer. The reactor was initially filled with 12.5 g of soybean oil, which was heated to 65 ℃ for 1 h while

stirring at 900 rpm. All of the experiments were performed under atmospheric pressure.

2.3 Analytical methods

The base strength (H_) of the catalyst was determined by Hammett indicators [13]. Fatty acid methyl ester (FAME) concentration expressed as the biodiesel purity of the product was determined by gas chromatography (Thermo trace GC ultra, Thermo Co.) with a flame ionization detector (FID) according to method CNS 15051.

3 Results and Discussion

3.1 catalysts characterization

The sodium bismuthate and sodium metavanadate were characterized with scanning electron-microscopy (SEM-EDS), shown in Figure 1 and Figure 2. The morphology was irregular and diverse, such as large pore and convex surface. The thermogravimetric analyses of sodium bismuthate and sodium metavanadate were shown in Figure 3 and Figure 4. The BET surface area, pore volume, and pore diameter of sodium bismuthate and sodium metavanadate were measured (Table 1). Basic strength of sodium bismuthate was assigned $9.8 < H_- < 15$ and sodium metavanadate was assigned $7 < H_- < 9.8$ by Hammett indicators method.

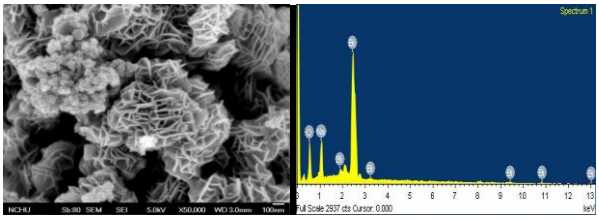

Figure 1: SEM-EDS imagine of the NaBiO3.

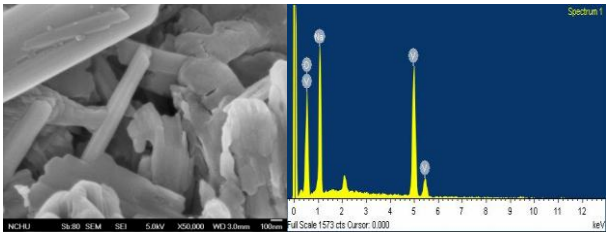

Figure 2: SEM-EDS imagine of the NaVO3.

Table 1: BET of NaBiO3 and NaVO3.

Sample	Weight	BET(m^2/g)	Pore size(Å)	Pore volume(cm^3/g)
$NaBiO_3$	0.3255	12.8648	252.5576	0.000119
$NaVO_3$	0.2264	2.2396	525.6549	0.000046

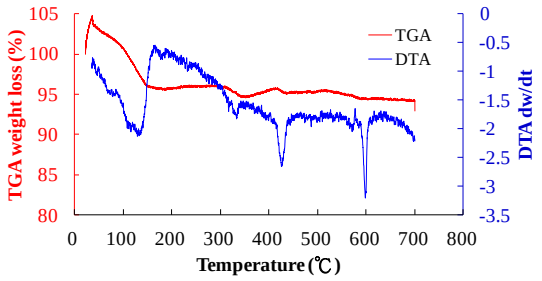

Figure 3: TGA of Sodium bismuthate

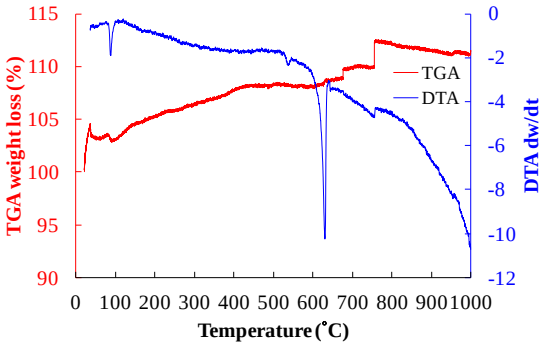

Figure 4: TGA of sodium metavanadate

3.2 Traditional heating for transesterification with sodium bismuthate as catalyst

The reaction temperature was treated from 40 to 65 ℃. The temperature 65 ℃ was heated by a hot plate for providing the surface temperature up to 200 ℃, and circulating water bath kept methanol refluxing in the reactor. As shown in Figure 5, the FAME conversion reached a plateau value at the reaction temperature 65 ℃. We also found that the most efficiency of the catalyst amount was 0.5 wt% in Figure 6. On account of transesterification reactions being a reversible reaction, excess methanol would be advantageous to the yield of FAME formation. As shown in Figure 7, the molar ratio of methanol to oil needed to be higher than 1:24 to reach the optimal FAME conversion. Finally, the FAME conversion was 97.22 % for 1 hour

