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Hydrolysis of cellulosic bamboo biomass into reducing sugars via a combined alkaline solution and ionic liquid pretreament steps

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ABSTRACT

Dilute acid hydrolysis of cellulosic biomass is not only controlled by the reaction conditions such as temperature, concentration of acidic catalyst and hydrolysis time but also by changing the physical aspects of the reaction media. Therefore, overcoming the insolubility of cellulose by the use of effective solvent without having to derivatize their basic functional groups is of tremendous advantage in the utilization of lignocellulosic biomass. Ionic liquids are considered as the most suitable solvents to dissolve cellulosic biomass and overcome the recalcitrant nature of lignocellulosic biomass. This study investigates the valorisation of bamboo biomass regenerated from alkaline solution and ionic liquid pretreament steps followed by dilute sulphuric acid hydrolysis. Lignin removal from the biomass as a result of pretreatment steps was analysed by crystallinity index determination, surface morphology and thermal stability analysis. The solid biomass materials were characterized using FTIR, XDR, SEM, TGA and Elemental analysis techniques to investigate the effect of the pretreatment steps on the properties of the original bamboo biomass. Alkaline treatment was found to be effective against lignin and hemicellulose removal. However, it did not remove the complexity of the cellulosic portion of the biomass with equal success. The crystallinity of the recovered cellulosic biomass could be effectively reduced by using the ionic liquid pretreatment. Investigation revealed that the yield of total reducing sugars increased to 64% after alkaline solution pre-treatment in comparison to only 30% yield of reducing sugar in the untreated biomass sample. After both pretreatment steps, the yield of reducing sugar further increased to 80%.

1. Introduction

The potential of biomass as feedstock for transportation fuels and platform chemical production had not been given enough attention because of the historic shift towards petroleum based resources in the twentieth century [1]. However, more recently, limited availability and environmental concern are the compelling factors in the pursuit of substituting fossil based energy dependency [2]. Lignocellulosic biomass is the ideal substitution for fossil based transportation fuel and platform chemicals production due to its abundance, low cost, even distribution and carbon-neutrality [3] [4]. Lignocellulosic biomass is a porous micro-structured composite which is composed of three biopolymers; lignin (15–25%), hemicelluloses (23–32%) and cellulose (38–50%) [5] [6]. These constituents form three-dimensional polymeric composites to provide structural rigidity and stability to the cell wall of the plant. Cellulose and hemicellulose combined (holocellulose) forms the carbohydrate portion of the lignocellulosic biomass which can be depolymerized into simple sugars such as glucose and xylose. Lignin serves as a binder to hold together the cellulose and hemicellulose in the cell wall through the complex intra and inter-hydrogen bonding networks [7].

The complex nature of the lignocellulosic biomass creates a major challenge in developing a competitive process technology to convert lignocellulosic biomass into fuels and chemicals in economically feasible and environmentally friendly manner [8]. In addition, lignocellulosic biomass cannot be directly converted into bioethanol due to the presence of lignin and the recalcitrant nature of the cellulosic portion of the biomass [9] and these obstacles have been long standing challenges on the utilization of lignocellulosic biomass. However, more recently the discovery of ionic liquids for biomass transformation has opened a new area of research to utilize lignocellulosic biomass for intermediate chemical production such as sugars and furan derivatives. Ionic liquids are special

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solvents that can dissolve materials that are otherwise considered insoluble in conventional solvents. Ionic liquids have special properties such as broader liquid temperature, high thermal stability and negligible vapour pressure which are the vital properties required in the transformation lignocellulosic biomass [10].

In the conversion process of lignocellulosic biomass into transportation fuel and platform chemicals, pretreatment is most important step for conditioning biomass. Pretreatment plays an important role in fractionating the lignocellulosic biomass to its components and improve accessibility of cellulosic portion for downstream processes. However, it is the most energy intensive and economically expensive process [11]. Biomass pretreatment processes are categorized into different methods ranging from physical, physico-chemical, and chemical to biological methods based on the techniques applied. Alkaline solution pretreatment is a type of chemical pretreatment effective in the delignification of biomass without significantly affecting cellulosic structure of the biomass [12,13]. However, this method of pretreatment has limited effect on the reduction of the crystallinity of pretreated biomass at mild concentration and temperature to reduce the recalcitrant behaviour of cellulosic biomass rendering resistance in the hydrolysis process. Therefore, ionic liquid pretreatment which is also a type of chemical pretreatment method known for its specific purpose in dissolving and reducing the crystallinity of cellulose is incorporated following the alkaline solution pretreatment. This method reduce the crystallinity index of the cellulosic biomass so that the reactivity of the biomass could be enhanced during acid hydrolysis [15,16].

