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ARTICLE TYPE

# Efficient and selective alcoholysis of furfuryl alcohol to alkyl levulinates catalyzed by double $SO_3H$-functionalized ionic liquids

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The production of alkyl levulinates from furfuryl alcohol (FAL) in alcohol media was investigated at moderate temperature in the presence of Brønsted acidic ionic liquids. The reaction was examined and optimized under batch conditions, where it was found that furfuryl alcohol was rapidly and almost quantitatively converted into intermediate products including 2-alkoxymethylfuran and 4, 5, 5-trialkoxypentan-2-one, and a high alkyl levulinates yield of 95% can be achieved after achieving steady state in 2 h. An advantage of this catalyst system is that undesired dialkyl ether (DEE) formed by side reaction of the dehydration of alcohol is negligible. The Hammett method was used to determine the acidities of these ionic liquids, which indicated that the acidity and molecular structure have strong effects on the catalytic activity of ionic liquids. Based on the experimental results, a possible mechanism for the alcoholysis of FAL is proposed.

## 1. Introduction

With the diminishing fossil fuels and concern from greenhouse gas caused global warming, the strategy of utilizing renewable biomass resources via catalytic processes is promising, which not only provides the chemical product as feedstocks for chemical industry, but also can ease the $CO_2$ burden due to the neutral characteristic of this strategy [1]. Of the numerous approaches, biomass-derived carbohydrates are attractive as fuel and chemicals because they are cost-effective, sustainable and abundant [2]. Moreover, these carbohydrates do not compete with the food chain, in contrast to the sugar, starch, and vegetable oils that are used for the first generation of bio-fuels and biochemicals [3]. In particular, Levulinic acid derived from these carbohydrates has been recognized as the promising platform molecule for fuels, e.g., ethyl levulinate and methyl tetrahydrofuran, as well as chemical intermediates including γ-valerolactone, methylene valerolactone, pyrrolidones, and pentenoate esters [4]. Efforts have been made to produce levulinic acid from carbohydrates including glucose, sucrose, fructose and biomass, such as wood, starch, grain sorghum and agricultural wastes. Jow *et al*. studied the production of levulinic acid from fructose over a LZY zeolite catalyst, and high yield of 56% was obtained after 13 h in a batch reactor at 140 °C due to the strong Lewis acidity of the silica/alumina support, as well as the molecular sieving capability of the Y-type zeolite. Van de Vyver *et al*. showed that levulinic acid can be produced directly from cellulose with 25% carbon molar yield at mild temperatures using sulfonated hyperbranched poly(arylene oxindole)s, this value is very close to the theoretical value (30%). Recently, the literature discloses the strategies of converting furfural to levulinic acid via hydrogenation to FAL over copper-based catalysts and subsequent acid catalyzed conversion of FAL to levulinic acid in aqueous solution [2, 4a, 5]. Such a reaction would allow increasing the yield of a levulinic acid plant by converting a minor coproduct, furfural, into its main product.

In industry, alkyl levulinates was mainly obtained by esterification of levulinic acid with the corresponding alkyl alcohol in the presence of acid catalysts. However, levulinic acid is of high cost as raw material for this purpose. So converting carbohydrates to alkyl levulinates in the presence of alcohol is addressed as well, because alkyl levulinates have been successfully used as plasticizing agents, solvents, odorous substances, and fuel additives [6]. In addition, alkyl levulinates are also the feedstock/precursors towards the synthesis of various chemicals and drugs because of their functional groups [7]. Numbers methods have been developed for the production of alkyl levulinates with a wide range of source including renewable biomass feedstock such as cellulose, saccharides, HMF, and furfuryl alcohol catalyzed with various acids in alcohols. Up to date, homogenous or heterogeneous catalysts including sulfonic acid-functionalized ionic liquids, zeolites, mixed-acid, mesoporous aluminosilicates Al-TUD-1, $SO_4^{2-}/ZrO_2$ were reported. Riisager group achieved a direct conversion of mono- and disaccharides into ethyl levulinate (EL) with sulfonic acid-functionalized ionic liquids and zeolite [8], Tominaga and coworkers studied mixed-acid systems, consisting of both Lewis and Brønsted acids, as efficient catalysts for direct synthesis of methyl levulinate from cellulose [9]. Valente and coworkers found that mesoporous aluminosilicates (Al-TUD-1) are effective for the production of useful bio-based levulinate esters from 5-hydroxymethyl-2-furfural (HMF) or furfuryl alcohol (FAL) with aliphatic alcohols [10]. Lin *et al.* reported the ethyl levulinate production from glucose in ethanol using a series of $SO_4^{2-}/ZrO_2$ based solid acid catalysts [11]. Recently, Chen and coworkers studied sulfonic acid-functionalized carbon materials ($C-SO_3H$) catalyzed conversion of fructose to alkyl levulinates and the catalyst can preserve the catalytic efficiency after five cycles [12]. It

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is revealed that the acidic catalysts, especially the strength and amount of acid, are crucial to the production of alkyl levulinates. Therefore, it is inspired reveals that the development of an efficient acid catalyst and suitable feedstock is the key to this progress. Based on chemical statistics, FAL is not fully utilized and oversupplied in the chemical market [5, 13]. Therefore it is necessary to find a new approach to convert low value added FAL to alkyl levulinates. Consequently, several popular catalysts including mineral acid [14], organic-inorganic hybrid solid acid [15], ion-exchange resins [3a], commercial sulfonic resin [16] and solid superacid [11b, 17] were extensively studied in terms of their catalytic performances. The mineral acids, such as $H_2SO_4$, HF, and $H_3PO_4$ are the least inexpensive and homogeneous catalysts for the synthesis of alkyl levulinates. However, these acids are extremely corrosive and contaminative, and thus the neutralization is required [18]. Organic-inorganic hybrid solid acids including methylimidazolebutylsulfate phosphotungstate ($[MIMBS]_3PW_{12}O_{40}$) demonstrated an efficient catalyst for the alcoholysis of FAL with a high yield of 93%. However, the catalyst shows a poor recyclability and the catalytic activity could not be restored because the catalyst can easily adsorb insoluble substances. Ion-exchange resins, commercial sulfonic resin and solid superacid have been widely used due to their excellent thermal stability and low cost characteristics for industrialization [11, 19]. However, this process still suffers from activity loss, catalyst deactivation and mass transfer issues.

