Catalysis Letters (2018) 148:680–690
https://doi.org/10.1007/s10562-017-2284-1

Sulphonic Acid-Functionalized Benzimidazolium Based Poly Ionic Liquid Catalyzed Esterification of Levulinic Acid

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Received: 3 November 2017 / Accepted: 17 December 2017 / Published online: 4 January 2018
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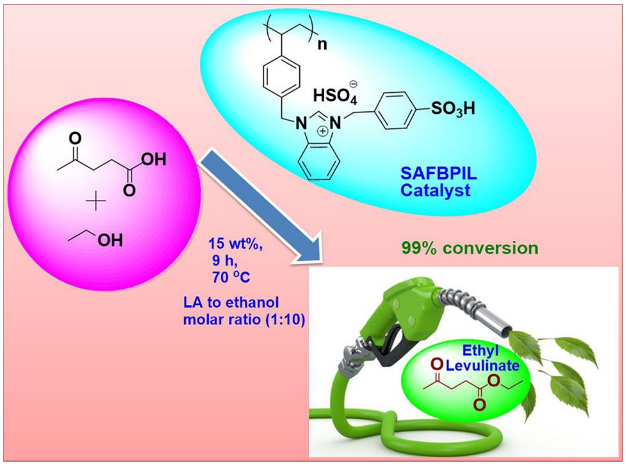
Abstract

Esters of levulinic acid (LA) are bio-based compounds having widespread applications and have the remarkable potential to be blended with commercial diesel or gasoline. In this study, a sulphonic acid-functionalized benzimidazolium based poly ionic liquid (SAFBPIL) catalyst was prepared and characterized by NMR, FT-IR, elemental analysis (C, H, N, S), TGA and BET surface area. Brønsted acidity was determined by anion-exchange/neutralization titration method and was found to be 5.55 mmol/g. The heterogeneous ionic liquid catalyst showed an excellent thermal stability up to 270 °C. Experiments were carried at different temperatures, LA to ethanol molar ratios, catalyst loadings and duration of the reaction in a batch reactor. The highest conversion was obtained at 70 °C using an initial LA:ethanol molar ratio of 1:10 and a catalyst loading of 15 wt% in 9 h. It was observed that ethyl levulinate (EL) could be effectively obtained over SAFBPIL with a selectivity higher than 99.5%. This is due to more acidic sites exhibited on SAFBPIL catalyst under optimized conditions. Herein, we are reporting for the first time an esterification of LA to EL using a new SAFBPIL as a catalyst. The catalyst was recycled for five runs without significant loss of catalytic activity.

Graphical Abstract



Keywords Sulphonic acid-functionalized · Levulinic acid · Benzimidazolium · Poly ionic liquid · Esterification · Brønsted acid

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Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10562-017-2284-1) contains supplementary material, which is available to authorized users.

Extended author information available on the last page of the article

1 Introduction

Even today, researchers are continuing to devote more attention on sustainable methods for the production of fuels, fuel additives and chemicals from renewable resources due to the depletion of non-renewable resources. In this respect, lignocelluloses have been recognized as valuable resources for fuels, fuel additives and chemicals [1, 2]. Out of various specialty chemicals derived from the hydrolysis of cellulose, 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 [3, 4]. LA containing both highly reactive functional groups [5] has become an inexpensive renewable resource in recent times for the synthesis of many value added chemicals such as 1,4-pentanediol, 2-methyl tetrahydrofuran-valerolactone, γ-Valerolactone [6–8] angelica lactone (α, β), δ-amine LA, acrylic acid, β-acetyl acrylic acid and levulinate esters [9, 10]. These valuable compounds can be obtained by different methods like esterification, oxidation, hydrogenation and reductive amination etc. In particular, esters of LA are valuable compounds which are used as solvents, plasticizers and fuel additives. Moreover, 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 [11–16]. The alkyl levulinate has been usually achieved by inorganic acids like H_2SO_4 [17–21] or homogeneous Brønsted acid catalysts [22–24].

Likewise, the literature on butyl levulinate (BL) synthesis is sparse: first attempts at synthesis were undertaken with homogeneous catalysts [25] and a kinetic model for the esterification of LA with butanol (BuOH) was proposed by Bart et al. [22]. Some effort has been made in BL synthesis directly from cellulose with homogeneous catalysts. The main drawbacks associated with the use of these acids are their corrosiveness, lack of reusability, neutralization and difficulty in the separation after the reaction. Therefore, the replacements of homogeneous with heterogeneous catalysts are beneficial due to ease of processing after the reaction, simple separation and recyclability. A number of heterogeneous catalytic systems have been reported in the literature [26–30] and although the sulphated catalysts were found to be efficient, leaching of the catalyst was noticed.

