CHAPTER 3

Esterification of Levulinic Acid using Sulphonic Acid-Functionalized Benzimidazolium based Poly(ionic liquid) as a Catalyst

3.1 Introduction

Nowadays the researchers are giving more attention to sustainable methods for the production of fuels, fuel additives and chemicals from renewable resources due to depletion of non-renewable resources. In this respect, lignocelluloses have been known as valuable resources for fuels, fuel additives and chemicals (Ragauskas et al., 2006). Out of the various speciality chemicals derived from the hydrolysis of cellulose, levulinic acid (LA) is given major significance due to its broad range of applications in flavoring agents, plasticizers, solvents and fragrances etc. as well as in the production of chemicals, fuels and fuel additives Pasquale et al., (2012). Levulinic acid containing both highly reactive functional groups has become an inexpensive renewable resource in recent times for the synthesis of many values added chemicals Hayes et al., (2006) like 1,4-pentanediol, 2-methyl tetrahydrofuran-valerolactone, γ-valerolacton Mohan (2014) angelica lactone (α, β), δ-amine levulinic acid, acrylic acid, β-acetyl acrylic acid and levulinate esters. These valuable compounds can be obtained by different methods like esterification, oxidation, hydrogenation, reductive amination etc. Ethyl levulinate (EL) is suitable due to its diesel miscibility, in order to reduce the dependence on petroleum derived fuels; researchers are concentrating on the esterification of LA by using various acid catalysts (Weingarten et al., 2012). The synthesis of the alkyl levulinate has been usually achieved by inorganic acids like H₂SO₄ or homogeneous Brønsted acid catalysts.

Various heterogeneous catalysts, solid acid catalysts have been tested, that includes supported heteropoly acids Su et al., (2014), zeolites Li et al., (2017) metal supported Piskuna et al., (2016) sulfated carbon nanotubes Oliveira, and Da Silva (2014), sulfated metal oxides Yadav and Yadav (2014). Leng et al. (2009) had reported recyclable green solid catalysts for esterifications from solid organic-
inorganic hybrid materials by combining PS functionalized IL-forming organic cations with Keggin-structured heteropolyanions. The synthesis of EL from the esterification of levulinic acid and ethanol was achieved under batch conditions at 353 K using a C–SO₃H acid acquired from a glycerol-based catalyst (Varkolu et al., 2017). The reusable catalyst assigned the high catalytic performance to the Brønsted acidity of the –SO₃H groups and also supports the esterification of levulinic acid with other alcohols.

Shagufta et al. (2017) have given very strong evidence in the review about esterification and transesterification of alcohols with carboxylic acids using several heterogeneous sulfonic acid-functionalized solid acid catalysts in the field of organic transformation. These testified catalysts are ecologically benevolent and cleaner than traditional homogeneous catalysts.

The present chapter is dedicated to the synthesis of sulphonate acid functionalized benzimidazolium based poly(ionic liquid) (SAFBPIL) and to evaluate the catalytic activity in liquid phase synthesis of ethyl levulinate by the reaction of the levulinic acid with ethanol in a batch process. Moreover, the effects of various experimental parameters including catalyst loading, reaction time, reaction temperature and LA:ethanol molar ratio as well as catalyst reusability towards the efficiency of reaction were also investigated.