In view of both the advantages and disadvantages of homogenous and heterogeneous catalysts, and to be aware of the importance and applications of FAL alcoholysis reaction from industrial as well as academic viewpoints, it is urgent to find an efficient, inexpensive, stable and environmentally benign catalyst system for this imperative reaction. Ionic liquids have been widely recognized as green reaction catalysts or media due to their negligible volatility and excellent thermal stability. $SO_3H$-functionalized ionic liquids (SFILs) with strong Brønsted acidity were firstly reported as the competing acid catalyst in comparison of conventional acidic catalysts, because they are flexible, recyclable, and can act as solvent and catalysts [20]. Therefore, the use of recoverable SFILs has economical and environmental benefits. Rode and coworkers studied single $SO_3H$-functionalized ionic liquids varied with different anions as efficient catalysts for direct synthesis of methyl levulinate from furfuryl alcohol [21]. However, none all these ILs can achieve a simultaneous high conversion and selectivity from FAL to Me-LA because of divergences in Brønsted acidity. The introduction of multi-alkyl sulfonic acid groups to cations enhanced the Brønsted acidity, thus resulting in high activity. Here, four kinds of SFILs based on trimethylsilylimidazole, pyridine and 1, 1, 3, 3-tetramethylguanidine are applied to catalyze the alcoholysis of FAL with various alcohols. It is proved that this is a simple method of synthesis of alkyl levulinates with excellent yields (95%) in the presence of ILs (~3 mol%) for a relatively short reaction time (2 h). The acidities of SFILs based on various anions including $HSO_4^-$, $CF_3COO^-$ were determined using the Hammett method with UV-vis spectroscopy and their acidity-catalytic activity relationships were systematically discussed. Moreover, multiple reaction pathways where formation of 4, 5, 5-triethoxypentan-2-one in parallel to the other intermediate ethoxymethylfuran (EMF) is converted to desired products ethyl levulinate together were proposed based on experimental results.

## 2. Experimental

### 2.1 Materials

Furfuryl alcohol (98%), 1, 3-propanesulfonate (99%), trimethylsilylimidazole (99%), 1, 1, 3, 3-tetramethylguanidine (99%), trifluoroacetic acid (99%) were purchased from Aladdin Industrial Corporation and 1, 4-butane sultone (99%) from J&K Chemical Ltd. Sulphuric acid (95-98%, AR), tetrafluoroboric acid (AR) ethyl ether (99.5%), acetic ether (99.5%) were supplied by Sinopharm Chemical Reagent Co., Ltd.. All alkyl alcohols were freshly distilled before use.

### 2.2 Synthesis of functionalized ILs

Ionic liquid 1,3-bis(3-sulfopropyl)-1H-imidazol-3-ium hydrogensulfate, $[(HSO_3\text{-}p)_2im][HSO_4]$ was prepared according to George methods [20a, 22]: trimethylsilylimidazole (150 mmol) was added to a solution of 1, 3-propanesultone (150 mmol) dissolved in anhydrous toluene (100 mL) by dropwise at 0 °C. The resulting solution was slowly heated to 65 °C and stirred for 24 h. Afterwards, the white products were obtained after filtration, washing with ethyl ether and acetic ether three times, respectively, followed by drying at 65 °C under vacuum (0.1 mmHg) for 24 h. 150 mmol of zwitterionic intermediate (150 mmol) was dissolved in anhydrous toluene (50 mL), a stoichiometric amount of sulfuric acid was slowly added and the solution was stirred first at 25 °C for 30 min, then at 70 °C for 24 h. The product was finally obtained via rotary evaporation and drying at 65 °C in vacuum for 24 h.

Other ionic liquids were prepared under the same protocols as described above.

### 2.3 Alcoholysis of furfuryl alcohol

Alcoholysis of furfuryl alcohol was operated in a Teflon-lined autoclave reactor. 20 mmol of furfuryl alcohol (2.0 g, 20 mmol), 0.6mmol of $[(HSO_3\text{-}p)_2im][HSO_4]$ (0.246 g, 0.6 mmol), and 0.88 mol of ethanol were added into the reactor, and then the reactor was heated to 110 °C in an oil batch and held isothermal for 2 h. After cooling down to room temperature, the IL was extracted with n-hexanes (10 × 15 mL) from the solution. Products were identified on a HP 6890/5793 GC-MS with a DB-5MS column and on a Varian NMR spectrometer (9.4 T, 400 MHz for $^1H$, 100 MHz for $^{13}C$) equipped with a $^{13}C$-{$^1H$, $^{19}F$} TXO probe head. The detected products were EL, ethoxymethylfuran, 4, 5, 5-triethoxypentan-2-one (TOP), diethyl ether and a small amount of furfuran resin.

### 2.4 Characterization

1-(4-sulfobutyl) pyridinium hydrogensulfate, ($[BsPy][HSO_4]$): $^1H$ NMR (400 MHz, $D_2O$), δ (TMS, ppm): 2.21-2.26 (m, 2H), 2.79 (t, J = 7.2 Hz, 2H), 4.56 (t, J = 7.2 Hz, 2H), 7.84 (t, 2H), 8.30 (t, 1H), 8.62 (d, J = 7.6 Hz, 2H); $^{13}C$ NMR (100 MHz, $D_2O$), δ (TMS, ppm): 27.23, 48.34, 61.55, 129.73, 145.43, 147.56.

