Application of Sulfated tin oxide in Transesterification of Waste Cooking oil: An Optimization Study

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Abstract— **Biodiesel is a biodegradable and non-toxic fuel which can be produced through transesterification reaction. However, it is impractical to use the refined vegetable oils as the feedstock for biodiesel production due to its high production cost and priority for food products. Thus, low-grade oil with high free fatty acids (FFA) content, typically waste cooking oil has been a promising choice to improve the economical feasibility of biodiesel. In the present study, superacid sulfated tin oxide catalyst, SO_4^{2-}/SnO_2 has been successfully prepared through impregnation method. Bimetallic effect was also studied at which SnO_2 mixed with SiO_2 and Al_2O_3, respectively at different weight ratio in order to enhance the catalytic activity of SnO_2. The effect of different reaction parameters such as calcinations temperature and period, reaction temperature, catalyst loading, methanol to oil ratio and reaction time were studied to optimize the reaction conditions. It was found that SO_4^{2-}/SnO_2-SiO_2 with weight ratio 3 exhibited an exceptional high activity with optimum yield 92.3% at reaction temperature 150°C, catalyst loading 3 wt%, methanol to oil ratio 15 and reaction time 3 hours.**

Keywords- solid acid catalys; sulfated tin oxide; biodiesel; waste cooking oil

I. INTRODUCTION

Rapid diminishing of energy reserves and fluctuating petroleum prices has intensified the search for renewable energy sources, globally. Fatty acid methyl ester (FAME) or better known as biodiesel can be a potential renewable energy re-placing petroleum-derived diesel [1-4]. Biodiesel can be easily synthesized through transesterification of virgin vegetable oils, animal fats or even recycled grease from the food industry [1, 5-6] in the presence of short chain alcohol and catalyst. However, high cost of the most common biodiesel feedstock, virgin vegetable oil, has hindered wider utilization and commercialization of future biodiesel plant [7]. Therefore, to overcome this limitation, cheaper feedstock such as low-grade oil, typically waste cooking oil can be a better option as this can reduce the overall biodiesel production cost significantly.

Recently, researchers in this field are focusing on developing solid acid catalyst for heterogeneous transesterification reaction, typically from low-grade oil [2, 6-7]. The advantages of solid acid instead of liquid acid catalyst are; (1) the catalyst is insensitive to FFA content, (2) can simultaneously catalyze esterification and transesterification reactions, (3) easier catalyst separation and (4) easily incorporated into a packed bed reactor for continuous production of biodiesel [1,7]. Among various solid acid catalysts available, many studies have highlighted the application of sulfated metal oxides in biodiesel production, especially sulfated zirconia (SO^{2-}_4/ZrO_2) due to its high catalytic activity [1, 6, 8, 9]. Sulfated tin oxide (SO^{2-}_4/SnO_2) is another potential catalyst for transesterification reaction due to its strong surface acidity that is reported to be stronger than SO^{2-}_4/ZrO_2 [10-12]. Nevertheless, study concerning the usage of SO^{2-}_4/SnO_2 catalyst in biodiesel production is still very limited.

Thus, this study is aimed to provide supplement technical information on the application of SO^{2-}_4/SnO_2 catalyst for transesterification reaction. Firstly, the effects of calcination temperature and calcination period towards the reaction performance were studied. This is followed by optimizing transesterification process variables including reaction temperature, catalyst loading, alcohol to oil ratio and reaction period. The effect of using mixed-metal was also investigated.

II. EXPERIMENTAL

A. Materials

Waste cooking oil was collected from cafeteria of Engineering Campus, Universiti Sains Malaysia, Penang. Methanol (purity 99.8%) and n-hexane (purity 99%) were purchased from Medina Jaya Sdn. Bhd. Methyl heptadecanoate which was used as internal standard for gas chromatography (GC) and sulfuric acid with purity 95-97% was purchased from Fluka Chemie, Germany. Pure methyl esters (references for GC analysis) such as methyl myristate, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate with purity more than 99%, tin (IV) oxide (SnO_2) with purity 99.9%, quartzsand (SiO_2) with purity 99.8% and alumina oxide (Al_2O_3) with purity 98% were purchased from Sigma Aldrich, Malaysia.

