



Acid catalysed alcoholysis of wheat straw: Towards second generation furan-derivatives



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ABSTRACT

The acid-catalysed alcoholysis of wheat straw has been studied in 95% methanol and 94% ethanol (w/w) in the presence of various amounts of H₂SO₄ and compared to the alcoholysis of wheat straw-derived organosolv pulp and commercially available celluloses. Substrate liquefaction and the product distribution were found to depend mainly on the temperature and the amount of H₂SO₄ added compared to the acid neutralisation capacity (ANC) of the substrate. The process was optimised for the one-step conversion of wheat straw into methyl glucosides, defined as the sum of α and β anomers. The maximum total methyl glucosides yield from wheat straw was 56 mol-% based on initial glucan after 120 min methanolysis at 175 °C and 40 mM H₂SO₄. Concurrently, furfural was formed at 40 mol-% yield based on initial xylan. The solid residue consisted of mainly acid insoluble (pseudo)lignin, humins and minerals. Switching to ethanol resulted in a shift from glycosides to furfural, 5-(alkoxymethyl)-2-furfural and levulinates. Addition of MgCl₂, as well as substituting H₂SO₄ by HCl led to poorer biomass liquefaction and lower glucosides yield presumably due to consumption of protons under the typical reaction conditions. Alcoholysis of delignified, cellulose-enriched pulp obtained via organosolv fractionation resulted in higher glucosides yields and more concentrated product streams, as higher glucan loadings are possible and undesired side-reactions are minimised. Furthermore, organosolv fractionation prior to alcoholysis allows for the separation and valorisation of the lignin fraction. The glucosides can be separated, e.g. by means of chromatography, and may be converted into furan building blocks, for example for the production of plastic precursors, such as 2,5-furandicarboxylic acid.

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1. Introduction

A growing world population and its persistent drive for increasing the standard of living and the growing needs for mobility are putting a large claim on the natural resources. It is commonly believed that resources such as clean water, food, energy and raw materials will become scarce in the foreseeable future. Worries about running out of natural resources have been from all ages, but has never led to insurmountable problems due to the adaptability and ingenuity of men. These days, declining known oil and gas reserves are a major topic in international discussions. In the light of anthropogenic global warming an obvious switch to alternative fossil carbon sources for energy production and petrochemical building blocks is not recommendable.

In many instances, a petrochemical building block can be substituted by natural alternatives. In this light, the U.S. Department of Energy published two reports identifying promising

renewable building blocks that can be produced from biomass sugars [1] and lignin [2]. Furan derivatives are considered to be high-potential building blocks for bio-based fuels and polymers [1]. A key intermediate in the production of biomass-derived furans is HMF (5-(hydroxymethyl)-2-furaldehyde) [3], which can be used to produce, for example, 2,5-dimethylfuran (DMF) [4] and 2,5-furandicarboxylic acid (FDCA) [5]. DMF is regarded as a potential bio-gasoline [6] and FDCA can replace the petrochemical terephthalic acid, a precursor to the polyester PET, to make clothing and plastic bottles [7].

HMF is an intermediate in the conversion of hexoses to levulinic acid and is produced in aqueous solution via acid-catalysed dehydration of hexoses, such as fructose and glucose [8–12]. Herein, glucose first needs to be converted to fructose by isomerisation. Under typical reaction conditions, the glucose–fructose isomerisation is rate-limiting, and HMF yields from fructose are higher than starting from glucose [11–13]. Addition of a base is beneficial for the production of HMF from glucose, by selectively accelerating the isomerisation reaction [8,14]. Increasing the temperature will speed up both glucose isomerisation and dehydration to form HMF, but even more the successive HMF

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polymerisation and decomposition yielding levulinic and formic acid [9].

Preferably, HMF is produced from non-edible natural resources, such as cellulose. When starting from lignocellulosic biomass, such as wheat straw or wood chips, or from cellulose the first step is depolymerisation. Typical aqueous acid hydrolysis methods for producing HMF from (ligno)cellulose are based on high temperatures. Consequently, the rate of HMF degradation via hydrolysis and polymerisation reactions is high and the yield is limited. In short, HMF is not stable under the typical acidic conditions required for its formation from cellulose or lignocellulosic biomass in water and the maximum yield from D-glucose is typically below 30% [8,11,15]. The yield can be improved by reactive extraction of HMF in a non-aqueous phase, preventing HMF degradation by hydration and subsequent decomposition. Fan et al. [13] reported a 68% yield of HMF from glucose in aqueous methyl isobutyl ketone, using the solid heteropoly acid salt $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$.

Recently, organic solvents such as N,N-dimethylacetamide (DMA) [11,13,16] and ionic liquids [11,17–19] were shown to have potential for the selective production of HMF from glucose and cellulose, especially in the presence of a metal chloride catalyst. Herein, the improved yields originate from improved cellulose solubility, enhanced glucose–fructose isomerisation, repressed HMF hydration, or a combination of those. The influence of loosely ion-paired halide ions, such as chloride, was explained by effective hydrogen bond disruption within the solid thus enabling cellulose hydrolysis at reduced temperatures, while simultaneously lowering HMF degradation. In DMA/LiCl, the maximum HMF yield from cellulose was circa 30% in the presence of $\text{Zr}(\text{O})\text{Cl}_2$ or CrCl_3 [16]. For a combination of CrCl_3 , HCl and LiBr in DMA/LiCl a maximum HMF yield of 37% was reported [11]. In both cases, the presence of large amounts of 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) and 1-butyl-3-methylimidazolium ([BMIm]Cl) resulted in a HMF yield increase to 54–57%. A mixture of CuCl_2 and CrCl_2 in [EMIm]Cl yielded a maximum HMF of 55% from cellulose after 8 h at 120 °C [19]. After 1 h at 140 °C, maximum HMF yields of respectively 53% and 42% were reported for cellulose and corn stover in CrCl_3 and HCl containing [EMIm]Cl [11]. While in pure ionic liquids HMF can easily be produced from fructose using a variety of metal chlorides, the production from glucose and polymers thereof seems to specifically require the presence of chromium chloride [17,18]. Next to the environmental disadvantages of chromium salts, the high cost of ionic liquids limits the industrial application of such solvents systems.

