

## Esterification of Levulinic Acid to Levulinate Esters in the Presence of Sulfated Silica Catalyst

(Pengesteran Asid Levulinik kepada Ester Levulinat dengan Kehadiran Pemangkin Silika Sulfat)

NUR AAINAA SYAHIRAH RAMLI, NUR IRSALINA HISHAM & NOR AISHAH SAIDINA AMIN\*

### ABSTRACT

*Levulinic acid (LA) is one of biomass derived building block chemicals with various applications. Catalytic esterification of LA with alkyl alcohol produces levulinate ester which can be applied as fragrance, flavouring agents, as well as fuel additives. In this study, a series of sulfated silica ( $\text{SiO}_2$ ) catalyst was prepared by modification of  $\text{SiO}_2$  with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) at different concentrations; 0.5 M to 5 M  $\text{H}_2\text{SO}_4$ . The catalysts were characterized, and tested for esterification of LA with ethanol to ethyl levulinate (EL). The effect of various reaction parameters including reaction time, catalyst loading and molar ratio of LA to ethanol on esterification of LA to EL were inspected. The catalyst with high concentration of acid sites seemed suitable for LA esterification to EL. Among the sulfated  $\text{SiO}_2$  catalysts tested (0.5 M- $\text{SiO}_2$ , 1 M- $\text{SiO}_2$ , 3 M- $\text{SiO}_2$  and 5 M- $\text{SiO}_2$ ), 3 M- $\text{SiO}_2$  exhibited the highest performance with the optimum EL yield of 54% for reaction conducted at reflux temperature for 4 h, 30% 3 M- $\text{SiO}_2$  loading and LA to ethanol molar ratio of 1:20. Besides, the reusability of 3 M- $\text{SiO}_2$  catalyst for LA esterification with ethanol was examined for five cycles. Esterification of LA with methanol and 1-butanol were also carried out for methyl levulinate (ML) and butyl levulinate (BL) productions with 69% and 40% of ML and BL yields, respectively. This study demonstrates the potential of sulfated  $\text{SiO}_2$  catalyst for levulinate ester production from LA at mild process condition.*

*Keywords: Esterification; levulinic acid; levulinate ester; sulfated silica*

### ABSTRAK

*Asid levulinik (LA) ialah bahan kimia asas daripada biojisim dengan pelbagai aplikasi. Pengesteran bermangkin asid levulinik dengan alkil alkohol menghasilkan ester levulinat yang dapat digunakan sebagai bahan pewangi dan perasa, juga aditif bahan api. Dalam kajian ini, satu siri pemangkin silika ( $\text{SiO}_2$ ) sulfat telah dihasilkan melalui pengubahsuaian  $\text{SiO}_2$  bersama asid sulfurik ( $\text{H}_2\text{SO}_4$ ) berkepekatan yang berbeza; 0.5 M hingga 5 M. Pemangkin tersebut telah dicirikan dan diuji bagi pengesteran LA dengan etanol kepada etil levulinat (EL). Kesan pelbagai parameter tindak balas termasuk masa tindak balas, suapan pemangkin dan nisbah molar antara LA dan etanol terhadap pengesteran LA kepada EL telah dikaji. Pemangkin dengan kepekatan yang tinggi bagi tapak asid tampak sesuai untuk pengesteran LA. Antara  $\text{SiO}_2$  sulfat yang telah diuji (0.5 M- $\text{SiO}_2$ , 1 M- $\text{SiO}_2$ , 3 M- $\text{SiO}_2$  dan 5 M- $\text{SiO}_2$ ), 3 M- $\text{SiO}_2$  menunjukkan prestasi tertinggi dengan hasil optimum EL sebanyak 54% untuk tindak balas yang dijalankan pada suhu refluks selama 4 jam, menggunakan 30% 3 M- $\text{SiO}_2$  suapan dan nisbah molar 1:20 antara LA dan etanol. Selain itu, kebolehgunaan semula 3 M- $\text{SiO}_2$  telah dikaji untuk 5 kitaran. Pengesteran LA dengan metanol dan 1-butanol untuk penghasilan metil levulinat (ML) dan butil levulinat (BL) turut ditunjukkan dengan hasil masing-masing sebanyak 69% dan 40% bagi ML dan BL. Kajian ini menunjukkan potensi  $\text{SiO}_2$  sulfat untuk penghasilan ester levulinat daripada LA pada keadaan proses yang sederhana.*

*Kata kunci: Asid levulinik; ester levulinat; pengesteran; silika sulfat*

### INTRODUCTION

Conversion of carbohydrate derived biomass for basic chemical production has received a great attention as biomass is regarded as alternative source for the depleting fossil fuels (Cirujano et al. 2015a; Wang et al. 2015). Levulinic acid (LA) is a versatile platform chemical and considered as one of the top twelve building block chemicals derived from biomass (Ahlkvist et al. 2016; Ramli & Amin 2017). LA can be used in several applications including fuel additives, pharmaceutical agents, resin precursors, fragrance and flavouring agents (Cirujano et al. 2015a; Wang et al. 2015). Esters of LA

(levulinate esters) are the important compounds among the LA derivatives which are employed in fragrance and flavouring industry and can be applied as fuel additives (Démolis et al. 2014; Song et al. 2015). For instance, ethyl levulinate (EL), one of the LA esters can be used directly in a regular diesel car engines as diesel miscible biofuel up to 5 wt. % (Démolis et al. 2014).

