Esterification of Free Fatty Acids in Crude Palm Oil Using Alumina-Doped Sulfated Tin Oxide as a Catalyst

Worawoot Prasitturattanachai and Kamchai Nuithitikul

Abstract—The conventional production of biodiesel from crude palm oil which contains large amounts of free fatty acids in the presence of a homogeneous base catalyst confronts the problems of soap formation and very low yield of biodiesel. To overcome these problems, free fatty acids must be esterified to their esters in the presence of an acid catalyst prior to alkaline-catalyzed transesterification. Sulfated metal oxides are a promising group of catalysts due to their very high acidity. In this research, alumina-doped sulfated tin oxide (SO_4^{2-}/Al_2O_3-SnO_2) catalysts were prepared and used for esterification of free fatty acids in crude palm oil in a batch reactor. The SO_4^{2-}/Al_2O_3-SnO_2 catalysts were prepared from different Al precursors. The results showed that different Al precursors gave different activities of the SO_4^{2-}/Al_2O_3-SnO_2 catalysts. The esterification of free fatty acids in crude palm oil with methanol in the presence of SO_4^{2-}/Al_2O_3-SnO_2 catalysts followed first-order kinetics.

Keywords—Methyl ester, Biodiesel, Esterification, Sulfated tin oxide, Fatty acid.

I. INTRODUCTION

TO lower the production cost, biodiesel is manufactured from low-quality oil which contains large amounts of free fatty acids (FFA) such as used cooking oil, crude palm oil. Such production, however, needs a two-steps process. FFA must be converted to their methyl esters (biodiesel) via esterification with an acid catalyst prior to transesterification with a homogeneous base catalyst. In the first step, FFA must be typically esterified to an acceptable level, e.g. 1 wt% [1], in order to prevent soap formation and increase the biodiesel yield in the following alkaline catalyzed transesterification. A suitable heterogeneous acid catalyst is preferred to a conventional homogeneous acid catalyst such as H_2SO_4 for the esterification because the heterogeneous catalyst is easily separated from the reaction mixture and recycled. The biodiesel production process therefore is simplified. Unlike a homogeneous acid catalyst, the use of a heterogeneous acid catalyst does not require neutralization of the remaining acid. Moreover, heterogeneous acid catalysts such as sulfated metal oxides are less corrosive and toxic than conventional acids.

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Therefore, reactor corrosion is minimized.

Sulfated tin oxide (SO_4^{2-}/SnO_2) is an interesting candidate in a sulfated metal oxides family for esterification reactions owing to its very high acidity, which is called superacidity [2]. Numerous papers have suggested that the superacidity is responsible for its unique catalytic activities [3]. SO_4^{2-}/SnO_2 has been reported to have stronger acid strength than sulfated zirconia, SO_4^{2-}/ZrO_2 [2], which well catalyzes esterification reactions of carboxylic acids [4], [5]. Therefore, the activity of SO_4^{2-}/SnO_2 is expected to be higher than SO_4^{2-}/ZrO_2. However, the studies on the structure and applications of SO_4^{2-}/SnO_2 are relatively few, compared to SO_4^{2-}/ZrO_2 and other SO_4^{2-}/M_xO_y-type solid superacids [6]. Moreover, SO_4^{2-}/SnO_2 is not commercially available, unlike SO_4^{2-}/ZrO_2. With these reasons, more attentions should be given to SO_4^{2-}/SnO_2.

Khder and coworkers [7] and Moreno and coworkers [8] have conducted intensive studies in the synthesis and characterization of SO_4^{2-}/SnO_2 as well as its activity for esterification reactions. The catalytic activity of SO_4^{2-}/SnO_2 strongly depends on its acidity, which is greatly affected by the sulfate concentration and calcination temperature. The maximum activity was achieved when the SO_4^{2-}/SnO_2 catalyst contained 30 wt% sulfate and was calcined at 550°C, giving about 92% conversion of acetic acid [7]. In the esterification of oleic acid with ethanol, the highest activity of SO_4^{2-}/SnO_2 catalyst occurred when it contained 0.3 wt% sulfate and was calcined at 500°C, giving 49% conversion of oleic acid [8].