3.2 Results and Discussion

3.2.1 Characterization of SAFBPL

The synthesized SAFBPL catalyst was confirmed by various characterization techniques such as NMR, FT-IR, BET and TGA analysis. The presence of olefinic protons in compound 1 and 2 observed at 5.74 to 6.70 and 5.30 to 6.76 ppm respectively. However, ¹H NMR of compound 3 revealed, a complete disappearance of these signals corresponding to the olefinic protons shown in Fig. 3.1 and the appearance of a broad signal at 0.77-1.43 ppm due to the polymeric backbone of aliphatic protons (compound 3). Justification of the monomer ratio by ¹H NMR yet was difficult at this step since the polymer (polystyrene) backbone protons overlapped with other signals in the spectrum. The broadness of the ¹H NMR spectrum of compound 4, confirms the sulphonation of the compound 3 and also the peak at 3.75 ppm in SAFBPL exhibit due to the –OH of the sulphonic acid.
The FT-IR spectrum of SAFBPIL (Fig. 3.2C) shows a broad band between 3600-3300 cm\(^{-1}\), which is ascribed to –OH groups of –SO\(_3\)H and water molecules adsorbed on the surface. The broadness of band at 3412 cm\(^{-1}\) indicates the presence of -OH Zillillah et al., (2012) group in the sample (Fig. 3.2C) while in FT-IR spectra of Fig 3.2A and 3.2B, the peak corresponding to –OH do not exist. The intense peaks at 2926 and 2968 cm\(^{-1}\) are characteristic to aliphatic -C-H and 3120 cm\(^{-1}\) is attributed to the aromatic =C-H group in the spectrum of SAFBPIL. The region around 574, 1016 and 1182 cm\(^{-1}\) relates to the S-O symmetric vibration and S=O asymmetric and symmetric stretching frequency of the –SO\(_3\)H group separately (Vafaeezadeh and Hashemi, 2014).
Specific surface area and pore size distribution of SAFBPIL was measured through adsorption and desorption isotherm of nitrogen molecules. The BET specific surface area of synthesized SAFBPIL is found to be 2.753 m²/g (Fig. 3.3). The obtained specific surface area is comparatively greater than that of the reported method and similar to another method (Leng et al., 2012; Wang et al., 2008). The total pore volume of SAFBPIL is 0.004 cm³/g and average pore diameter is 3.535 nm respectively (Fig. 3.4).
3.2.2 Determination of Acidity of SAFBPIL

The concentration of acidic site on SAFBPIL was determined by using an ion-exchange/neutralization titration technique. In this method, 300 mg of SAFBPIL was dried at 105-110 °C for 1 h. The dried catalyst was suspended in 10 mL volume of a 20 wt% NaCl solution in a conical flask and kept under agitation at 150 rpm, for 24 h on a mechanical shaker. Then, the aqueous solution was filtered and titrated with 0.15 wt% standardized NaOH solution (Suwannakarn et al., 2007).

3.2.3 Optimization of Reaction Parameters

3.2.3.1 Effect of Catalyst Loading

The influence of catalyst loading on esterification was studied by changing the amount of SAFBPIL catalyst from 5 to 20 wt%. Initially, esterification was performed without catalyst that yielded around 26% conversion of the LA. The result indicated that the rate of esterification of LA was significantly influenced by the amount of catalyst and the optimum dose was observed at 15 wt% of catalyst with 99% conversion. An increase in the amount of catalyst provided more sulphonic acid sites on the catalyst surface for accelerating the esterification which in turn enhances the rate of reaction significantly (Fig. 3.5).
3.2.3.2 Effect of Reaction Time

The effect of reaction time on the esterification of LA with ethanol is illustrated in (Fig. 3.6). The rate of conversion of LA and selective formation of EL as the main product increases with time up to 9 h. At this stage the rate of conversion remains more or less persistent till 24 h, under the given reaction conditions. The liquid phase esterification reaction covers the surface of the solid oxide, leads to effective use of a catalyst (Cunill et al., 2016).
3.2.3.3 Effect of Reaction Temperature

The influence of temperature on the rate of esterification and selectivity of formation of EL was investigated by varying temperature from 40 to 80 °C. Temperature is vital with respect to the rate of reaction, product conversion, and dissemination of heat energy. It was observed that raising the temperature signifies positive impact on esterification of LA using SAFBPIL catalyst. The conversion of LA to EL improved from 27 to 99% as the temperature increased from 40 to 70 °C (Fig. 3.7). This is due to the fact that higher temperature provides more energy for the reactant molecules to overcome activation energy. However, a further increase in temperature has no significant effect on the esterification.

![Graph showing the effect of temperature on LA conversion with ethanol over SAFBPIL Catalyst](image)

**Fig. 3.7** Effect of Temperature on LA Conversion with Ethanol over SAFBPIL Catalyst

Reaction Conditions: Dose 15 wt%, Time 9 h and LA:Ethanol Molar Ratio (1:10)