B. Transesterification reaction

50 ml of waste cooking oil and a pre-determined amount of catalyst and methanol (parameters to be varied) were charged into a 300 ml stainless steel batch reactor equipped with thermocouple and magnetic stirrer. The reactor was then pressurized to 10 bars to ensure that all reactants remain in liquid phase for the entire duration of reaction. The reactants were stirred at 350 rpm in order to maintain uniform temperature and suspension. The reactor temperature was controlled by a heater with a programmable PID temperature controller. After running the reaction for a desired duration, the reactor was cooled to room temperature. After cooling, the product was discharged out and filtered using filter paper to separate the solid catalyst from the mixture of FAME-glycerol.

C. Method of analysis

The identity and relative composition of fatty acids present in the methyl ester product were analyzed by Perkin-Elmer Clarus 500 gas chromatograph equipped with flame ionization detector (FID) and Nukol^{TM} column (15 m × 0.53 mm × 0.5 µm). Helium was used as carrier gas. Oven temperature were held at 110 ^oC (0.5 minutes) and was then heated at a rate of 10^oC/min to 220^oC (8 minutes). The temperature of injector and detector were set at 220^oC and 250^oC, respectively.

III. RESEULT AND DISCUSSION

A. Effect of reaction temperature and mixed metal oxide

Fig. 1 shows the effect of transesterification reaction temperature (100 to 200°C) on the yield of FAME using various bi-metalic catalysts at different weight ratio. When the reaction was increased from 100 to 150°C, there is a significant increase in the yield of FAME for all types of catalyst. However, beyond 150°C, except for bi-metalic catalyst prepared with ratio 1, the yield of FAME seems to level off as the batch of reactants had reached its equilibrium conversion. On the other hand, the increase in yield when reaction temperature increased from 100 to 150^oC could be justified as follows. Waste cooking oil and methanol are immiscible, therefore reaction with heterogeneous catalyst would create a 3-phase system at which the mass transfer rate of reactant molecules between the three phases is very limited [13]. As the reaction temperature is increased, all reactant molecules will gain more kinetic energy that will eventually accelerated the mass transfer rate between the oil-methanol-catalyst phases that resulted in the formation of more FAME in a shorter time.

The effect of mixed metal oxide (bi-metal oxide) on the yield of FAME was also studied and the results are given in Fig. 1. SiO_2 and Al_2O_3 were chosen to mix with SnO_2 at different weight ratio as both metal oxides were reported to be able to stabilize the crystalline structure of SnO_2 [14, 15]. The weight ratio of SnO_2:SiO_2 and SnO_2:Al_2O_3 were varied at 1:1, 3:1 and 5:1 (hereafter refer to as 1, 3 and 5) and impregnated with 2.0 M H_2SO_4 to become sulfated mixed metal oxide. Since 150°C was found to be the minimum temperature to achieve equilibrium conversion, discussion in this section will focus on the data trend for reaction temperature above 150°C. Furthermore, when the reaction temperature was below 150°C, no significant data trend can be observed. From Fig. 1, it is obvious that the weight ratio between the bi-metal affect the yield of FAME significantly. For all sulfated mixed metal with ratio 1, the yield of FAME was even lower than SO_4^{2-}/SnO_2 with exceptional at the extreme end of higher reaction temperature. However for sulfated mixed metal with ratio 3 and 5, the yield was significantly higher than SO_4^{2-}/SnO_2 with ratio 3 giving higher yield. These results showed that with appropriate amount of SiO_2 and Al_2O_3, acid sites on the surface of SnO_2 can be enhanced and therefore increases its contact with reactants that led to higher reactivity [16]. The optimum yield for SO_4^{2-}/SnO_2-SiO_2 (3) and SO_4^{2-}/SnO_2-Al_2O_3 (3) was 82.1% and 79.6%, respectively at 150^oC.

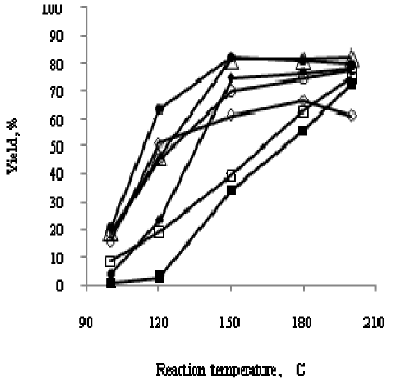

Figure 1. Effect of reaction temperature on FAME yield using SO_4^{2-}/SnO_2 and its sulfated mixed metal oxide. Reaction condition: methanol:oil ratio 10, catalyst loading 3 wt %, reaction time 3 hours. All samples were calcined at 300 °C for 2 hours.

