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Efficient hydrolysis of Babool wood (Acacia nilotica) to total reducing sugars using acid/ionic liquid combination catalyzed by modified activated carbon

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ABSTRACT

This study aims to examine the potential of Babool wood (*Acacia nilotica*) as an alternative and sustainable resource to produce value added chemicals and/or useful intermediates like sugars. The performance of Babool wood digestability and hydrolysis to sugars was compared using three acids: H_2SO_4/H_3PO_4/HCl and ionic liquid [Bmim] Cl catalyzed by modified activated carbon. Hydrolysis using sulphuric acid treated Babool wood leads to the formation of total reducing sugar (TRS) ranging from 53.34% to 83.67% yield under different conditions. Babool wood treated with acid was characterized using Fourier Transformation Infrared Spectroscopy, X- Ray Diffraction and Lignocellulosic compositional analysis. Further, the effect of process variables such as acid strength, acid concentration, acid to Babool wood ratio, Babool wood particle size, hydrolysis time, and temperature on the TRS yield was explored. Maximum TRS yield was observed to be 83.67% in a reaction time of 60 min using $-80 + 100$ mesh of Babool wood at 393 K. Kinetic results were successfully simulated with literature model ($R^2 > 0.9$) for rate of formation of sugar. This study provides a single step approach for Babool wood hydrolysis to sugars.

1. Introduction

The use of petrochemicals has increased exponentially in last few decades but depletion of conventional resources has forced researchers to look for alternative sustainable sources. Lignocellulosic materials are the most efficient renewable clean resource due to its potential stability and carbon neutrality [1,2]. Significant efforts are being made globally for the conversion of lignocellulosic components to hydrocarbons such as total reducing sugar, 2, 5-Dimethyl furan, Levulinic acid, 2, 5 Furan dicarboxylic acid [3–5]. Complex structure of hemicellulose-lignin along with highly ordered inter and intra hydrogen network of cellulose is a hindrance for the hydrolysis of lignocellulosic biomass [6–10]. To overcome the recalcitrant nature of lignocellulosic material, pretreatment and hydrolysis is important for production of value added products [6,11–13]. Literature reports various pretreatment techniques such as steam explosion, liquid hot water pretreatment, ammonia fibre expansion and microbial pretreatment but due to challenges and disadvantages associated with these processes such as excessive degradation of physiochemical properties of cellulose and hemicellulose, high energy input and slow reaction time required appropriate and potential candidate for disintegrating biomass matrix [14–16]. Utilization of ionic liquids and/or mineral acids pretreatment (dilute or concentrated) has gained attention and are commonly used methods to reduce the crystallinity of biomass matrix [17–19].

The hydrolysis of bamboo biomass in ionic liquid media catalyzed with chitosan based solid acid catalyst has been reported and maximum TRS yield was found to be 73.42% in 24 h at 120 °C [3]. Also, the pretreatment of softwood using [Bmim] Cl has been studied and 78% of glucose yield was reported at 130 °C in 15 h [20].

These studies conclude that ionic liquid helps in breaking the recalcitrance nature of biomass but requires long reaction time. Some studies have been reported using only mineral acids. Sulphuric acid hydrolysis on olive biomass has been studied and 17.2% of TRS yield was observed in a reaction time of 4 h at 90 °C [21]. Also, the pretreatment effect on wheat straw using 5 wt% of H_2SO_4 at 50 °C was reported and maximum glucose yield of 96% was

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observed in a reaction time of 72 h [22]. These studies also indicate that long reaction time is a major drawback for biomass hydrolysis.

Literature reports that combination of ionic liquid and mineral acid has a synergistic effect on the hydrolysis process [2,23–25]. The combined effect of [C_4mim] Cl and dilute hydrolchloric acid was studied and maximum TRS yield of 4% in 0.5 h was observed using cornstalk and 85% TRS yield in 1 h using pinewood at 100 °C [26]. Hydrolysis of Bamboo biomass was also studied using dilute hydrochloric acid in [Bmim] Cl media and maximum TRS yield of 67.1% was obtained in a reaction time of 4 h at 100 °C [1].

Some studies reported utilization of heterogeneous catalyst and ionic liquid for the hydrolysis of lignocellulosic biomass. Literature reports that chemical treatment of activated carbon using mineral acids provide appropriate amount of brØnsted acid and hence leads to fast hydrolysis [27,28]. Switchgrass hydrolysis catalyzed by activated carbon modified with sulphonic acid was reported and maximum glucose yield of 16.91% was observed in a reaction of 15 min at 90 °C [29]. Also, hydrolysis of microcrystalline cellulose catalyzed by sulphuric acid treated activated carbon in [Bmim] Cl medium was also studied and maximum yield of TRS (44.57%) and 5-Hydroxymethyl Furfural (36.33%) was observed in a reaction time of 1 h at 120 °C [28].

In the present work, combination of acid/IL catalyzed by modified activated carbon was studied on hydrolysis of Babool (*Acacia Nilotica*) wood for the production of sugars. Also, a comparative study was conducted to examine the effect of acid strength using different acids namely; H_2SO_4, H_3PO_4 and HCl on hydrolysis in [Bmim] Cl ionic liquid and modified activated carbon. Lastly, kinetic study was conducted to determine rate of formation of TRS.

