



# Synergistic effect of ionic liquid and dilute sulphuric acid in the hydrolysis of microcrystalline cellulose



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## ABSTRACT

Hydrolysis of microcrystalline cellulose (MCC) using dilute sulphuric acid in ionic liquid was studied in a batch reactor. Imidazolium based ionic liquid (1-butyl-3-methylimidazolium chloride, [BMIM] Cl) was synthesized by nucleophilic substitution reaction and characterized by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). MCC was dissolved in [BMIM] Cl and subsequently hydrolyzed by catalytic amount of dilute sulphuric acid. The effect of [BMIM] Cl on the crystallinity index, chemical and thermal properties was studied using XRD, FTIR and TGA analysis by regenerating the dissolved MCC. The amount of total reducing sugar (TRS) produced by the dilute acid hydrolysis was determined by 3, 5-dinitrosalicylic acid (DNS) method using UV–Visible spectroscopy. It was observed that prior dissolution of MCC with [BMIM] Cl resulted with high yield of TRS (92%) compared with the direct mixing of MCC, [BMIM] Cl and sulphuric acid catalyst which result in lower yield of TRS (25%).

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## 1. Introduction

Non-renewability of fossil fuels and challenges associated with its utilization such as price fluctuation due to political instability of oil rich regions, environmental concerns, imbalance between energy supply and population growth and uneven distribution of fossil resources in the globe are some of the compelling factors for researchers in the area of renewable energy [1]. Biomass is one of the most promising candidates along with solar, wind and hydrothermal energies for sustainable and renewable energy demand [2]. Being the most abundant and bio-renewable resource, lignocellulosic biomass has the potential to serve as feed stock for the production of second generation bioethanol and platform chemicals without competing with food supply [3]. Lignocellulosic biomass is composed of three bio-polymeric components: cellulose (35–50%), hemicellulose (20–35%) and lignin (5–30%) [4].

Cellulose (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub> is the major component of lignocellulosic biomass which forms microfibrils in plant cell wall to provide strength [5]. It is the most abundant renewable resource and has a potential to be used as feedstock for the production of sugar and platform chemicals [6]. Structurally, cellulose is a linear bio-polymer of anhydroglucose units (AGUs) jointed together in long chains by β-1, 4-glycosidic bonds (or acetal bonds). The number of repeating units of AGUs is termed as the degree of polymerization and it varies from 1000 to 15,000. Each glucose molecule contains five hydroxyl groups and

depending on the degree of polymerization, large hydroxyl groups form inter- and intra-molecular hydrogen bonding [7]. The hydrogen bonding is very strong and forms a large number of networks throughout the cellulose strands [7,8]. As a result of these strong bonding and the co-existence of crystalline and amorphous area, cellulose is recalcitrant for physical as well as chemical treatment. As a result it exhibits low level of activation to hydrolyse into glucose molecules. This challenge continues to be the bottleneck for limited utilization of lignocellulosic biomass [9,10].

In current biomass processing technology, the hydrolysis of cellulose is carried out mainly using enzymatic hydrolysis method which has tremendous advantages with respect to high yield and mild operation conditions. However, this method suffers from slow rate, high cost of enzymes and limited conversion [3]. The use of mineral acids is another alternative approach for hydrolysing cellulosic biomass which demands less time and energy which consequently reduce processing cost. Liquid mineral acids such as sulphuric and hydrochloric acid served for cellulose depolymerisation and degradation for more than a couple of centuries. Sulphuric acid is widely used due to its high catalytic activity, acid strength, hydrogen ion releasing efficiency and lower cost [11].

Several research works have been carried out on the application of sulphuric acid for lignocellulosic biomass processing including pretreatment and hydrolysis stages [12]. With regard to cellulose hydrolysis, dilute and concentrated acids have been investigated so far [13]. Concentrated acid hydrolysis is effective in swelling up cellulose and providing easy breakage of the glycosidic bond to release glucose molecules. However, there are several disadvantages associated such as difficulty in

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product/catalyst separation, reactor corrosion, non-recyclability, waste treatment requirement and consumption of large amount of neutralizing agents [14]. Similarly, dilute sulphuric acid hydrolysis requires high temperature and moderate pressure for efficient hydrolysis of cellulose. However, the higher temperature results in the decomposition of sugar molecules into undesired products such as humins and furan chemicals. This incompatibility between the harsh hydrolysis condition and lower product stability has been a longstanding problem in cellulose hydrolysis using dilute acids. But more recently this old method has been reignited due to the discovery of ionic liquids for lignocellulosic biomass transformation into useful chemicals [15].

Ionic liquids are a new class of material capable of dissolving cellulose [16]. Ionic liquids have unique physico-chemical properties such as; good chemical and thermal stability, non-flammability and low vapour pressure. The application of ionic liquid for cellulose deconstruction was first investigated by Graenacher in 1934 [17]. However, his work was not able to attract much attention at the time due to the high melting point of the ionic liquid. Interestingly, Rogers and co-workers came up with new ionic liquid formulation which has reasonable suitability such as low melting point, extended liquid phase range and unique ability of dissolving cellulose without derivatization which are very crucial properties for biomass transformation. This finding opened a new avenue in utilization of ionic liquids for biomass processing. Several kinds of ionic liquids with a variety of structures have been reported as novel solvent for cellulose dissolution, such as alkylimidazolium salts containing chloride, bromide and fluoride [8,16].

This paper presents the hydrolysis of microcrystalline cellulose (MCC) into reducing sugars using dilute sulphuric acid in 1-butyl-3-methylimidazolium chloride ([BMIM] Cl) media. The effect of hydrolysis temperature, time and prior dissolution of MCC in [BMIM] Cl were investigated in depth. Furthermore, the effect of prior dissolution of MCC on structural, thermal and chemical properties were investigated using SEM, TGA, FTIR and XRD characterization techniques by regenerating the dissolved cellulosic material.