B. Effect of catalyst loading

Catalyst loading is an important parameter that needs to be optimized to increase the FAME yield. Fig. 2 shows the effect of catalyst loading on the yield of FAME. The value of catalyst loaded into the reaction mixture was varied from 1 to 8 wt% (based on weight of waste cooking oil). From the figure, it can be noted that the yield of FAME increased with higher catalyst loading up until a value in which higher increment no longer increase the yield of FAME. This is because with more catalyst addition, the total number of available active sites increased resulted in faster reaction rate to reach reaction equilibrium [17]. However, further increase in catalyst loading beyond its optimum value will have negligible increase in FAME yield. This might be due to the immiscibility of waste cooking oil and methanol, which causes the reaction to be rate limiting step at the beginning of the reaction. However, as catalyst is introduced in the reaction mixture, it provides an external contact surface area that facilitates the formation of FAME. As more FAME is produced, it eventually acted as co-solvent, by dissolving both reactants to become a single phase reaction system. Subsequently, the reaction rate is being controlled by the diffusion of the reactants to the active sites, instead of catalyst loading. Hence, increasing the dosage of catalyst in the reaction mixture will have an insignificant effect on the yield of FAME. The optimum catalyst loading for SO_4^{2-}/SnO_2, $SO_4^{2-}/SnO_2\text{-}SiO_2$ (3), and $SO_4^{2-}/SnO_2\text{-}Al_2O_3$ (3) are 6, 3 and 3 wt %, respectively.

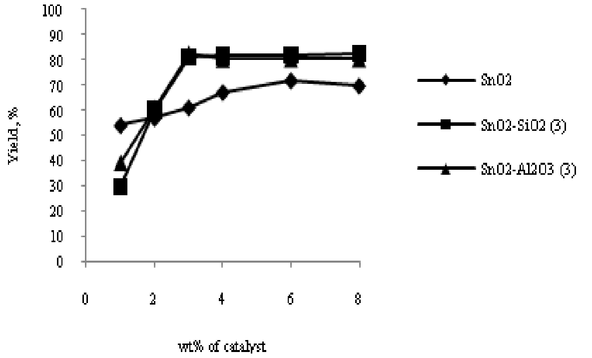

Figure 2. Effect of catalyst loading on FAME yield using SO_4^{2-}/SnO_2 and its sulfated mixed metal oxide. Reaction condition: reaction temperature 150°C, methanol:oil ratio 10, reaction time 3 hours.

C. *Effect of methanol:oil ratio*

Basically, for a reversible reaction like transesterification [1], reactants (methanol) are normally used in excess to push the reaction forward for formation of products (FAME). However, care must be taken as to how much excess methanol is to be used because too much methanol may dilute the system and eventually cause a drop in the yield of FAME due to slower reaction [18]. Fig. 3 shows the effect of methanol to oil ratio on the yield of FAME using three types of catalyst. In the present work, methanol to oil ratio were set at 5, 10, 15, 20, 25 and 30 in order to optimize the transesterification reaction as shown in Fig. 5. From the figure, the yield of FAME catalyzed by SO_4^{2-}/SnO_2 increased abruptly from 69.0% to 91.5% as the methanol to oil ratio increased from 5 to 30. Nevertheless, the observation for transesterification reaction catalyzed by $SO_4^{2-}/SnO_2\text{-}SiO_2$ (3) and $SO_4^{2-}/SnO_2\text{-}Al_2O_3$ (3) showed a different pathway as the yield of FAME decreased at a certain ratio, indicating an optimum value. The maximum yield obtained by $SO_4^{2-}/SnO_2\text{-}SiO_2$ (3) was 92.3% at ratio 15 whereas for $SO_4^{2-}/SnO_2\text{-}Al_2O_3$ (3) was 82.3% at ratio 10. It can be clearly seen that due to the high reactivity of sulfated $SnO_2\text{-}SiO_2$ catalyst, methanol to oil of 15 is sufficient to achieve a high yield as compared to the original sulfated SnO_2 whereby this can only be achieve at a ratio of more than 30.

D. *Effect of reaction time*

Fig. 4. shows that the yield of FAME increased steadily as the reaction time was increase from 1 to 3 hrs of reaction time. After 3 hrs., the yield level off as near-equilibrium composition was achieved. This shows that sulfated SnO_2 is a very suitable solid catalyst that has a very high reactivity to catalyze transesterification reaction as typical solid catalyst requires more than 10 hrs. of reaction time. The optimum yield obtained for reaction catalyzed by SO_4^{2-}/SnO_2, $SO_4^{2-}/SnO_2\text{-}SiO_2$ (3) and $SO_4^{2-}/SnO_2\text{-}Al_2O_3$ (3) was 91.5%, 92.3% and 87.4%, respectively corresponding to their optimum reaction time.