N-(bis(dimethylamino)methylene)-4-sulfobutan-1-aminium trifluoromethanesulfonate, ($[BsTmG][CF_3COO]$): $^1H$ NMR (400 MHz, $D_2O$), δ (TMS, ppm): 1.38-1.50 (m, 4H), 2.63 (t, J = 13.6 Hz, 2H) 2.66 (s, 12H), 2.94 (t, J = 7.2 Hz, 2H); $^{13}C$ NMR (100

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MHz, $D_2O$), δ (TMS, ppm): 21.62, 28.73, 40.51, 45.31, 51.33, 120.58, 163.24, 165.46.

N-(bis(dimethylamino)methylene)-4-sulfobutan-1-aminium hydrogensulfate, ([BsTmG][$HSO_4$]): $^1$H NMR (400 MHz, $D_2O$), δ (TMS, ppm): 2.77-2.75 (s, 3H), 1.63-1.51 (m, 2H), 3.05 (t, J = 7.2 Hz, 2H), 2.73 (t, J = 7.2 Hz, 2H); $^{13}$C NMR ($D_2O$, 400 MHz), δ (TMS, ppm): 21.72, 28.34, 39.53, 44.36, 50.62, 161.83.

1-methyl-3-(4-sulfobutyl)-1H-imidazol-3-ium hydrogensulfate, ([BsMIm][$HSO_4$]): $^1$H NMR (400 MHz, $D_2O$), δ (TMS, ppm): 1.37-1.45 (m, 2H), 1.65-1.73 (m, 2H), 2.61 (t, J = 7.2 Hz, 2H), 3.56 (s, 3H), 3.92 (t, J = 7.3 Hz, 2H), 7.11 (s, 1H), 7.16 (s, 1H), 8.39 (s, 1H); $^{13}$C NMR (100 MHz, $D_2O$), δ (TMS, ppm): 21.11, 28.32, 35.39, 49.51, 50.63, 122.23, 123.84, 136.13.

1,3-bis(3-sulfopropyl)-1H-imidazol-3-ium hydrogensulfate, [($HSO_3$-p)$_2$im][$HSO_4$]: $^1$H NMR (400 MHz, $D_2O$), δ (TMS, ppm): 2.05-2.08 (t, J = 13.2 Hz, 4H), 2.65-2.69 (t, J = 13.6 Hz, 4H), 4.09-4.13 (t, J = 13.6 Hz, 4H), 7.31 (s, 2H), 8.59 (s, 1H); $^{13}$C NMR (100 MHz, $D_2O$), δ (TMS, ppm): 24.45, 46.48, 47.29, 121.99, 135.01.

3-butyl-1-methyl-1H-imidazol-3-ium hydrogensulfate, ([BMIm][$HSO_4$]): $^1$H NMR (400 MHz, $D_2O$), δ (TMS, ppm): 0.69 (t, J = 7.4 Hz, 3H), 0.98 (m, 2H), 1.61 (m, 2H), 3.65 (s, 3H), 3.96 (t, J = 7.2 Hz, 2H), 7.19 (s, 1H), 7.24 (s, 1H), 8.47 (s, 1H); $^{13}$C NMR (100 MHz, $D_2O$), δ (TMS, ppm): 12.82, 18.93, 31.44, 35.82, 49.56, 122.47, 123.78, 136.08.

4, 5, 5-triethoxypentan-2-one: $^1$H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 1.15 (t, J = 6.8 Hz, 3H), 1.20 (t, J = 9.8 Hz, 3H), 1.23 (t, J = 13.6 Hz, 3H), 2.09 (s, 3H), 2.68 (d, J = 5.4 Hz, 2H), 3.59 (m, 3H), 3.72 (m, 3H), 3.84 (m, 1H), 4.41 (d, J = 7.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 15.04, 15.05, 15.33, 31.01, 43.96, 64.08, 64.09, 66.61, 76.16, 103.35, 208.28.

2-ethoxymethylfuran: $^1$H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 1.23 (t, J = 4.1 Hz, 3H), 3.54 (q, J = 7.2 Hz, 2H), 4.44 (s, 2H), 7.40 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 142.62, 110.53, 108.94, 152.21, 70.23, 64.84, 14.55.

### 2.5 Analytic methods

The products were analyzed on gas chromatography instrument (Agilent, 7890A) equipped with a HP-5 column (30 m × 0.320 mm × 0.25 μm) and a flame ionization detector. In terms of the operation conditions, $N_2$ as the carrier gas was 1.0 mL·min$^{-1}$, the injection port temperature was 250 $^{o}$C, the oven temperature was 190 $^{o}$C, and the detector temperature was 300 $^{o}$C. Combining the analyses of GC-MS and NMR, FAL, DEE, EL, EMF and 4, 5, 5-trithoxypentan-2-one were identified. In order to calculate FAL conversion and product yield accurately, ethyl benzoate as internal standard was applied and the reactive correction factors of the products were summarized in Table 1. FAL conversion and products selectivity were calculated using the following equations:

$$\text{conversion (\%)} = \frac{\text{sum of C-based moles of all products}}{\text{sum of C-based moles of reactant and all products}} \times 100$$

$$\text{selectivity (\%)} = \frac{\text{C-based moles of specific products}}{\text{sum of C-based moles of all products}} \times 100$$

Only selectivity to EMF, 4, 5, 5-triethoxypentan-2-one and DEE was discussed in this study in view of their relative large amounts detected in the products.