However, the modification of SO_4^{2-}/SnO_2 with other metal oxides is hardly found in the literature. The introduction of Al_2O_3 onto SO_4^{2-}/SnO_2 and its application for benzoylation have been reported by Guo and coworkers [6]. Another previous study of alumina-doped sulfated tin oxide (SO_4^{2-}/Al_2O_3-SnO_2) for acylation was performed by Zhao and coworkers [9]. Introducing Al_2O_3 to SO_4^{2-}/SnO_2 offers the benefit of cost saving. To the best of our knowledge, there has been no study in catalytic esterification with SO_4^{2-}/Al_2O_3-SnO_2. Therefore, the present study focuses on the activity of SO_4^{2-}/Al_2O_3-SnO_2 for esterification of FFA in crude palm oil to produce methyl esters for the first time. Since palm oil is an abundant resource in Southeast Asian countries, it is an economic and commercially feasible feedstock for biodiesel production. In this study, types of aluminum precursors used in the preparation of SO_4^{2-}/Al_2O_3-SnO_2 catalysts were varied. Three precursors were investigated: $AlCl_3$, $Al(NO_3)_3$ and $Al_2(SO_4)_3$. The activities of these catalysts were then tested for

esterification of FFA in crude palm oil in a batch reactor under reflux condition. The reaction kinetics was also studied.

II. Experimental

A. Preparation of SO_4^{2-}/Al_2O_3-SnO_2

The preparation of SO_4^{2-}/Al_2O_3-SnO_2 was adapted from the procedure of Furuta and coworkers [10]. A mixture of $SnCl_4.5H_2O$ (20 g) and aluminum precursor, $AlCl_3$ or $Al(NO_3)_3$ or $Al_2(SO_4)_3$ (corresponding to 2, 4, 10 and 20 mol% Al) was dissolved in 600 ml of distilled water. An ammonia solution (30 wt%) was added under vigorous stirring until the pH was 8. The precipitate was separated, suspended in CH_3COONH_4 solution (4 wt%), filtered and dried at 100^oC for 24h, yielding aluminum-tin compound. The compound then was immersed in H_2SO_4 solution (30 wt% sulfates) to form gels. The gels were further stirred for 1h, filtered, dried at 100 ^oC for 2h and calcined at 500^oC for 3h to give alumina-doped sulfated tin oxide. In this study, the designations of SO_4^{2-}/Al_2O_3-SnO_2 (x) are used. The Roman number x stands for the type of aluminum precursor, I = $AlCl_3$, II = $Al(NO_3)_3$ and III = $Al_2(SO_4)_3$.

B. Esterification of FFA

Activity of SO_4^{2-}/Al_2O_3-SnO_2 to catalyze esterification of FFA in crude palm oil to produce methyl esters was determined in a round bottom flask fitted with a magnetic stirrer and a reflux condenser. A mixture of 25 ml crude palm oil (10 wt% of FFA), 45ml methanol and 1g SO_4^{2-}/Al_2O_3-SnO_2 catalyst was added to the flask. The mixture was heated to 80^oC. The reaction was initiated by stirring (250rpm) and stopped after a specific reaction time (1, 2 and 3h). The product mixture was filtered, washed with water several times and evaporated. The FFA contents in crude palm oil before and after the reaction were evaluated by titration method (ASTM D 5555). The conversion of FFA (X_{FFA}) was calculated from (1)

$$X_{FFA}(\%) = \frac{FFA_0 - FFA_t}{FFA_0} \times 100 \qquad (1)$$

where FFA_0 and FFA_t (wt%) are the concentrations of free fatty acids in crude palm oil before and after the reaction, respectively.

III. Results and Discussion

The activity of SO_4^{2-}/Al_2O_3-SnO_2 (I) catalysts prepared from $AlCl_3$ precursor with varied molar ratio of Al (from 2% to 20%) for esterification of FFA in crude palm oil is shown in Fig. 1. It was found that the conversion of FFA significantly increased with the reaction time. The maximum activity of SO_4^{2-}/Al_2O_3-SnO_2 (I) catalysts prepared from $AlCl_3$ precursor was observed when 2% Al was added to SnO_2; the conversions varied from 61% to 87% when the reaction time increased from 1 to 3h. The conversion of FFA is likely to

