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ESTERIFICATION OF RENEWABLE LEVULINIC ACID TO LEVULINATE ESTERS USING AMBERLYST-15 AS A SOLID ACID CATALYST

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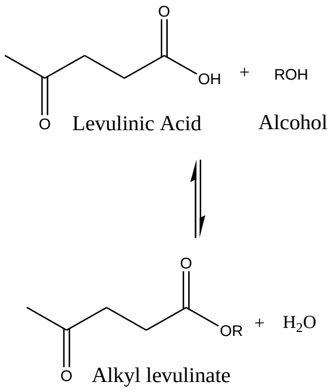
Graphical abstract



Abstract

Levulinic acid (LA) is a versatile biomass-derived building block as it can be used for the synthesis of organic chemicals as alternative to the depleting fossil fuel resources. Levulinate esters, obtained from catalytic esterification of LA with alcohol, can be used in many applications such as fragrance and fuel additives. In this study, ion-exchange resins Amberlyst-15 was employed as solid acid catalyst for esterification of LA with methanol for methyl levulinate (ML) production. The effect of reaction time, catalyst loading, and molar ratio of LA to methanol, was investigated on LA esterification to ML at the reflux condition. The optimum ML yield of 82% was obtained from reaction conducted at reflux temperature for 5h, using 30% of Amberlyst-15 loading, and 1:20 of LA to methanol molar ratio. The reusability of Amberlyst-15 for ML production was examined for five successive reactions. In addition, Amberlyst-15 catalyst, employed in the esterification of LA with ethanol and 1-butanol for ethyl levulinate (EL) and butyl levulinate (BL), respectively, registered good performance. Yields of 71% and 55% have been obtained for EL and BL, respectively. Amberlyst-15 is a promising solid acid catalyst for production of biomass derived levulinate esters at mild process conditions.

Keywords: Esterification, levulinic acid, solid acid catalyst, Amberlyst-15, levulinate ester

Abstrak

Asid levulinik (LA) merupakan bahan asas daripada biojisim yang serba guna dimana ia boleh digunakan bagi sintesis bahan kimia organik sebagai alternatif kepada sumber bahan api fosil yang semakin menyusut. Ester levulinat yang diperoleh daripada pengesteran bermangkin LA dengan alkohol dapat digunakan di dalam banyak aplikasi seperti wangian dan aditif bahan api. Dalam kajian ini, resin pertukaran ion Amberlist-15 telah digunakan sebagai pemangkin asid pepejal untuk pengesteran LA dengan metanol bagi penghasilan metil levulinat (ML). Kesan masa tindak balas, suapan pemangkin, dan nisbah molar antara LA dan metanol telah dikaji terhadap pengesteran LA kepada ML pada keadaan refluks. Hasil optima ML sebanyak 82% telah diperoleh daripada tindakbalas yang telah dijalankan pada suhu refluks selama 5 j, menggunakan 30% suapan Amberlist-15, dan 1:20 nisbah antara molar LA terhadap metanol. Kebolehgunaan semula Amberlist-15 untuk penghasilan ML telah diperiksa untuk lima tindakbalas berturutan. Di samping itu, pemangkin Amberlist-15 telah digunakan dalam pengesteran LA dengan etanol dan 1-butanol untuk penghasilan etil levulinat (EL) dan butil levulinat (BL) dengan prestasi yang baik. Hasil sebanyak 71 dan 55% masing-masing telah dicapai untuk EL dan BL. Amberlist-15 merupakan pemangkin asid pepejal yang berpotensi bagi penghasilan ester levulinat daripada biojisim pada keadaan proses yang sederhana.

Kata kunci: Pengesteran, asid levulinik, pemangkin asid pepejal, Amberlist-15, ester levulinat

1.0 INTRODUCTION

The continuous depletion of fossil fuel resources and increasing global energy consumption have led to considerable attention on utilization of lignocellulosic biomass for production of chemicals, fuels, and energy [1, 2]. Levulinic acid (LA) is lignocellulosic biomass derived chemical and regarded as one of the top twelve building block chemicals [3-5]. From energy to manufacturing, LA can be used in the preparation of resins, pharmaceutical agents, and biofuels [1, 2, 6]. Levulinate ester or alkyl levulinate is one of the LA derivatives synthesized from esterification reaction of LA with various alkyl alcohols (Figure 1) [7]. These levulinate esters have extensive application either in flavoring and fragrance industries or as additives in gasoline and biodiesel [8, 9].