Among the various heterogeneous catalysts, solid acid catalysts have been tested including supported heteropolyacid (HPA) [31], metal organic framework [32], zeolites [33], metal-based catalyst [34–37], zirconia [38], graphene oxide based [19], sulfated carbon nanotubes [39], starbon mesoporous materials functionalized with sulfonated groups [40] and silicas [41, 42]. For example, Wang et al. [43] had reported recyclable green solid catalysts for esterifications from solid organic–inorganic hybrid materials by combining polystyrene functionalized IL-forming organic cations with Keggin-structured heteropolyanions. A novel and environmentally benign heterogeneous catalytic method were developed [44] for the direct conversion of carbohydrates biomass into methyl levulinate (ML) as biofuels and/or high-value chemicals. The heterogeneous catalyst, (SO_4^{2-}/TiO_2) was easily recovered by filtration and reused for the next run after calcination. In the same year, an effective catalytic protocol was identified for the practicality of converting glucose to EL using a series of sulphated solid acid catalysts [30]. Bokade and Dharne [45] have described a promising HPA supported on acid-treated clay montmorillonite (K10) for the synthesis of *n*-butyl levulinate by esterification of LA with *n*-butanol. The catalyst was found to be the most effective with 97% LA conversion and 100% selectivity to *n*-butyl levulinate.

The synthesis of ethyl levulinate (EL) from the esterification of LA with ethanol was achieved under batch conditions at 353 K using a bio-glycerol derived carbon $–SO_3H$ catalyst [46]. The reusable catalyst assigned high catalytic performance to Brønsted acidity of the $–SO_3H$ groups and also supports the esterification of LA with other alcohols. Another research group [47] tested ZrO_2/SBA-15 catalysts with different ZrO_2 loadings for the esterification of LA in a fixed-bed reactor in vapor phase conditions at atmospheric pressure. The catalyst with 7 wt% ZrO_2 securing more number of moderate acidic sites showed 100% conversion of LA and 96% selectivity to ML. Zheng and his co-workers [48] fabricated a novel catalyst by immobilizing 12-silicotungstic acid ($H_4SiW_{12}O_{40}$, HSiW) in the mesoporous molecular sieves MCM-41 using an open synthesis method without hydrothermal process. The HSiW/MCM-41 catalysts maintained hexagonal mesoporous features of MCM-41 and the usual Keggin structure of bulk HSiW and displayed admirable catalytic activity with 81.2% methyl oleate with recyclability.

Recently, liquid-phase synthesis of BL was described [49] by using a set of 0.8% acidic ion exchange catalyst resins at 80 °C and 2.5 MPa in a batch reactor with an initial AL/BuOH molar ratio of 1:3. It was observed that BL could be effectively attained over ion-exchange resins with selectivity greater than 99.5%. Very recently, a series of metal-zeolite hybrids was obtained by impregnation and deposition–precipitation methods and characterized with various techniques [34]. Acid–base bifunctional zirconia-zeolite hybrid $ZrY_6(0.5)$ with high stability and porosity demonstrated superior activity towards the production of ML from carbohydrates. Moreover, the catalyst could be reused for at least five times with stable conversion rates and ML yields. Shagufta et al. [50] have stated strong evidence in their 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 scope of these catalysts makes the industrial procedures easier and cleaner by an increasing recyclability; surface area and sulfonic acid content. A novel Brønsted acidic polymeric hybrid catalyst was invented by coupling task-specifically designed SO_3H-functionalized polymeric ionic liquid with Keggin-structured heteropolyanion [51]. The heterogeneous polymeric hybrid was shown to be a highly competent solid catalyst for numerous esterification reactions contributing to the advantages of easy retrieval and steady recycle. Among a variety of heterogeneous Brønsted acidic catalysts, polymer supported ionic liquids consisting of sulfonic acid groups are of great interest [52].

Conversely, to the best of our knowledge very few works reported the applications of polymer-supported IL catalysts for biofuel production from esterification reaction. In our latest work [53] we have reported the catalytic performance of polymer-supported benzimidazolium based ionic liquid catalyst for the synthesis of 3,4-dihydropyrimidine-2(1H)-one/thione derivatives. Presently, commercially available heterogeneous Brønsted acid catalysts mainly include ion-exchange resin and ZSM-5. The ion-exchange resin is not durable and long-lasting at high temperature due to its relatively poor thermal stability. Esterification of the carboxyl group is comparatively sluggish and needs initiation either by high temperature or by a catalyst to attain equilibrium conversion in a practical time. Owing to an existence of these complications, it is particularly significant and necessary to cultivate an environmentally benevolent catalyst with high activity for the direct production of alkyl levulinates. Accordingly, this paper is dedicated to the synthesis of sulphonic acid functionalized poly ionic liquid and to evaluate the catalytic activity in liquid phase synthesis of EL by the reaction of LA with ethanol in a batch process. Moreover, the effects of various process parameters comprising catalyst loading, reaction time, reaction temperature and LA to ethanol molar ratio as well as catalyst reusability towards the efficiency of reaction were investigated.

