

10-1-2019

Factors Influencing Cellulosic Sugar Production during Acid-Catalyzed Solvent Liquefaction in 1,4-dioxane


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Abstract

This work explores the use of 1,4-dioxane to depolymerize cellulose into solubilized carbohydrates. This low boiling point solvent offers inexpensive and simple separation compared to higher boiling point solvents such as γ -valerolactone previously considered for acid-catalyzed depolymerization of cellulose. In the present study, several key reaction parameters, including reaction temperature, catalyst concentration, and water content, were studied as major factors influencing sugar production from cellulose. A maximum yield of 51% for levoglucosan, the major product of cellulose depolymerization, was achieved at higher temperature, shorter reaction time and lower acid concentration in the ranges tested for these parameters. Addition of water as co-solvent enhanced solubilization of cellulose and increased solubilized carbohydrate production, which could potentially enable processing of cellulose at high feedstock loadings and milder operating conditions.

Keywords

Cellulose, solubilized carbohydrates, liquefaction, parameters, 1, 4-dioxane, depolymerization, catalysis

Disciplines

Bioresource and Agricultural Engineering | Catalysis and Reaction Engineering | Polymer Science

Comments

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3 **Factors Influencing Cellulosic Sugar Production during Acid-Catalyzed Solvent**
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5 **Liquefaction in 1,4-Dioxane**
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12 Arpa Ghosh¹ and Robert C. Brown^{1, 2*}
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Abstract

This work explores the use of 1,4-dioxane to depolymerize cellulose into solubilized carbohydrates. This low boiling point solvent offers inexpensive and simple separation compared to higher boiling point solvents such as γ -valerolactone previously considered for acid-catalyzed depolymerization of cellulose. In the present study, several key reaction parameters, including reaction temperature, catalyst concentration, and water content, were studied as major factors influencing sugar production from cellulose. A maximum yield of 51% for levoglucosan, the major product of cellulose depolymerization, was achieved at higher temperature, shorter reaction time and lower acid concentration in the ranges tested for these parameters. Addition of water as co-solvent enhanced solubilization of cellulose and increased solubilized carbohydrate production, which could potentially enable processing of cellulose at high feedstock loadings and milder operating conditions.

Keywords

Cellulose, solubilized carbohydrates, liquefaction, parameters, 1,4-dioxane, depolymerization, catalysis

Introduction

Lignocellulosic biomass is a promising source of fermentable sugars for production of biofuels and value-added chemicals.¹ Thermal depolymerization in solvents has drawn increasing attention as a promising approach for production of water-soluble sugars and anhydrosugars from cellulosic feedstock.^{2,3} Anhydrosugars can be hydrolyzed to glucose prior to fermentation to ethanol production although recently it has been shown that levoglucosan and cellobiosan, the most abundant anhydrosugars from cellulose depolymerization, can be directly fermented using engineered microbes.^{4,5}

Cellulose, the most abundant polysaccharide of lignocellulosic biomass, consists of D-glucose units joined by β -glycosidic linkages. The highly compact and crystalline structure of cellulose is the result of intermolecular hydrogen bonding among cellulose fibrils. Enzymatic hydrolysis is the conventional pathway of biomass deconstruction for soluble sugar production.⁶⁻⁹ Although physical and chemical pretreatments can be used to increase the susceptibility of cellulose to enzymatic hydrolysis,¹⁰⁻¹² the high cost of enzymes, slow rates of enzymatic hydrolysis and end-product inhibition are barriers to commercialization of this technology.¹³⁻¹⁵

Concentrated acid hydrolysis is an effective approach to saccharification.^{16,17} However, the corrosiveness and difficulty of recovering concentrated acid has discouraged its commercial development. Ionic liquids readily solubilize cellulose and, in combination with catalysts, can produce high yields of fermentable sugars.¹⁸⁻²⁰ Nevertheless, the high cost of ionic liquids requires recovery at high efficiency, which has slowed its commercial development.¹⁹ A relatively simple and rapid thermal depolymerization process is fast pyrolysis, which can also deconstruct cellulose into anhydrosugars.²¹⁻²⁴ The high temperature of pyrolysis (500-700°C) requires careful control of operating conditions to avoid undesired secondary degradation reactions that adversely affect the yield and selectivity of anydrosugars.²⁵⁻²⁷

