

Methanesulfonic acid-catalyzed conversion of glucose and xylose mixtures to levulinic acid and furfural



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ABSTRACT

Methanesulfonic acid (MSA) was compared with sulfuric acid for the conversion of glucose and xylose mixtures to produce levulinic acid and furfural. The interactions of glucose and xylose, the predominant sugars found in biomass, were found to influence product yields with furfural degradation reactions enhanced under higher reactant loadings. Fast heating rates allowed maximal yields (>60 mol%) of levulinic acid and furfural to be achieved under short reaction times. Under the range of conditions examined, sulfuric acid produced a slight increase in levulinic acid yield by 6% ($P=0.02$), although there was no significant difference ($P=0.11$) between MSA and sulfuric acid in levulinic acid formed from glucose alone. The amount and type of the solid residue is similar between MSA and sulfuric acid. As such, MSA is a suitable alternative because its use minimizes corrosion and disposal issues associated with mineral acid catalysts. The heating value of the residue was 22 MJ/kg implying that it is a suitable source of fuel. On the basis of these results, a two-stage processing strategy is proposed to target high levulinic acid and furfural yields, and other chemical products (e.g. lactic acid, xylitol, acetic acid and formic acid). This will result in full utilization of bagasse components.

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1. Introduction

The conversion of lignocellulosic biomass into chemical products proceeds through the fractionation of lignin and carbohydrates, and the depolymerization to monomeric sugars and conversion of these to targeted compounds. Acid hydrolysis of the latter is the most effective method for biomass depolymerization to sugars, as this occurs in relatively shorter times than enzymatic hydrolysis (Mamman et al., 2008). Under harsher processing conditions the monomeric sugars formed in situ can be converted to useful chemicals such as levulinic acid (from hexose sugars derived from cellulose) and furfural (from pentose sugars derived from hemicellulose). Typically the conversion of hexose sugars proceeds via isomerization and dehydration routes through either cyclic or acyclic structures to the intermediate hydroxymethylfurfural (HMF), which is subsequently hydrolyzed to both levulinic acid and formic acid (Kuster, 1990) as shown in Scheme 1. Likewise, pentose sugars are readily converted via dehydration to furfural (Nimlos et al., 2006). Other typical products from the acid-catalyzed conversion of biomass include acetic acid, glycolic acid, lignin and lignin degradation products (Girisuta et al., 2013).

The reactive nature of levulinic acid makes it suitable for the production of other chemicals that can replace similar chemicals

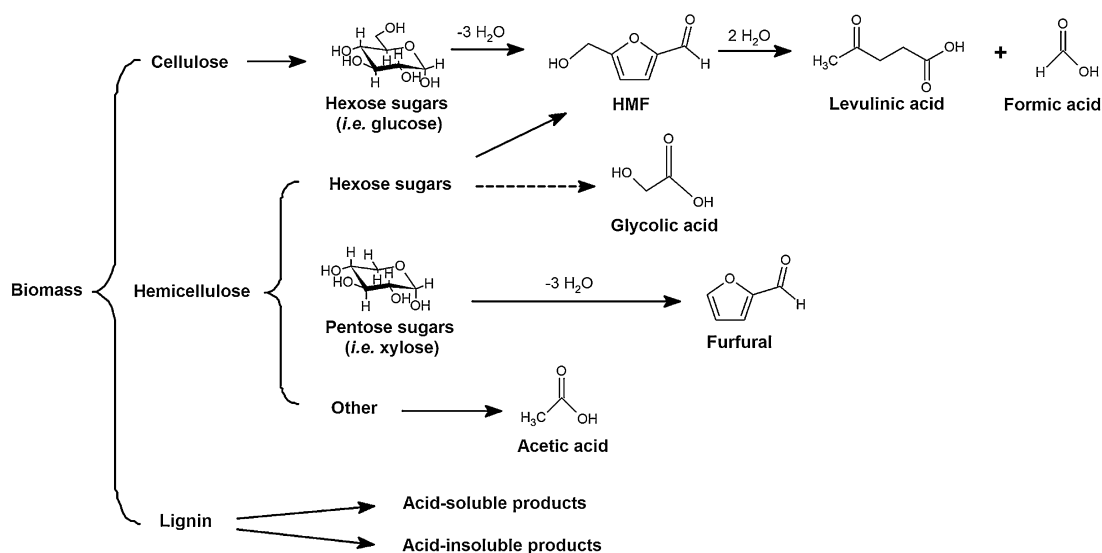
currently sourced from the petrochemical industry for use as fuels, solvents, and pharmaceutical and agricultural products (Bozell and Petersen, 2010). However, its production has high equipment cost associated with its recovery, and the recovery of the mineral acid catalyst normally used.

The only attempted semi-commercial production of levulinic acid from cellulosic feedstocks is based on the Biofine process. This process uses a two-stage acid-catalyzed process to optimize conditions to achieve up to 70–80 mol% yields of levulinic acid and furfural (Hayes et al., 2006). The major drawback of the Biofine process is the inability to effectively separate and recover levulinic acid under dilute aqueous solutions (Mamman et al., 2008; Rackemann and Doherty, 2011). The recovery of the mineral acid catalyst requires specific processing equipment and the sticky residue associated with lignin and humic acids tend to block the reactor and piping systems. Also, conditioning of these residues by neutralization is required prior to combustion, if it is to be used for the production of power and heat. This treatment process results in the production of gypsum, which is increasingly becoming an environmental nuisance as lime is used to neutralize sulfuric acid used as the catalyst.