Levulinate esters can be synthesized from catalytic esterification of LA with alkyl alcohol (Figure 1); such as methanol, ethanol, and butanol, to give methyl levulinate (ML), ethyl levulinate (EL) and butyl levulinate (BL), respectively (Fernandes et al. 2012; Pasquale et al. 2012;

Ramli et al. 2017b; Yadav & Yadav 2014; Zainol et al. 2016). Esterification of LA can be carried out in the presence of homogeneous acid catalyst such as mineral acids (Bart et al. 1994; Chang et al. 2012). It is known that the drawbacks from the use of homogenous catalyst are environmental problems related with handling, disposal, and regeneration practices. Thus, considerable efforts were made to tackle the drawbacks of homogeneous catalysts and to develop environmentally friendly heterogeneous catalysts with considerable catalytic activity and reusable properties (Dharne & Bokade 2011; Nandiwale & Bokade 2015a; Su et al. 2014; Varkolu et al. 2016).

The most employed heterogeneous catalysts for LA esterification with alkyl alcohols are zeolites and heteropolyacid based catalysts. These types of catalysts have reported several advantages such as adjustable acidity and recyclability other than substantial performance on the reaction (Maheria et al. 2013; Nandiwale & Bokade 2015b; Pasquale et al. 2012; Yan et al. 2013). However, the treatment of zeolites is necessary in order to introduce mesoporosity structure and favor the LA esterification (Patil et al. 2014). Meanwhile, heteropolyacid based catalysts undergo leaching of the acid from the catalyst support (Dharne & Bokade 2011). Therefore, there are necessities to develop new catalysts and to improve the catalytic performance of LA esterification in terms of activity, stability, and reusability. Attempts to prepare an effective catalyst for esterification of LA can be achieved using mesoporous materials such as silica and modification of the mesoporous materials to give a catalyst with high acidic sites.

The objective of this study was to examine the potential of sulfated silica ( $\text{SiO}_2$ ) catalyst for esterification of LA with alkyl alcohols for the production of levulinate esters. Herein, a series of sulfated  $\text{SiO}_2$  catalyst was prepared by modification of  $\text{SiO}_2$  with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and characterized based on their surface area and acidity. Subsequently, sulfated  $\text{SiO}_2$  and parent  $\text{SiO}_2$  were employed as catalysts for esterification of LA with ethanol at reflux temperature for EL production. From the catalyst screening, the activity of selected sulfated  $\text{SiO}_2$  catalyst was further inspected by varying the reaction parameters in order to maximize the EL production. The reaction parameters include reaction time (1 to 6 h), catalyst loading (10 to 50%), and molar ratio of LA to ethanol (1:5 to 1:25). The reusability of sulfated  $\text{SiO}_2$  was inspected for five successive cycles. Besides, the catalytic performance of sulfated  $\text{SiO}_2$  for esterification of LA with other alkyl alcohols such as methanol and 1-butanol were also inspected.

## MATERIALS AND METHODS

### MATERIALS

All chemicals were used as received without any further purification. The chemicals used for the preparation of sulfated silica were silicon dioxide ( $\text{SiO}_2$ ) and  $\text{H}_2\text{SO}_4$  (96%) purchased from QRec, New Zealand. Ethanol (99%), methanol (99%), 1-butanol (99%), and LA (99%), were employed in the catalytic tests and purchased from Merck, Germany. In sample analyses, standard analytical grade of ethyl levulinate (EL, 99%), methyl levulinate (ML, >98%), and butyl levulinate (BL, 98%) were obtained from Sigma Aldrich. Distilled water was used in the preparation of solutions.

### CATALYST PREPARATION AND CHARACTERIZATION

A series of sulfated  $\text{SiO}_2$  catalyst was prepared by modification of  $\text{SiO}_2$  with  $\text{H}_2\text{SO}_4$  at different concentrations of 0.5 M to 5 M. For each catalyst, 10 g of  $\text{SiO}_2$  was mixed with 100 ml of  $\text{H}_2\text{SO}_4$  at different concentrations (0.5 M, 1 M, 3 M, and 5 M). The mixture was stirred overnight at room temperature. Then, the catalyst was centrifuged and washed with distilled water, and finally dried at 160°C. The properties of sulfated  $\text{SiO}_2$  (0.5 M- $\text{SiO}_2$ , 1 M- $\text{SiO}_2$ , 3 M- $\text{SiO}_2$ , 5 M- $\text{SiO}_2$ ) and parent  $\text{SiO}_2$  were characterized based on their surface area and acidity. The Brunauer Emmett Teller (BET) surface area of the catalysts were evaluated using Micromeritics 3Flex 3.01 instrument based on nitrogen ( $\text{N}_2$ ) adsorption and desorption at -196°C. The acid properties of the catalyst samples were determined via temperature-programmed desorption (TPD) of ammonia ( $\text{NH}_3$ );  $\text{NH}_3$ -TPD (Micromeritics AutoChem II 2920) by passing 10%  $\text{NH}_3$ /helium gas up to 900°C and quantified using a thermal conductivity detector (TCD).

### CATALYTIC TEST AND PRODUCT ANALYSIS

The catalytic esterification of LA was carried out in a 250 mL batch reactor flask and equipped with a condenser, magnetic stirrer, and thermocouple. The reactor flask was loaded with predetermined amounts of LA, alcohol and catalyst. The solution was stirred at 200 rpm and heated to the reflux temperature of respective alcohol. After the reaction was completed, the mixture was to cool to room temperature. The reflux temperature of ethanol, methanol and 1-butanol are 78.3°C, 64.7°C and 117.7°C, respectively. All samples were filtered before further analysis using gas chromatography. For catalyst reusability

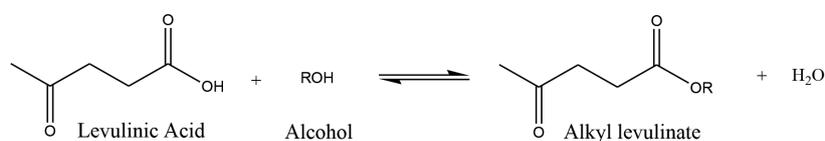


FIGURE 1. Reaction scheme of LA esterification to alkyl levulinate

test, the catalyst was recovered by centrifugation, washed with ethanol and dried overnight at 120°C before being returned to the subsequent cycle. The experimental runs were conducted in triplicate and results in the figures were expressed as the mean value and standard deviation.