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3 Solvent liquefaction has emerged as a promising pathway to cellulosic sugar production. Solvent-
4 assisted depolymerization of biomass employs relatively moderate reaction conditions, typically
5 between 105 and 350°C, with or without homogeneous catalyst.^{28,29} Liquefaction in a solvent
6 medium allows recovery of non-volatile sugars as solubilized carbohydrates and helps suppress
7 secondary dehydration reactions by dispersing reactive species in the solvent phase. These features
8 provide distinctive advantages compared to other cellulose depolymerization pathways.^{30,31}
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17 While water is an effective solvent for hydrolysis of cellulose, the need for special alloys to avoid
18 metal corrosion and operation at elevated pressures results in expensive reactors.³²⁻³⁴ Operation at
19 subcritical conditions helps avoid some of these problems but accelerates dehydration of
20 monosaccharides into 5-hydroxymethylfurfural, a precursor to water-insoluble humins, an
21 undesirable by-product of hydrothermal processing of cellulose.^{35,36} Several researchers have
22 suggested that polar aprotic solvents could be efficient media for acid-catalyzed production of
23 carbohydrates from cellulose. Aprotic solvents serve primarily as chemically inert media in which
24 cellulose is depolymerized to anhydrosaccharides.^{2,37-39} Compared to water, polar aprotic solvents
25 significantly enhance the rate of hydrolytic depolymerization of $\beta(1\rightarrow4)$ bonds to liberate
26 monosaccharides from cellobiose units while suppressing secondary dehydration of
27 monosaccharide products.³⁹
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41 A variety of polar aprotic solvents including sulfolane, 1,4-dioxane, THF, acetone, gamma
42 valerolactone and acetonitrile have been used under hot, pressurized conditions to convert cellulose
43 and/or lignocellulosic biomass into solubilized carbohydrates.^{2,3,30,38,40,41} In particular, high polarity
44 aprotic solvents produce the highest yields of monomeric anhydrosugars, up to 38% from cellulose
45 at 350°C without catalysts.² Recently, we have demonstrated that dilute acid catalyst reduces
46 differences in levoglucosan yields among aprotic solvents of different polarities, allowing low
47 polarity solvents to be competitive alternatives to high polarity solvents.⁴² The above phenomenon
48 was attributed to considerably lower degradation rates of levoglucosan in low polarity solvents
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3 compared to high polarity ones. The lower boiling point of low polarity aprotic solvents offers
4 advantages in recovering products and recycling the solvent.^{43–45} Additionally, LG is highly stable
5 in low polarity solvents even in the presence of acid catalysts. For instance, the rate of LG
6 degradation never exceeded 0.02–0.12 mg min⁻¹ in 1,4-dioxane and THF, in contrast to the rapid
7 decomposition of LG (0.20–0.31 mg min⁻¹) in the high polarity solvents GVL and acetonitrile.⁴²
8 This suggests low polarity solvents as solvents of choice for processing cellulose under acid-
9 catalyzed production of solubilized carbohydrates.
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19 Despite these promising results, the use of low polarity solvents to thermally deconstruct cellulose
20 has not been optimized. While several polar aprotic solvents have been investigated, the literature
21 contains little information on the influence of reaction variables on acid-catalyzed cellulosic sugar
22 production in polar aprotic solvents. We have recently demonstrated that reaction time is among
23 the most important parameters governing yield of solubilized carbohydrate,^{2,30,42} with distinct
24 optimal times for maximizing yields of desired monosaccharides. Bai et al.³⁰ presented the effects
25 of reaction temperature, reaction time, water content and mass loading on the yields of
26 monosaccharides during switchgrass liquefaction in 1,4-dioxane. However, the effect of acid
27 catalyst was not investigated and the temperature range was very small. Additionally, the effects
28 of these variables on depolymerization of individual polysaccharides in biomass were not
29 adequately explained. Solvent liquefaction studies also indicate that low polarity solvents usually
30 require processing at high temperature and pressure with relatively low feedstock loading for
31 effective conversion of cellulose to sugars.^{30,40,42} These constraints entail high capital and operating
32 costs.
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50 Our previous work suggests that several low polarity and low boiling point solvents, 1,4-dioxane,
51 THF and acetone, are suitable for acid-catalyzed cellulose depolymerization.⁴² Since 1,4-dioxane
52 exhibited the largest initial rate of LG production and a low LG degradation rate, it was chosen for
53 this study. Additionally, 1,4-dioxane is stable in the presence of acid catalyst and elevated
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3 temperatures and represents a relatively green solvent that can be produced from biomass.^{2,30,46–48}

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5 The parameters investigated in the present study include temperature, concentration of acid catalyst
6 (sulfuric acid), and the amount of water used as co-solvent. The size of cellulose particles and the
7 type of reactor can also influence product distributions, but including them was beyond the scope
8 of this study. Other kinds of acid might also be effective as catalysts, but sulfuric acid was selected
9 because it is inexpensive and representative of homogeneous acid catalysts.
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17 Although operation at low temperature is desired to keep pressure low, it could also significantly
18 decrease solubilization capability of carbohydrate products in the primary solvent phase. We
19 hypothesize that polar solvents such as water could promote solubilization of cellulose products at
20 relatively low temperatures, which readily dissolve and disperse in the aqueous phase of a mixture
21 of 1,4-dioxane and water.^{49,50} Additionally, water should enhance production of solubilized
22 carbohydrates via acid-catalyzed hydrolysis at 200-300°C through its well-known catalytic effect
23 at modest temperatures.^{32,51} Use of water as a co-solvent may allow the use of smaller amounts of
24 acid, mitigating acid-catalyzed dehydration of sugar products.^{52,53} The guiding hypothesis of this
25 research is that use of water as co-solvent both mitigates solubilization problems and enhances
26 cellulose depolymerization under conditions of low temperature liquefaction in 1,4-dioxane.
27 Furthermore, recent literature shows that adding water as co-solvent with a n organic solvent could
28 help in formation of local solvent domains enriched with water near the hydrophilic reactant (e.g.
29 carbohydrates) and increase the strength of hydrogen bonding between the reactant and local water
30 molecules.⁵⁴ This type of solvation effect in co-solvent system could also augment the reactivity of
31 cellulose at lower temperatures. It is important to note that subcritical water may also incur some
32 undesired dehydration effects of the carbohydrate products due to its catalytic activity.
33 Accordingly, a detailed study of the effect of water under various reaction conditions will provide
34 information important to the design of a robust thermal deconstruction process based on acid-
35 catalyzed solvent liquefaction.³²
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Experimental section