## 2. Materials and methods

### 2.1. Materials

Microcrystalline cellulose (extra pure, average particle size of 90  $\mu\text{m}$ ) is purchased from Alfa Aesar (A Johnson Matthey Company, Heysham, Lancashire, United Kingdom). 1-Chlorobutane, N-methyl imidazole, toluene, acetone, acetonitrile, ethyl acetate, 3, 5-dinitrosalicylic acid, sodium hydroxide, sodium potassium tartrate and phenol were purchased from Spectrochem (Anand Bhuvan, Princess Street Mumbai, India). 1-butyl-3-methylimidazolium chloride ([BMIM] Cl) was synthesized and characterized as reported in the literature with some modification [18].

### 2.2. Methods

#### 2.2.1. [BMIM] Cl synthesis

1-butyl-3-methylimidazolium chloride ([BMIM] Cl) was synthesized from equimolar concentration of 1-chlorobutane and N-methylimidazole in a toluene under atmospheric pressure in reflux condenser. First the N-methylimidazole was dissolved in 65 ml toluene vigorously stirring at 750 rpm at room temperature for 30 min and then 1-chlorobutane was added dropwise. The solution was heated to reflux at 110  $^{\circ}\text{C}$  for 36 h. The reaction product was then placed in a freezer at  $-5^{\circ}\text{C}$  for 12 h. Toluene and [BMIM] Cl formed two separate phases and toluene was removed by simple decantation process. The remaining viscous [BMIM] Cl solution was washed with acetonitrile three times and finally with ethyl acetate to yield a white and clean [BMIM] Cl. Finally, [BMIM] Cl was dried in vacuum at 100  $^{\circ}\text{C}$  and crystallized by adding 0.05 g of pure [BMIM] Cl as crystallization seed and left to stand for 24 h.

#### 2.2.2. MCC dissolution and regeneration

[BMIM] Cl and MCC were dried in oven at 105  $^{\circ}\text{C}$  for 12 h. MCC (5 wt.%) dissolved in [BMIM] Cl was heated at 120  $^{\circ}\text{C}$  through vigorously stirring at 500 rpm for 30 min. After treatment, MCC was regenerated using 20 ml distilled water through vigorously stirring for 15 min at room temperature. The regenerated cellulosic material was filtered using vacuum filtration and washed with distilled water three times and dried under vacuum at 100  $^{\circ}\text{C}$  for 12 h.

#### 2.2.3. Dilute acid hydrolysis

MCC (0.1 g) was dissolved in [BMIM] Cl (2 g) and stirred for 30 min until homogenous solution is observed and then 10 ml of 5% v/v dilute sulphuric acid was added and refluxed at predetermined hydrolysis temperature ( $^{\circ}\text{C}$ ) maintained constant using oil bath. After the completion of the reaction time, the reaction mixture was quenched in ice bath for 15 min followed by PH neutralization using calcium carbonate. Then pure hydrolysate was collected by vacuum filtration. Finally, the hydrolysate was centrifuged at 10,000 rpm for 10 min at room temperature and then stored under refrigerator for further analysis.

#### 2.2.4. Product analysis

The total reducing sugar produced was quantitatively analysed using dinitrosalicylic acid (DNS) assay method in which 1 ml of hydrolysate and 2 ml of DNS reagent mixed followed by heating in boiling water for 10 min [19]. The resulting solution was cooled in ice bath and the absorbance of the solution was measured using UV-Vis spectroscopy (CARY 100 Conc) at 540 nm wavelength. The total reducing sugar yield was determined from calibration curve formed using four point concentration of standard glucose solutions. The percent reducing sugar yield from the hydrolysis was calculated using Eq. (1) [20]. The analytical error in the TRS yield was evaluated to be in the  $\pm 1.4\%$  range.

$$\text{TRS Yield}(\%) = \frac{\text{Reducing sugar weight} \times \frac{162}{180} \times 100}{\text{Dry cellulose weight}} \quad (1)$$

#### 2.2.5. Characterization of [BMIM] Cl

The synthesized [BMIM] Cl was characterized by FTIR and TGA. The FTIR analysis was performed using NICOLET iS50 FTIR and the spectra was collected in a wave number ranging from 400 to 4000  $\text{cm}^{-1}$  at a resolution of 32  $\text{cm}^{-1}$ . The analysis was performed by applying a drop of [BMIM] Cl on KBr pellet.

The TGA analysis was performed using TGA-Q600 instrument (supplied by Waters LLC, USA) with a  $\text{N}_2$  flow of 40 ml/min from room temperature to 600  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ . The TGA analysis was performed to investigate the thermal stability and the upper temperature limit of [BMIM] Cl to determine the minimum decomposition temperature of [BMIM] Cl.

#### 2.2.6. Characterization of original and regenerated MCC

**2.2.6.1. FTIR analysis.** FTIR of original and regenerated MCC were performed to get important information on how the hydrogen bonding in cellulose strands affected during the dissolution process [21]. The FTIR reflectance spectra of original and regenerated MCC were collected for a wave number ranging from 400 to 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  using Thermoscientific NICOLET iS50 Attenuated Total Reflectance-Fourier transform spectroscopy (ATR-FTIR). The samples were measured as a thin film using diffuse reflectance mode of the infrared spectroscopy. During the analysis, the effects of moisture and air were prevented by measuring the background spectra before each sample.

**2.2.6.2. XRD analysis.** The crystallinity index (CrI) of the original and regenerated MCC was measured using X-ray diffraction analysis. The CrI

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