2 Experimental

2.1 Materials

4-Vinylbenzyl chloride (90%) containing 500 ppm of tert-butyl catechol was obtained from Sigma-Aldrich India. Levulinic acid (LA) 98% and Azobisisobutyronitrile (AIBN) (98%) were obtained from Avra synthesis (India) PVT Ltd. AIBN was recrystallized from methanol before use. *n*-Nonane (Internal standard) was obtained from TCI chemicals (India) PVT Ltd. Sodium hydride (60% suspension in paraffin oil), benzimidazole, benzyl chloride and sulphuric acid (98%) were purchased from S D Fine chemicals India. Ethanol used was procured from Changshu Hongsheng fine chemical Co., Ltd. Other solvents used were of commercial grade and used as supplied unless it is specified.

2.2 Instrumentation

NMR spectra were recorded in DMSO-d_6 and $CDCl_3$ on Bruker spectrometer operating at 400 MHz with TMS as an internal standard. The TGA analysis of the SAFBPIL catalyst was obtained in the range of 30–800 °C with an increase in temperature at the rate of 10 °C min^{-1} in a N_2 atmosphere on TG/DTA thermoanalyzer SII, 7200 (Seiko, Japan). FT-IR spectra were recorded on IR affinity-1 Shimadzu FT-IR spectrophotometer using KBr pellet method. EL in the reaction products was analyzed on a GC (Shimadzu GC-2010 plus instrument) equipped with a column model Rtx-1 (crossbond 100% dimethylpolysiloxane) with a flame ionization detector. Elemental analysis (C, H, N and S) was performed on the Elementar Vario EL III model. Brunauer–Emmett–Teller (BET) surface area was measured at the temperature of 77 K liquid N_2 using a Quanta chrome nova-1000 instrument analyzer. Specific surface area, average pore diameter and pore volume are measured using N_2 adsorption–desorption isotherms. Before analysis, the sample was degassed at 250 °C for 5 h under vacuum for the removal of moisture and unwanted adsorbents from the sample.

2.3 Synthesis of Sulphonic Acid Functionalized Benzimidazolium Based Poly Ionic Liquid (SAFBPIL)

2.3.1 Synthesis of 1-(4-Vinylbenzyl)-1H-benzimidazole (1)

1-(4-Vinylbenzyl)-1H-benzimidazole was synthesized according to our previously reported procedure [54]. The detailed procedure and the corresponding spectral data are given in the supplementary information (Yield: 9.36 g, 80%).

2.3.2 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 the dirty white solid compound 2 formed was separated by removal of acetonitrile with a rotary evaporator. The separated product was washed repeatedly 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%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 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) δ: 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.

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

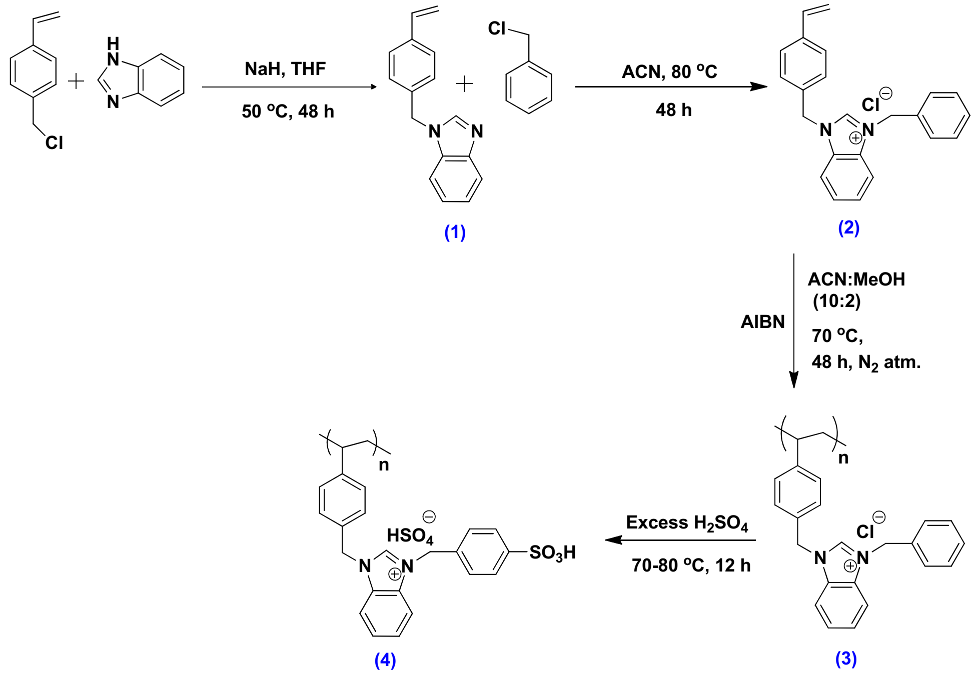
3-Benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride (2) (12 g, 33.33 mmol) was suspended in 120 mL mixture of acetonitrile and methanol (10:2) followed by charging of 4 mol% AIBN (0.328 g, 2 mmol). The polymerization was carried out at 70 °C for 48 h under N_2 atmosphere. After this period, the solvents were removed by rotary evaporator and the resultant viscous yellow liquid dried in 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%). The NMR spectrum of compound 3 is given in supplementary information (Fig. S4). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 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) δ: 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.