To overcome the issue of levulinic recovery, Dumesic's group recently proposed a solvolytic approach to produce γ -valerolactone (GVL) that doubles as the solvent in the conversion of cellulose to levulinic acid (Alonso et al., 2013). The levulinic acid is hydro-generated in situ to GVL over noble metal catalysts, which are expensive. The use of such systems is also costly because of solvent

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Scheme 1. Acid catalyzed conversion of lignocellulosic biomass.

losses during recovery. Alternative to direct production of levulinic acid from lignocellulosics is the production of chloromethylfurfural (CMF) which was developed using biphasic system based on halogenated acids and solvents (Mascal and Nikitin, 2010). The CMF can subsequently be converted to levulinic acid. However, the use of concentrated mineral acid as the catalyst, as in the Biofine process, possesses serious environmental concerns and issues surrounding acid recovery and handling.

Regardless of the approach (aqueous- or organic-solvent based), the production of high yields of levulinic acid is typically catalyzed by mineral acids which have corrosion and waste-disposal problems. Corrosion issues could be minimized by developing environmentally friendly processes through the utilization of less corrosive homogeneous or heterogeneous catalysts. To date, the use of heterogeneous catalysts has so far been unable to overcome low product yields or operate economically at high biomass loadings (Rackemann and Doherty, 2011). Therefore, low corrosivity homogeneous catalysts are viable alternatives if product selectivity can be maintained, and the catalyst readily recovered.

Sulfonic acids are strong, non-oxidizing, biodegradable acid catalysts that are more environmentally friendly, less corrosive, and minimize charring and other undesirable side reactions that occur in mineral acids such as sulfuric acid (Arkema, 2013). Both methanesulfonic acid (MSA) and *p*-toluenesulfonic acid have been used in the solvolysis liquefaction of cellulose and biomass, and were found to play an important role in reducing condensation reactions in comparison to mineral acids (Mun et al., 2006). These properties of sulfonic acids may offset their higher cost compared to mineral acids. The cost of MSA is ~\$4 per kg (Gernon et al., 1999) while that of sulfuric acid is ~\$1 per kg. A recently developed environmentally friendly commercial process based on air oxidation of dimethylsulfide (synthesized from sulfur and methanol) produces MSA and water with no wastes or impurities (BASF, 2010).

Despite these advantages of sulfonic acids, there has been limited work reported on their use for the production of levulinic acid from carbohydrates (Lai et al., 2011). Heterogeneous catalysts with sulfonic acid functionalized groups have been used to produce levulinic acid and its ester from glucose (Hu and Li, 2011) in high yields but extension to more complicated feedstocks like cellulose resulted in very low yields due to insufficient access of the feed material to the catalyst.

This work reports on the evaluation of MSA as an effective catalyst for the conversion of glucose and xylose mixtures (the two

predominant sugars in sugarcane bagasse) to levulinic acid and furfural using conditions that allows integration with utilities of sugar factories. Both ethanesulfonic acid ($pK_a = -2$) and *p*-toluenesulfonic acid ($pK_a = -2.8$) are expected to be comparable in performance to MSA, and so were not included in the present study. Besides, these two acids cannot be classed as environmentally friendly. The interaction between the sugar monomers on product yields was examined for the first time in this work. This is to provide data as to whether it would be beneficial to fractionate bagasse in a step-wise fashion prior to being hydrolyzed. Preliminary screening tests with the individual sugar monomers were also conducted. The characteristics of the solid residues originating from conversion of sugar monomers and their mixtures were also examined, as these residues are a valuable source of fuel. The information obtained from the study was used to propose a two-stage conceptual design of a sugarcane bagasse biorefinery.

2. Materials and methods

2.1. Materials

Chemicals used for analyses include ultra pure Millipore-Q water, D-(+)-xylose (99%), D-(+)-glucose (99%), L-arabinose (99%), D-(+)-mannose (99%), L(+)-lactic acid (98%), levulinic acid (98%) and 5-(hydroxymethyl)furfural purchased from Sigma Aldrich; formic acid (98%) and 2-furaldehyde (99%) purchased from Fluka Analytical; maleic acid (99%) purchased from Merck; and glacial acetic acid (99.7%) purchased from Chem Supplies. All the chemicals were used as received. Catalysts for the trials included sulfuric acid (98%) from Merck and methanesulfonic acid (~70%) from BASF. Deuterated dimethylsulfoxide (DMSO-d₆) were purchased from Sigma Aldrich (99.9 at% D).

2.2. Experimental equipment

Experiments were carried out in 10 mL sealed glass ampoules of 9.6 mm inner diameter and 150 mm long. The ampoules were loaded with ~3.5 mL total of reactants, solvent and catalyst and heated in a fluidised sand bath (Model number: SBL-2D, Techne Inc., Burlington, NJ) to a set temperature and reaction time. At the end of the reaction time (starting from after operating temperature

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