



## Research paper

# Glucose production from lignocellulosic biomass using a membrane-based polymeric solid acid catalyst



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## ABSTRACT

Large-scale production of biomass-derived fuels and chemicals requires the economical and efficient depolymerization of lignocellulosic biomass into sugars and fuels. Catalytic hydrolysis of raw wheat straw for the production of glucose was conducted using a designed porous membrane-based polymeric solid acid catalyst consisting of poly (ionic liquid) and polysulfonic acid chains. The catalyst demonstrated superior activity and selectivity with glucose yield reached over 50% from the un-pretreated raw straw. Under the optimal conditions, over 80% of cellulose and over 90% of xylan were converted to soluble sugars and furans with over 60% glucose or xylose yields reached respectively from pretreated straw biomass. Our catalyst demonstrates high glucose and total reducing sugar (TRS) yields from lignocellulosic biomass with promising application for the future lignocellulosic biorefinery.

## 1. Introduction

Lignocellulosic biomass represents the largest renewable carbon resource in the biosphere. It has been presented as the most promising alternative to petroleum for the production of liquid fuels, chemicals and materials during the current energy crisis and climate change [1]. The widely available lignocellulosic biomass is mainly composed of three polymers: cellulose (35–50 wt%), hemicellulose (20–35 wt%) and lignin (5–30 wt%) (variation in the percentages is due to the difference in species, varieties, plant parts and environmental conditions) [2–4]. Conversion of the polysaccharide fraction of biomass, i.e. cellulose and hemicelluloses, for production of soluble sugars has been intensively investigated due to the fact that biomass-derived soluble sugars can serve as the versatile intermediates for the production of cellulosic biofuels and value-added products via biochemical or chemical conversions [5–7].

A typical biochemical conversion process includes pretreatment to reduce biomass recalcitrance, enzymatic hydrolysis to produce soluble carbohydrates and fermentation to produce fuels or bio-based products. However, both pretreatment and enzymatic hydrolysis steps entail many limitations such as the corrosive nature of the acid or base used for pretreatment with high material and construction cost, the high cost of enzyme cocktail and slow reaction rate during enzymatic digestion

[1]. Chemical conversion process involves the use of mineral acid or metallic catalyst for producing soluble sugars from biomass. Mineral acids such as H<sub>2</sub>SO<sub>4</sub> have long been used for catalytic production of sugars from biomass [8–10]. Environment-friendly solid acid catalyst, however, is emerging as a substitute for mineral acid because of many advantages it possesses over mineral acid, such as the easy recovery of catalyst for reuse, non-corrosive, no waste acid to dispose [11,12]. The major problem associated with using solid acid catalyst for biomass conversion is that it is a solid-solid reaction in the liquid phase leading to inefficient catalytic conversion. However, if a solvent can partially dissolve the lignocellulosic biomass or disperse the catalyst, the catalytic conversion will be significantly enhanced. Moreover, earlier studies [13–17] demonstrate that solvent and solvent mixtures play a critical role in biomass fractionation and conversion. It is known that ionic liquids (ILs) and  $\gamma$ -valerolactone (GVL), both are considered green solvents, can promote biomass conversion by solubilizing biomass components including cellulose and lignin effectively. They have been implemented as solvent systems for catalytic transformation of lignocellulosic biomass into a wide variety of products [3,5,18–20]. In contrast to the high cost of ILs, GVL can be produced at potentially low cost from biomass and can be recycled and reused after purification [21,22]. Earlier studies indicate that GVL speeds up the cellulose hydrolysis and prevents the formation of humins [23]. There is evidence

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that GVL affects the activation energy of sugar reactions [24].

Previous studies [25–27] focused on catalytic conversion of crystalline cellulose to glucose using solid acid catalysts, however, to the best of our knowledge, there have been very few literature reports on producing glucose or xylose using actual lignocellulosic biomass with a solid acid catalyst. Schneider et al. depolymerized barley straw using several solid acids and obtained a maximum total reducing sugars (TRS) yield of 42% using oxalic acid dihydrate as catalyst [28]. Several other studies focused on synthesizing carbonaceous solid acid through carbonation of biomass materials or sugars followed by sulfonation, and conducted the hydrolysis of corn cobs as well as rice straw using water or [BMIM][Cl] as solvent [29–32]. Victor et al. [33] prepared activated carbon supported tungstenphosphoric acid ( $H_3PW_{12}O_{40} \cdot nH_2O$ ) and optimized glucose production from rice straw. Ramli and Amin [34] catalyzed the hydrolysis of oil palm biomass for the production of reducing sugars in the presence of 1-butyl-3-methylimidazoliumbromide ([BMIM]Br) and Fe/HY (one type of H-form zeolite) catalyst. Li et al. [35] carried out catalytic hydrothermal saccharification of rice straw using sulfonated mesoporous silica (SBA-15) in water. Rinaldi et al. [36] applied macroreticulated styrene–divinylbenzene resins functionalized with sulfonic groups (Amberlyst 15DRY) to hydrolyze wood spruce in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) to produce reducing sugars. Lai et al. [37] prepared  $Fe_3O_4$ -SBA- $SO_3H$ , a magnetic solid acid catalyst, and used it for saccharification of corn cob in water. However, all the previous studies using solid acid catalysts only focused on total reducing sugar (TRS) yields and with less than 65% obtained [32]. The reported glucose yields from a couple of studies [29,33] demonstrated only with less than 35%.