Table 1. Reactive correction factors of the products of FAL conversion

| Entry | Name | Reactive correction factor |
|---|---|---|
| 1 | FAL | 1.416 |
| 2 | DEE | 1.303 |
| 3 | EL | 1.591 |
| 4 | EMF | 1.294 |
| 5 | 4,5,5-trithoxypentan-2-one | 1.312 |

### 2.6 Hammett acidity of Brønsted acidic ILs

The acidities of Brønsted-acidic ILs were measured at room temperature on a Perkin-Elmer Lambda 650S UV-Vis spectrometer equipped with Labsphere intergrating over the spectral range 300-650 nm using p-nitroaniline as the indicator and molecular probe [23]. The ILs and p-nitroaniline were dissolved in methanol to achieve the concentration of 3.0 × 10$^{-2}$ mol·L$^{-1}$ and 7.5 × 10$^{-5}$ mol·L$^{-1}$, respectively. Then, the solutions were mixed for 2 h with magnetic stirring, and then the UV spectrum of mixed solution was recorded. The Hammett acidity function ($H_0$) can be expressed on the basis of the following equation:

$$H_0 = pK_a(In) + \log([In]/[InH^+])$$

Where $pK_a$(In) is the $pK_a$ value of the p-nitroaniline indicator solution (about 0.99), [In] and [$InH^+$] are the molar concentration of the protonated and unprotonated form of p-nitroaniline indictor, respectively.

### 2.7 Recycling and reuse of the ionic liquid

After the reaction, the water was firstly removed by molecular sieve via adsorption dehydration (3 Å). The resulting low boiling point components including diethyl ether (34.6 $^{o}$C) and ethanol (78.4 $^{o}$C) were separated depending on their different boiling points. Then IL was extracted from the remaining EL, ethoxymethylfuran (EMF), 4, 5, 5-triethoxypentan-2-one (TOP) with 5 mL of n-hexane 10 times. Finally, the catalyst was then heated at 65 $^{o}$C in vacuum until the water in this system was removed absolutely. The dried catalyst was re-used directly for the next run by adding fresh feedstock under the same reaction conditions.

## 3. Results and discussion

### 3.1 The Hammett acidity function-activity relationship

Characterization including Hammett method, and $NH_3$-TPD were employed to analyze the amount and strength of the acidity and the acidity is very important to FAL alcoholysis [6b]. Haan *et al.* [3a] found that EL was preferentially produced at the acid sites at the surface of the pores. Valenta [10] tested porous aluminosilicates as acid catalysts for the reaction of FAL with ethanol, higher EL yield was obtained on the catalysts with the higher total amount of acid sites (L + B) identified with pyridine-adsorption. Taking the results (Table 2) and literature together, the functionalized ionic acids influences the catalytic yield of EL to different extent because of the acidic properties of functionalized ionic acids stemming from divergences in structures of cations (e.g., [($HSO_3$-p)$_2$im], [BsMIm] and [BsTmG]) and varieties of anions([$HSO_4$], and [$CF_3COO$]). To shed light on the impact of acidity on catalytic performance (EL yield), Brønsted acidity was measured with UV visible spectroscopy and summarized in Figure 1 and Table 2. High intensity of absorbance of p-nitroaniline indicates the synthesized ionic acid has poor acidity. The ILs bearing none alkyl sulfonic acid group ([BMIm][$HSO_4$]) on the cation exhibited lower activity than these corresponding single $SO_3H$-functionalized ionic acids ([BsMIm][$HSO_4$], [BsTmG][$HSO_4$] and [BsPy][$HSO_4$]). While the ILs bearing two alkyl sulfonic acid groups have higher activity than single $SO_3H$-functionalized ionic acids, this indicates the significant effect of the number of alkyl sulfonic acid groups on the catalytic performance of the ILs. The catalytic performance of the ILs with the anions of [$HSO_4$] was stronger than that of the corresponding ILs with [$CF_3COO$]. This is possibly due to the weak acidity of trifluoroacetic acid compared with $H_2SO_4$. Therefore, double $SO_3H$-functionalized ILs exhibited a stronger catalytic performance than other tested ILs. As shown in Table 2, the acidity of ionic acids decreases in the order: [$(HSO_3\text{-}p)_2$im][$HSO_4$] > [BsMIm][$HSO_4$] ≈ [BsTmG][$HSO_4$] ≈ [BsPy][$HSO_4$] > [BMIm][$HSO_4$] > [BsTmG][$CF_3COO$], and the yield of EL also follows the same trend. It is concluded that the sequence of the catalytic performance observed in the alcoholysis of FAL was in good agreement with the Brønsted acidity order determined by the Hammett method, and [$(HSO_3\text{-}p)_2$im][$HSO_4$] was determined to be the most suitable catalyst for the alcoholysis of FAL to EL in ethanol [24].

### 3.2 Influence of substrate on catalytic yield of alkyl levulinate

The alcoholysis of furfuryl alcohol with different alkyl alcohols in order to explore the scope of this method was carried out using catalytic amount of ionic liquids [$(HSO_3\text{-}p)_2$im][$HSO_4$]. When the reactions were carried out for 2 h, yields were achieved for the investigated solvents (80%-95%), this difference is probably attributed to the boiling point and steric effects of the substrates [17]. To attenuate the differences of activities, shorter reaction time (0.5 h) was employed (Table 3, entries 1, 3, 7 and 15). In the case of linear alcohol, with the increasing of carbon length, the alkyl levulinates yield was decreased gradually (Table 3, entries 2, 4, 8 and 16). This difference is associated with the difficulty of the conversion from 2-alkoxymethylfuran and 4, 5, 5-trialkoxypentan-2-one to alkyl levulinates and it is confirmed with the fast consumption of FAL in the first several minutes.

