

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

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**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 ( $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$ ) catalysts were prepared and used for esterification of free fatty acids in crude palm oil in a batch reactor. The  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  catalysts were prepared from different Al precursors. The results showed that different Al precursors gave different activities of the  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  catalysts. The esterification of free fatty acids in crude palm oil with methanol in the presence of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  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  $\text{H}_2\text{SO}_4$  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.

Therefore, reactor corrosion is minimized.

Sulfated tin oxide ( $\text{SO}_4^{2-}/\text{SnO}_2$ ) 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].  $\text{SO}_4^{2-}/\text{SnO}_2$  has been reported to have stronger acid strength than sulfated zirconia,  $\text{SO}_4^{2-}/\text{ZrO}_2$  [2], which well catalyzes esterification reactions of carboxylic acids [4], [5]. Therefore, the activity of  $\text{SO}_4^{2-}/\text{SnO}_2$  is expected to be higher than  $\text{SO}_4^{2-}/\text{ZrO}_2$ . However, the studies on the structure and applications of  $\text{SO}_4^{2-}/\text{SnO}_2$  are relatively few, compared to  $\text{SO}_4^{2-}/\text{ZrO}_2$  and other  $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ -type solid superacids [6]. Moreover,  $\text{SO}_4^{2-}/\text{SnO}_2$  is not commercially available, unlike  $\text{SO}_4^{2-}/\text{ZrO}_2$ . With these reasons, more attentions should be given to  $\text{SO}_4^{2-}/\text{SnO}_2$ .

Khder and coworkers [7] and Moreno and coworkers [8] have conducted intensive studies in the synthesis and characterization of  $\text{SO}_4^{2-}/\text{SnO}_2$  as well as its activity for esterification reactions. The catalytic activity of  $\text{SO}_4^{2-}/\text{SnO}_2$  strongly depends on its acidity, which is greatly affected by the sulfate concentration and calcination temperature. The maximum activity was achieved when the  $\text{SO}_4^{2-}/\text{SnO}_2$  catalyst contained 30 wt% sulfate and was calcined at  $550^\circ\text{C}$ , giving about 92% conversion of acetic acid [7]. In the esterification of oleic acid with ethanol, the highest activity of  $\text{SO}_4^{2-}/\text{SnO}_2$  catalyst occurred when it contained 0.3 wt% sulfate and was calcined at  $500^\circ\text{C}$ , giving 49% conversion of oleic acid [8].

However, the modification of  $\text{SO}_4^{2-}/\text{SnO}_2$  with other metal oxides is hardly found in the literature. The introduction of  $\text{Al}_2\text{O}_3$  onto  $\text{SO}_4^{2-}/\text{SnO}_2$  and its application for benzoylation have been reported by Guo and coworkers [6]. Another previous study of alumina-doped sulfated tin oxide ( $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$ ) for acylation was performed by Zhao and coworkers [9]. Introducing  $\text{Al}_2\text{O}_3$  to  $\text{SO}_4^{2-}/\text{SnO}_2$  offers the benefit of cost saving. To the best of our knowledge, there has been no study in catalytic esterification with  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$ . Therefore, the present study focuses on the activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  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  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  catalysts were varied. Three precursors were investigated:  $\text{AlCl}_3$ ,  $\text{Al}(\text{NO}_3)_3$  and  $\text{Al}_2(\text{SO}_4)_3$ . The activities of these catalysts were then tested for

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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 $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$

The preparation of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  was adapted from the procedure of Furuta and coworkers [10]. A mixture of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (20 g) and aluminum precursor,  $\text{AlCl}_3$  or  $\text{Al}(\text{NO}_3)_3$  or  $\text{Al}_2(\text{SO}_4)_3$  (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  $\text{CH}_3\text{COONH}_4$  solution (4 wt%), filtered and dried at  $100^\circ\text{C}$  for 24h, yielding aluminum-tin compound. The compound then was immersed in  $\text{H}_2\text{SO}_4$  solution (30 wt% sulfates) to form gels. The gels were further stirred for 1h, filtered, dried at  $100^\circ\text{C}$  for 2h and calcined at  $500^\circ\text{C}$  for 3h to give alumina-doped sulfated tin oxide. In this study, the designations of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (x) are used. The Roman number x stands for the type of aluminum precursor, I =  $\text{AlCl}_3$ , II =  $\text{Al}(\text{NO}_3)_3$  and III =  $\text{Al}_2(\text{SO}_4)_3$ .