Materials

Microcrystalline cellulose of size 50 μm was purchased from Sigma Aldrich. Levoglucosan (LG, purity > 99.6%) and cellobiosan (purity > 98.7%) were obtained from Carbosynth, UK. Furfural (purity > 99%), levoglucosenone (LGO, purity > 99.2%), 5-hydroxymethylfurfural (5-HMF, purity > 99%) were purchased from Sigma Aldrich. Cellobiose (purity > 98%) from Acros Organics and D-Glucose (purity > 99%) from Fisher Scientific were acquired. Polyethylene glycol standards were obtained from Agilent Technologies. HPLC grade and submicron filtered 1,4-dioxane, acetone and methanol were provided from Fisher Scientific. Sulfuric acid (H_2SO_4 , purity 96.6 wt%) was received from Fisher Scientific and DI water (18.2 M Ω) was available on site.

Solvent processing methodology

Experiments were conducted in microreactors assembled from Swagelok (316 SS) fittings. A reactor constituted of a 3/8-inch tube fitting union and two sealed plugs. Reactor capacity was 2.5 mL. Microcrystalline cellulose (10-50 mg) was added to 1.2 mL of solvent. Non-aqueous reactions were conducted at temperatures ranging from 250 to 375°C for up to 15 min with 0-5 mM sulfuric acid added to the solvent to serve as catalyst. The reactor pressures were estimated elsewhere for pure 1,4-dioxane system.² For experiments in co-solvent mixtures of 1,4-dioxane and water, water content ranged from 0 to 50 vol% of the mixture. The effect of water was studied at several temperatures in the range of 250 to 350°C with 0.25 mM sulfuric acid. Relatively long reaction times of 10 to 30 min were used, as depolymerization of cellulose is significantly slower at low temperatures. Experiments with water as co-solvent increased mass loadings 20-50 mg cellulose. It is important to note that these reactors do not have stirrer attached to them and thus could incur some mass transfer limitation effects on the reaction kinetics. Therefore, a diluted mass loading has been used whenever possible to keep mass transfer effects low. A simple flow chart (Figure S1) is provided in Supplementary Information to help explain the scheme of experimental design in this

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3 study. It is important to note that these microreactors have limited application as we could not
4 accommodate in-line pressure measurement during the reaction and thus the effect of pressure on
5 reaction rate and pathways could not be studied. We suggest use of an Autoclave reactor with
6 continuous pressure control for any future work aimed at investigating pressure effects on cellulose
7 depolymerization in polar aprotic solvent.
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15 Reactors were sealed and shaken for 1 h prior to experiments. The mini-reactors were heated in a
16 fluidized sand bath (Techne Industrial Bed 51) to the desired reaction temperature. Temperature
17 profiles in the reactors were measured with a type K thermocouple inserted in the reactor. Initial
18 heating rates of the reactor contents were 5-7°C s⁻¹. The normal boiling points and estimated
19 pressures at reaction conditions for each solvent are given in Table S1. The methodology for
20 determining reactor pressure is elucidated elsewhere.² Reaction time was measured as the time
21 interval between dropping the reactor into the hot fluidized bed and removing and immersing it in
22 cold water. The reactors, once cooled, were slowly opened to allow non-condensable gases to
23 escape prior to extracting the liquid and solid contents of the reactor. Liquid was extracted and
24 solids washed from the bottom of the reactor using the same solvent used in the experiment. The
25 liquid fraction consisted of both the solvent and solubilized products from cellulose deconstruction.
26
27 The liquid fraction was filtered using Whatman syringe-filters of pore size 0.45 μm. The solid
28 residue was dried overnight in an oven at 50°C and weighed. Gas products were quantified by the
29 difference in the mass of the reactor before and after the non-condensable gases escaped. Since the
30 influence of reaction time on LG production was significant, time evolution was evaluated for each
31 experimental condition investigated. The experiments were repeated two or three times and average
32 reported. For all experiments, standard error was within 10% of the mean.
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51 Thermal stability of 1,4-dioxane at reaction conditions was tested to verify its robustness. The
52 solvent with 0.25 mM sulfuric acid was employed in three cycles of solvent processing at 350°C,
53 each lasting four minutes. A decomposition of 0.02-0.32% of the solvent to low molecular weight
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3 products based on GC-MS peak area analysis was observed per cycle of 1,4-dioxane processing at
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5 250-350°C in presence of 0-10 mM acid catalyst and 10 vol% water as co-solvent. The main
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7 degradation product was methyl substituted 1,3-dioxolane. Thus, the solvent system appeared to be
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9 relatively robust against decomposition.
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11 12 ***Analytical methods***