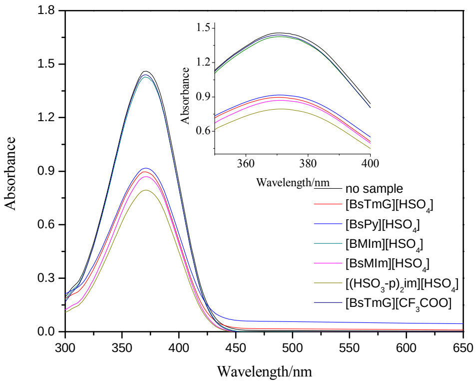

**Figure 1.** The UV/Vis spectra according to the Hammett method (the amplified peaks are presented at the top right corner).

**Table 3** Impact of substrate on catalytic yield of alkyl levulinates

| No. | Substrate | Boiling point [°C] | Time [h] | Yield [%] |
|---|---|---|---|---|
| 1 | ethanol | 78.4 | 0.5 | 60 |
| 2 | ethanol | 78.4 | 2 | 92 |
| 3 | n-propanol | 97.1 | 0.5 | 59 |
| 4 | n-propanol | 97.1 | 2 | 95 |
| 5 | isopropanol | 82.5 | 0.5 | 57 |
| 6 | isopropanol | 82.5 | 2 | 90 |
| 7 | n-butanol | 117.3 | 0.5 | 55 |
| 8 | n-butanol | 117.3 | 2 | 93 |
| 9 | isobutanol | 107.9 | 0.5 | 70 |
| 10 | isobutanol | 107.9 | 2 | 92 |
| 11 | 2-butyl alcohol | 108 | 0.5 | 67 |
| 12 | 2-butyl alcohol | 108 | 2 | 89 |
| 13 | tert-butanol | 83 | 0.5 | 53 |
| 14 | tert-butanol | 83 | 2 | 87 |
| 15 | 1-pentanol | 137.3 | 0.5 | 56 |
| 16 | 1-pentanol | 137.3 | 2 | 80 |

Reaction conditions: Furfuryl alcohol (20 mmol) and catalyst [$(HSO_3\text{-}p)_2$im][$HSO_4$] (0.6 mmol) in different alcohol (40 mL), reaction time = 2 h, temperature = 110 °C.

**Table 2** Hammett acidity of synthesized ionic acid catalysts and yield of ethyl levulinate

| No. | Catalysts | Absorbance | [In] [%] | [$InH^+$] [%] | Hammett acidity | Yield [%] |
|---|---|---|---|---|---|---|
| 1 | none | 1.44 | 100 | 0 | - | 0 |
| 2 | [BsTmG][$CF_3COO$] | 1.43 | 99.3 | 0.7 | 3.1 | 24 |
| 3 | [BMIm][$HSO_4$] | 1.40 | 97.2 | 2.8 | 2.5 | 34 |
| 4 | [$(HSO_3\text{-}p)_2$im][$HSO_4$] | 0.79 | 54.9 | 45.1 | 1.0 | 95 |
| 5 | [BsMIm][$HSO_4$] | 0.87 | 60.4 | 39.6 | 1.2 | 92 |
| 6 | [BsTmG][$HSO_4$] | 0.90 | 62.5 | 37.5 | 1.2 | 93 |
| 7 | [BsPy][$HSO_4$] | 0.92 | 63.9 | 36.1 | 1.2 | 93 |

Reaction conditions: Furfuryl alcohol (20 mmol) and catalyst [$(HSO_3\text{-}p)_2$im][$HSO_4$] (0.6 mmol) in alcohol (40 mL), reaction time = 2 h, temperature = 110 °C.

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The effect of boiling point becomes controlling factor, thus solvents with longer carbon length results in lower activity.

The steric effect becomes obvious in the case of $C_4$ alcohol (n-butanol, isobutanol, 2-butyl alcohol, tert-butanol). With the increasing of molecular volume, the conversion of intermediates required in the production of corresponding alkyl levulinates becomes restricted and hindered.

### 3.3 The effect of catalyst amount on the yield of product distribution

The amount of catalyst definitely impacts the acidic concentration in reaction solution, correspondingly influences the product distribution. Additionally, the reaction time is a crucial factor influencing product species. As shown in Figure 2, the concentration of $[(HSO_3\text{-}p)_2im][HSO_4]$ ranges from 0.1 to 0.6 mmol, while the other conditions keep constants. A maximum EL yield of 65.5% to 94% within 3 h with ILs ranging from 0.1 mmol and 0.6 mmol is achieved respectively (Figure 2d), attributed to an increase of the number of active sites. The yields of EMF, 4, 5, 5-triethoxypentan-2-one could respectively reach to maxima of 36.4% and 34.7% with 0.1 mmol catalyst in 7 minutes. Increasing the amount of catalyst further, i.e. 0.6 mmol, the yields of EMF and 4, 5, 5-triethoxypentan-2-one begin to decrease. Meanwhile, DEE yield increases. It was worthy of noting that EMF and 4, 5, 5-triethoxypentan-2-one were first formed, and then decreased with reaction time for all the experiments in Figure 2, and the yield of EL increased rapidly from zero to stable concentration. This demonstrates that alcoholysis of FAL to EL proceeded mainly through EMF and 4, 5, 5-triethoxypentan-2-one as suggested by Dumesic [16].