2.3.4 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 [55]. In 100 mL round bottom flask, poly(3-benzyl-1-(4-vinylbenzyl)-1H-benzimidazolium chloride) (3) (10 g) was suspended in water and stirred for half an hour at ice-cold condition. To this, an excess of H_2SO_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 at 50 °C for 12 h (Scheme 1). The formation of SAFBPIL catalyst was confirmed by negative silver nitrate test for chloride anion (Fig. S11). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 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) δ: 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. Anal. Calcd for $C_{22}H_{28}N_2O_7S_2$ (%): 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.

2.4 Esterification of LA with Ethanol

LA esterification was carried out in a two-neck round-bottom flask with a reflux condenser kept at 70 °C for the specified period of time. The catalytic assessments were



Scheme 1 Schematic representation of the synthesis of sulphonic acid functionalized poly ionic liquid catalyst

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 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 × 0.32 mm × 0.5 µm and a flame ionization detector 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,

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

3 Results and Discussion

3.1 Characterization of SAFBPIL

The synthesized SAFBPIL 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 between 5.74 and 6.70 and 5.30–6.76 ppm respectively. However, ^{1}H NMR of compound 3 revealed a complete disappearance of these signals corresponding to the olefinic protons as shown in Fig. 1 and the appearance of the broad signal between 0.77 and 1.43 ppm due to the polymeric backbone of aliphatic protons (compound 3). Justification of the monomer ratio by ^{1}H NMR was yet difficult at this step since the polymer (polystyrene) backbone protons overlapped with other signals in the spectrum. The broadness of ^{1}H NMR spectrum of compound 4 confirmed the sulphonation of compound 3 and also the peak at 3.75 ppm in SAFBPIL exhibited due to –OH of sulphonic acid.

The FT-IR spectrum of SAFBPIL (Fig. 2C) showed a broad band of 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} indicated the presence of –OH [56] group in the sample (Fig. 2c) while in FT-IR spectra of Fig. 2a, b, the peak corresponding to –OH does 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 –SO$_3$H group separately [57, 58].

Scheme 2 Esterification of LA with ethanol using SAFBPIL catalyst

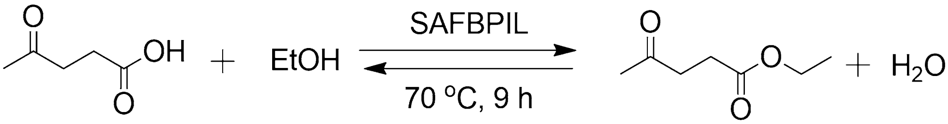
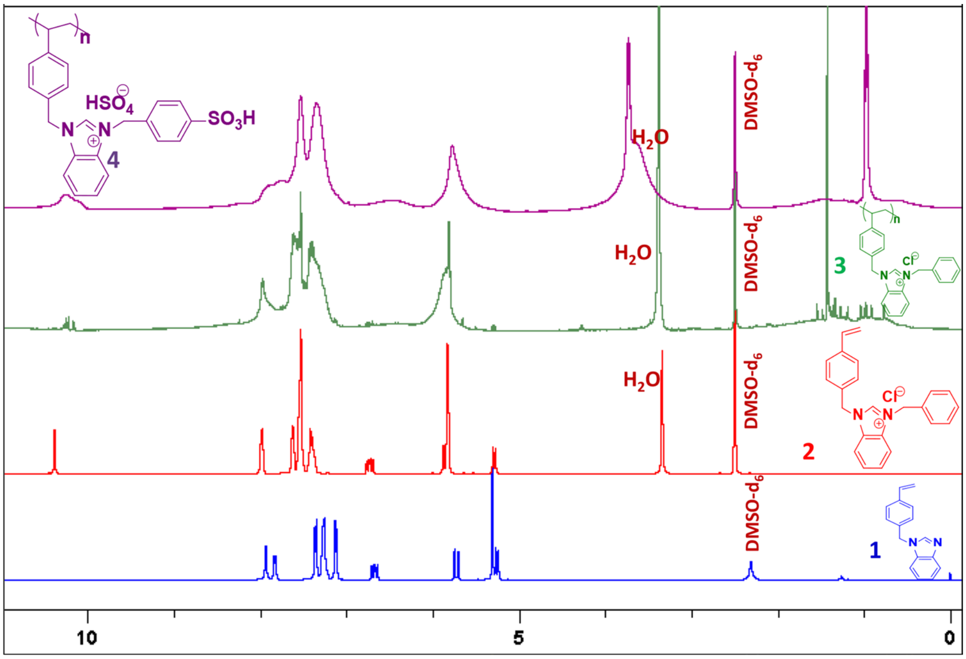


Fig. 1 ^{1}H NMR overlay of compound 1, 2, 3 and 4 (SAFBPIL)