3.2.3.4 Effect of Molar Ratio of Levulinic Acid to Ethanol

The molar ratio of LA to ethanol is one of the most important parameters that affect the esterification reaction. Stoichiometrically, 1 mol of ethanol is required for each mole of LA, but in practice, higher molar ratio is utilized in order to drive the reaction towards good performance and produce more ethyl levulinate. The gradual increase in the conversion of LA to EL with respect to variation in the LA to ethanol molar ratio is shown in Fig. 3.8. The ratio was varied from 1:6 to 1:14. The results illustrated that the highest conversion (99%) of LA to EL was obtained at 1:10 molar ratio. On the other hand, as the molar ratio increased further to 1:14, no substantial progress was observed.
Fig. 3.8 Effect of LA to Ethanol Molar Ratio on LA to EL Conversion with Ethanol over SAFBPIL Catalyst. Reaction Conditions: Dose 15 wt%, Time 9 h and Temperature 70 °C

Thus, it was found that an excess ethanol feed was productive to a certain extent. The formation of EL dropped from 99 to 97% which may be affected by excessively ethanol-diluted LA. This does not favor the reaction; consequently, conversion of LA to EL has been dropped (Liu et al., 2016).

Scheme 3.1 Plausible Mechanism for Esterification of LA to EL
3.2.3.5 Recyclability and Stability of SAFBPIL

The reaction between LA and ethanol was carried out to investigate the recyclability and deactivation of the heterogeneous catalyst which is equally essential when supported catalysts are employed. To examine the catalyst reusability, the separated SAFBPIL catalyst was washed with ethyl acetate (3 x 10 mL), filtered and dried in an oven for 12 h and reuse for the next run. It was observed that less significant changes in the conversion of LA to EL after each cycle and the catalyst was reused for five successive runs (Fig. 3.9).

![Bar chart showing recyclability of SAFBPIL after esterification]

Fig. 3.9 Recyclability of SAFBPIL after Esterification

To determine the thermal stability of catalyst, thermogravimetric analysis (TGA) of the compound 2, 3 and 4 (SAFBPIL) was conducted in the range of 30 °C to 800 °C with an increase in temperature at the rate of 10 °C min\(^{-1}\) in a N\(_2\) atmosphere. The TGA thermogram of SAFBPIL (Fig. 3.10 C) displayed continuous decrease in weight from 100-800 °C. The initial weight loss (9.056%) at lower temperature range (up to 100 °C) relates to the removal of moisture content of the sample while the weight loss (45.20%) from 200 to 402 °C may be due to decomposition of benzyl group on SAFBPIL. The final weight loss of 31.60% was observed from 400 to 680 °C would correspond to the decomposition of poly(1-(4-vinylbenzyl)-1H-benzimidazole) in the SAFBPIL (Muskawar et al., 2016). Since the decrease in weight of the SAFBPIL commences from 270 °C, it could conclude that the polymer is stable up to 270 °C. Additionally, thermogram of ionic liquid monomer...
(compound 2) and poly(ionic liquid), prior to sulphonation (compound 3) have been studied. In the thermogram of compound 2, the initial weight loss was observed up to 203 °C (Fig. 3.10 A) while thermal stability of the compound 3 was noticed up to 232 ° (Fig. 3.10 B). From the thermogram Fig. 3.10 C it could be recognized that thermal stability of the SAFBPIL is more compared to ionic liquid monomer (compound 2) and poly(ionic liquid) (compound 3).

![Thermogram of compounds](image)

**Fig. 3.10** TGA Spectrum of A) Compound 2, B) Compound 3 and C) Compound 4 SAFBPIL

### 3.3 Conclusions

In the present work we have successfully synthesized the sulphonic acid functionalized poly(ionic liquid) and characterized by NMR, FT-IR, elemental analysis (C, H, N, S), TGA and BET surface area and Brønsted acidity was determined by titration method. The synthesized catalyst was effectively used for the esterification of LA with ethanol with selectivity higher than 99.5%. Among the optimized conditions, the best parameters were found to be: 15 wt% of the catalyst, 70 °C temperature, 9 h reaction time and LA to Ethanol molar ratio of 1:10. The high conversion of EL (99%) was obtained due to availability of more Brønsted acidic sites of the catalyst. The heterogeneous catalyst was reused up to five runs without significant loss in the catalytic activity. The thermal stability of the catalyst was investigated and it was found that the catalyst was stable up to 270 °C. Therefore, SAFBPIL catalyst can be considered as a competent catalyst for the esterification of LA giving a substitute of inorganic acid to the synthesis of EL.
3.4 Experimental Section

3.4.1 Esterification of Levulinic Acid with Ethanol

LA esterification was carried out in two necks round-bottom flask with a reflux condenser kept at 70 °C for the specified period of time. The catalytic assessments were performed by using LA (5 mmol) and ethanol (50 mmol) (LA:ethanol molar ratio 1:10) under stirring at 500 rpm and 15 wt% (87 mg) of catalyst (scheme 3.2).