### B. Esterification of FFA

Activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  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  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  catalyst was added to the flask. The mixture was heated to  $80^\circ\text{C}$ . 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 ( $X_{\text{FFA}}$ ) was calculated from (1)

$$X_{\text{FFA}}(\%) = \frac{\text{FFA}_0 - \text{FFA}_t}{\text{FFA}_0} \times 100 \quad (1)$$

where  $\text{FFA}_0$  and  $\text{FFA}_t$  (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  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (I) catalysts prepared from  $\text{AlCl}_3$  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  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (I) catalysts prepared from  $\text{AlCl}_3$  precursor was observed when 2% Al was added to  $\text{SnO}_2$ ; 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  $\text{SnO}_2$  was increased from 4% to 20%, the activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (I) catalysts decreased. The lowest activity was found when 20% Al was added to  $\text{SnO}_2$ . Too much ratio of Al is expected to decrease the activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (I) catalysts probably due to the decreased acidity of the catalyst.  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$  was reported to be less active than  $\text{SO}_4^{2-}/\text{ZrO}_2$  for esterification of FFA in used vegetable oil [11].  $\text{SO}_4^{2-}/\text{ZrO}_2$  gave lower activity than  $\text{SO}_4^{2-}/\text{SnO}_2$  for esterification of FFA in crude palm oil [12].  $\text{SO}_4^{2-}/\text{SnO}_2$  has been reported to have stronger acid strength than sulfated zirconia,  $\text{SO}_4^{2-}/\text{ZrO}_2$  [2]. Therefore, it is likely that the greater the addition of  $\text{Al}_2\text{O}_3$ , the lower the acidity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$ .

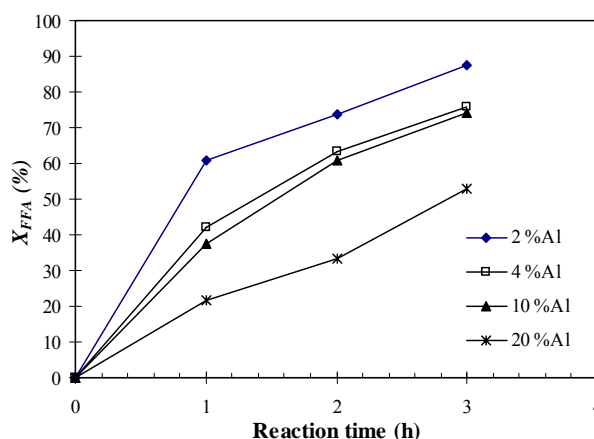


Fig. 1 Effect of Al molar ratio added to  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (I) catalysts

The activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (II) catalysts prepared from  $\text{Al}(\text{NO}_3)_3$  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  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (II) catalysts prepared from  $\text{Al}(\text{NO}_3)_3$  precursor was observed when 4% Al was added to  $\text{SnO}_2$ ; the conversions varied from 53% to 82% when the reaction time increased from 1 to 3h. When the molar ratio of Al added to  $\text{SnO}_2$  was too low (2%), the activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (II) catalyst was lower. In contrast, when too much molar ratio of Al was added to  $\text{SnO}_2$  (10%, 20%), the activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (II) catalysts decreased. This case is different from that of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (I) catalyst. Therefore, different types of Al precursors affect the activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  catalyst differently.

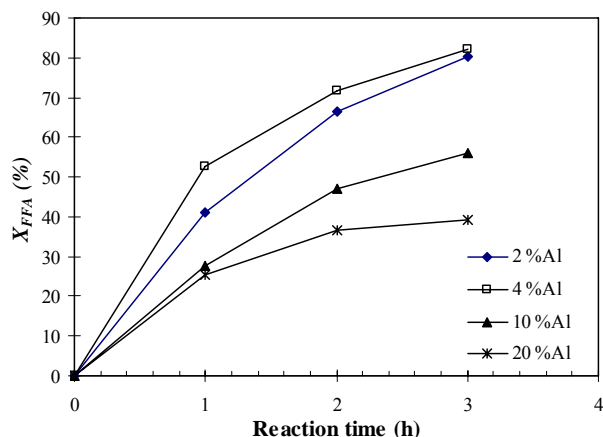


Fig. 2 Effect of Al molar ratio added to  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (II) catalysts

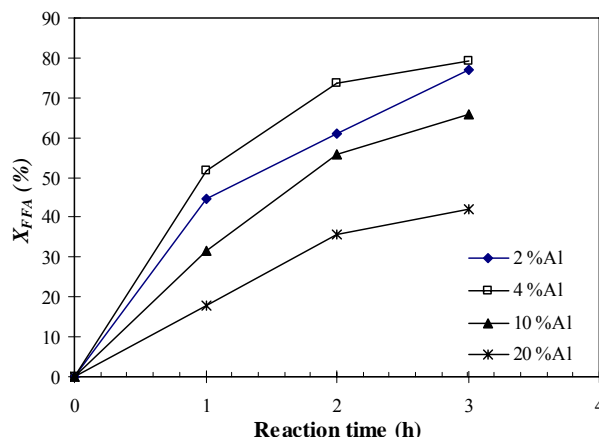


Fig. 3 Effect of Al molar ratio added to  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (III) catalysts

The activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (III) catalysts prepared from  $\text{Al}_2(\text{SO}_4)_3$  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  $\text{Al}(\text{NO}_3)_3$  precursor. The  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (III) catalysts prepared from  $\text{Al}_2(\text{SO}_4)_3$  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  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (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  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  for esterification of FFA in crude palm oil. For the high activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  catalyst for esterification of FFA in crude palm oil, the amounts of  $\text{Al}_2\text{O}_3$  added to  $\text{SnO}_2$  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  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  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  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  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.

$$-r_{\text{FFA}} = -\frac{dC_{\text{FFA}}}{dt} = kC_{\text{FFA}}^n C_{\text{CH}_3\text{OH}}^m \quad (2)$$

where  $-r_{\text{FFA}}$  is the reaction rate of FFA,  $C_{\text{FFA}}$  and  $C_{\text{CH}_3\text{OH}}$  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 initial concentration of methanol is much higher than that of FFA ( $C_{\text{CH}_3\text{OH},0} \gg C_{\text{FFA},0}$ ), (2) becomes (3).

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

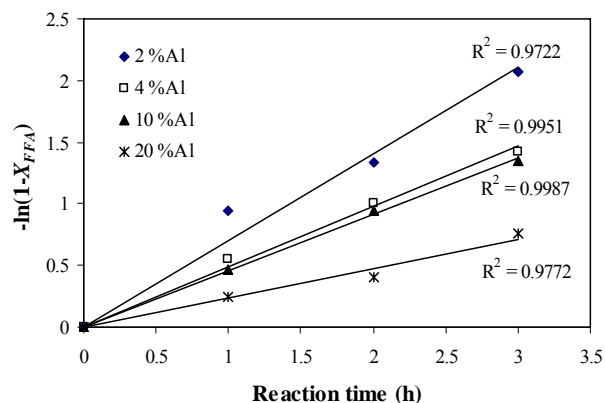
$$k' = kC_{\text{CH}_3\text{OH},0}^m \quad (4)$$

Substituting  $C_{\text{FFA}} = C_{\text{FFA},0}(1 - X_{\text{FFA}})$  and  $n = 1$  into (3) and integrating (3) from  $t = 0$  to  $t$  yields (5).

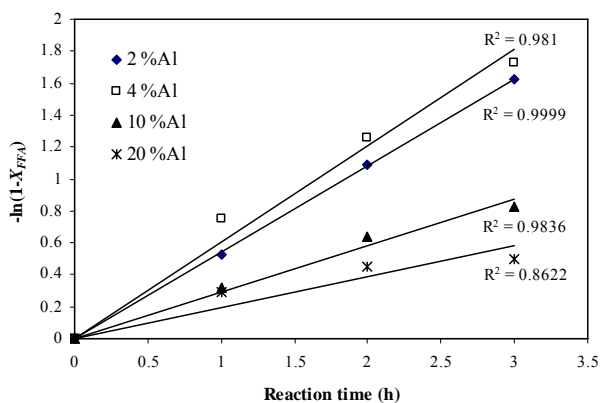
$$-\ln(1 - X_{\text{FFA}}) = k't \quad (5)$$

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

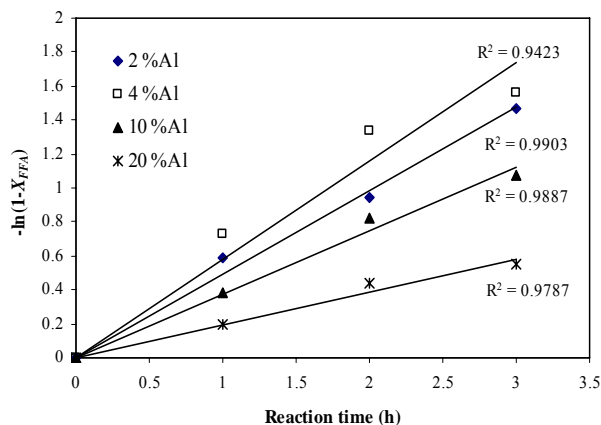
shown in Fig. 4.



(a)



(b)



(c)

Fig. 4 First-order kinetics for esterification of FFA with methanol in the presence of: (a)  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (I); (b)  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (II); (c)  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  (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  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  catalysts obeyed first-order kinetics.

#### IV. CONCLUSION

The  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  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  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$ . Regardless the types of Al precursors, the amounts of  $\text{Al}_2\text{O}_3$  added to  $\text{SnO}_2$  should be kept lower than 4 mol% of Al for the high catalytic activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$ . The esterification of FFA with methanol in the presence of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  catalyst obeyed first-order kinetics.

Further investigation should be performed to evaluate the activity of  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$  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.

#### ACKNOWLEDGMENT

The authors would like to thank King Mongkut's University of Technology North Bangkok and Energy Policy and Planning Office, Ministry of Energy, Thailand for financial supports.

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