The concentration of EL, ML and BL were determined using gas chromatography (GC) equipped with flame ionization detector (FID) (Agilent 7820A) and a capillary column (HP-5; 30 m × 0.32 mm × 0.25 μm). The carrier gas was N<sub>2</sub> at 1.0 mL/min. The oven temperature of GC was held at initial temperature of 80°C then ramped to 170°C (13°C/min) and finally reached 300°C (40°C/min). The total retention time was 10 min. The levulinate ester (EL, ML, BL) yield was calculated according to (1).

$$\text{Levulinate ester yield (mol\%)} = \frac{\text{Final levulinate ester amount (mol)}}{\text{Initial LA amount (mol)}} \times 100\% \quad (1)$$

## RESULTS AND DISCUSSION

### CATALYST CHARACTERIZATION

The SiO<sub>2</sub> and sulfated SiO<sub>2</sub> catalysts were characterized using BET method and NH<sub>3</sub>-TPD for inspecting their specific surface area and acidity, respectively. These two characterizations technique were carried out since it is signified that surface area and acidity play important roles in the LA esterification to EL (Liu et al. 2013; Ramli et al. 2017a). The SiO<sub>2</sub> obtained from QRec is a mesopore compound with mean pore size of 6 nm. As listed in Table 1, the specific surface area of SiO<sub>2</sub> gradually decreased after the modification with different concentrations of H<sub>2</sub>SO<sub>4</sub>. The decrease in specific surface area was due to the blockage of SiO<sub>2</sub> pores by the SO<sub>3</sub>H groups. A notable surge in catalyst acidity from 71.2 μmol/g to 170.7 μmol/g was observed when SiO<sub>2</sub> was modified with 3 M H<sub>2</sub>SO<sub>4</sub>. It is suggested that uniform dispersion of SO<sub>3</sub>H groups increased with higher H<sub>2</sub>SO<sub>4</sub> concentration and increased the number of acidic sites. Meanwhile, there was no substantial increase in acidity when the H<sub>2</sub>SO<sub>4</sub> loading was further increased from 3 M to 5 M. The further increase in H<sub>2</sub>SO<sub>4</sub> loading might resulted in the formation of sulfates multilayer on the catalyst surface. Since NH<sub>3</sub> is adsorbed on the catalyst surface during the NH<sub>3</sub>-TPD analysis, the sulfates multilayer possibly hindered NH<sub>3</sub> to access the

TABLE 1. Surface area and acidity of SiO<sub>2</sub> and sulfated SiO<sub>2</sub> catalysts

Catalyst	Specific surface area (m <sup>2</sup> /g)	Acidity (μmol/g)
Si <sub>0</sub> 2	485	71.2
0.5M-SiO <sub>2</sub>	436	89.8
1M-SiO <sub>2</sub>	369	111.5
3M-SiO <sub>2</sub>	294	170.7
5M-SiO <sub>2</sub>	137	176.2

acid sites. Thus, only marginal increase in catalyst acidity was observed for 5 M-SiO<sub>2</sub> compared to 3 M-SiO<sub>2</sub>. The same catalyst acidity trend has been reported in a previous study on increasing heteropolyacid loading on the catalyst support (Nandiwale et al. 2013).

### CATALYST SCREENING FOR LEVULINIC ACID ESTERIFICATION WITH ETHANOL

The sulfated SiO<sub>2</sub> catalysts were screened for esterification of LA with ethanol to EL at predetermined condition. Besides, parent SiO<sub>2</sub> catalyst was also utilized to examine the effect of sulfating treatment on LA esterification to EL. The overall trend of EL yield over different catalysts are as follows; 5 M-SiO<sub>2</sub> > 3 M-SiO<sub>2</sub> > 1 M-SiO<sub>2</sub> > 0.5 M-SiO<sub>2</sub> > SiO<sub>2</sub> (Figure 2). The parent SiO<sub>2</sub> presented only 9% of EL yield, which is far lower compared to the sulfated SiO<sub>2</sub> catalysts. In previous studies, it was reported that high total acidity enhances the EL yield, which associated to the high surface area with strong acid sites (Cirujano et al. 2015b; Neves et al. 2014; Su et al. 2013a). From the characterization test, the catalyst surface area of sulfated SiO<sub>2</sub> decreased after the modification, while the catalyst acidity increased after the modification. The results from catalyst screening test indicates that the sulfating treatment was essential to improve the activity towards EL production. A small increase in the EL yield (<1%) was recorded when 5 M-SiO<sub>2</sub> was employed in contrast to 3 M-SiO<sub>2</sub>. Due to the environmental aspect, 3 M-SiO<sub>2</sub> is utilized in the subsequent tests in order to avoid the use of higher H<sub>2</sub>SO<sub>4</sub> concentration during catalyst preparation.