The esterification reactions are usually performed in presence of homogeneous acid catalyst [10, 11]. The homogeneous acid catalyst is effective but it endures several drawbacks such as difficult catalyst recovery and corrosive to equipment. Heterogeneous catalyst is highly recommended as a substitute since it is easily separated from product mixture, can be used in subsequent reactions, and less corrosive compared to homogeneous acid [12-14]. Zeolites and heteropolyacid based catalysts [15-18] are the most employed for catalytic esterification of LA with Amberlyst-15 usually used as the reference acidic catalyst [9, 14, 19, 20]. Amberlyst-15, an ion-exchange resin, contains sulfonic acid groups on its surface and is regarded as a strong Brønsted acid catalyst [14].

Herein, Amberlyst-15 was tested for LA esterification with methanol for methyl levulinate (ML) production at the reflux temperature by varying several reaction parameters. The effect of several reaction parameters on ML production was inspected. The reaction parameters including reaction time (1 – 7h), catalyst loading with respect to LA (10 – 35%), and LA to methanol molar ratio (1:5 – 1:30) were optimized accordingly. The reusability of Amberlyst-15 for ML production was also scrutinized for five consecutive cycles. At the optimum conditions, Amberlyst-15 was employed for LA esterification with ethanol and 1-butanol to produce ethyl levulinate (EL) and butyl levulinate (BL), respectively. Based on the results, the competency of Amberlyst-15 for levulinate ester production from LA was revealed.

2.0 METHODOLOGY

2.1 Materials

All chemicals were used as received without any further purification. Amberlyst-15 was purchased from Sigma Aldrich. LA (99%), ethanol (99%), methanol (99%), and 1-butanol (99%) were obtained from Merck and employed in the catalytic tests. H_2SO_4 (96-98%) obtained from Merck was used for the preparation of HPLC mobile phase.

2.2 Catalytic Test and Product Analysis

The batch catalytic esterification of LA with alcohol over Amberlyst-15 catalyst was carried out in a 250 mL flask equipped with a condenser, thermocouple, and magnetic stirrer. Figure 2 illustrated the experimental setup for LA esterification used in this study. The flask was loaded with predetermined amounts of LA, alcohol, and catalyst. The solution was heated to the reflux temperature of the respective alkyl alcohols at a constant stirring speed of 200 rpm. The reflux temperature of methanol, ethanol, and 1-butanol are 64.7, 78.4, and 117.7 °C, respectively. After the reaction was completed, the mixture was cooled to room temperature. All samples were filtered before further analysis with HPLC. For Amberlyst-15 reusability test, the catalyst was recovered by centrifugation, washed with methanol, and dried overnight at 120 °C before tested in the subsequent cycle.

The concentration of LA in the product mixture was determined using HPLC (Agilent) under the following conditions: organic acid Aminex HPX-87H column; mobile phase; 5 mM H_2SO_4 at 0.6 ml/min, detector; UV210 nm; retention time 30 min; column temperature, 60 °C. LA conversion was calculated according to Eq. (1). The levulinate ester yield was considered to be equal to the LA conversion of the respective reaction owing to the assumption of 100% levulinate ester selectivity.

$$\text{LA conversion (\%)} = \frac{\text{Initial mol LA - final mol LA}}{\text{Initial mol LA}} \times 100\% \quad (1)$$

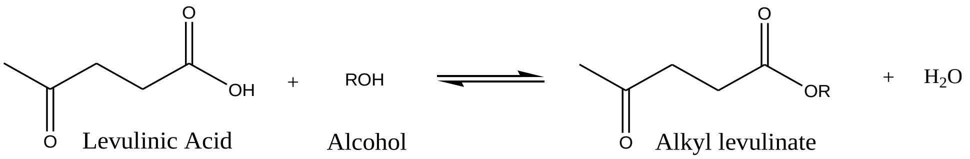


Figure 1 Reaction scheme of LA esterification to alkyl levulinate.