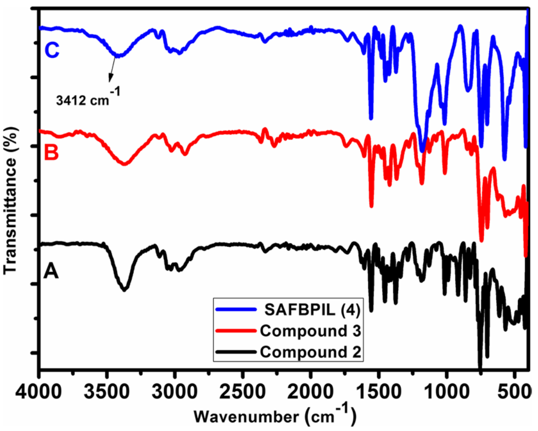


Fig. 2 Comparative FT-IR spectra of (*a*) compound 2, (*b*) compound 3 and (*c*) compound 4 SAFBPIL

Specific surface area and pore size distribution of the SAFBPIL was measured using adsorption and desorption isotherm of nitrogen molecules. The BET specific surface area of synthesized SAFBPIL was found to be 2.75 m²/g (Fig. 3). The obtained specific surface area was comparatively greater than that of the reported method [53]. The total pore volume and average pore diameter of SAFBPIL were 0.004 cm^3/g and 3.53 nm respectively (Fig. 4).

3.2 Determination of Acidity of SAFBPIL

It is well known that the sulphonic acid functionalized ionic liquids containing HSO_4^- counter anion enhances the Brønsted acidity of the catalyst [59]. Therefore we have synthesized the SAFBPIL and the acidic site 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 [60]. The acidity of SAFBPIL was found to be 5.55 mmol/g which is higher than the reported heterogeneous acidic catalyst [61].

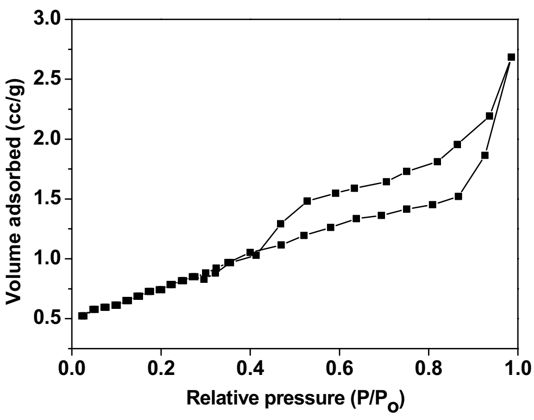


Fig. 3 BET isotherm of SAFBPIL

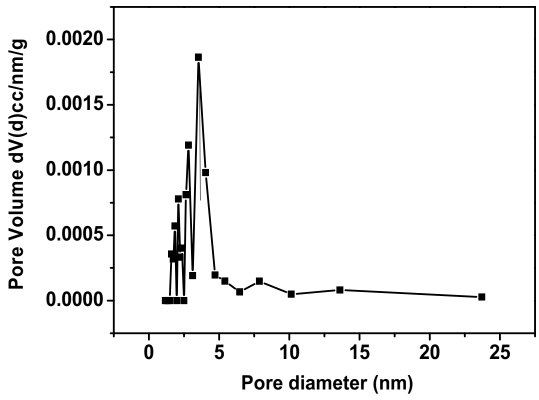


Fig. 4 Pore diameter and pore volume of SAFBPIL

3.3 Optimization of Reaction Parameters

3.3.1 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 the 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 enhanced the rate of reaction significantly (Fig. 5).

3.3.2 Effect of Reaction Time

The effect of reaction time on the esterification of LA with ethanol is illustrated in (Fig. 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 that leads to effective use of catalyst [50].

3.3.3 Effect of 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

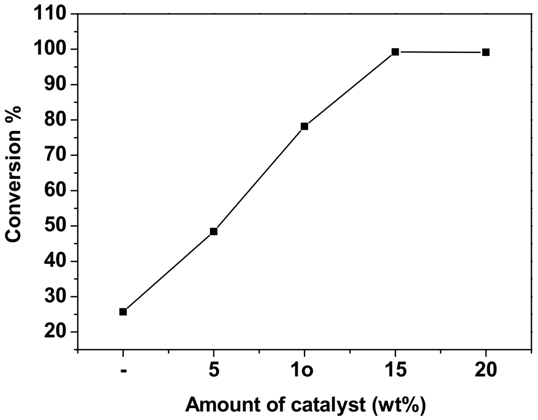


Fig. 5 Effect of amount of catalyst on LA conversion with ethanol over SAFBPIL catalyst. Reaction conditions: temperature 70 °C: time 24 h, LA: ethanol molar ratio (1:10)

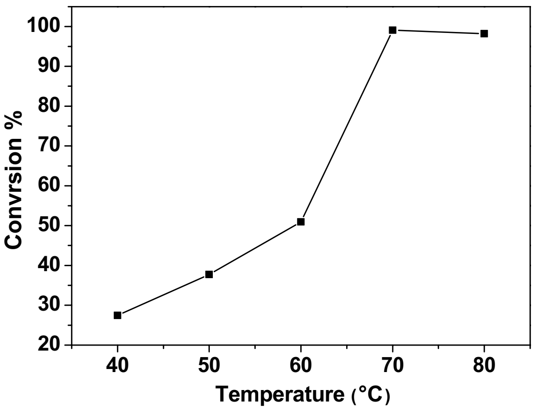


Fig. 7 Effect of temperature on LA conversion with ethanol over SAFBPIL catalyst. Reaction conditions: dose 15 wt%, time 9 h and LA:ethanol molar ratio (1:10)