Alternatively, in acidified methanol and ethanol hexose-containing material can be converted into stable HMF ethers [20]. These ethers can be isolated and converted further into valuable building blocks, such as FDCA [7,12]. Thus far, etherification of HMF has been shown successful with good yield and selectivity starting from fructose [21]. Etherification starting from glucose remains challenging. Within the national Dutch Catfur project, ECN, Avantium Technologies and Utrecht University cooperate to develop glucose-based, second generation furan-derivatives. Herein, the first step is liquefaction of lignocellulosic biomass using short-chain alcohols. Garves reported that the main products from the cellulose fraction are alkyl glucosides or alkyl levulinates, depending on the process conditions [22]. Under water-lean conditions the formation of levulinic acid and humins is reduced [23]. The suppression of humins formation is a major benefit in the economics of biomass valorisation, since humins are typically considered suitable for low-value applications only, such as heat and power generation. It is noteworthy that obtained alkylated sugars are highly soluble in alcohol and may be further converted to yield the same HMF ethers as from glucose and fructose.

Liquefaction of lignocellulosic biomass in alcohols results in product streams that also contain solubilised lignin fractions and

hemicellulose derivatives. Their presence may lead to a loss of sugars due to undesired condensation reactions. Alternatively, prior to alcoholysis the biomass can be fractionated. Organosolv fractionation enables separation of the three main constituents of lignocellulosic biomass, viz. lignin, hemicellulose and cellulose [24,25]. The pulp can be used for the production of alkyl glucosides, whereas the lignin and hemicelluloses can be valorised separately. When performing alcoholysis on delignified pulp, undesired side-reactions are expected to be minimised, the sugar yields increased and more concentrated product streams will be possible compared to alcoholysis on the whole biomass. Whereas methanol seems the solvent of choice in alcoholysis of hexose-containing material, ethanol is interesting when starting with lignocellulosic biomass, due to the higher lignin solubility [26]. Besides, ethanol is considered less toxic and can easily be obtained from renewable resources. Moreover, in acid catalysed alcoholysis at elevated temperature the use of ethanol is preferred over methanol because of its lower tendency to form dialkylether [27].

Previously, H_2SO_4 , HCl, and MgCl_2 have been compared and tested as catalyst in organosolv fractionation of wheat straw in ethanol/water (60% ethanol, w/w) [25]. Herein, the effect of the acid catalysts was found to be primarily due to their effect on the pH of the organosolv liquor rather than the type of anion. H_2SO_4 was found to be a weaker acid than HCl in 60% (w/w) aqueous ethanol. The use of MgCl_2 was found to enhance fractionation and enzymatic digestibility of the resulting pulp, however, to a lesser extent than both acid catalysts.

In this study cellulose containing material is processed in acidified methanol and ethanol, targeting maximum total glucosides yields. Herein, no difference is made between the yields of the α and β anomer of the glucosides; both anomers can be used simultaneously as precursor for the formation of furan-derivatives. The effect of substrate, catalyst concentration, temperature and reaction time are studied, as well as the effect of HCl and MgCl_2 addition.

2. Experimental

2.1. Materials

Wheat straw was selected as a representative lignocellulosic biomass substrate, because it is an abundant agricultural residue in Europe. The wheat straw used in this study was dried winter wheat straw grown in the vicinity of Delftzijl, the Netherlands, and cut to <2 cm pieces. The average moisture content was ~8% (w/w) dry biomass. The bulk composition of the wheat straw was: 8.4% water extractives, 2.0% ethanol extractives, 36.9% glucan, 19.9% xylan, 1.9% arabinan, 0.7% galactan, 0.2% mannan, 0.1% rhamnan, 16.7% acid-insoluble lignin, and 1.1% acid-soluble lignin. The ash content was 6.1%. The elemental composition of the biomass was 44.3% carbon, 42.7% oxygen, 5.4% hydrogen, 2.2% silicon, 0.2% potassium, 0.2% calcium (other elements <0.1%) [25]. All percentages are based on dry biomass weight. The straw was stored dry in closed bags at room temperature until use. The material was used without further treatment.

Cellulose-enriched lignocellulosic pulp (68.9%, w/w glucan; 7.9%, w/w xylan, 15.7%, w/w acid-insoluble lignin, and 0.4%, w/w acid-soluble lignin) was obtained from organosolv pulping of wheat straw [28]. For this, the wheat straw was mixed with 50% (w/w) aqueous ethanol in a ratio of 10L/kg dry biomass and the slurry was heated to 210 °C while being mixed. The reactor was kept isothermal for 90 min and then cooled to below 40 °C. After organosolv treatment, the product was filtered. The solid fraction was washed with 50% (w/w) aqueous ethanol and dried in vacuo at 50 °C. The pulp was stored in closed vessels until further use. As lignin and hemicellulose-free reference samples Avicel PH-101

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