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Can cellulose be a sustainable feedstock for bioethanol production?

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ABSTRACT

Bioethanol is a promising substitute for conventional fossil fuels. The focus of this work was to convert commercial cellulose (Avicel® PH-101) to ethanol. In the first step, cellulose was selectively converted to glucose. Cellulose hydrolysis was carried out under microwave irradiation using hydrochloric acid as catalyst. Process parameters – acid concentration, irradiation time, and power consumption – were optimized. A yield of 0.67 g glucose/g cellulose was achieved under modest reaction conditions (2.38 M acid concentration, irradiation time – 7 min, 70% of power consumption). The glucose thus produced was then converted to ethanol by fermention with yeast (*Saccharomyces cerevisiae*). The speed, selective nature of the process and the attractive overall yield indicate that cellulose, a vast carbohydrate source, could indeed be a sustainable feedstock for bioethanol production.

1. Introduction

The world's energy resources are depleting, and a diligent search for alternative and renewable energy sources is essential. Ethanol obtainable by fermentation of sugars is one such promising energy source. Bioethanol is already being used as a transportation fuel in Brazil, and is blended into petroleum in the US. Cellulose is the most abundant organic material on earth and can be found in terrestrial plants, algae, and waste materials (agricultural waste and newspapers). It is therefore considered a promising starting material for the production of glucose and ethanol [1–10]. Hydrolysis of cellulose, a polymer of β1-4 linked glucose units, to glucose is a challenge. The inter and intra molecular hydrogen bonds are responsible for the highly crystalline structure and water insolubility of cellulose [11]. Optimal temperature and pressure for the conversion of waste cellulose to glucose in an autoclave were found to be 220–240 °C and 500 psi respectively [12]. In general, dilute acid hydrolysis of cellulose requires high temperatures and long reaction time. The use of concentrated acid permits lower temperatures and shorter reaction times but then more glucose degradation takes place [13].

Zhang et al. [14] reported the conversion of cellulose into glucose with a 37% yield in an ionic liquid [C4mim]Cl, employing a solid acid catalyst under microwave irradiation. Amarasekara et al. [15] used Bronsted acidic ionic liquids, namely, 1-(1-propylsulfonic)-3-methylimidazolium chloride and 1-(1-butylsulfonic)-3-methylimidazolium chloride, to convert cellulose (Sigmacell) under conventional heating for 1 h into 14% glucose yield and to a 62% yield of total reducing sugars.

Orozco et al. [16] reported the conversion (maximum of 50%) of cellulose and grass clippings into glucose in a closed vessel microwave system using phosphoric acid and a temperature of 175 °C. Sugar degradation is the major reaction at reaction temperatures of 150–200 °C. Vitz et al. [17] explored the efficacy of a variety of ionic liquids as solvents for Avicel® PH-101. Li et al. [18] converted cellulose to glucose by ball milling the cellulose to reduce the crystal size, followed by the hydrolysis under microwave irradiation for a period of 3 h at a high concentration of catalyst, $H_3PW_{12}O_{40}$, (88 wt.%). The development of a fast and green process for cellulose hydrolysis which avoids pretreatment or special solvents or harsh hydrolysis reaction conditions was therefore the objective of the current research work which reports the conversion of highly crystalline, Avicel® PH-101 (commercial cellulose) obtained from cotton linters, into glucose in the presence of hydrochloric acid under microwave (MW) irradiation. The hydrolysis of cellulose is conducted at approximately 100 °C and atmospheric pressure in a domestic microwave (MW) oven. MW heating consumes less energy than conventional heating, offers lower reaction time, and generates uniform heating without creating hot spots. The heating is generated within the material itself, and flows from the center to the circumference.

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Consequently, thermal gradients and heat flow are different than in conventional heating [19].

2. Experimental

2.1. Materials

Avicel® PH-101, glucose, horseradish peroxidase (HRP) and glucose oxidase (GOx) were purchased from Sigma–Aldrich and used as procured. Aqueous solutions of HCl of varying concentrations were prepared from a 32 wt.% concentrated HCl solution. Baker's yeast was purchased from the supermarket. Stock solutions of enzymes HRP, GOx were prepared using commercially available enzymes.

2.2. Cellulose hydrolysis

Typical cellulose hydrolysis reaction was carried out by dispersing Cellulose (Avicel® PH-101, 1.0 g) in 20 mL, of 1 M HCl. The mixture was subjected to microwave irradiation for 5 min. under stirring in a 100 mL RB flask., The contents of the RB flask were then filtered (Whatman paper no 1), and the hydrolyzate was analyzed using ^{13}C NMR. The residue was dried and weighed using Precisa 205 ASCS electronic balance to estimate the conversion of cellulose. Energy consumption measurements were performed using a Hioki 3334 power hitester.