Upon completion of reaction, the mixture was allowed to cool to room temperature. The heterogeneous catalyst was separated and n-nonane was added to the reaction mixture as an internal standard. EL formed in the reaction was analyzed on a GC (Shimadzu GC-2010 plus instrument) equipped with a column model Rtx-1 (crossbond 100% dimethylpolysiloxane) with dimensions of 30.0 m x 0.32 mm x 0.5 μm and a flame ionization detector (FID) operating at max prog. temp. 350 °C. The carrier gas was nitrogen with a flow rate of 0.5 mL/min. The conversion of LA was calculated based on the following formula,

\[
\text{Conversion of LA (\%) = } \frac{\text{Initial area of LA} - \text{Final area of LA}}{\text{Initial area of LA}} \times 100
\]

![Scheme 3.2 Esterification of LA with Ethanol using SAFBPIL Catalyst](image)

3.4.2 Synthesis of Sulphonic Acid Functionalized Poly(Ionic Liquid) (SAFBPIL)

3.4.2.1 Synthesis of 1-(4-vinylbenyl)-1H-benzimidazole (1)

1-(4-vinylbenyl)-1H-benzimidazole was synthesized according to our previously reported procedure (Khiratkar et al., 2016) (Yield: 9.36 g, 80%).
3.4.2.2 Synthesis of 3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride (2)

In 250 mL two neck round bottom flask 1-(4-vinylbenzyl)-1H-benzimidazole (11.7 g, 50 mmol) and acetonitrile (150 mL) were allowed to stir for 10 min at 80 °C and benzyl chloride (6.93 g, 55 mmol) was added drop-wise under stirring and continued for 48 h. After completion of the reaction, the mixture was cooled to room temperature and dirty white solid compound 2 was formed after distillation of acetonitrile using rotary evaporator. The obtained product was repeatedly washed with ethyl acetate to get white amorphous powder of 3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride, filtered and dried in an oven at 50 °C for 10 h (Yield: 15 g, 83.33%).

3.4.2.3 Synthesis of poly(of 3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride) (3)

3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride (2) (12 g, 33.33 mmol) was suspended in 120 mL mixture of acetonitrile and methanol (10:2) followed by charging of (4 mol%) AIBN (0.328 g, 2 mmol). The polymerization was carried out at 70 °C for 48 h under N\textsubscript{2} atmosphere. After this period, the solvents were removed by rotary evaporator and the resultant viscous yellow liquid dried under vacuum for half an hour. It is further dried in an oven at 50 °C for 12 h to get yellowish crystalline polymer (Yield: 10 g, 87.5%).

3.4.2.4 Synthesis of SAFBPIL (4) by sulphonation of poly(3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride) (3)

Synthesis of SAFBPIL was carried out by adapting the method proposed by Kore and Shrivastava (2011). In 100 mL round bottom flask, poly(3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride) (3) (10 g) was suspended in minimum amount of water and stirred for half an hour at ice cold condition. To this, an excess of H\textsubscript{2}SO\textsubscript{4} (16.66 g, 170 mmol) was added drop-wise and stirred for half an hour. The resulting reaction mixture was then stirred at 70-80 °C for 12 h. The yellowish SAFBPIL solid was obtained by washing viscous reaction mass with deionized water several times, followed by drying overnight in hot air oven at 50 °C for 12 h (Scheme 3.3). The formation of SAFBPIL catalyst was confirmed by negative silver nitrate test for chloride anion (Fig. 3.11).
Scheme 3.3 Schematic Representation of Synthesis of Sulphonic Acid Functionalized Benzimidazolium based Poly(Ionic Liquid) Catalyst

Fig. 3.11 Silver Nitrate Test Image of Compound 2, 3 and 4 SAFBPIL Catalyst
3.5 Characterization of Compounds

3.5.1 Synthesis of 1-(4-vinylbenyl)-1H-benzimidazole (1)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.92 (s, 1H), 7.83-7.81 (d, 2H), 7.36-7.34 (d, 2H), 7.25-7.23 (d, 2H), 7.12-7.10 (d, 2H) 6.70-6.63 (dd, 1H), 5.74-5.69 (d, 1H), 5.30 (s, 2H), 5.26-5.23 (d, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 144.02, 143.26, 137.72, 136.09, 134.90, 133.98, 127.40, 126.88, 123.19, 122.39, 120.48, 114.70, 110.13, 48.68.