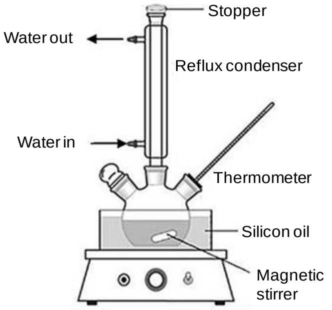


Figure 2 Experimental setup for LA esterification

3.0 RESULTS AND DISCUSSIONS

3.1 Effect of Reaction Parameters on LA Esterification with Methanol Catalyzed by Amberlyst-15

The catalytic activity of Amberlyst-15 on esterification of LA to ML at reflux condition was inspected by varying reaction time, catalyst loading, and LA to methanol molar ratio.

3.1.1 Effect of Reaction Time

Figure 3 illustrates the effect of reaction time from 1 to 7 h on LA esterification with methanol at reflux temperature, 20% Amberlyst-15 loading, and 1:15 LA to methanol molar ratio. LA conversion increased with prolonged reaction time from 1 to 5 h. Since the LA conversion from 5 to 7 h was insignificant, reaction time of 5 h was selected as the optimum reaction time and retained for all further experiments.

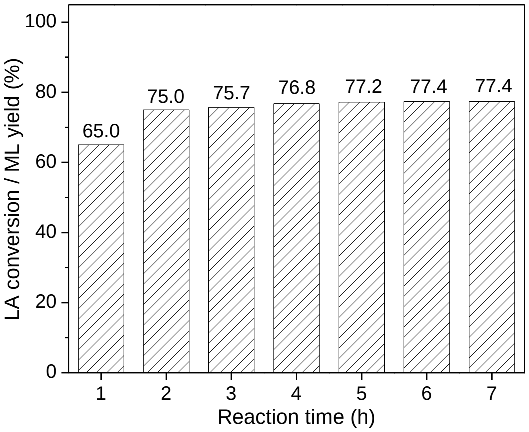


Figure 3 Effect of reaction time on LA conversion/ML yield (reflux temperature, 20% Amberlyst-15 loading, 1:15 of LA to methanol molar ratio)

3.1.2 Effect of Catalyst Loading

The effect of Amberlyst-15 loading on LA esterification with methanol is exhibited in Figure 4. The Amberlyst-15 loading with respect to LA was varied from 10 to 35% for reaction conducted at reflux temperature, reaction time of 5 h, and LA to ethanol molar ratio 1:15. LA conversion improved from 76 to 80% as Amberlyst-15 loading increased from 10 to 30%. No increase in LA conversion was observed when 35% Amberlyst-15 loading was applied. Hence, further reactions were performed at the optimum Amberlyst-15 loading of 30%. Increase in Amberlyst-15 loading resulted in more viscous reaction mixture and impeded the esterification reaction. Besides, excess catalyst limits the mass transfer rate, and hinders the catalytic activity. The increase in reaction mixture viscosity and mass transfer limitation resulted from excess catalyst loading and their consequences on the reaction have been discussed in previous studies [3, 21, 22]. It is reported that ML production from LA esterification with methanol can occur without the presence of catalyst, due to the competency of LA to catalyze the reaction itself [16, 20]. Thus, a blank reaction of LA esterification with methanol was conducted herein at reflux temperature using 1:15 of LA to methanol molar ratio. The blank reaction registered LA conversion of 4% after 6 h of reaction.

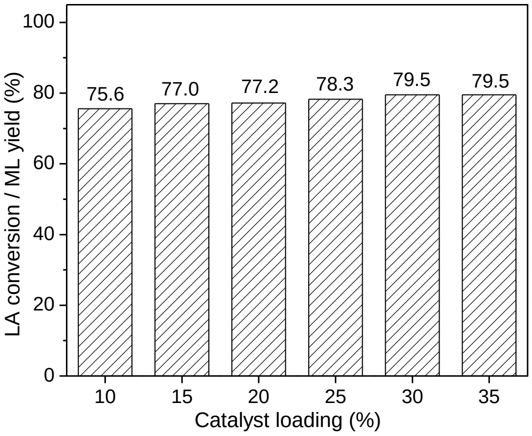


Figure 4 Effect of catalyst loading on LA conversion/ML yield (reflux temperature, 5 h reaction time, 1:15 of LA to methanol molar ratio)

3.1.3 Effect of Molar Ratio

Since LA esterification with alcohol is a reversible reaction, high LA conversion could be achieved by minimizing the backward reaction. Immediate elimination of water or excess amount of alcohol in the reaction could increase the LA conversion [23]. In this study, excess methanol was utilized to accelerate the forward reaction since it is not easy to eliminate water in the reaction system. The effect of LA to methanol molar ratio from 1:5 to 1:30 on LA esterification is illustrated in Figure 5. LA conversion rose from 78 to 82% when molar ratio increased from 1:5 to 1:20. This surmise that excess methanol is favorable for the forward reaction of LA esterification. But, a slight decrease in LA conversion was observed when molar ratio up to 1:30 was employed. Additional decrease in LA conversion is expected if excess methanol (molar ratio higher than 1:30) is used due to higher amount of methanol might dilute the reactant and inhibit the ML production [16, 24].