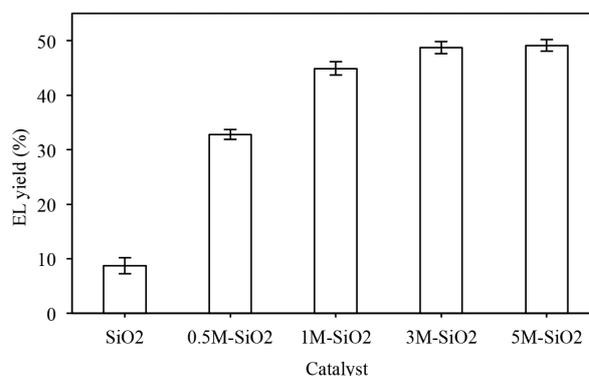


FIGURE 2. LA esterification to EL using different catalysts (reflux temperature, reaction time 6 h, 20% catalyst loading, 1:20 of LA to ethanol molar ratio)

It was presumed that other side reactions also occurred in the presence of sulfated SiO<sub>2</sub> catalysts. Thus, 100% selectivity of EL was not attained from the reaction. The side reactions included dehydration of alcohol in the presence of acid catalyst (Siva Sankar et al. 2016; Su et al. 2013a), transfer hydrogenation of LA and EL to γ-valerolactone (GVL) (Siva Sankar et al. 2016) and dehydration of LA to α-angelica lactone (Enumula et al. 2017). Furthermore, it is reported that the increase in catalyst acidity facilitated

the side reaction involving dehydration of LA to angelica lactone rather than esterification of LA (Siva Sankar et al. 2016). The amounts of other by-products were not further quantified in this study as the main aim is to examine the EL production from LA esterification.

#### EFFECT OF REACTION PARAMETERS ON LA ESTERIFICATION WITH ETHANOL

The catalytic activity of 3 M-SiO<sub>2</sub> on LA esterification to EL at reflux condition was further scrutinized by varying several reaction parameters including reaction time, catalyst loading and LA to ethanol molar ratio. The effect of reaction time on LA esterification with ethanol using 3 M-SiO<sub>2</sub> is given in Figure 3. The EL yield linearly increased with reaction time from 1 h to 4 h. When extending the reaction time from 4 h to 6 h, there is only a slight increase in the EL yield. The formation of water molecules during the esterification might cause the occurrence of hydrolysis and reversible reaction thus resulted in the small increase of EL production for reaction conducted over 4 h (Maheria et al. 2013). The addition of water caused the breaking of the ester link into its parents functional groups - carboxylic acid and alcohol (Maheria et al. 2013). Thus, prolonged reaction time was not feasible to the reaction. The same trend has been reported previously for esterification of LA with alcohols (Maheria et al. 2013; Ramli et al. 2017a, 2017b). As the difference between EL yield from 4 h to 6 h was insignificant, 4 h of reaction was selected as the optimum reaction time and used for all further experiments.

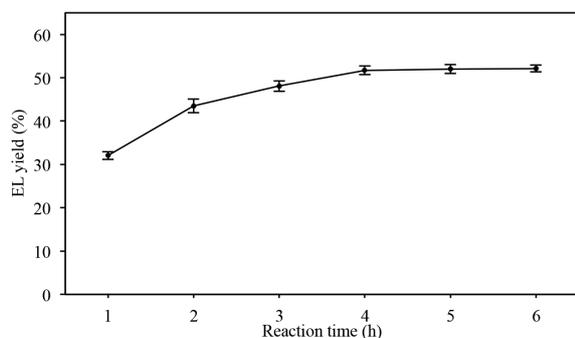


FIGURE 3. Effect of reaction time on EL yield (reflux temperature, 20% 3 M-SiO<sub>2</sub> loading, 1:20 of LA to ethanol molar ratio)

The implication of 3 M-SiO<sub>2</sub> loading; varied from 10% to 50% was studied on LA esterification with ethanol for EL production (Figure 4). The EL yield increased from 43% to 54% with increasing 3 M-SiO<sub>2</sub> loading from 10% to 30%. Above 30% of 3 M-SiO<sub>2</sub> loading, a small decrease in the EL yield was observed. Higher catalyst loading resulted in more viscous reaction mixture and might limit the mass transfer rate. The increase in reaction mixture viscosity and mass transfer limitation subsequently could hinder the catalytic activity (Li et al. 2013; Ramli et al. 2017b; Ya'aini et al. 2012). Further reactions were performed at the optimum 3 M-SiO<sub>2</sub> catalyst loading of 30%. It is

implied that LA esterification with ethanol can take place even in the absence of catalyst due to the fact that LA has the competency to catalyze the reaction (Fernandes et al. 2012; Nandiwale & Bokade 2015b). Previous studies have reported the blank reaction of LA esterification with alkyl alcohol resulted in a small yield of levulinate ester (Fernandes et al. 2012; Nandiwale & Bokade 2015b). A blank reaction was performed in this study and 4% of EL yield was obtained after 6 h of reaction.

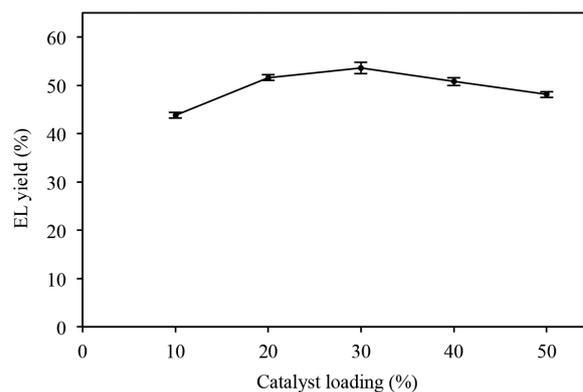


FIGURE 4. Effect of 3 M-SiO<sub>2</sub> catalyst loading on EL yield (reflux temperature, 4 h reaction time, 1:20 of LA to ethanol molar ratio)