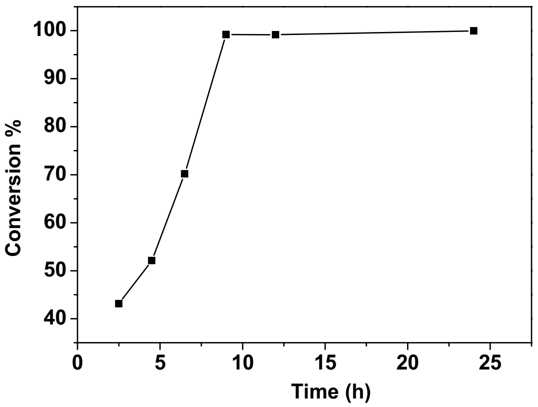


Fig. 6 Effect of reaction time on LA conversion with ethanol over SAFBPIL catalyst. Reaction conditions: amount of catalyst 15 wt%, temperature 70 °C and LA:ethanol molar ratio (1:10)

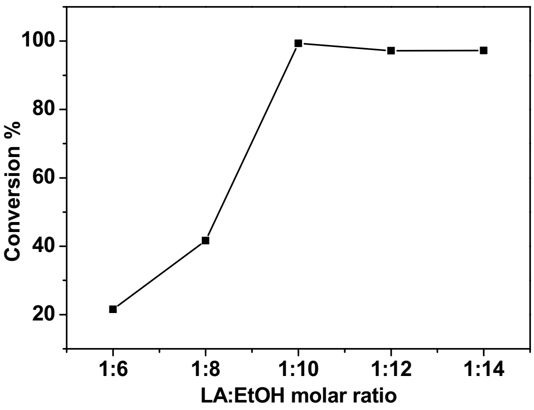


Fig. 8 Effect of LA to ethanol molar ratio on LA conversion with ethanol over SAFBPIL catalyst. Reaction conditions: dose 15 wt%, time 9 h and temperature 70 °C

with respect to 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. 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.

3.3.4 Effect of LA to Ethanol Molar Ratio

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, the higher molar ratio is utilized in order to drive the reaction towards good performance and produce more EL. 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. 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 was increased further to 1:14, no substantial progress was observed. Additionally, we have performed the esterification reaction using isopropyl alcohol and 1-pentanol under optimized conditions. However, isopropyl levulinate obtained with 16% conversion and 1-pentanol did not give satisfactory conversion.

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 [38]. The formation of EL was confirmed by ^{1}H NMR and ^{13}C NMR spectra (Figs. 9, 10). The plausible mechanism of esterification of LA using SAFBPIL is given in the Scheme 3.

3.3.5 Recyclability and Stability of the 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 × 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. 11). Whereas in normal esterification using H_2SO_4, we could not recover and reuse the catalyst hence the present