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14 A Gas Chromatograph with Mass Spectrometer and Flame Ionization Detector (Agilent 7890B GC-
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16 MS/FID) was employed to analyze the liquid fraction. The GC was equipped with two capillary
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18 columns of type Phenomenex ZB 1701 (60 m x 0.250 mm and 0.250 μm film thickness), one
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20 connected to each the MS and FID. The back detector of FID was held at 250°C while the injection
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22 port of GC was kept at 300°C. The flow rate of helium, used as carrier gas, was maintained at 1 mL
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24 min^{-1} . The volume of liquid sample injected for analysis was 1 μL . The temperature of the GC oven
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26 was increased from 40°C (3 min hold) to 240°C (4 min hold) using a heating rate of 3°C min^{-1} .
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28 Quantitative calibration was performed in GC-FID with LG, LGO, 5-HMF, and furfural standards
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30 in diluent methanol or acetone as appropriate. In absence of calibration standard for 1,6-anhydro-
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32 β -D-Glucofuranose (AGF), LG was used for quantification of this anhydrosugar. Anhydrosugar
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34 monomers quantified by GC-FID was not used in the analysis of effect of water as co-solvent on
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36 sugar yields in order to avoid inconsistency. We performed GC-MS/FID on liquid samples
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38 from reaction with the solvent (with acid) to quantify levoglucosan,
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40 levoglucosenone, AGF, 5-HMF and furfural whereas used high performance liquid
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42 chromatography (HPLC) for solvent/water reactions to quantify levoglucosan, glucose
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44 and anhydro-oligosaccharides.
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52 Yield of a solubilized product was calculated as:
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$$\text{Carbon molar yield (\%)} = \frac{C_{sp}}{C_i} \times 100\% \quad (1)$$

where

C_{sp} = moles of carbon in solubilized product

C_i = initial moles of carbon in cellulose as feedstock

Semi-volatile and non-volatile sugars including LG, glucose, cellobiosan and cellobiose were analyzed using HPLC. The HPLC was equipped with a HyperREZ XP Carbohydrate H+ 8 μm (300 x 7.7 mm) column. The flow rate of the matrix, DI water, was 0.2 ml min^{-1} at 25°C and 8 bar pressure. A refractive index (RI) detector was used for identification of sugars. LG, D-glucose, cellobiose, cellobiosan were quantified directly using calibration curves developed with standards of these carbohydrates. High molecular weight solubilized carbohydrates which could not be identified directly in HPLC were analyzed by dilute acid hydrolysis test. In this type of analysis, solubilized oligosaccharides (anhydro- or hydrolyzed) were quantified using HPLC subsequently described. Due to unavoidable uncertainty of measurement, this procedure was only suitable for relatively large sample sizes such as obtained from processing 50 mg cellulose samples.

Dilute acid hydrolysis was conducted in Ace glass reactors (6 mL capacity) containing about 0.5 mL unfiltered solvent liquefaction product solution. The concentration of acid in the hydrolysis test was optimized to be 100 mM for conversion of the anhydrosugars in aqueous 1,4-dioxane system (Figure S2). For hydrolysis, 2.5 mL of 100 mM H_2SO_4 was added in the glass reactor already loaded with solvent liquefaction sample. Triangular stir bars were placed inside the reactors, which were then tightly sealed. These were placed in an oil bath set at 135°C and processed for 44 min. LG and cellobiosan were hydrolyzed individually to confirm complete hydrolysis of the anhydrosugars at the hydrolysis condition employed. Additionally, a blank reactor with 100 mM sulfuric acid solution was used as control. The reactors were taken out of the oil bath and placed inside a freezer for 15 min to bring the contents to room temperature. Hydrolysis samples were filtered and

analyzed in HPLC with a duplicate for each sample. In addition, the entire process of solvent liquefaction followed by hydrolysis was repeated once or twice to report an average for each test condition.

Undetectable solubilized carbohydrates produced from cellulose depolymerization were converted to glucose using dilute acid hydrolysis. They were quantified from the difference in amounts of equivalent glucose pre- and post-hydrolysis as follows:

$$\text{Anhydro – oligosaccharides carbon molar yield (\%)} = \frac{G_{\text{post}} - G_{\text{pre}}}{C_i} \times 100\% \quad (2)$$

where

G_{pre} = moles of glucose equivalence from solvent liquefaction quantified pre-hydrolysis

G_{post} = moles of glucose quantified post-hydrolysis

C_i = initial moles of cellulose as feedstock

A correction factor of 0.9 was applied to convert from glucose-equivalence to anhydro-equivalence. HPLC was used instead of GC-FID to quantify LG in products for all experiments investigating the effect of water co-solvent on cellulose depolymerization to ensure a common chromatographic separation was employed.