3.5.2 Synthesis of 3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chlorides (2)

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$: 10.38 (s, 1H), 7.98 (d, 2H), 7.63 (d, 2H), 7.53 (s, 5H), 7.42 (d, 3H), 6.76 (dd, 1H), 5.88 (s, 1H), 5.83 (s, 4H), 5.30 (d, 1H).

$^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$: 142.82, 137.49, 135.86, 133.95, 133.34, 130.98, 128.91, 128.66, 128.23, 126.69, 126.60, 155.20, 113.98, 49.92, 49.70.

3.5.3 Synthesis of Poly(of 3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride) (3)

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$: 10.22 (s, 1H), 7.98 (d, 2H), 7.63 (d, 2H), 7.53 (s, 5H), 7.42 (d, 3H), 6.76 (dd, 1H), 5.88 (s, 1H), 5.83 (s, 4H), 5.30 (d, 1H).

$^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$: 142.81, 137.56, 135.91, 133.99, 133.37, 131.05, 130.01, 129.00, 128.73, 128.29, 126.78, 126.68, 119.87, 115.30, 114.03, 49.99, 49.78, 47.53, 24.43, 22.02.

3.5.4 Synthesis of SAFBPIL (4) from Sulphonation of Poly(3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride) (3)

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$: 10.25 (br, 1H), 7.88 (br, 1H), 7.74 (br, 1H), 7.53 (br, 1H), 7.34 (br, 1H), 6.53 (br, 2H), 6.51 (br, 2H), 6.49 (br, 2H), 6.44 (br, 2H), 5.77 (br, 2H), 1.45 (br, 1H), 0.99 (br, 2H), 0.74 (br, 3H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$: 142.81, 137.56, 135.91, 133.999, 133.37, 131.05, 130.01, 129.00, 128.73, 128.29, 16.78, 126.68, 119.87, 115.30, 114.03, 49.99, 49.78, 47.53, 24.43, 22.02. Anal. Calcd for C$_{22}$H$_{28}$N$_2$O$_7$S$_2$ (%): C, 56.37, H, 5.30, N, 5.26, S, 12.04. Found: C, 58.31, H, 5.75, N, 6.32, S, 7.30.
3.6 Spectral Data of Compounds

**Fig. 3.12** $^1$H NMR Spectrum of 3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride

**Compound 2**

**Fig. 3.13** $^{13}$C NMR Spectrum of 3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride

**Compound 2**
Fig. 3.14 FT-IR Spectrum of 3-benzyl-1-(4-vinylbenzyl)-1H-benimidazolium chloride

Compound 2

Fig. 3.15 TGA Thermogram of Compound 2
Fig. 3.16 $^1$H NMR Spectrum of Poly(3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride)

Compound 3

Fig. 3.17 $^{13}$C NMR Spectrum of Poly(3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride)

Compound 3
Fig. 3.18 FT-IR Spectrum of Poly(3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride) Compound 3

Fig. 3.19 TGA Thermogram of Compound 3
**Fig. 3.20** $^1$H NMR spectrum of SAFBPIL Compound 4

**Fig. 3.21** $^{13}$C NMR Spectrum of SAFBPIL Compound 4
Fig. 3.22 FT-IR Spectrum of SAFBPIIL Compound 4

Fig. 3.23 TGA Thermogram of Compound 4
Fig. 3.24 GC Chromatogram of Esterification Reaction Mixture

Fig. 3.25 GC-MS Chromatogram of Ethyl Levulinate
Fig. 3.26 Mass Spectrum of Ethyl Levulinate

Calc. mass = 144.16
Obs. Mass = 144.21
Fig. 3.27 $^1$H NMR Spectrum of Ethyl Levulinate

Fig. 3.28 $^{13}$C NMR Spectrum of Ethyl Levulinate