Fig. 9 ^{1}H NMR spectrum of EL

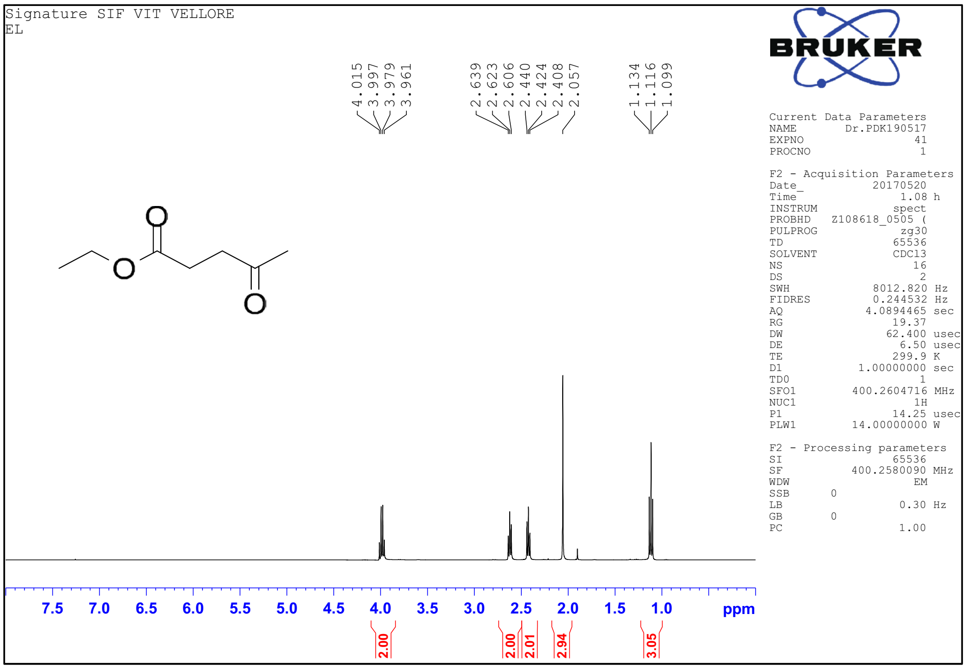


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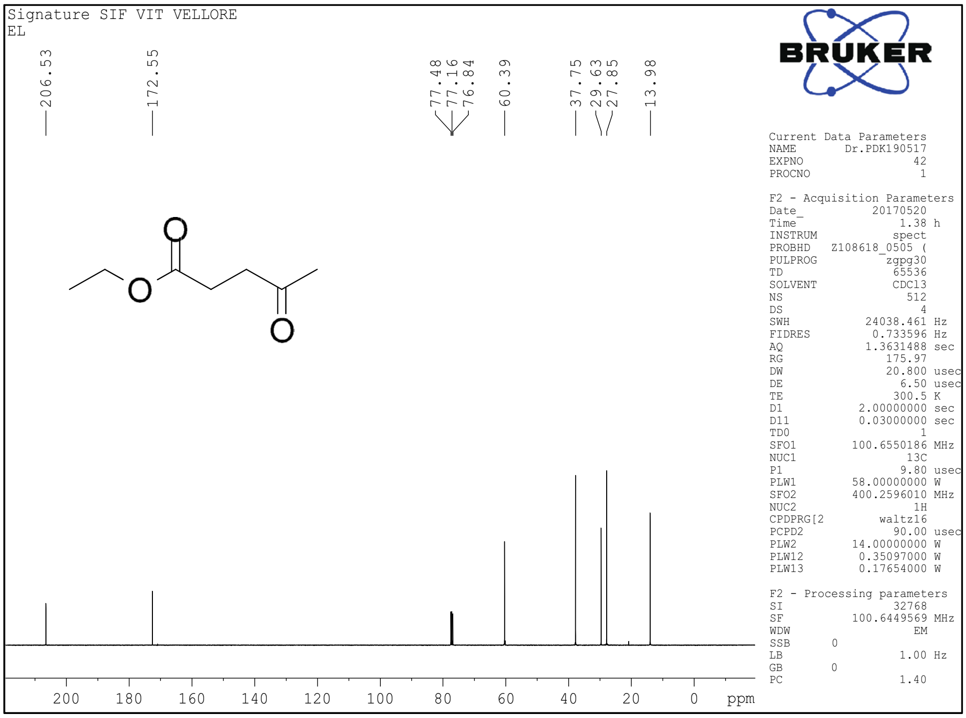
Fig. 10 ^{13}C NMR spectrum of EL



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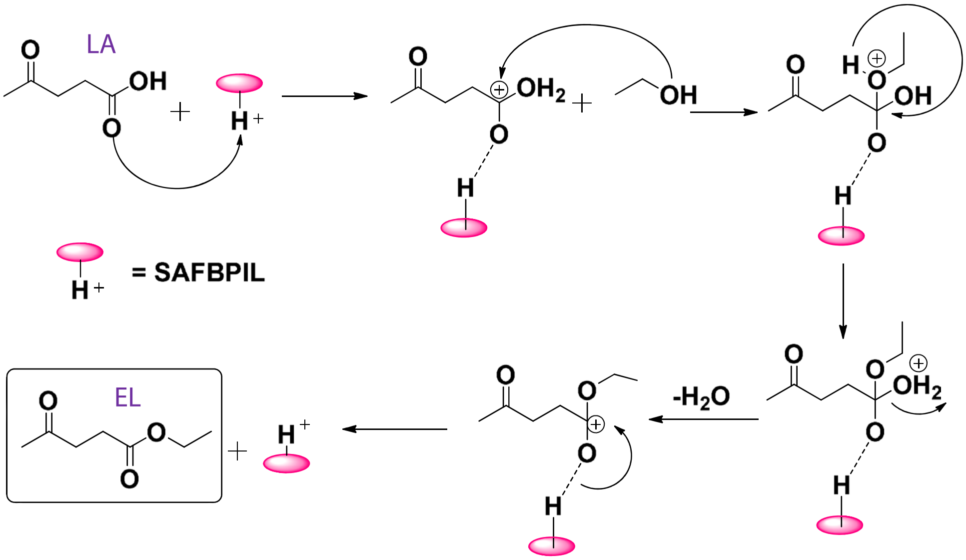
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ               1.3631488 sec
RG                  175.97
DW                  20.800 usec
DE                    6.50 usec
TE                   300.5 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1           100.6550186 MHz
NUC1                   13C
P1                    9.80 usec
PLW1           58.00000000 W
SFO2           400.2596010 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           14.00000000 W
PLW12           0.35097000 W
PLW13           0.17654000 W

F2 - Processing parameters
SI                   32768
SF             100.6449569 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