2.3. Microwave heating

The cellulose hydrolysis was carried out in a domestic microwave (MW) oven operated at 2.45 GHz in batch mode in air under atmospheric pressure. The output of the domestic microwave reactor was 1200 W. The microwave oven was modified so as to accommodate a reflux condenser passing through its roof (for enhanced safety of operation and to condense evaporation from the reaction vessel) and was equipped with a stirring facility [20].

2.4. Fermentation of the glucose produced from cellulose

Glucose fermentation was carried out with the aid of baker's yeast, *Saccharomyces cerevisiae* purchased from the supermarket. Fermentation was carried out in a 100 mL Erlenmeyer flask. The fermentation medium comprises of 20 mL of neutralized hydrolyzate (pH-7). To this medium, 0.2 g of yeast is added. The contents were stirred for 12 h at 30 °C. The concentration of glucose in the fermentation broth is quantified at regular intervals of time to moniter the fermentation process. An aliquot was collected after 12 h and analyzed by ^{1}H NMR to determine the fermentation products.

2.5. Glucose quantification using an enzymatic assay

The glucose assay suggested by Frost [21] was employed for glucose estimation in the hydrolyzate and the fermentation broth. Typical method involves the oxidation of glucose to δ-gluconolactone using the FAD-dependent enzyme glucose oxidase. The glucose oxidase is regenerated in its oxidized form via molecular oxygen to produce hydrogen peroxide. The hydrogen peroxide is then used by a horseradish peroxidase to catalyze the oxidation *o*-phenylenediamine dihydrochloride (OPD), which produces an orange brown coloration with typical absorption at 450 nm.

2.6. ^{13}C And ^{1}H NMR analysis

Samples from the hydrolyzate were collected after the microwave irradiation and analyzed by ^{13}C NMR spectroscopy for the confirmation of glucose formation. Aliquots of sample from the fermentation broth were analyzed using ^{1}H NMR to confirm the formation of ethanol produced form glucose fermentation. D_2O was employed as solvent. Typical sample for analysis comprise of 400 μL of the analyte and 200 μL of the solvent. Spectral analysis was carried out at room temperature. ^{13}C and ^{1}H NMR spectra were recorded on Bruker Avance DPX 300.

3. Results and discussion

3.1. Characterization of the hydrolyzate

The hydrolyzate obtained from the microwave irradiation (5 min.) of aqueous dispersion of cellulose (1.0 g) in the presence of 1 M HCl (20 mL) was subjected to ^{13}C NMR analysis. Peaks typical of D-glucose (60.2 (C6), 69.0 (C4), 70.7, 72.2 (C2), 73.6 (C3), 75.1 (C5) and 95.1 (C1, β), 91.4 (C1α) ppm) only were observed (Fig. 1). For comparison the ^{13}C NMR spectrum of an authentic sample of glucose is also depicted in Fig. S1. No other products such as hydroxy methyl furfural (HMF) or levulinic acid or formic acid were observed indicating that the process of hydrolysis is selective. In order to obtain maximum glucose yield, various reaction parameters, such as concentration of the acid (HCl), irradiation time and microwave power were optimized.

3.2. Effect of dilute acid concentration on glucose amount

To evaluate the influence of the acid concentration on the amount of glucose, different concentrations (1, 2.5, 3.14, 5, 7.5 wt.% (0.3–2.5 M)) of acid were used with an irradiation time of 7 min. The amount of glucose obtained in each case is depicted in Fig. 2. The highest glucose yield (0.67 g/g of cellulose) is obtained for the 7.5 wt.% HCl. The cellulose conversion was found to be 67%. The unreacted residue (33 wt.%) was found to be cellulose. Although no significant rise in glucose amount is seen in the concentration range of 0.3–0.789 M, a steep rise in glucose formation is observed beyond 1 M concentration of HCl.

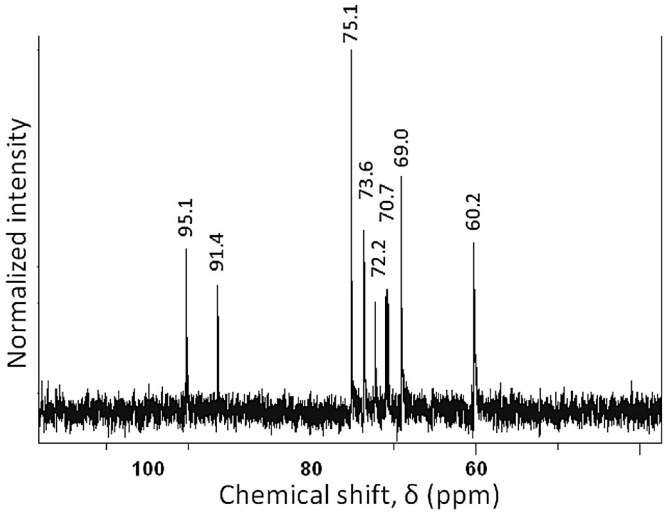

Fig. 1. ^{13}C NMR spectrum of the hydrolyzate from cellulose hydrolysis.