2. Materials and methods

2.1. Materials

Babool wood was acquired from GGSIP University, New Delhi, Glucose standard solutions (1%), 3, 5 Dinitro Salicylic Acid, 1-Butyl-3-Methylimidazolium chloride, Sulfuric acid, Phosphoric acid and Hydrochloric acid were purchased from Central Drug House Pvt. Ltd. (CDH) Vadodara, Gujarat. Activated carbon (AC) was purchased from Merck Life Sciences Pvt. Ltd, Darmstadt, Germany.

2.2. Methodology

2.2.1. Screening of Babool wood

The Babool wood (Acacia nilotica) was thoroughly washed with distilled water for the removal of impurities followed by drying in hot air oven at 100 °C for 12 h. Dried Babool wood was crushed in ball mill and sieved to fractions with particle size ranging from (i) −20 mesh (ii) −20 to +40 mesh (iii) −40 to +60 mesh (iv) −60 to +80 mesh (v) −80 to +100 mesh (vi) −100 to +120 mesh and used as feed.

2.2.2. Preparation of catalyst

Modified activated carbon was prepared and characterized as reported in our previous work [28] and denoted as ACS. The procedure is as follows: 20 g of activated carbon was mixed thoroughly using 18 M of sulfuric acid in 100 ml of deionised water and refluxed for 4 h at 75–80 °C. The resultant solution was washed thoroughly using deionised water to prevent ions elution in reaction system. Finally, resultant modified activated carbon (ACS) was filtered through vaccum filter and dried for 12 h at 120 °C.

2.2.3. Characterization of Babool wood

Untreated and acid treated Babool wood using three different acids namely; H_2SO_4, H_3PO_4 and HCl were characterized using Fourier Transformation Infrared Spectroscopy (FT-IR) and X- Ray Diffraction (XRD). FT-IR analysis was conducted to determine change in functional groups before and after acid treatment. A reflectance spectrum was performed for wavenumber ranging from 400 to 4000 cm^{-1} with resolution of 4 cm^{-1} using Thermoscientific Nicolet IS50 Fourier transform spectroscopy, Thermo Fisher Scientific, Massachusetts, United States. The crystallinity of untreated and acid pretreated biomass was measured using X- Ray Diffraction (Xpert pro PAN Analytical model), Malvern Panalytical Ltd. United Kingdom. The diffracted intensity of Cu Kα radiation generated at 40 kV and 15 mA was recorded with diffracted angle ranging from 10 to 90° with scanning speed of 2°/minute. Lignocellulosic composition was determined using TAPPI (Technical Association of the Pulp and Paper Industry) standards.

2.2.3.1. Compositional analysis.

2.2.3.1. Compositional analysis. Extractives present in Babool wood were determined using solvent extraction method according to TAPPI 204 cm-97 [30]. Samples were thoroughly washed with distilled water for removing impurities and dried at 100 °C for 12 h in hot air oven. Water soluble compounds such as nitrogeneous materials, inorganic and non-structural compounds were determined using 100 ml of distilled water for 6 h in a soxhlet apparatus. The sample was then dried again at 105 °C for 2 h and was referred as water soluble compounds. Ethanol extractives were determined using another set of soxhlet extraction for the removal of waxes and chlorophyll using 100 ml of ethanol (95%) for 6 h and the final extractive content was measured as total mass loss during the procedure [31]. The sample was then removed from soxhlet apparatus and dried again at 105 °C for 2 h and referred to as ethanol extractives.

For determination of total solids, Babool wood sample was dried at 100 °C for 12 h in hot air oven according to the National Renewable Energy Laboratory procedure (ASTM E1756-01 and T412 om-02) [32]. As per the procedure, the sample was heated at 105 °C in hot air oven for 4 h and then allowed to cool at room temperature to determine total solid percentage in the Babool wood.

The total content of cellulose present in Babool wood, based on TAPPI standard, was determined as the amount of α-cellulose which is soluble in 17.5% NaOH solution. Analysis of α-cellulose was conducted by stirring 1 gm of biomass in beaker with 20 ml of 17.5% NaOH solution at 30 °C for 45 min in water bath. Then, 10 ml of distilled water was added in to the solution and shaken again for another 15 min. Finally, the solution was washed with 10 ml of 10% acetic acid and filtered using whatman filter paper. The obtained sample (α-cellulose) was dried in hot air oven for 12 h at 80 °C and weighed. Similarly, total content of holocellulose in Babool wood was determined as the sum of hemicellulose and cellulose. In this analysis, initially 1 gm of Babool wood was treated with 30 ml of distilled water that contains 0.04 ml of acetic acid and 0.4 g of sodium chlorite for 60 min at 75 °C. Further, same proportion of acetic acid and sodium chlorite (0.04 ml; 0.4g) was added in the mixture successively in every 60 min for 3 h. Finally, the obtained sample (holocellulose) was filtered and dried in hot air oven for 12 h at 80 °C and weighed [24].

Total content of lignin in Babool wood was determined as klason lignin in the form of acid insoluble residue according to TAPPI method; T 222 om-02 [32]. Initially, 1 g of Babool wood was dissolved in 15 ml of 72% H_2SO_4 and the mixture was stirred at 20 °C for 4 h. Then, sample was diluted with water up to 3% H_2SO_4 and subsequently 575 ml of water was added in to the mixture and refluxed for 4 h. Finally, samples were dried in hot air oven at 105 °C for 5 h and weighed [31].