increase further if the reaction time is longer than 3h because the reaction equilibrium is not reached yet. When the molar ratio of Al added to SnO_2 was increased from 4% to 20%, the activity of SO_4^{2-}/Al_2O_3-SnO_2 (I) catalysts decreased. The lowest activity was found when 20% Al was added to SnO_2. Too much ratio of Al is expected to decrease the activity of SO_4^{2-}/Al_2O_3-SnO_2 (I) catalysts probably due to the decreased acidity of the catalyst. SO_4^{2-}/Al_2O_3 was reported to be less active than SO_4^{2-}/ZrO_2 for esterification of FFA in used vegetable oil [11]. SO_4^{2-}/ZrO_2 gave lower activity than SO_4^{2-}/SnO_2 for esterification of FFA in crude palm oil [12]. SO_4^{2-}/SnO_2 has been reported to have stronger acid strength than sulfated zirconia, SO_4^{2-}/ZrO_2 [2]. Therefore, it is likely that the greater the addition of Al_2O_3, the lower the acidity of SO_4^{2-}/Al_2O_3-SnO_2.
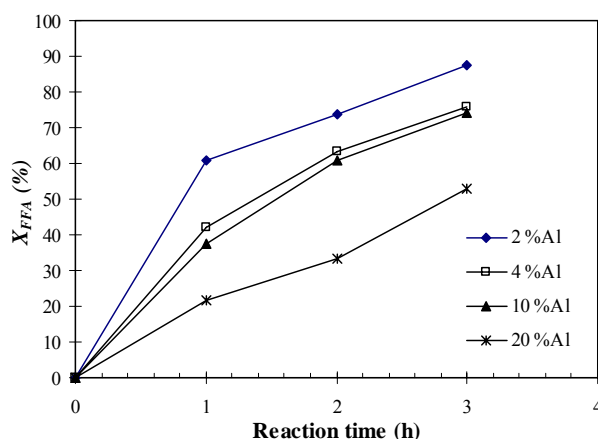

Fig. 1 Effect of Al molar ratio added to SO_4^{2-}/Al_2O_3-SnO_2 (I) catalysts

The activity of SO_4^{2-}/Al_2O_3-SnO_2 (II) catalysts prepared from $Al(NO_3)_3$ precursor with varied molar ratio of Al (from 2% to 20%) for esterification of FFA in crude palm oil is shown in Fig. 2. The conversion of FFA was found to considerably increase with the reaction time. The maximum activity of SO_4^{2-}/Al_2O_3-SnO_2 (II) catalysts prepared from $Al(NO_3)_3$ precursor was observed when 4% Al was added to SnO_2; the conversions varied from 53% to 82% when the reaction time increased from 1 to 3h. When the molar ratio of Al added to SnO_2 was too low (2%), the activity of SO_4^{2-}/Al_2O_3-SnO_2 (II) catalyst was lower. In contrast, when too much molar ratio of Al was added to SnO_2 (10%, 20%), the activity of SO_4^{2-}/Al_2O_3-SnO_2 (II) catalysts decreased. This case is different from that of SO_4^{2-}/Al_2O_3-SnO_2 (I) catalyst. Therefore, different types of Al precursors affect the activity of SO_4^{2-}/Al_2O_3-SnO_2 catalyst differently.
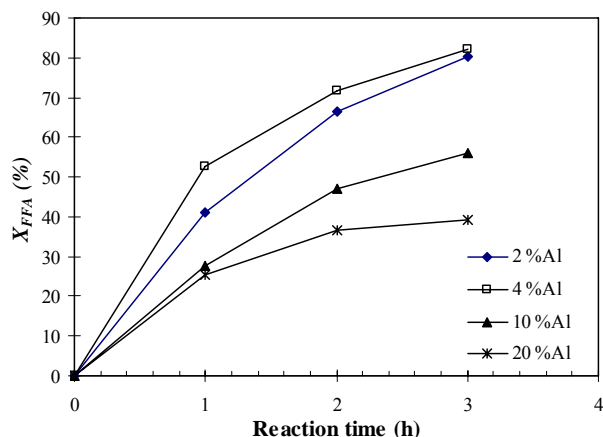
Fig. 2 Effect of Al molar ratio added to SO_4^{2-}/Al_2O_3-SnO_2 (II) catalysts
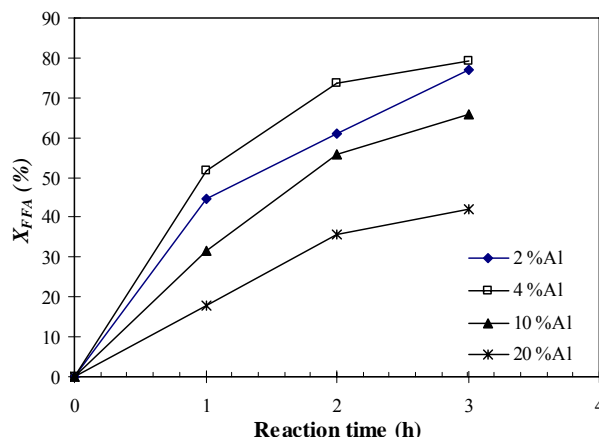
Fig. 3 Effect of Al molar ratio added to SO_4^{2-}/Al_2O_3-SnO_2 (III) catalysts