The esterification of LA with alkyl alcohol is a reversible reaction (Figure 1). High rate of LA conversion could be attained by minimizing the backward reaction through simultaneous elimination of the water by-product or by using excess ethanol in the reaction (Nandiwale et al. 2013). Excess ethanol was used in this study to accelerate the forward reaction since it is difficult to remove water in the present reaction system. The effect of LA to ethanol molar ratio on EL yield is given in Figure 5. The EL yield increased from 35% to 54% when molar ratio of LA to ethanol is increased from 1:5 to 1:20. This reiterated excess ethanol is favorable for the forward reaction of LA esterification. With increasing molar ratio up to 1:30, a slight reduction in the EL yield by 8% was recorded. Further decrease in EL yield is expected if surplus of ethanol (LA to ethanol molar ratio higher than 1:30) is employed in the reaction. This is due to the fact that higher amount of ethanol might dilute the reactant and lower the concentration of LA (Nandiwale & Bokade 2015b; Patil et al. 2014; Ramli et al. 2017b). This condition could cause poor accessibility of LA with regards to adsorption onto the catalyst thus inhibit the EL production. The backward reaction of LA esterification was favoured with high amount of ethanol thus decreasing the LA conversion to EL (Su et al. 2013a). Besides, other side reactions could also take place such as dehydration of ethanol and transfer hydrogenation of LA (Siva Sankar et al. 2016; Su et al. 2013a). In a previous study (Siva Sankar et al. 2016), further increase in methanol for methyl levulinate production catalyzed by ZrO<sub>2</sub>/SBA-15 resulted in low formation of GVL. This is due to excess methanol served as a hydrogen source

for the transfer hydrogenation of LA. Small amount of dimethylether was also detected due to the intermolecular dehydration reaction (Siva Sankar et al. 2016).

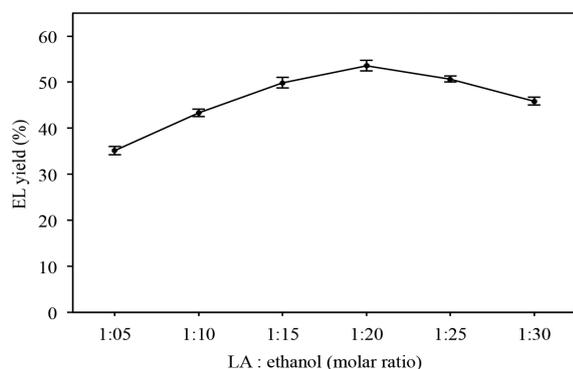


FIGURE 5. Effect of LA to ethanol molar ratio on EL yield (reflux temperature, 4 h reaction time, 30% 3 M-SiO<sub>2</sub> loading)

Although using excess ethanol accelerated the forward reaction, it also increases production cost. From the economic point of view, LA esterification to EL relies on the ethanol recovery. In an ideal practice, the unreacted ethanol should be recovered and recycled back into the process to reduce operating cost and minimize environmental impacts. In previous study on esterification reaction for biodiesel production, the recovery of alcohols was carried out through distillation - vacuum or conventional (Musa 2016). Besides, the crude alkyl levulinate from LA esterification could be recovered by evaporation of solvent under reduced pressure and then

purified to afford pure levulinate product (Maheria et al. 2013). This could be a good option to further recover excess ethanol from the esterification of LA as well as to obtain purified EL.

The modification of SiO<sub>2</sub> with Brønsted H<sub>2</sub>SO<sub>4</sub> has induced new acid sites. It is suggested that Brønsted acid sites played significant roles for the LA esterification. The plausible reaction mechanism of catalytic esterification of LA with ethanol in the presence of 3 M-SiO<sub>2</sub> can be described by several steps as illustrated in Figure 6. The reaction proceeds according to the mechanism proposed previously (Enumula et al. 2017; Pasquale et al. 2012; Siva Sankar et al. 2016; Su et al. 2013b). The first step involves the adsorption of LA on the Brønsted acid sites of the catalyst for the formation of protonated LA intermediate. The protonation increases the electrophilicity of carbonyl carbon. Next, the nucleophilic oxygen of ethanol attacks the carbonyl carbon to form the oxonium ion. Then, a new oxonium ion is formed through a proton transfer from the former oxonium ion. Finally, the loss of water and successive deprotonation leads to the formation of EL. The acid sites of the catalyst are being regenerated from the deprotonation step (Pasquale et al. 2012; Song et al. 2015). The presence of catalyst in the reaction mixture augments the reaction rate since the catalyst acid sites improve the proton accessibility for catalyzing the esterification reaction (Melero et al. 2013; Pasquale et al. 2012; Song et al. 2015). As for Lewis acid sites played significant roles in the LA esterification reaction, the reaction mechanism might follow different pathway as has been described elsewhere (Enumula et al. 2017; Su et al. 2013b).