Analysis of high molecular weight solubilized carbohydrates was also performed using GFC methodology. A Dionex Ultimate 3000 series HPLC served for GFC analysis. The eluent used in GFC column was DI water. Liquid fractions from solvent liquefaction were diluted to 10 vol% in DI water. Two type PL-aquagel-OH-20 5 μm columns were connected in series in the HPLC and were maintained at 25°C. The mobile phase was DI water with flow rate set at 0.8 mL min⁻¹. Refractive index was used for detection of water-soluble carbohydrates. Polyethylene glycol standards were employed to design a calibration curve for molecular weight distribution of solubilized carbohydrates. Expected sugar products (LG, D-glucose, cellobiosan and cellobiose)

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3 were identified by comparing their retention times with that of their individual standards. The
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5 procedure of determining presence of solubilized carbohydrates is described elsewhere.²
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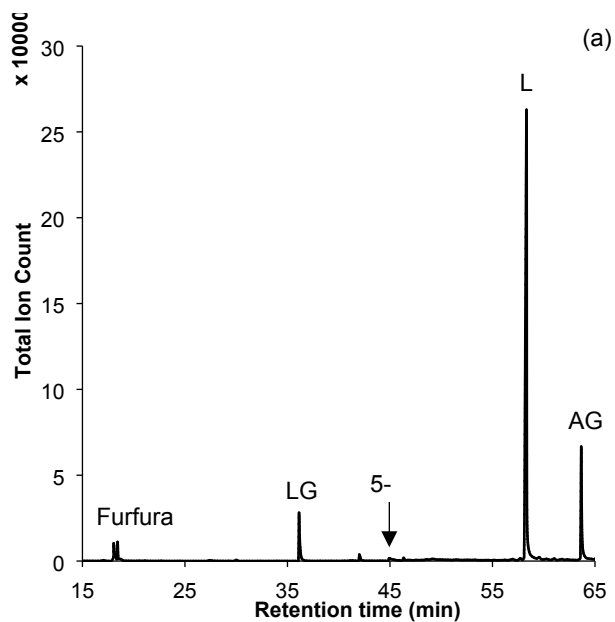
8 Thermogravimetric analysis was performed on the solid residues from cellulose solvent
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10 liquefaction to determine ash and moisture content of the solids. Elemental analysis was also
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12 conducted on solid residues in a CHNS Analyzer to determine carbon, hydrogen and oxygen
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14 content of the solids on ash and moisture-free basis.
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17 18 **Results and Discussion**

19 20 *Product distribution of acid-catalyzed cellulose solvent liquefaction*

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23 Product distributions for acid-catalyzed solvent liquefaction of cellulose in 1,4-dioxane are
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25 presented in Figure 1. The GC chromatogram is for liquefaction in pure 1,4-dioxane (Figure
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27 1 (a)) while the HPLC chromatogram represents the products obtained for liquefaction in
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29 mixtures of 1,4-dioxane and water (Figure 1 (b)). The GC-MS spectrum shows that the
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31 major carbohydrate product of depolymerization of cellulose was the anhydro-
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33 monosaccharide, LG. When water was present as co-solvent, glucose appeared along with
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35 LG as a major carbohydrate product. Minor products included AGF, LGO, 5-HMF and
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37 furfural, which originated from secondary reactions that degraded carbohydrate products,
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39 but these were at significantly lower concentrations than LG or glucose, as shown in Figure
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41 1 (a). Additionally, large molecular weight carbohydrates in the form of anhydro-
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43 oligosaccharides were detected in the GFC spectra (Figure S3) for depolymerization of
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45 cellulose in pure 1,4-dioxane. Anhydro-oligosaccharides could not be directly detected in
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47 the experiments with water as co-solvent because the retention time of the glucose
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49 formed in these experiments strongly overlapped with the retention times of the anhydro-
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3 oligosaccharides. Nevertheless, dilute-acid hydrolysis of the liquid product from the
4 aqueous co-solvent system revealed that anhydro- or hydrolyzed oligomers of C₆ sugar
5 were likely present (see Figure S4). The distribution of these large molecular weight
6 solubilized carbohydrates and monomer carbohydrates in either pure or aqueous 1,4-
7 dioxane solutions indicate that monomers were the main products of acid-catalyzed cellulose
8 decomposition. Thus, the above monomer sugars were used as proxies for analyzing the extent of
9 cellulose depolymerization, which was convenient as these are easy to measure in solution.
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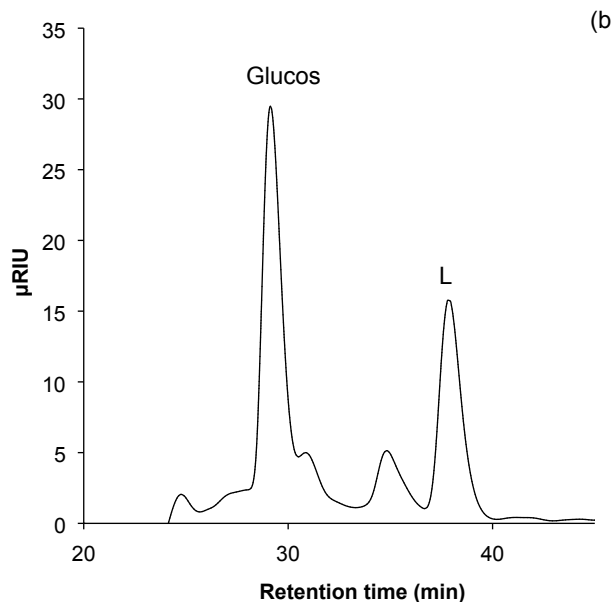


Figure 1. Analysis of solubilized products from acid-catalyzed solvent liquefaction of cellulose in 1,4-dioxane. (a) GC-MS chromatogram (0.25 mM H₂SO₄; no water; 350°C; 1 min reaction); (b) HPLC chromatogram (0.25 mM H₂SO₄; 10% vol water; 250°C; 10 min reaction).