(Figure 8). Furthermore, this study also used different vegetable oil to produced biodiesel, and the results were shown in Figure 9.

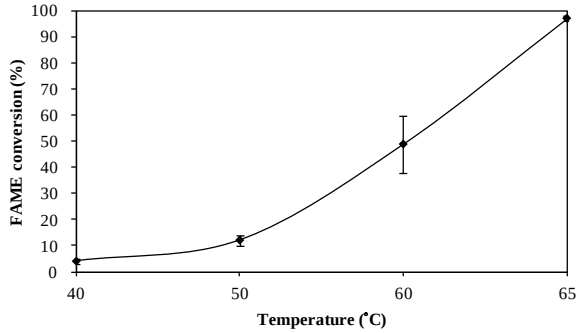

Figure 5: Effects of different reaction temperatures on biodiesel production with soybean oil, sodium bismuthate amount of 0.5 wt%, oil/methanol molar ratio of 1:24 and reaction time 1 hour.

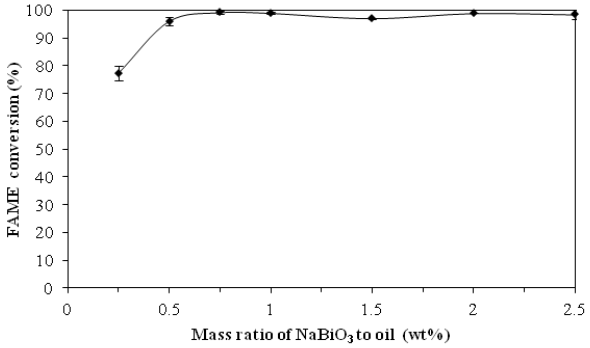

Figure 6: Effects of different sodium bismuthate amounts on biodiesel production with soybean oil, reaction temperature 65 °C, oil/methanol molar ratio of 1:24 and reaction time 1 hour.

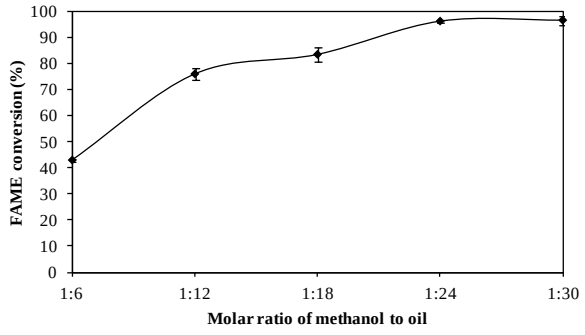

Figure 7: Effects of different molar ratios of methanol to oil on biodiesel production with soybean oil, reaction temperature 65 °C, sodium bismuthate amount of 0.5 wt% and reaction time 1 hour.

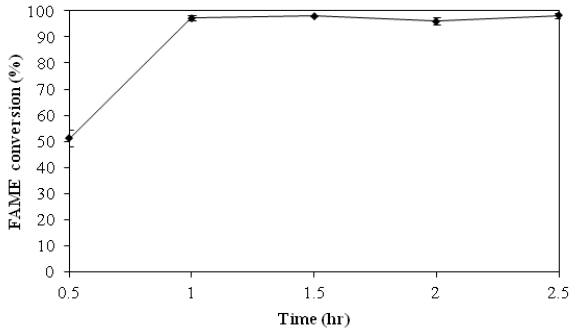

Figure 8: Effects of different reaction time on biodiesel production with soybean oil, reaction temperature 65 °C, sodium bismuthate amount of 0.5 wt% and oil/methanol molar ratio of 1:24.