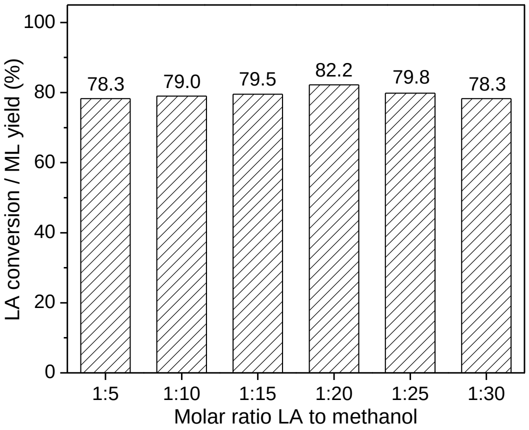


Figure 5 Effect of LA to methanol molar ratio on LA conversion/ML yield (reflux temperature, 5 h reaction time, 30% Amberlyst-15 loading).

From the analysis of effect of reaction parameters, the optimum conditions to maximize the LA esterification with methanol are 5h reaction time, 30% Amberlyst-15 loading, and 1:20 of LA to methanol molar ratio.

3.2 Proposed Mechanism of LA Esterification with Methanol

The proposed mechanism of catalytic esterification of LA with methanol catalyzed by Amberlyst-15 can be elucidated as in Figure 6. Initially, the adsorption of LA on the catalyst Brønsted acid sites resulted in the formation of protonated LA intermediate thus increases the electrophilicity of carbonyl carbon. The carbonyl carbon then attacked by the nucleophilic oxygen of ethanol to form oxonium ion. A proton transfer from the oxonium ion yielded a new oxonium ion. Next, ML is formed through the loss of water followed by the deprotonation step. As a result, the regeneration of catalyst acid sites occurred from the deprotonation step [9, 18]. The acid sites of catalyst improve the proton accessibility and enhance the overall reaction accordingly [18].