Effect of acid concentration on levoglucosan production

The effect of acid concentration on solvent liquefaction in 1,4-dioxane was investigated at a reaction temperature of 350°C using 20 mg cellulose. We have chosen 350 °C as the fixed temperature for this part of the study in order to compare the effects of acid concentration with our previous results from non-catalytic 1,4-dioxane system.² Further, setting the reaction time ranges carefully for each acid concentration helped in capturing the LG optimum in each case. As shown in Figure 2, very low acid concentrations were adequate to enhance depolymerization of cellulose to LG. An acid concentration as low as 0.1 mM produced a 2.7-fold increase in maximum LG yield (41%) compared to non-catalyzed solvent liquefaction (15%). However, 0.25 mM acid appeared to be optimal, increasing yield to 43% and decreasing reaction time four fold as well as reducing secondary reactions that would otherwise decompose LG over longer reaction times. On the other hand, increasing acid concentration to 2 mM significantly reduced maximum LG yield to 27% while 5 mM acid dropped maximum LG to only 12% - lower than the yield for non-catalytic solvent

liquefaction. These reductions are attributed to acid-catalyzed dehydration of LG to LGO, 5-HMF, furfural, and isomerization to AGF,^{30,38,52} which were found to increase from 7% to 44% as acid concentration was increased from 0.1 to 5 mM (Figure S5).

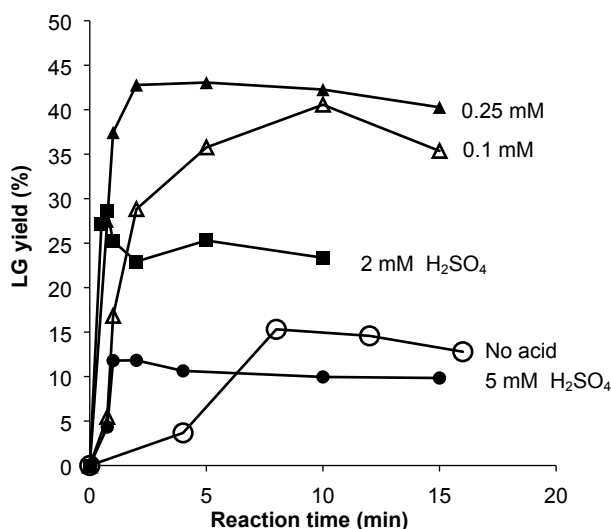


Figure 2. Yields of LG from acid-catalyzed solvent liquefaction of cellulose in 1,4-dioxane as a function of reaction time and acid catalyst concentration (350°C).

A detailed analysis of rates of LG formation and degradation at different acid concentrations is given in Section 7 (see Figure S6) of the Supplementary Information. While low acid concentrations led to low rates of LG degradations, high acid concentrations resulted in more LG degradation. The highest LG formation rate and lowest LG degradation rate were observed at 0.25 mM sulfuric acid, which corresponded to maximum yield of LG yield at this acid concentration. Thus, 0.25 mM was chosen as an optimal acid concentration for subsequent solvent liquefaction experiments.

Effect of temperature

Figure 3 illustrates the effect of reaction temperature on LG yields at increasing reaction times. Like the study of acid concentration effects, the reaction times in this part of the study were also chosen carefully to successfully capture the LG optimum at each temperature. As shown in Figure

3, reaction rates increased with temperature. At temperatures less than 300° C, several minutes were required to reach maximum LG yields. The rate of LG formation was only 0.5 mg min⁻¹ at 250°C increasing to 1.8 mg min⁻¹ at 300°C. At temperatures above 350°C, maximum yields were reached within 1 minute, representing a dramatic increase in rate to 9.9 mg min⁻¹. Furthermore, temperature tended to enhance maximum LG yields, increasing from 25% at 250°C to 51% at 350°C. However, as temperature further increased to 375°C, maximum LG dropped to 46%, possibly due to increased dehydration of LG.

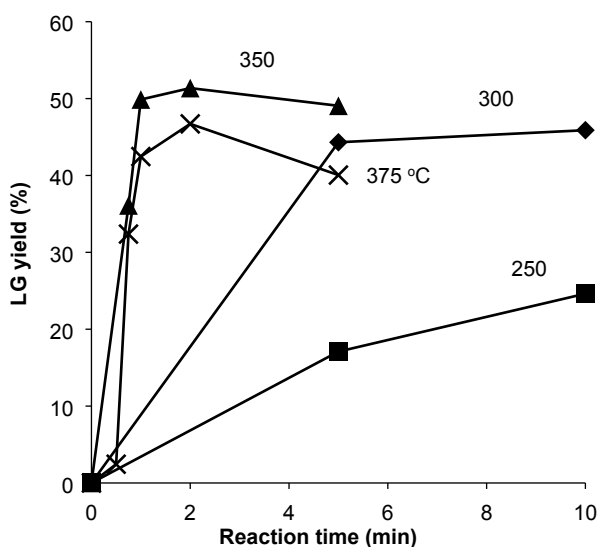


Figure 3. Yields of LG from acid-catalyzed solvent liquefaction of cellulose in 1,4-dioxane as a function of reaction time and temperature (0.25 mM H₂SO₄; no water).