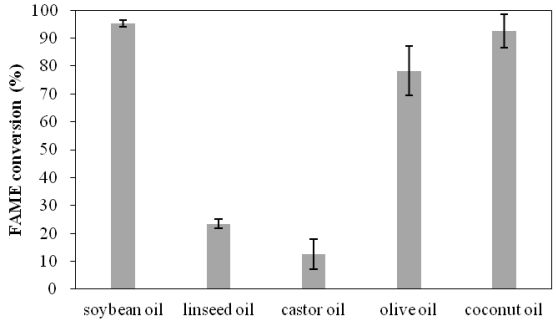

Figure 9: Effects of different vegetable oil on biodiesel production with reaction temperature 65 °C, the sodium bismuthate amount 0.5 wt% and oil/methanol molar ratio of 1:24 for 1 hour.

3.3 Microwave heating for transesterification with sodium bismuthate as catalyst

The results of transesterification with different reaction time by microwave heating (50W) are shown in Figure 10, and we also changed the microwave power to estimate the formation of FAME, as shown in Figure 11. Moreover, the effect of different oil/methanol molar ratios was shown in Figure 12. In this work, 94.95 % FAME conversion was obtained by using microwave heating to produce biodiesel when microwave power was 50 W under 1 hour and

oil/methanol molar ratio of 1:24.

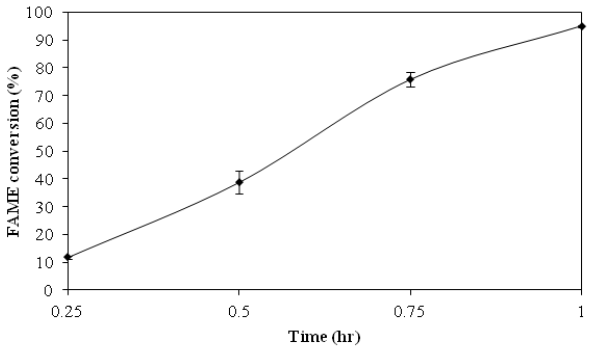

Figure 10: Effects of different reaction time on biodiesel production with soybean oil, microwave power 50 W, sodium bismuthate amount of 0.5 wt% and oil/methanol molar ratio of 1:24.

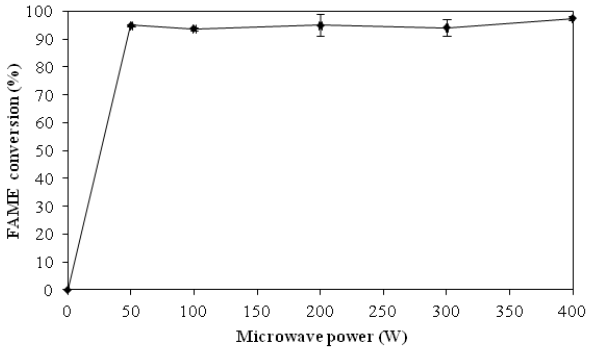

Figure 11: Effects of different microwave power on biodiesel production with soybean oil, reaction time 1h, sodium bismuthate amount of 0.5 wt% and oil/methanol molar ratio of 1:24.

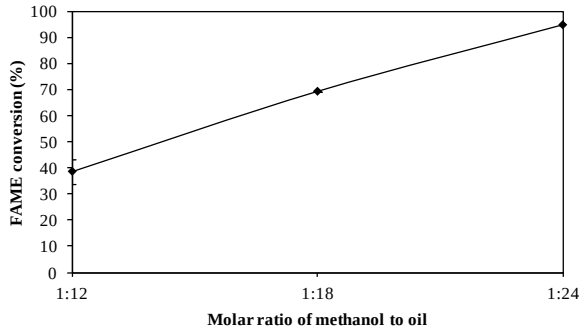

Figure 12: Effects of different molar ratios of methanol to oil on biodiesel production with soybean oil, reaction time 1h, microwave power 50 W and sodium bismuthate amount of 0.5 wt%.

