Continuous, solvent free, high temperature synthesis of ionic liquid 1-butyl-3-methylimidazolium bromide in a microreactor

Chemical Engineering Division

Abstract

In this work, feasibility of continuous, solvent free high-temperature synthesis of an imidazolium-based ionic liquid 1-butyl-3-methylimidazolium bromide ([BMIM][Br]) in a microreactor is explored. [BMIM][Br] could be produced continuously at 120°C. Effects of residence time, reaction temperature and feed molar ratio on space time yield are studied. Maximum space time yield obtained is 506 kgs/lit-day, which is much higher compared to space time yield reported in conventional batch synthesis.

1. Introduction

Ionic liquids (ILs) has been an arena of intense research in the recent past. ILs have intrinsic ionic conductivity at room temperature, offer a wide electrochemical window, and are non-volatile. Their chemical and physical properties can be readily adjusted by selection of suitable cation and anion. ILs find numerous applications as novel solvents in organic synthesis, catalysis, and electrochemistry. Several studies reported in literature suggest potential applications of ionic liquids in nuclear fuel cycle. Synthesis of imidazolium based ionic liquid usually involves a highly exothermic and fast alkylation reaction. In batch synthesis a solvent has to be used to ensure low operational temperature to avoid thermal degradation of the product. Use of solvent, however, reduces reaction rate. For example in the synthesis of 1-butyl 3-methylimidazolium bromide ([BMIM]Br), time required for complete conversion is reported to be more than 50 hours. Additionally, solvent needs to be separated to get a pure product. Several studies on solvent free continuous synthesis of ionic liquids in miniaturized or microreactors have been reported.

Microreactors are extremely useful for continuous, solvent free and high temperature synthesis of ionic liquids due to high surface to volume ratio ensuring intensified heat transfer. This preempts the possibility of thermal degradation of the product if wall temperature is controlled. Also this obviates the need of using a solvent to prevent thermal runaway.

In this work, we report continuous solvent free high temperature synthesis of 1-butyl-3-methylimidazolium bromide ([BMIM]Br) (Fig. 1) in a microreactor. The heat of reaction is -96 kJ/mol. The study consists of three parts. In part-1, feasibility of continuous solvent free synthesis of [BMIM]Br is demonstrated. In part-2, parametric studies to quantify the effects of reaction temperature, residence time, and feed molar ratio on yield are reported. In the part-3, the different combinations of residence time and temperature are tried to find out the maximum space time yield possible with the microreactor.

Fig. 1: Reaction for synthesis of 1-butyl-3-methylimidazolium bromide ([BMIM]Br)
2. Experimental Procedure

2.1 Chemicals

The reactants, 1-bromobutane (purity > 99 %) and 1-methylimidazole (purity > 99 %), were purchased from Merck. The reactants were used directly without any further purifications.

2.2 Experimental Setup

Schematic diagram of the experimental setup and microreactor are shown in Fig. 2. Two positive displacement pumps (0-10 ml/min flow rate range) feed reactants to the microreactor. The product from the microreactor is collected in a bottle kept in an ice bath to quench the reaction. Residence time, reaction temperature and feed molar ratio are varied to study their effect on yield. Residence time is varied by varying the flow rate. The microreactor used in this study has serpentine microchannels etched in glass chip. The volume of the microreactor is 250µL. Out of the three inlets of the microreactor, only two are used in the present study and the third one is kept closed. The microreactor is mounted on a hotplate to maintain reaction temperature.

2.3 Analysis

The yield of the synthesized ionic liquid [BMIM]Br is evaluated using Volhard titration (for the estimation of Br⁻ ion). The presence of [BMIM]Br in the product obtained in the part-1 of the study is confirmed using a proton NMR spectrum.

3 Results and Discussion

3.1 Demonstration of Synthesis of [BMIM]Br in the Microreactor

Reaction was carried out at two different temperatures of 90°C and 120°C, by keeping the residence time (500 sec) and reactant feed molar ratio (1.2) constant. Unreacted 1-bromobutane phase was at the top of the collected sample due to the density difference and was discarded. The bottom layer was analyzed. Yield was found to be 53% and 72% at 90°C and 120°C respectively. To get the pure product, ionic liquid phase was washed thrice with hot ethyl acetate to remove any unreacted 1-methylimidazole. Then the product was evaporated under vacuum to remove any volatile impurities and thereafter, kept at 10°C for overnight. This process yielded a solid product of [BMIM]Br. The observed m.p. of the product 65-70°C, is very close to the value reported for pure [BMIM]Br. Proton NMR spectrum of the product (Fig. 3) confirms the formation of the desired product [BMIM]Br.
3.2 Parametric Studies

Parametric studies are carried out to find out the effects of residence time, reaction temperature, and feed molar ratio on yield. One parameter is varied at a time by keeping the other two parameters constant. Fig. 4, Fig. 5 and Fig. 6 show the variation of yield with reaction temperature, residence time, and feed molar ratio, respectively.