Effect of water as co-solvent on solubilized carbohydrates production

Effect of water on yields of solubilized products

As evident from the earlier sections, sugar production from cellulose is only enhanced at high temperatures and low acid concentration if pure 1,4-dioxane is used. In order to explore solvent liquefaction of cellulose at lower temperatures, we further investigated the effects of adding water as a co-solvent to 1,4-dioxane in presence of acid-catalyst. Figure 4 presents the effect of water addition on acid-catalyzed cellulose solubilization in 1,4-dioxane at 250°C. Water clearly enhanced

the solubilization of cellulose compared to pure 1,4-dioxane. Yield of solubilized products increased from 27% to 62% after 10 min of reaction as a result of including 10 vol% water. The yield of solubilized products after 30 minutes increased from 36% to 65% as a result of including 10 vol% water as co-solvent. Most of the enhanced yield was achieved within 10 minutes.

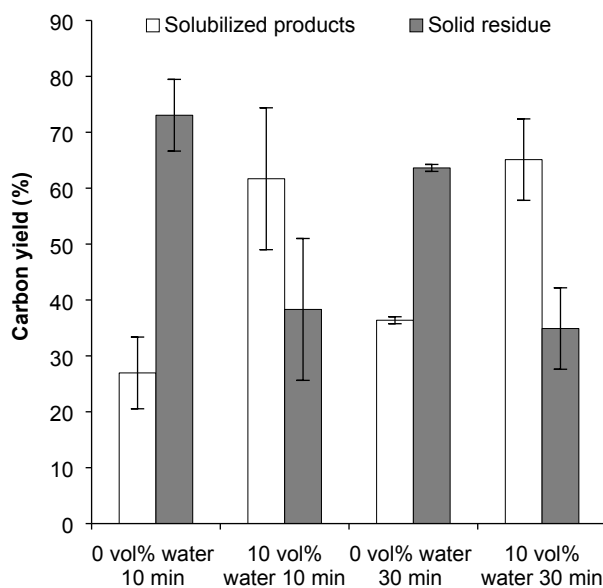


Figure 4. Yields of solid residue and solubilized products from acid-catalyzed solvent liquefaction of cellulose in 1,4-dioxane and water (0.25 mM H₂SO₄; 250°C).

Effect of water on solubilized carbohydrate yield

Water had a significant effect on solubilized carbohydrate yield for acid catalyzed solvent liquefaction of cellulose at 250°C, increasing from 21 mol% to 45 mol% as water increased from zero to 10 vol% (Figure 5). Part of this increase was due to the appearance of glucose in the products, which was wholly absent when water was excluded. Although water clearly promoted acid hydrolysis of cellulose to glucose, it also appears that it promoted anhydrosugar production for modest additions of water.

When water increased above 10 vol% of the solvent mixture, the yield of solubilized carbohydrate decreased to only 13 mol% at 50 vol% water. Oligosaccharides completely disappear from the solubilized carbohydrates while levoglucosan is substantially reduced from a maximum yield of 19.0 mol% to only 4.1 mol% when water makes up 50 vol% of the solvent mixture. Glucose also underwent a precipitous decline from a high of 19.7 mol% to only 8.9 mol% when water increased to 50 vol%. One might suspect anhydro-oligosaccharides to increasingly undergo hydrolysis to glucose with increasing water concentration. However, it is not clear whether levoglucosan directly decomposed or first hydrolyzed to glucose followed by decomposition of this monosaccharide. It is well known that mineral acids in aqueous media both catalyze cellulose depolymerization as well as accelerate secondary dehydration reactions of C₆ monosaccharides.^{35,55–57} Glucose dehydrates to 5-HMF while both glucose and LG can dehydrate to furfural.^{38,53}

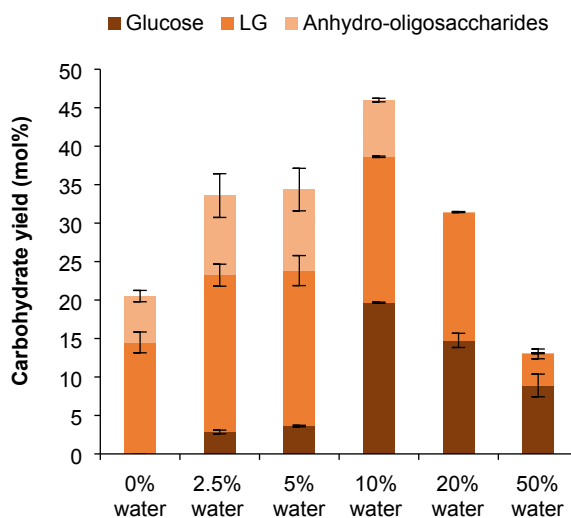
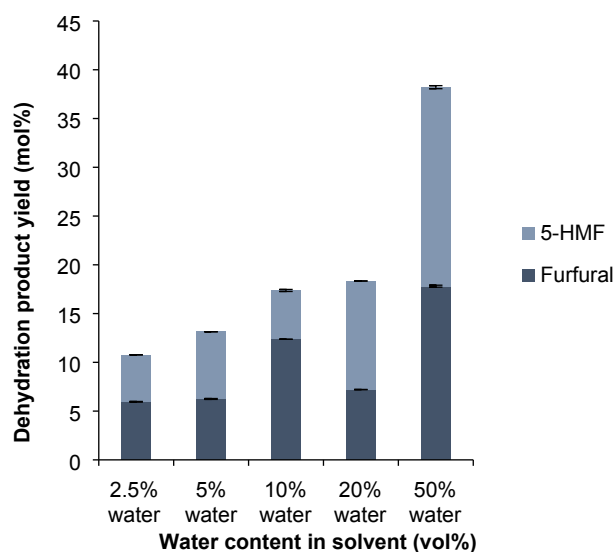