3.4 Traditional heating for transesterification with sodium metavanadate as catalyst

We found that $NaVO_3$ calcined at different temperatures had no obvious effect on the transesterification (Figure 12). The reaction temperature was treated from 40 to 65 ℃. As shown in Figure 13, the FAME conversion reached a plateau value at the reaction temperature 65 ℃. We also found that the most efficiency of the catalyst amount was 6 wt%, Figure 14. As shown in Figure 15, the molar ratio of methanol to oil needed to be higher than 1:24 to reach the optimal FAME conversion. Finally, the FAME conversion was 93.68 % for 2 hours (Figure 16).

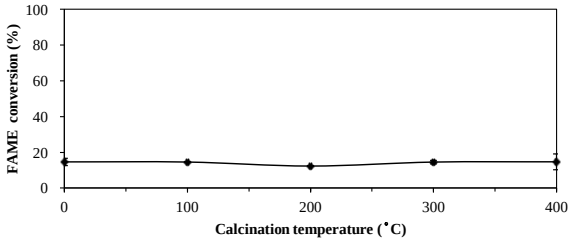

Figure 13: Effects of different calcination temperatures ($NaVO_3$) on biodiesel production with soybean oil, reaction temperature 65 ℃, the amount of sodium metavanadate 1.5 wt% and oil/methanol molar ratio of 1:24 for 2 hours.

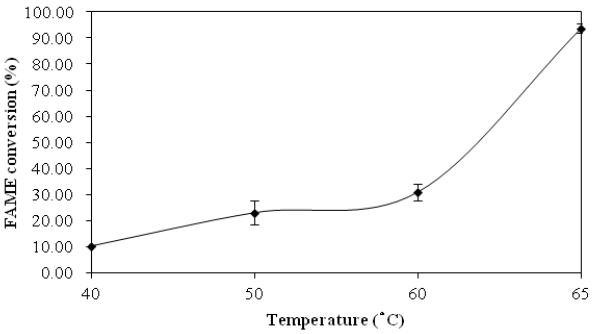

Figure 14: Effects of different reaction temperatures on biodiesel production with soybean oil, sodium metavanadate amount of 6 wt%, oil/methanol molar ratio of 1:24 and reaction time 2 hours.

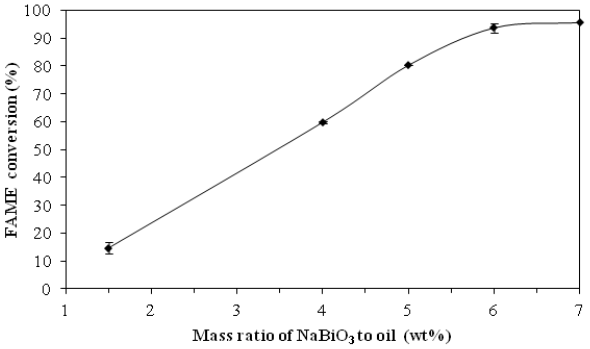

Figure 15: Effects of different sodium metavanadate amounts on biodiesel production with soybean oil, reaction temperature 65 °C, oil/methanol molar ratio of 1:24 and reaction time 2 hours.

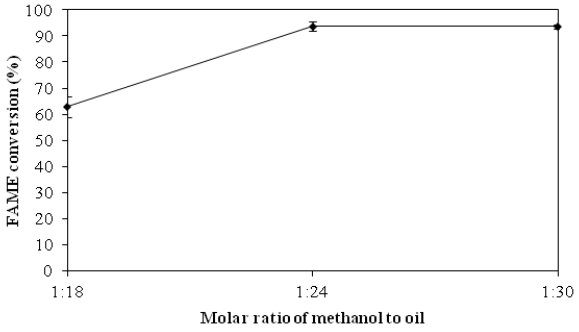

Figure 16: Effects of different molar ratios of methanol to oil on biodiesel production with soybean oil, reaction temperature 65 °C, sodium metavanadate amount of 6 wt% and reaction time 2 hours.