### 3.4 Influence of reaction temperature on conversion and product distribution

Temperature appears to have a profound effect on both the reaction rate and the product distribution. Therefore, a systematic study was conducted to understand the effect of reaction temperature on FAL alcoholysis and abundance of the main products at 70 °C, 90 °C, 110 °C and 130 °C respectively. Figure 3 shows the temporal evaluation of the products. As expected, the higher temperature there is, the higher the conversion of EL is. FAL not only form intermediates including EMF and 4, 5, 5-triethoxypentan-2-one but also is converted to EL simultaneously. Moreover, the consumption rate of FAL at the initial time and EL

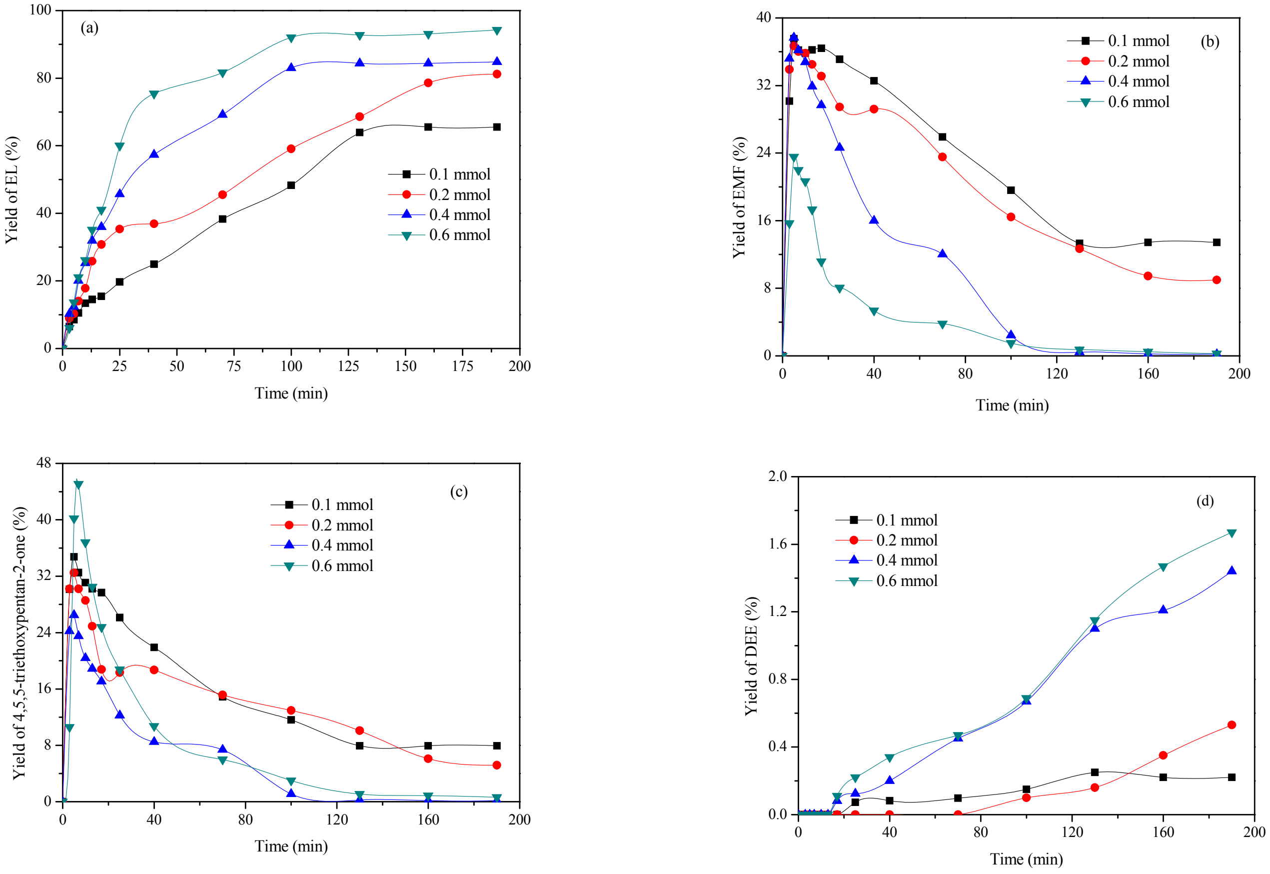

**Figure 2.** The influences of catalyst amounts in the reaction on time-dependent product distribution in the presence of $[(HSO_3\text{-}p)_2im][HSO_4]$: (a) yield of EL, (b) yield of EMF, (c) yield of 4, 5, 5-triethoxypentan-2-one, (d) yield of DEE. Reaction conditions: Furfuryl alcohol (20 mmol) and catalyst $[(HSO_3\text{-}p)_2im][HSO_4]$ (set amount) in alcohol (40 mL), reaction temperature = 110 °C

yield increase with the reaction temperature increasing. The ratio of EL formation was rather slow at 70 °C (Figure 3b), Even with a prolonged reaction time, a low yield of 32% was achieved with 6 h. It is speculated that the alcoholysis of furfuryl alcohol with ethanol may experience the formation of intermediates firstly, which then was converted into the final product, and the step from intermediates to EL is the rate-determining, this is confirmed by the relatively amount of EMF and 4, 5, 5-triethoxypentan-2-one (38% and 33%, respectively).

Increasing the temperature to 90 °C, 110 °C and 130 °C, the reaction rate of FAL alcoholysis and formation rate of EL were enhanced significantly. As depicted in Figure 3b, FAL was almost completely converted into the EL after 3 h with a yield of 95%, and equilibriums reached. Interestingly, despite the increase of reaction rate was observed as expected, the yield of EL was constant (95%). To sum up, the distribution of products can be kinetically adjusted by controlling the temperature.

### 3.5 Recycling and reuse of $[(HSO_3\text{-p})_2im][HSO_4]$

Recycle experiments were conducted to investigate the catalyst's stability and lifetime of the ionic liquids, the cyclic tests were conducted for six times. As show in Figure 4, the catalytic activity of $[(HSO_3\text{-p})_2im][HSO_4]$ for the alcoholysis of FAL did not decrease after the six run, demonstrating that the catalyst was stable in this reaction. The EL yield in the recycling test was even higher than in the 1st run, which might be due to the retention of EL and unreacted feedstock in the previous run [24].