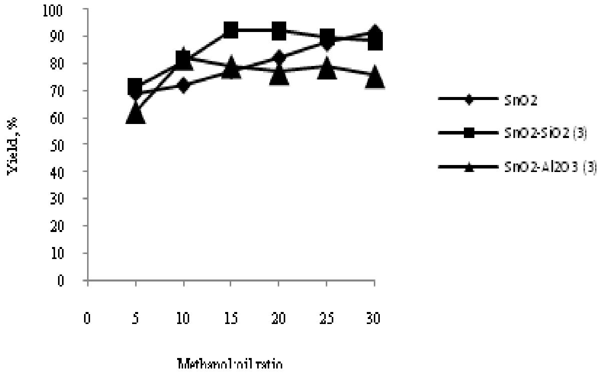

Figure 3. Effect of methanol to oil ratio on FAME yield using SO_4^{2-}/SnO_2 and its sulfated mixed metal oxide. Reaction condition: reaction temperature 150°C, catalyst loading 6 wt % for SO_4^{2-}/SnO_2 and 3 wt % for $SO_4^{2-}/SnO_2\text{-}SiO_2$ (3) and $SO_4^{2-}/SnO_2\text{-}Al_2O_3$ (3), reaction time 3 hours.

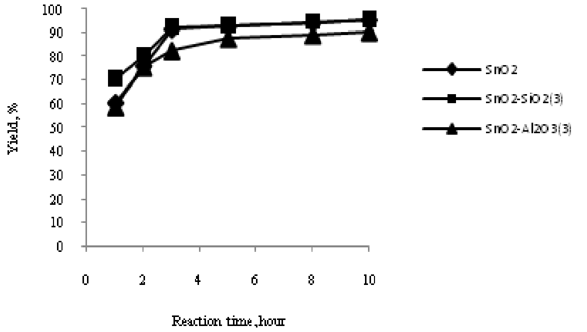

Figure 4. Effect of reaction time on FAME yield using SO_4^{2-}/SnO_2 and its mixed metal oxide. Reaction condition: reaction temperature 150°C, methanol:oil ratio 10 for $SO_4^{2-}/SnO_2\text{-}Al_2O_3$ (3), 15 for $SO_4^{2-}/SnO_2\text{-}SiO_2$ (3) and 30 for SO_4^{2-}/SnO_2, catalyst loading 6 wt % for SO_4^{2-}/SnO_2 and 3 wt % for $SO_4^{2-}/SnO_2\text{-}SiO_2$ (3) and 30 for $SO_4^{2-}/SnO_2\text{-}Al_2O_3$ (3).

E. *FAME Properties*

Table 2 summarized some of the FAME properties produced from $SO_4^{2-}/SnO_2\text{-}SiO_2$ (3) catalyst. From the table, it was found that all the listed properties met the specification of standard En 14214.

TABLE I. FAME PROPERTIES

Property	**Unit**	**Value**	**EN 14214**
Density at 15ºC	Kg/m^3	885.5	860-900
Viscosity at 40ºC	mm^2/s	4.08	3.5-5.0
Flash point	ºC	201	>101
Sulfur	mg/kg	0.5	<10
Sulfated ash	% mass	0.01	<0.02
Iodine value	-	70.9	<120
Methanol content	% mass	0.1	<0.2

IV. CONCLUSION

The present study had open a new synthetic route in application of modified SO_4^{2-}/SnO_2 as a promising catalyst in biodiesel production, typically from low grade oil with high free fatty acid content. It was found that adding appropriate amount of SiO_2 or Al_2O_3 to SO_4^{2-}/SnO_2 will eventually enhance the catalytic activity of the catalyst leading to higher yield of FAME with minimum catalyst loading and methanol to oil molar ratio. The highest FAME yield of 92.3 % was obtained by using $SO_4^{2-}/SnO_2\text{-}SiO_2$ (3) catalyst in which the catalyst was calcined at 300°C for 2 hours, while the optimum transesterification reaction condition was at 150°C, 3 wt% catalyst, 15:1 methanol to oil ratio and 3 hours reaction time.

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