The activity of SO_4^{2-}/Al_2O_3-SnO_2 (III) catalysts prepared from $Al_2(SO_4)_3$ precursor with varied molar ratio of Al (from 2% to 20%) for esterification of FFA in crude palm oil is shown in Fig. 3. The conversion of FFA was found to increase significantly with the reaction time. The optimum molar ratio of Al was 4%, which is similar to the case of $Al(NO_3)_3$ precursor. The SO_4^{2-}/Al_2O_3-SnO_2 (III) catalysts prepared from $Al_2(SO_4)_3$ precursor (4% Al) gave the highest conversions of FFA (52% to 79%) when the reaction time increased from 1 to 3h. After 3h of reaction, the conversion of the SO_4^{2-}/Al_2O_3-SnO_2 (III) (4% Al) seems to level off, indicating the approach of the reaction equilibrium.

Compared the results of Figs. 1 to 3, it can be concluded that different types of Al precursors gave different activities of SO_4^{2-}/Al_2O_3-SnO_2 for esterification of FFA in crude palm oil. For the high activity of SO_4^{2-}/Al_2O_3-SnO_2 catalyst for esterification of FFA in crude palm oil, the amounts of Al_2O_3 added to SnO_2 should be kept lower than 4 mol% of Al. In a typical biodiesel production from oil containing large amounts of FFA, FFA must be esterified to an acceptable level, e.g. 1 wt% [1], in order to prevent soap formation and increase the biodiesel yield before the oil is fed to the following alkaline catalyzed transesterification. With this criterion, the FFA content in our crude palm oil which initially was 10 wt% must be reduced to 1 wt% (or 90% conversion of FFA). The results of Figs. 1 to 3 show the potential of SO_4^{2-}/Al_2O_3-SnO_2 to be used as a commercial catalyst to reduce FFA content in crude palm oil when more reaction time is allowed. However, further investigation in the activity of reused SO_4^{2-}/Al_2O_3-SnO_2 catalyst is strongly needed before it is actually used on the commercial scale. Catalyst reuse is an important step because it reduces the cost of the process [13].

Since several studies have successfully described pseudo homogeneous, first-order kinetics for esterification reaction [14], [15], we attempted to determine the reaction order with respect to FFA based on the power-law model. We assumed a pseudohomogeneous behavior: no mass transfer limitation, the absence of adsorption/desorption effects of the heterogeneous catalyst and the total reaction mixture acting as a homogeneous system. In our study, FFA is the limiting reactant while methanol is fed in excess amount. Therefore, the reaction order with respect to FFA at a constant reaction temperature is necessary while the concentration of methanol is assumed to be constant.

$$-r_{FFA} = -\frac{dC_{FFA}}{dt} = kC_{FFA}^n C_{CH_3OH}^m \qquad (2)$$

where $-r_{FFA}$ is the reaction rate of FFA, C_{FFA} and C_{CH_3OH} are the concentrations of FFA and methanol at the reaction time t. n and m are reaction orders with respect to FFA and methanol. If the initical concentration of methanol is much higher than that of FFA ($C_{CH_3OH,0} >> C_{FFA,0}$), (2) becomes (3).