Previously we designed and synthesized an enzyme mimic polymeric solid acid catalyst for cellulose hydrolysis [38] as well as hydrolysis of pretreated cellulosic corn stover biomass [23] to produce reducing sugars. The catalyst consists of two polymer chains randomly grafted on the surface of a substrate. Poly (vinyl imidazolium chloride) ionic liquid (PIL) chain was grafted by UV-initiated polymerization to facilitate cellulose dissolution. Poly (styrene sulfonic acid) (PSSA) chain was grafted by atom-transfer radical polymerization (ATRP) to hydrolyze the cellulose substrate. The ratio of the two polymer chains, their respective densities and the polymer chain length can be varied to optimize the catalytic activity. TRS yields as high as 97% were obtained when the catalyst was used to depolymerize crystalline cellulose in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) solvent [38] at mild temperature of 130 °C. Moreover, near quantitative TRS yields were obtained for the depolymerization of acid- and base-pretreated corn stover biomass in [EMIM]Cl and [EMIM]Cl/GVL mixed solvents [23]. However, these early studies focused only on total reducing sugars, not on the production of monosaccharides.

In the current study, the previously optimized polymeric solid acid catalyst was further used for hydrolysis of real biomass feedstock (wheat straw) with the focus on maximizing the glucose yield through optimizing reaction temperature, reaction solvent, water content in the solvent mixture, and the loadings of biomass and catalyst. Furthermore, catalytic conversion of alkali and acid pretreated wheat straw was also conducted and compared to that of raw straw in order to investigate the effects of pretreatment on biomass conversion. Finally, recyclability of the solid acid catalyst was demonstrated by reusing the catalyst for multiple times. The objective of present study was to investigate the catalytic performance of our polymeric solid acid catalyst for glucose production using real lignocellulosic biomass and optimize the catalytic conversion process.

## 2. Experimental

### 2.1. Materials

Natural wheat straw was purchased from Thunder Acres family farm located in south central Kansas, USA. Before hydrolysis

experiments, the straw was milled using a coffee grinder and dried in a VWR symphony vacuum oven (414004–582, Radnor, PA, USA) at 40 °C till the biomass weight no longer changes. Ceramic membrane used for modification was provided by A-Tech, Germany. Ionic liquid [EMIM]Cl with purity  $\geq 95\%$  and GVL with purity  $\geq 98\%$  were purchased from Sigma-Aldrich (St Louis, MO, USA) and Acros Organics (Geel, Belgium), respectively. Sulfuric acid ( $H_2SO_4$ ) and sodium hydroxide (NaOH), both are of ACS grade, were obtained from VWR International (West Chester, PA, USA). The information about chemicals used for preparation of polymeric solid acid catalyst can be found in our previous publication [23]. All the chemicals were directly used without further purification.

### 2.2. Synthesis of polymeric solid acid catalyst

Polymeric solid acid catalyst was prepared via 5 steps. The preparation details can be found elsewhere [23,38]. Briefly, UV initiator benzoin ethyl ether (BEE)-COOH was firstly synthesized via reaction of BEE with ethyl acrylate. Grafting of catalyst on ceramic membrane substrate was then conducted by firstly forming a self-assembled monolayer (SAM) possessing amino end groups. This was followed by the subsequent immobilization of ATRP and UV initiators on the SAM layer by conjugating with the amino end groups on the substrate surface. PSSA and PIL chains were then grown via ATRP and UV-initiated polymerization respectively.

### 2.3. Pretreatment of wheat straw

Acid and alkali pretreatment of straw were carried out at 10% (w/v) straw concentration with 2% (w/v)  $H_2SO_4$  and NaOH respectively at 121 °C for 60 min in a Tuttnauer 2540 EKP autoclave (Ronkahoma, NY, USA). After cooling down to room temperature, the pretreated slurry was filtered and washed with deionized (DI) water under vacuum through a Buchner funnel using a Whatman #1 filter paper (Buckinghamshire, UK) until the pH of the filtrate became neutral. The retained solid residue was vacuum-dried at 40 °C for 24 h for further use.

### 2.4. Hydrolysis of biomass

Batch biomass hydrolysis experiments were carried out in a 25 ml round-bottom glass reactor placed in an oil bath heated by a magnetic hot plate stirrer (VMS-C7, VWR International, West Chester, PA, USA). After adding raw straw (ranging from 0.4 to 1.0 g) to 10.00 g solvent consisting of [EMIM]Cl and GVL at different proportions, the reactants were mixed with a magnetic stirring bar in the sealed reactor. The reactions were performed at three different temperatures (140, 150 and 160 °C) with catalyst loading varying from 0.2 to 0.5 g. The reaction solvents consisted of 99.7 wt% organic solvent: 0.3 wt% water. The organic solvents that were chosen and compared were 100 wt% [EMIM]Cl, 80 wt% [EMIM]Cl: 20 wt% GVL and 50 wt% [EMIM]Cl: 50 wt% GVL.

When investigating the effects of water on biomass conversion, the added amount of water varied from 0.3 to 10 wt% with the corresponding amount of organic solvent ranged from 90 to 99.7 wt%. The weight ratio of [EMIM]Cl to GVL in the organic solvent was kept constant at 80%:20%.

When conducting hydrolysis of acid and alkali pretreated wheat straw, the amount of pretreated straw used has the equivalent cellulose to that in the 8 wt% raw straw (0.275 g) according to their respective cellulose compositions as shown in Table 1. The solvent contained 9.5 g organic solvent at 80 wt% [EMIM]Cl and 20 wt% GVL ratio and 0.5 g  $H_2O$ .

Samples were taken at different reaction times and diluted with DI water. The solid residues were removed using centrifugation (VWR Scientific model V mini centrifuge, West Chester, PA, USA). The products contained in supernatants were analyzed using High Performance

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