Scheme 3 A plausible mechanism for esterification of LA to EL



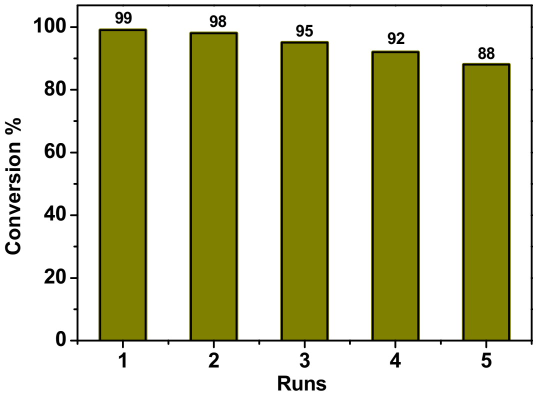


Fig. 11 Recyclability of SAFBPIL after esterification at 70 °C

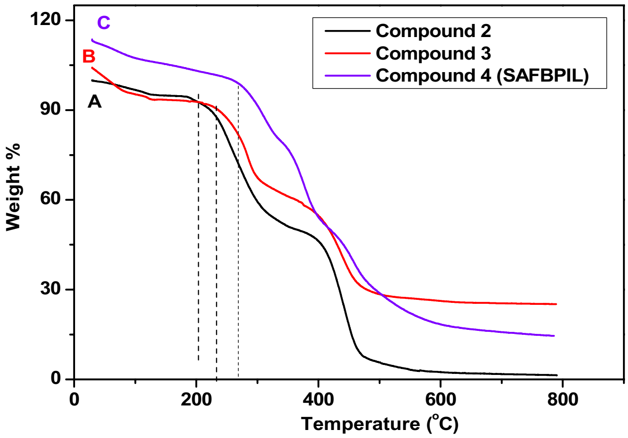


Fig. 12 TGA spectra of (*a*) compound 2, (*b*) compound 3 and (*c*) compound 4 (SAFBPIL)

methodology is advantageous over the normal esterification method. Additionally, sulphuric acid is corrosive to nature.

Further, to test leaching of the catalyst, we have performed Sheldon's hot filtration test [62] which includes filtration of the catalyst part way through a reaction of LA and ethanol under optimized conditions, followed by a continuation of the reaction with the filtrate. It was observed that the reaction stopping completely after filtration confirmed the inactive nature of filtrate. Accordingly, the hot filtration test can be taken as definite evidence that leaching of active catalyst did not occur during 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 30–800 °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. 12c) displayed a continuous decrease in weight from 100 to 800 °C. The initial weight loss (9.056%) at a lower temperature range (up to 100 °C) relates to the removal of moisture content of 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. Since, a decrease in weight of the SAFBPIL commenced 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. 12a) while thermal stability of the compound 3 was noticed up to 232 °C (Fig. 12b). From the thermogram (Fig. 12c) it could be recognized that thermal stability of the SAFBPIL is more compared to the ionic liquid monomer (compound 2) and poly ionic liquid (compound 3).

The catalytic activity of SAFBPIL towards esterification of LA to EL is better than or comparable with the literature reports (Table 1). Moreover, the reactivity of SAFBPIL has been compared with commercially available acidic Dowex® 50WX2 hydrogen form (Table 1, entry 1) and Amberlyst-15 (Table 1, entry 2). It was found that 84% of EL obtained using optimized conditions by Dowex catalyst.

To verify the potential application of EL as biofuels/oxygenated fuel additives [3], we have blended diesel samples with 7.5 and 10% EL and compared the properties with the real diesel sample. Among these, the cetane number, kinematic viscosity @ 40 °C, calorific values (MJ/Kg) and density of the blended samples were found to be comparable with those of the real diesel sample while the flash point and fire point of the blended samples were found to be better with respect to the real sample (Table S1).

4 Conclusions

In the present work, we have successfully synthesized new sulphonic acid functionalized benzimidazolium based poly ionic liquid and characterized by NMR, FT-IR, elemental analysis (C, H, N, S), TGA and BET surface area. Brønsted acidity was determined by using an ion-exchange/neutralization titration method and was found to be 5.55 mmol/g. 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. The heterogeneous catalyst was reused up to five cycles 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. Moreover, prospective application of EL as biofuels/oxygenated fuel additives was confirmed by blending 7.5 and 10% EL with real diesel sample and found to acquire comparable properties as those of the real diesel. 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.

Table 1 Comparison of esterification of LA to EL with various reported heterogeneous catalysts

Entry	Catalyst for the LA esterification	GC conversion (%)	Ref.
1	Dowex® 50WX2	84	–
2	Amberlyst-15	54	[63]
3	20 wt% $H_4SiW_{12}O_{40}$–SiO_2	75	[64]
4	15% (w/w) DTPA/DH-ZSM-597	94	[65]
5	DH-ZSM-5	95	[12]
6	Carbon–SO_3H	99	[3]
7	SAFBPIL	99	Present work

Acknowledgements We gratefully acknowledge SIF DST-VIT-FIST, VIT-Vellore for providing NMR, GC–MS, FT-IR. The authors also acknowledge the financial help provided by DST-SERB (ECR/2016/001866) and 'VIT SEED GRANT', VIT-Vellore for carrying out this research work. The authors express gratitude to "Smart Materials Laboratory for Bio-sensing and Catalysis" for providing basic facilities.

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