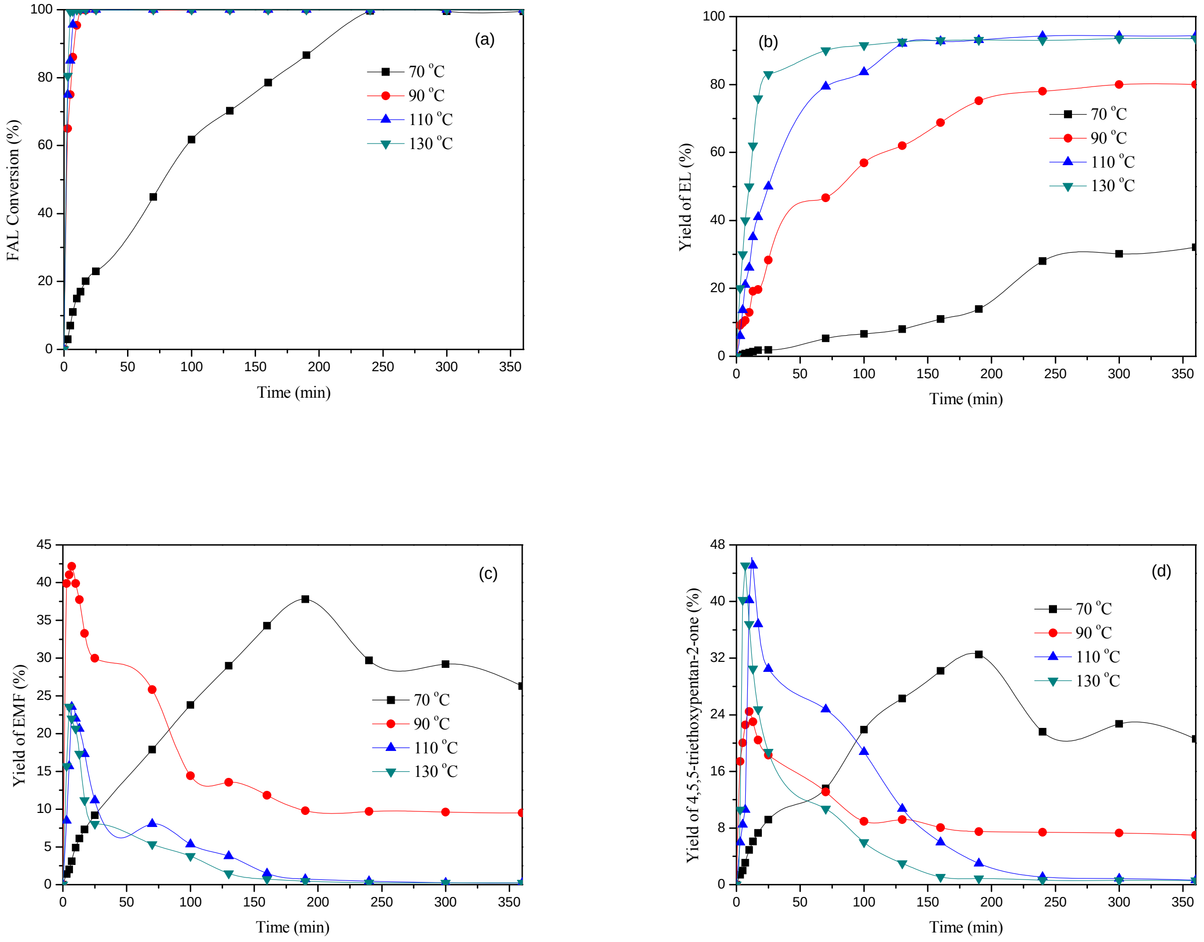

**Figure 3**. Influences of reaction temperatures on time-dependent product distribution in the presence of $[(HSO_3\text{-p})_2im][HSO_4]$, (a) FAL conversion, (b) yield of EL, (c) yield of EMF, (d) yield of 4, 5, 5-triethoxypentan-2-one. Reaction conditions: Furfuryl alcohol (20 mmol) and catalyst (0.6 mmol) in alcohol (40 mL).

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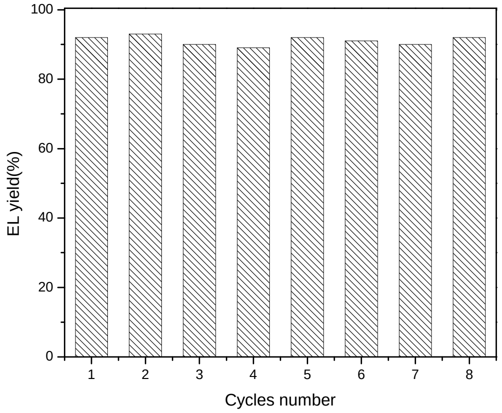