Fig. 4 shows that the reaction strongly depends on temperature, as the yield increased by a factor of 2.5, when the temperature is raised from 60°C to 120°C and a maximum yield of 64% is obtained at 120°C. The reaction is reported to be a homogeneous reaction initially. However, as IL is produced, reaction becomes bi-phasic with 1-methylimidazole predominantly dissolving in the IL phase. Under this bi-phasic condition, the observed reaction rate will depend on both both the mass transfer and intrinsic reaction rates. Fig. 4 shows clearly that the yield increases with increases in temperature. This may be either due to increase in reaction rate at higher temperatures or an increase in overall volumetric mass transfer coefficient due to lower values of viscosities and interfacial tension at higher temperature leading to finer dispersion or both. Hence, even in mass transfer controlled regime yield is likely to increase with increase in temperature. Further experiments involving imaging of two-phase flow pattern are required to ascertain whether the reaction for the conditions of the experiments reported in this study is mass transfer controlled or kinetically controlled. Fig. 5 shows clearly that the yield increases with increase in residence time and is as expected. Fig. 6 shows that on increasing feed molar ratio (1-bromobutane to 1-methylimidazole), the yield first reduces and then becomes constant. Since 1-bromobutane is less viscous, it is likely to be the dispersed phase. On increasing feed molar ratio keeping residence time constant, flow rate of 1-bromobutane increases while flow rate of 1-methylimidazole reduces. This is likely to make dispersion coarser which in turn may lead to reduced specific interfacial area. With reaction occurring at the interface, the yield is likely to come down due to reduction in specific interfacial area. However, on further increase in feed molar ratio, a stage is likely to come when 1-bromobutane no longer disperses and flow will be parallel or annular flow. Under this condition, the specific interfacial area will not change with increase in feed molar ratio and hence yield is
expected to become constant. However, these explanations need to be substantiated with flow visualization experiments.

### 3.3 Space Time Yields

After carrying out experiments to study the effects of various parameters, reaction was carried out at the low-low, low-high, high-low and high-high combinations of reaction temperature and residence time with the objective of studying the space time yields and production rate. In all experiments molar ratio was kept constant at 1.72 and the results are shown in Table 1.

It may be noted that while the yield is highest (about 72%) for the high-high combination of the residence time and temperature, the highest space time yield (506 kgs/lit-day) is obtained for the low-high combination of the residence time and reaction temperature. This corresponds to a production rate of about 127 grams/day of IL.

<table>
<thead>
<tr>
<th>Residence time (sec)</th>
<th>Reaction temperature (°C)</th>
<th>%Yield</th>
<th>Space time yield (kgs/lit-day)</th>
<th>Production rate (gm/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>60</td>
<td>36.2</td>
<td>57.56</td>
<td>14.39</td>
</tr>
<tr>
<td>500</td>
<td>120</td>
<td>71.6</td>
<td>113.86</td>
<td>28.46</td>
</tr>
<tr>
<td>60</td>
<td>60</td>
<td>24.8</td>
<td>315.17</td>
<td>78.79</td>
</tr>
<tr>
<td>60</td>
<td>120</td>
<td>40.0</td>
<td>506.65</td>
<td>126.66</td>
</tr>
</tbody>
</table>

Table 1: Yield, space time yield and production rate for different combinations of residence time and reaction temperature

4. Conclusions

Continuous, solvent free high temperature synthesis of [BMIM][Br] in a microreactor is demonstrated. Effects of reaction temperature, residence time and feed molar ratio on yield are studied and explained. A high space time yield of about 506 kgs/lit-day is achieved at residence time of 1 minute at 120°C, which is much higher compared to space time yield reported for batch synthesis. This space time yield corresponds to a production rate of about 127 grams/day of IL.

Acknowledgement

The authors gratefully acknowledge analytical support received from PCS, BOD and LSS, ChED of BARC.

References