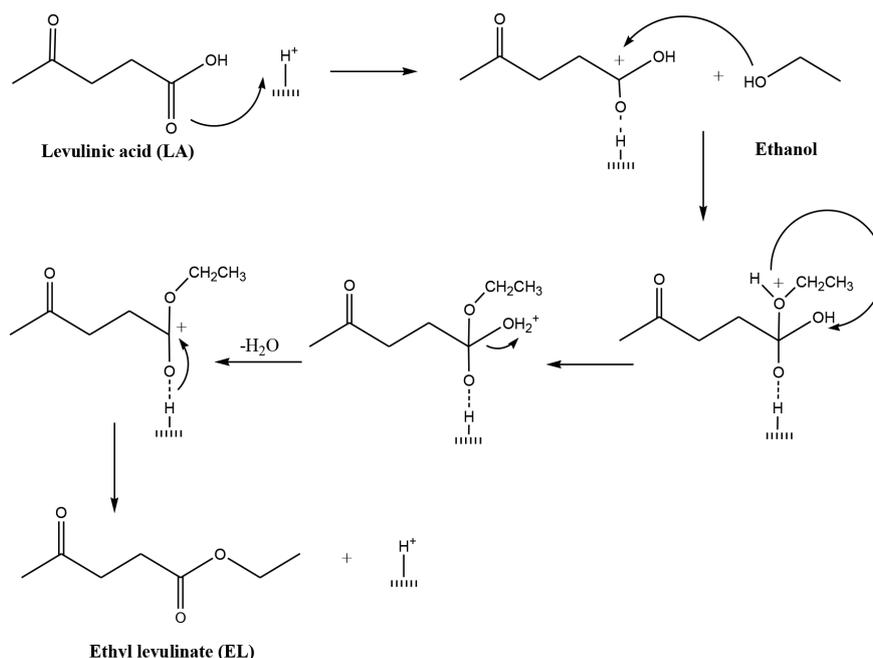


FIGURE 6. Plausible reaction mechanism of LA esterification with ethanol

## CATALYST REUSABILITY

The reusability of sulfated  $\text{SiO}_2$  for LA esterification with ethanol is evaluated for four times (Figure 7). The 3 M- $\text{SiO}_2$  is recovered by centrifugation, washed with ethanol, dried overnight, and returned to the subsequent cycles without further pretreatment with  $\text{H}_2\text{SO}_4$ . The catalytic activity of 3 M- $\text{SiO}_2$  is observed to be stable for five runs with slight decrease in the EL yield (54% to 38%) from first to fifth runs. The decrease in EL yield from the reused catalyst is probably due to the loss of catalyst during the filtration and washing steps. Besides, it can be implied that there is leaching of sulfonate group from the catalyst during the reaction and there is probability of reactant and product deposition on the catalyst active sites resulting in the decrease of catalyst activity (Fernandes et al. 2012). The inspection on leaching of sulfonate group is not included in the scope of this study. Besides, the used 3 M- $\text{SiO}_2$  catalyst was not further characterized in this study.

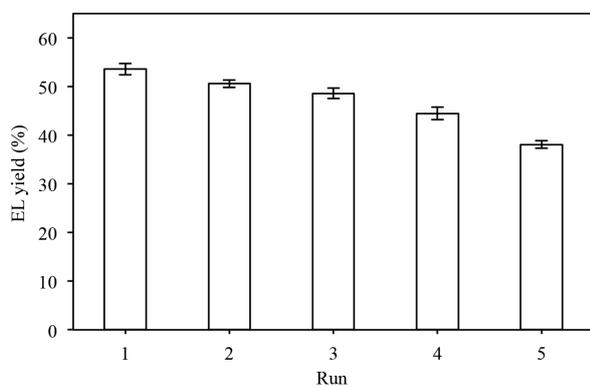


FIGURE 7. Reusability of 3 M- $\text{SiO}_2$  catalyst for LA esterification with ethanol (reflux temperature, 4h reaction time, 30% 3 M- $\text{SiO}_2$  loading, 1:20 of LA to ethanol molar ratio)

## LEVULINIC ACID ESTERIFICATION WITH DIFFERENT ALCOHOLS

As 3 M- $\text{SiO}_2$  exhibited good performance for LA esterification with ethanol, the former catalyst was further tested for LA esterification with methanol and 1-butanol for methyl levulinate (ML) and butyl levulinate (BL) productions, respectively. The reactions were conducted at reflux temperature of respective alcohols, reaction time of 4h, 30% 3 M- $\text{SiO}_2$  loading, and LA to ethanol molar ratio 1:20. As illustrated in Figure 8, the LA esterification with methanol, ethanol and 1-butanol yielded levulinate esters of 67%, 54% and 45%, respectively. It is disclosed that higher yields were attained from esterification of LA with shorter carbon chain alcohols. In previous studies, lower levulinate esters yield were reported from esterification of LA with longer chain alcohols (Melero et al. 2013; Ramli et al. 2017b; Siva Sankar et al. 2016). It is suggested that the occurrence of steric effect from LA esterification with longer carbon chain alcohol could impede the conversion of intermediates to alkyl levulinate (Melero et al. 2013). In a previous study, LA esterification with longer alcohol

chain resulted in the higher formation of GVL through the catalytic transfer hydrogenation (Siva Sankar et al. 2016). This is because in longer alcohol chains, the hydrogen is more readily to be transferred from the alcohol molecule to LA molecule for the formation of GVL.

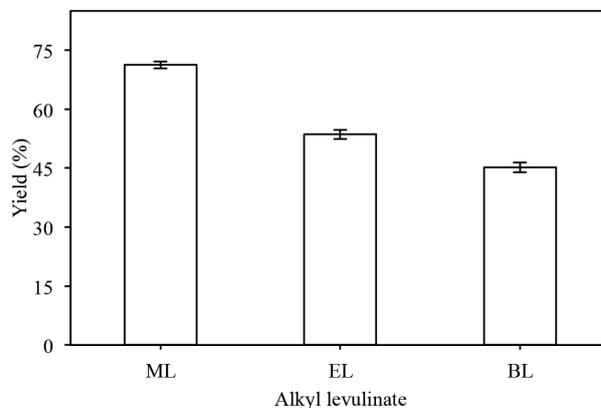


FIGURE 8. Esterification of LA with methanol, ethanol, and 1-butanol for ML, EL, and BL production using 3 M- $\text{SiO}_2$  as catalyst (reflux temperature, 4 h reaction time, 30% 3 M- $\text{SiO}_2$  loading, 1:20 of LA to alcohol molar ratio)