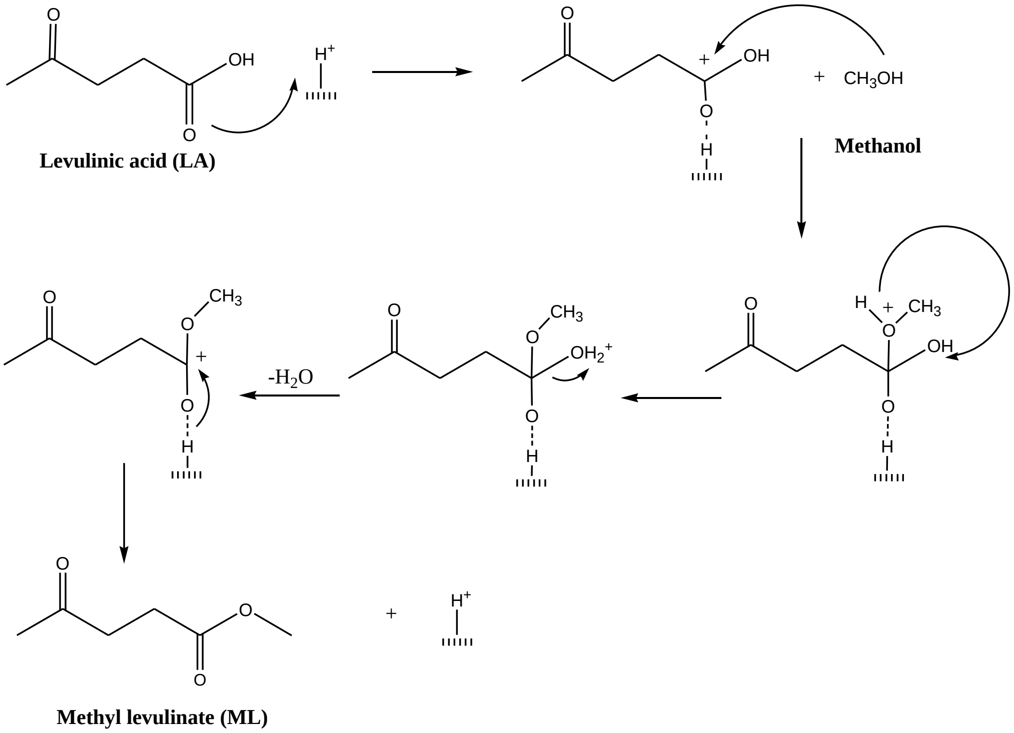


Figure 6 Proposed mechanism of LA esterification with methanol

3.3 Reusability of Amberlyst-15 for LA Esterification with Methanol

Since reusability is a key factor in heterogeneous catalysis, the stability of Amberlyst-15 was investigated by inspecting the performance of regenerated catalyst. Amberlyst-15 was reused for four times and the reactions were conducted at the optimum conditions (Figure 7). After each run, the catalyst was recovered by centrifugation, washed with methanol and dried overnight at 105 °C. The dried catalyst was then used directly in the next run under the same reaction conditions. The catalytic activity of recycled Amberlyst-15 did not decrease significantly after five runs, demonstrating its good stability for esterification of LA. The decrease in ML yield could be due to catalyst loss during the filtration and washing steps, as well as depositions of reactants and product on the catalyst active sites [20].

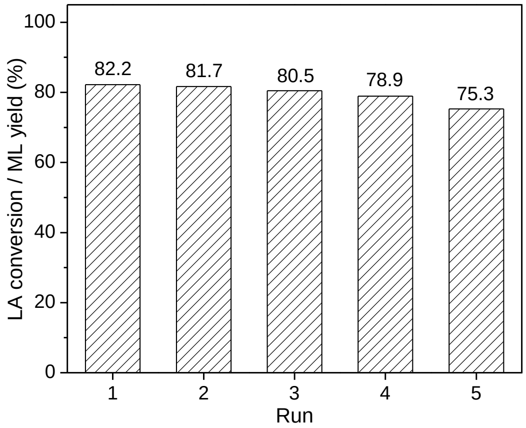


Figure 7 Reusability of Amberlyst-15 for esterification of LA with methanol (reflux temperature, 5h reaction time, 30% Amberlyst-15 loading, 1:20 of LA to methanol)

3.4 Esterification of LA with Ethanol and 1-butanol using Amberlyst-15

Amberlyst-15 has demonstrated substantial performance for LA esterification with methanol for ML production. Next, Amberlyst-15 was tested for LA esterification with ethanol and 1-butanol for the production of ethyl levulinate (EL), and butyl levulinate (BL), respectively (Table 1). The esterification reactions were carried out at reflux temperature of the alcohols, for 5h, 30% Amberlyst-15 loading with respect to LA, and 1:20 of LA to alcohol molar ratio. It is evident that higher LA conversions were achieved from LA esterification with shorter chain alcohol. From the analyses, 82% conversion was obtained from LA esterification with methanol compared to 71 and 55% for LA esterification with ethanol and 1-butanol, respectively. Longer chain alcohol might elevate the steric effect and hinders the alkyl levulinate production. The same trend has been reported where LA esterification with bulkier alcohols is slower as steric limitations leadi to a decrease of reaction rate [25].

Table 1 LA esterification with different alcohols for 5h reaction time using 30% Amberlyst-15 loading and 1:20 of LA to alcohol molar ratio

Alcohols	Reflux temperature (°C)	Alkyl levulinate (AL)	LA conversion / AL Yield (%)
Methanol	64.7	ML	82.2
Ethanol	78.4	EL	70.9
1-butanol	117.7	BL	55.3

4.0 CONCLUSION

Amberlyst-15 was employed for LA esterification with alkyl alcohols for methyl, ethyl, and butyl levulinate (ML, EL, BL) productions. At the optimum conditions of 5h reaction time, 30% of Amberlyst-15 loading, and 1:20 of LA to alcohol molar ratio, 82, 71, and 55% of ML, EL, BL yields were obtained, respectively from esterification of LA. Reusability of Amberlyst-15 was tested for five successive cycles of LA esterification to ML without significant decrease in the catalytic activity. Sulfonated ion-exchange resins Amberlyst-15 promotes the prospect of sulfonated based catalyst for the production of biomass-derived levulinate esters.

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