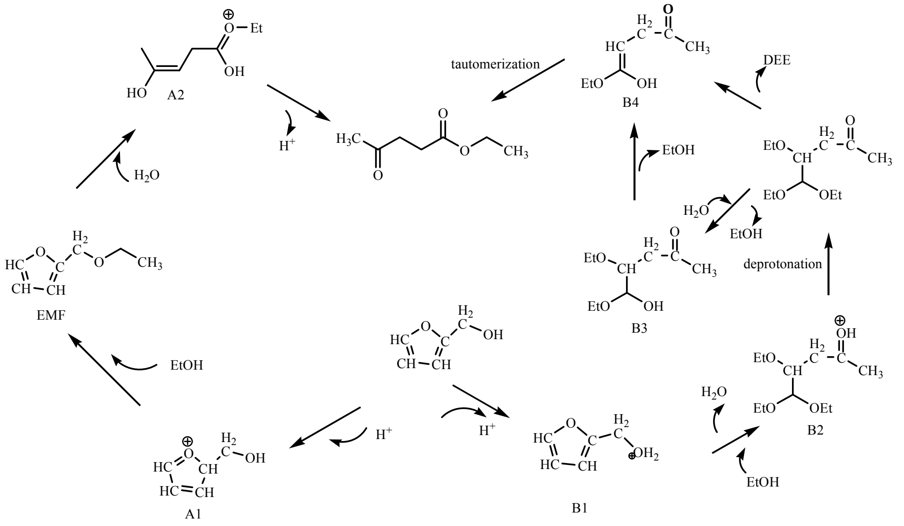
**Figure 4.** Cyclic performance of [$(HSO_3\text{-}p)_2im$][$HSO_4$] in the alcoholysis of FAL with ethanol. Reaction conditions: Furfuryl alcohol (20 mmol) and catalyst (0.6 mmol) in alcohol (40 mL).

### 3.6 Proposed mechanism for FAL alcoholysis

According to the literature, two possible reaction mechanisms for the alcoholysis of FAL to produce EL are proposed: (1) EMF route and (2) EMF and 4, 5, 5-triethoxypentan-2-one multi-path. The EMF route proposed by Zhao and co-workers [15] involves the first step of alcoholysis of FAL to form an intermediate of EMF and the second step of acidification of the intermediate to EL. The latter route proposed by James A. Dumesic *et al.* [4b, 14] indicates there are three different pathways for the production of EL. The initial step of the entire pathway is the protonation of the hydroxyl group to form intermediates including EMF and 4, 5, 5-triethoxypentan-2-one and this takes place in parallel to production of EL. In our conditions, GC-MS analyses allowed the identification of various products continuously, including diethyl ether (DEE), ethyl levulinate and the excessive alcohol. The DEE was the product of the inter-molecular dehydration reaction with ethanol. EMF and 4, 5, 5-triethoxypentan-2-one were detected and quantified using NMR. These both products indicate that the reaction is likely to proceed via the latter route, although our experimental results suggest the possible reaction mechanism is not in accord with above-mentioned. The results in Table 4 show that the amount of DEE is not equal to EMF or 4, 5, 5-triethoxypentan-2-one, this indicates that the conversion of FAL to EL are finished mainly through EMF and 4, 5, 5-triethoxypentan-2-one and the main pathway does not exist for the formation DEE. A reaction pathway for acid-catalyzed conversion of FAL into ethyl levulinate in ethanol is proposed, as illustrated in Scheme 1. In the first step, Protonation FAL with acidic group yields A1 and B1, which are attacked by EtOH to form EMF and B2, respectively. The next intermediate A2 formed from the partially detached protonated ethoxy group was then isomerized to form part of the product. Meanwhile, deprotonation of B2 results in the formation of the other intermediate 4, 5, 5-triethoxypentan-2-one which leads to species B4 by acid-catalyzed removal of ethanol from B3 or DEE directly. Subsequently, B4 is converted in a serial mode to ethyl levulinate due to tautomerization.

**Table 4** The influences of catalyst amounts in the reaction on the DEE to EMF and DEE to 4, 5, 5-triethoxypetan-2-one ratio in the presence of [$(HSO_3\text{-}p)_2im$][$HSO_4$]

| Catalyst amount/mmol | DEE yield/% | EMF yield/% | 4,5,5-triethoxypentan-2-one yield/% | DEE/EMF | DEE/4, 5, 5-triethoxypentan-2-one |
|---|---|---|---|---|---|
| 0.1 | 0.2 | 37.6 | 34.7 | 0.009 | 0.017 |
| 0.2 | 0.5 | 36.7 | 32.5 | 0.023 | 0.045 |
| 0.4 | 1.4 | 37.7 | 26.5 | 0.063 | 0.155 |
| 0.6 | 1.7 | 45.1 | 23.6 | 0.064 | 0.212 |



**Scheme 1.** proposed reaction pathway for the acid-catalyzed conversion of furfuryl alcohol to ethyl levulinate in alcohol.

## 4. Conclusion

Efficient conversion of furfuryl alcohol to alkyl levulinates was experimentally studied using double $SO_3H$-functionalized ILs as catalysts under mild conditions, where the highest yield of 95% was obtained when it was employed at 110 °C after 3 h. Double $SO_3H$-functionlized ILs are efficient catalysts for FAL conversion into EL, which facilitates the separation of ethyl levulinate and reuse of ionic liquids. Higher acidity of ILs measured by Hammett method promotes the conversion from FAL to EL. This approach offers significant improvements for production of EL from FAL, regarding high yield, product separation and catalyst recovery, thereby provides an economic, safe and environmentally friendly route to biomass utilization.

## Notes and references

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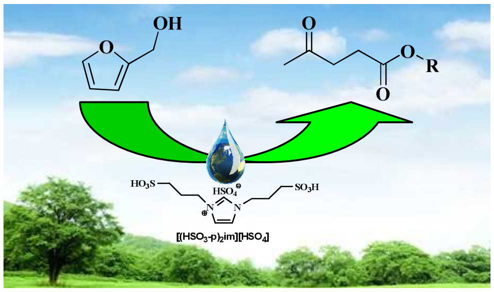
# Efficient and selective alcoholysis of furfuryl alcohol to alkyl levulinates catalyzed by double $SO_3H$-functionalized ionic liquids

**Guofeng Wang, Zhanquan Zhang, Linhua Song ***



An efficient synthesis of alkyl levulinates from furfuryl alcohol has been developed using double $SO_3H$-functionalized ionic liquids.