## CONCLUSION

A series of sulfated  $\text{SiO}_2$  catalysts (0.5 M- $\text{SiO}_2$ , 1 M- $\text{SiO}_2$ , 3 M- $\text{SiO}_2$ , 5 M- $\text{SiO}_2$ ) was prepared, characterized, and tested for esterification of LA with ethanol for EL production at reflux condition. Modification of  $\text{SiO}_2$  with  $\text{H}_2\text{SO}_4$  decreased the specific surface area and caused prominent increase in catalyst acidity. High acidity sulfated  $\text{SiO}_2$  catalyst exhibited better performance compared to the parent  $\text{SiO}_2$  catalyst for EL production. From the catalyst screening, the highest catalytic performance was observed from 3 M- $\text{SiO}_2$ . Using 3 M- $\text{SiO}_2$ , effect of reaction time, catalyst loading, and LA to ethanol molar ratio were further evaluated on EL production. At the optimum condition of 4 h, 30% of 3 M- $\text{SiO}_2$  loading and 1:20 molar ratio of LA to ethanol, the esterification of LA with ethanol at reflux temperature yields 53.6% of EL. Prolong reaction time over 4h might cause the occurrence of hydrolysis and reversible reaction thus resulted in small increase of EL yield. Besides, the limitation of mass transfer caused by more viscous reaction mixture and high catalyst loading hinder the overall catalytic activity. It is demonstrated that 3 M- $\text{SiO}_2$  can be reused up to four times without the need for  $\text{H}_2\text{SO}_4$  pretreatment. The reduce of catalyst activity of the reused 3 M- $\text{SiO}_2$  was due to the loss of catalyst during washing, leaching of sulfonate group, and deposition of reactant and product on catalyst active sites. Meanwhile, 3 M- $\text{SiO}_2$  employed for the production of ML and BL registers good activity, as 69% and 40% of ML and BL yields, respectively, were produced. This study reveals the ability of sulfated  $\text{SiO}_2$  for the transformation of renewable feedstock to levulinate ester as a fuel additive.

## ACKNOWLEDGEMENTS

The authors would like to express their sincere gratitude for the financial support received from Universiti Teknologi Malaysia under the Research University Grant (vote number 02E54).

## REFERENCES

- Ahlkvist, J., Wärnå, J., Salmi, T. & Mikkola, J.P. 2016. Heterogeneously catalyzed conversion of nordic pulp to levulinic and formic acids. *Reaction Kinetics, Mechanisms and Catalysis* 119: 415-427.
- Bart, H.J., Reidetschlager, J., Schatka, K. & Lehmann, A. 1994. Kinetics of esterification of levulinic acid with n-butanol by homogeneous catalysis. *Industrial & Engineering Chemistry Research* 33: 21-25.
- Chang, C., Xu, G. & Jiang, X. 2012. Production of ethyl levulinate by direct conversion of wheat straw in ethanol media. *Bioresource Technology* 121: 93-99.
- Cirujano, F.G., Corma, A. & Llabrés i Xamena, F.X. 2015a. Conversion of levulinic acid into chemicals: Synthesis of biomass derived levulinate esters over Zr-containing MOFs. *Chemical Engineering Science* 124: 52-60.
- Cirujano, F.G., Corma, A. & Llabrés i Xamena, F.X. 2015b. Conversion of levulinic acid into chemicals: Synthesis of biomass derived levulinate esters over Zr-containing MOFs. *Chemical Engineering Science* 124: 52-60.
- Démolis, A., Essayem, N. & Rataboul, F. 2014. Synthesis and applications of alkyl levulinates. *ACS Sustainable Chemistry & Engineering* 2: 1338-1352.
- Dharne, S. & Bokade, V.V. 2011. Esterification of levulinic acid to n-butyl levulinate over heteropolyacid supported on acid-treated clay. *Journal of Natural Gas Chemistry* 20: 18-24.
- Enumula, S.S., Gurram, V.R.B., Chada, R.R., Burri, D.R. & Kamaraju, S.R.R. 2017. Clean synthesis of alkyl levulinates from levulinic acid over one pot synthesized WO<sub>3</sub>-SBA-16 catalyst. *Journal of Molecular Catalysis A: Chemical* 426: 30-38.
- Fernandes, D.R., Rocha, A.S., Mai, E.F., Mota, C.J.A. & Teixeira da Silva, V. 2012. Levulinic acid esterification with ethanol to ethyl levulinate production over solid acid catalysts. *Applied Catalysis A: General* 425-426: 199-204.
- Li, Y., Liu, H., Song, C., Gu, X., Li, H., Zhu, W., Yin, S. & Han, C. 2013. The dehydration of fructose to 5-hydroxymethylfurfural efficiently catalyzed by acidic ion-exchange resin in ionic liquid. *Bioresource Technology* 133: 347-353.
- Liu, R., Chen, J., Huang, X., Chen, L., Ma, L. & Li, X. 2013. Conversion of fructose into 5-hydroxymethylfurfural and alkyl levulinates catalyzed by sulfonic acid-functionalized carbon materials. *Green Chemistry* 15: 2895-2903.
- Maheria, K., Kozinski, J. & Dalai, A. 2013. Esterification of levulinic acid to n-Butyl levulinate over various acidic zeolites. *Catalysis Letters* 143: 1220-1225.
- Melero, J.A., Morales, G., Iglesias, J., Paniagua, M., Hernández, B. & Penedo, S. 2013. Efficient conversion of levulinic acid into alkyl levulinates catalyzed by sulfonic mesostructured silicas. *Applied Catalysis A: General* 466: 116-122.
- Musa, I.A. 2016. The effects of alcohol to oil molar ratios and the type of alcohol on biodiesel production using transesterification process. *Egyptian Journal of Petroleum* 25: 21-31.
- Nandiwale, K.Y. & Bokade, V.V. 2015a. Environmentally benign catalytic process for esterification of renewable levulinic acid to various alkyl levulinates biodiesel. *Environmental Progress & Sustainable Energy* 34: 795-801.
- Nandiwale, K.Y. & Bokade, V.V. 2015b. Esterification of renewable levulinic acid to n-butyl levulinate over modified H-ZSM-5. *Chemical Engineering & Technology* 38: 246-252.
- Nandiwale, K.Y., Sonar, S.K., Niphadkar, P.S., Joshi, P.N., Deshpande, S.S., Patil, V.S. & Bokade, V.V. 2013. Catalytic upgrading of renewable levulinic acid to ethyl levulinate biodiesel using dodecatungstophosphoric acid supported on desilicated H-ZSM-5 as catalyst. *Applied Catalysis A: General* 460-461: 90-98.
- Neves, P., Russo, P.A., Fernandes, A., Antunes, M.M., Farinha, J., Pillinger, M., Ribeiro, M.F., Castanheiro, J.E. & Valente, A.A. 2014. Mesoporous zirconia-based mixed oxides as versatile acid catalysts for producing bio-additives from furfuryl alcohol and glycerol. *Applied Catalysis A: General* 487: 148-157.
- Pasquale, G., Vázquez, P., Romanelli, G. & Baronetti, G. 2012. Catalytic upgrading of levulinic acid to ethyl levulinate using reusable silica-included Wells-Dawson heteropolyacid as catalyst. *Catalysis Communications* 18: 115-120.
- Patil, C.R., Niphadkar, P.S., Bokade, V.V. & Joshi, P.N. 2014. Esterification of levulinic acid to ethyl levulinate over bimodal micro-mesoporous H/BEA zeolite derivatives. *Catalysis Communications* 43: 188-191.
- Ramli, N.A.S. & Amin, N.A.S. 2017. Optimization of biomass conversion to levulinic acid in acidic ionic liquid and upgrading of levulinic acid to ethyl levulinate. *BioEnergy Research* 10: 50-63.
- Ramli, N.A.S., Sivasubramaniam, D. & Amin, N.A.S. 2017a. Esterification of levulinic acid using ZrO<sub>2</sub>-supported phosphotungstic acid catalyst for ethyl levulinate production. *BioEnergy Research* 10: 1105-1116.
- Ramli, N.A.S., Zaharudin, N.H. & Amin, N.A.S. 2017b. Esterification of renewable levulinic acid to levulinate esters using Amberlyst-15 as a solid acid catalyst. *Jurnal Teknologi* 79: 137-142.
- Siva Sankar, E., Mohan, V., Suresh, M., Saidulu, G., David Raju, B. & Rama Rao, K.S. 2016. Vapor phase esterification of levulinic acid over ZrO<sub>2</sub>/SBA-15 catalyst. *Catalysis Communications* 75: 1-5.
- Song, D., An, S., Lu, B., Guo, Y. & Leng, J. 2015. Arylsulfonic acid functionalized hollow mesoporous carbon spheres for efficient conversion of levulinic acid or furfuryl alcohol to ethyl levulinate. *Applied Catalysis B: Environmental* 179: 445-457.
- Su, F., An, S., Song, D., Zhang, X., Lu, B. & Guo, Y. 2014. Heteropoly acid and ZrO<sub>2</sub> bifunctionalized organosilica hollow nanospheres for esterification and transesterification. *Journal of Materials Chemistry A* 2: 14127-14138.
- Su, F., Ma, L., Song, D., Zhang, X. & Guo, Y. 2013a. Design of a highly ordered mesoporous H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>-Si(Ph) Si hybrid catalyst for methyl levulinate synthesis. *Green Chemistry* 15: 885-890.
- Su, F., Wu, Q., Song, D., Zhang, X., Wang, M. & Guo, Y. 2013b. Pore morphology-controlled preparation of ZrO<sub>2</sub>-based hybrid catalysts functionalized by both organosilica moieties and Keggin-type heteropoly acid for the synthesis of levulinate esters. *Journal of Materials Chemistry A* 1: 13209-13221.
- Varkolu, M., Moodley, V., Potwana, F.S.W., Jonnalagadda, S.B. & van Zyl, W.E. 2016. Esterification of levulinic acid with ethanol over bio-glycerol derived carbon-sulfonic-acid. *Reaction Kinetics, Mechanisms and Catalysis* 120(1): 69-80.