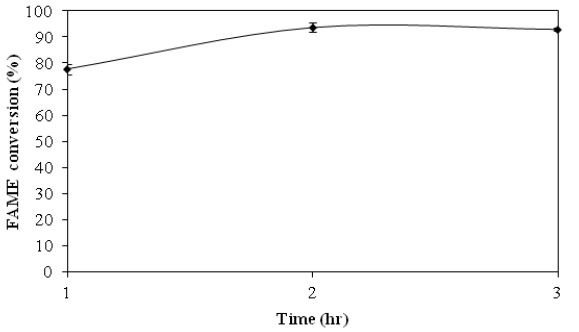

Figure 17: Effects of different reaction time on biodiesel production with soybean oil, reaction temperature 65 °C, sodium metavanadate amount of 6 wt% and oil/methanol molar ratio of 1:24.

3.5 Microwave heating for transesterification with sodium metavanadate as catalyst

The results of the transesterification with different reaction time by microwave heating (50W) are shown in Figure 18, and we also changed the microwave power to estimate the formation of FAME, Figure 19. Moreover, the effects of different oil/methanol molar ratios are shown in Figure 20. In this work, 97.16 % FAME conversion was obtained by using microwave heating to produce biodiesel when microwave power was 50 W under 1 hour and oil/methanol molar ratio of 1:24.

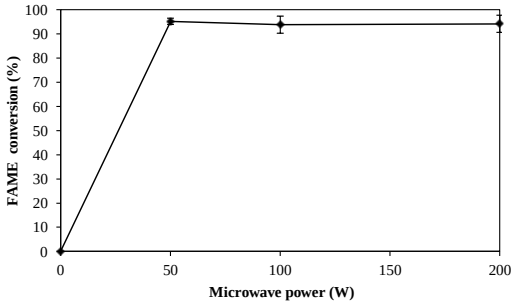

Figure 18: Effects of different microwave power on biodiesel production with soybean oil, reaction time 1h, sodium metavanadate amount of 6 wt% and oil/methanol molar ratio of 1:24.

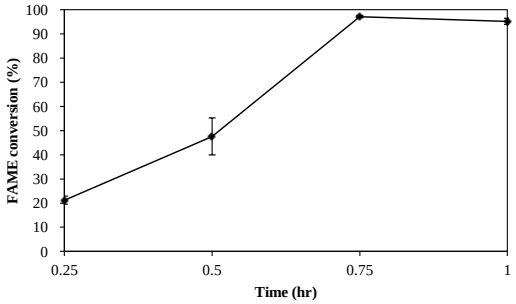

Figure 19: Effects of different reaction time on biodiesel production with soybean oil, microwave power 50 W, sodium metavanadate amount of 6 wt% and oil/methanol molar ratio of 1:24.

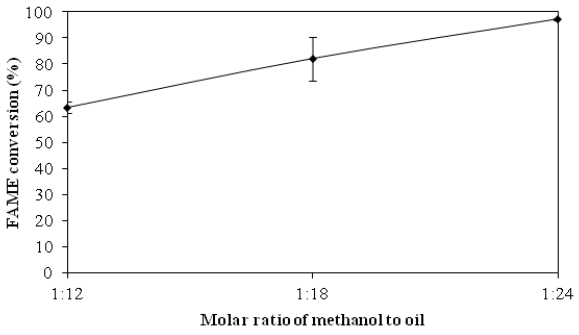

Figure 20: Effects of different molar ratios of methanol to oil on biodiesel production with soybean oil, reaction time 1h, microwave power 50 W and sodium metavanadate amount of 6 wt%.

4 Conclusions

The results of using traditional heating for transesterification showed that the best FAME conversion was 97.22 % under 65 ℃ with the sodium bismuthate amount 0.5 wt%, the oil/methanol molar ratio 1:24 for 1 hour, and 93.68 sodium metavanadate 6 wt% and the oil/methanol molar ratio 1:24 for 1 hour.

The performance of microwave heating for the transesterification was also found the best FAME conversion being 94.95 % under 1 hour, 50 W microwave power with the amount of sodium bismuthate 0.5 wt%, oil/methanol molar ratio of 1:24 and 97.16 % under 0.75 hour, and 50 W microwave power with the amount of sodium metavanadate for 6 wt% and oil/methanol molar ratio of 1:24.

To compare the reaction rates between traditional heating and microwave heating, our experiment indicated that microwave irradiation would be more efficient than traditional heating on biodiesel production.

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