In this study, bamboo biomass was pretreated in alkaline solution and ionic liquid solvent for the purpose of improving acid hydrolysis and reducing the recalcitrant behaviour of the biomass through the combined effect of pretreatment steps to partially remove lignin and reduce crystallinity index. The biomass obtained from Haryana, India was studied for structural, morphological, chemical and physical changes exhibited as the result of the pretreatment steps. All the three bamboo biomass samples (original bamboo biomass, alkaline pretreated and ionic liquid pretreated) were subjected to dilute acid hydrolysis in ionic liquid solvent media (1-butyl 3-methylimidazolium chloride ([BMIM] Cl)). The total reducing sugar yield (TRS) was estimated by 3, 5-dinitrisalcylic acid (DNS) array method using UV–Visible spectroscopy. The effects of hydrolysis temperature, time, acid concentration and substrate type on the TRS yield were studied in detail. The original bamboo biomass is referred as "Original bamboo biomass" (OBB), the solid biomass recovered from alkaline solution and [BMIM] Cl pretreatment was referred as "Recovered Biomass I" (RBI) and biomass obtained after acid treatment is referred as "Regenerated Biomass II" (RBII).

2. Materials, experimental and characterization

2.1. Materials

Sulfuric acid (98%), N-methylimidazolium, 1-chlorobutane, acetonitrile and ethyl acetate were purchased from Spectrochem (Anand Bhuvan, Princess Street Mumbai, India). Bamboo biomass (Dendrocalamus Strictus) was obtained from Haryana, India. All chemicals were used without further purification.

2.2. Experimental

2.2.1. [BMIM] Cl synthesis

1-butyl 3-methylimidazolium chloride ([BMIM] Cl) was prepared form 1-chlorobutane and N-methyl imidazole in a toluene media as reported in literature [16] [17].

2.2.2. Ash content

The ash content of the bamboo biomass was determined as part of the total composition of the bamboo biomass. The determination was performed using the National Renewable Energy Laboratory (NREL) procedure (Sluiter et al., 2008). In a typical ash content measurement, 2 g of the oven dried bamboo biomass was placed into weighed crucible and the sample was heated in muffle furnace (KHERA INSTRUMENTS PVT.LTD, INDIA) at 575 °C for 5 h. After carefully removing the sample in the crucible, both the sample and the crucible weighed. The ash content of the bamboo biomass was estimated as percent of residue from the heating process and calculated from the Equation (1):

$$\%Ash\,content = \frac{Weightcrucible\,plus\,ash - Weightcrucible}{Oven\,dried\,Weightsample} * 100\% \tag{1}$$

2.2.3. Extracts removal

Three step extractive removal procedure was used to remove extracts from the bamboo biomass. Soxhlet extraction setup was used to remove the extracts while water, ethanol and hexane were used as extraction solvents as reported in literature [18]. In a typical extraction procedure, 5 g of original bamboo biomass was extracted for 2 h in each solvent and the weight change was measured after drying the extracted biomass after 24 h at 105 °C in vacuum drying oven. Reduction in weight was observed after every treatment step as every step resulted in removal of some component of the biomass.

2.2.4. Pretreatment

Extractive removed bamboo biomass sample weighing 1 g was treated with different concentration of sodium hydroxide solution in a round bottomed flask at predetermined temperature and time in 1:20 wt ratio of biomass to alkaline solution loading. The solid biomass was recovered by vacuum filtration using porcelain Bucher funnel and then washed three times with distilled water. The wet biomass material was dried at 105 °C in vacuum dry oven for 24 h. Similarly, the precipitated lignin was separated using vacuum filtration and dried at 110 °C for 24 h. The supernatant obtained from the partially dissolved biomass was adjusted to a pH of 5 using a dilute solution of HCl and recovered as dark brown precipitate of lignin (Silverstein et al., 2007). The effect of temperature, time and alkaline solution concentration was studied to determine degree of delignification and the crystallinity index of the recovered biomass.

After determining the optimal condition for alkaline solution pretreatment, the biomass was treated in a larger volume batch reactor. Extracts removed biomass weighing 10 g was treated with 5% (W/V) of sodium hydroxide solution in a sealed AMAR Autoclave reactor for 30 min at 130 °C and all the other post-treatment processes followed as described above. Finally, the biomass recovered from alkaline pretreament step was further treated using [BMIM] Cl to reduce the crystallinity of the alkaline treated biomass (RBI) and overcome the recalcitrant nature of the biomass. In this step 2.5 g of RBI was dissolve in 12.5 g of [BMIM] Cl and heated at 120 °C for 6 h with continuous stirring. After completion of treatment time, 60 ml of Mill-Q water was added and stirred vigorously for 15 min to regenerate the cellulosic rich bamboo biomass (RBII). RBII was finally collected from the solution using vacuum filtration and washed with distilled water three times and then dried under vacuum at 105 °C for 24 h.