- Wang, Y., Vogelgsang, F. & Román-Leshkov, Y. 2015. Acid-catalyzed oxidation of levulinate derivatives to succinates under mild conditions. *ChemCatChem* 7: 916-920.
- Ya'aini, N., Amin, N.A.S. & Asmadi, M. 2012. Optimization of levulinic acid from lignocellulosic biomass using a new hybrid catalyst. *Bioresource Technology* 116: 58-65.
- Yadav, G.D. & Yadav, A.R. 2014. Synthesis of ethyl levulinate as fuel additives using heterogeneous solid superacidic catalysts: Efficacy and kinetic modeling. *Chemical Engineering Journal* 243: 556-563.
- Yan, K., Wu, G., Wen, J. & Chen, A. 2013. One-step synthesis of mesoporous  $H_4SiW_{12}O_{40}-SiO_2$  catalysts for the production of methyl and ethyl levulinate biodiesel. *Catalysis Communications* 34: 58-63.
- Zainol, M.M., Asmadi, M., Amin, N.A.S. & Ahmad, K. 2016. Carbon cryogel microsphere for ethyl levulinate production: Effect of carbonization temperature and time. *Journal of Engineering Science and Technology* 11: 108-121.

Nur Aainaa Syahirah Ramli  
Advanced Oleochemical Technology Division  
Malaysian Palm Oil Board  
No 6, Persiaran Institusi, Bandar Baru Bangi  
43000 Kajang, Selangor Darul Ehsan  
Malaysia

Nur Irsalina Hisham & Nor Aishah Saidina Amin\*  
Chemical Reaction Engineering Group (CREG)  
Faculty of Chemical and Energy Engineering  
Universiti Teknologi Malaysia  
81310 UTM Johor Bahru, Johor Darul Takzim  
Malaysia

\*Corresponding author; email; noraishah@cheme.utm.my

Received: 6 September 2017

Accepted: 11 December 2017