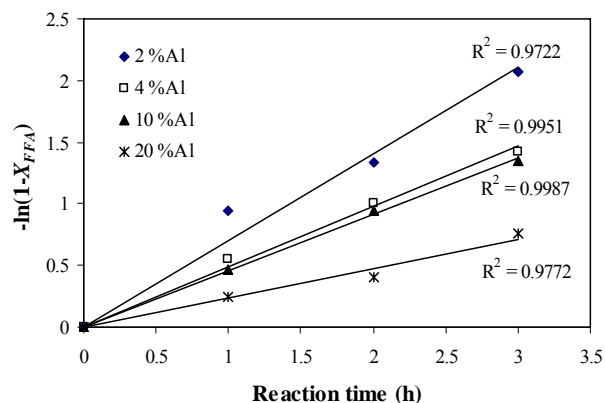$$-\frac{dC_{FFA}}{dt} = k'C_{FFA}^n \qquad (3)$$

$$k' = kC_{CH_3OH,0}^m \qquad (4)$$

Substututing $C_{FFA} = C_{FFA,0}(1 - X_{FFA})$ and n = 1 into (3) and integrating (3) from t = 0 to t yields (5).
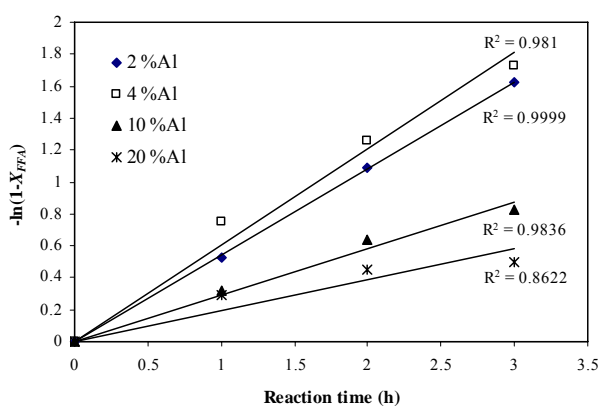
$$-\ln(1 - X_{FFA}) = k't \qquad (5)$$

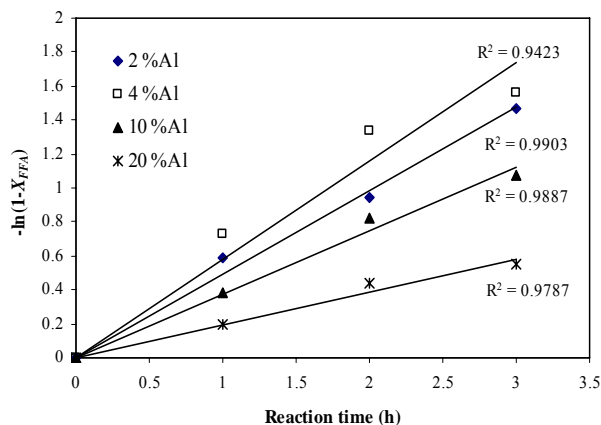The plot between $-\ln(1 - X_{FFA})$ and reaction time (t) is

shown in Fig. 4.

(a)

(b)

(c)

Fig. 4 First-order kinetics for esterification of FFA with methanol in the presence of: (a) SO_4^{2-}/Al_2O_3-SnO_2 (I); (b) SO_4^{2-}/Al_2O_3-SnO_2 (II); (c) SO_4^{2-}/Al_2O_3-SnO_2 (III) catalysts

As shown in Fig. 4, the regression coefficients (R^2) of the straight lines indicate a good fit to the first-order kinetics with

respect to FFA. Therefore, esterification of FFA with methanol in the presence of SO_4^{2-}/Al_2O_3-SnO_2 catalysts obeyed first-order kinetics.

IV. CONCLUSION

The SO_4^{2-}/Al_2O_3-SnO_2 catalyst could reduce the FFA content in crude palm oil via esterification to an acceptable level for alkaline catalyzed transesterification. Different types of Al precursors gave different catalytic activities of SO_4^{2-}/Al_2O_3-SnO_2. Regardless the types of Al precursors, the amounts of Al_2O_3 added to SnO_2 should be kept lower than 4 mol% of Al for the high catalytic activity of SO_4^{2-}/Al_2O_3-SnO_2. The esterification of FFA with methanol in the presence of SO_4^{2-}/Al_2O_3-SnO_2 catalyst obeyed first-order kinetics.

Further investigation should be performed to evaluate the activity of SO_4^{2-}/Al_2O_3-SnO_2 catalyst after recycle since the loss of sulfates which are the active sites for esterification reactions is widely reported in the literature [16]-[18]. This causes the catalyst deactivation which in turn prohibits the application of the sulfated metal oxide catalysts for liquid phase reactions to the commercial scale.

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