Figure 5. Yields of solubilized carbohydrates from acid-catalyzed solvent liquefaction of cellulose in 1,4-dioxane and water (0.25 mM H₂SO₄; 250°C; 30 min reaction time).

To investigate the question of solubilized carbohydrate decomposition, the yield of carbohydrate dehydration products (5-HMF and furfural) was determined as a function of water content. As shown in Figure 6 the total yield of these furanic products increased from 11% to 38% as water

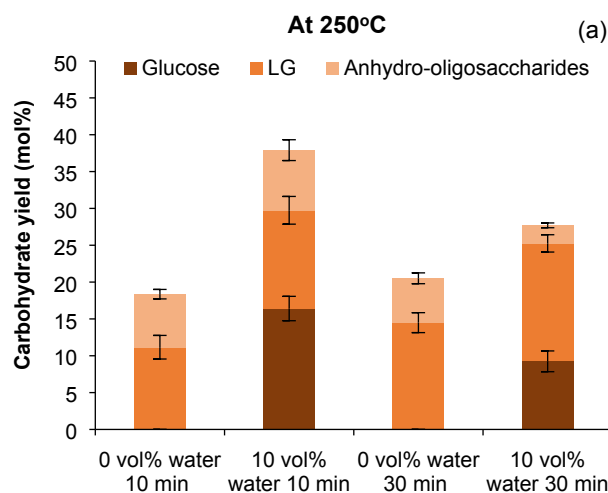
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3 increased from 2.5 vol% to 50 vol%. Figure 6 demonstrates that water also substantially increases
4 dehydration reactions, which has been previously suggested.³² The yield of furanic compounds
5 increased almost linearly with water content as shown in Figure S7 of the supplementary material.
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7 However, from this data it is difficult to surmise whether the anhydrosugars directly dehydrated or
8 first hydrolyzed to glucose followed by monosaccharide dehydration. In this context, two possible
9 pathways consisting of hydrolysis leading to reducing sugar (e.g. glucose) and furanics, and
10 glycosylation forming anhydrosugars could be evaluated based on product evolution over time to
11 help establish a hypothesis for the most possible reaction mechanism for cellulose conversion in
12 1,4-dioxane in presence of water.⁵⁸ Unfortunately, a full study on conversion of carbohydrate
13 products to furanics was out of the scope of this study. We propose that investigating the reaction
14 pathways of cellulose-derived carbohydrates in solvent/water mixture could be an important area
15 of future work to better understand the reactions of acid-catalyzed cellulose decomposition in 1,4-
16 dioxane and water.
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51 Figure 6. Yields of dehydration products from acid-catalyzed solvent liquefaction in 1,4-dioxane
52 and water (0.25 mM H₂SO₄; 250°C; 30 min reaction time).
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3 ***Effect of temperature and reaction time on solubilized carbohydrates when using water as co-***
4 ***solvent***
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8 Figure 7 explores the effect of both reaction time and temperature when using water as co-solvent
9 during acid-catalyzed solvent liquefaction in 1,4-dioxane. In the absence of water, extending
10 reaction time from 10 minutes to 30 minutes has relatively little effect on solubilized carbohydrates
11 although as reaction temperature increased from 250°C to 350°C there was about 12% loss in yield.
12
13 At the lowest temperature tested (250°C), water dramatically boosts solubilized carbohydrate yield
14 (110%) after 10 minutes of reaction, but as reaction proceeds for another 20 minutes the yield falls
15 by 25%, suggesting subsequent product dehydration. At 300°C and short reaction times (10
16 minutes) there is little difference in carbohydrate yield from using water as co-solvent and at longer
17 reaction times (30 minutes) water actually reduces carbohydrate yield, again suggesting the gradual
18 progression of secondary dehydration reactions. At the highest temperature tested (350°C), use of
19 water as co-solvent is counterproductive, cutting carbohydrate yields in half even after only 10
20 minutes of reaction and by 78% after 30 minutes. At these high temperatures, hydrolysis may
21 proceed faster in presence of water producing enough glucose monomers that could help in
22 accelerating dehydration reactions to produce 5-HMF and furfural.⁵⁹
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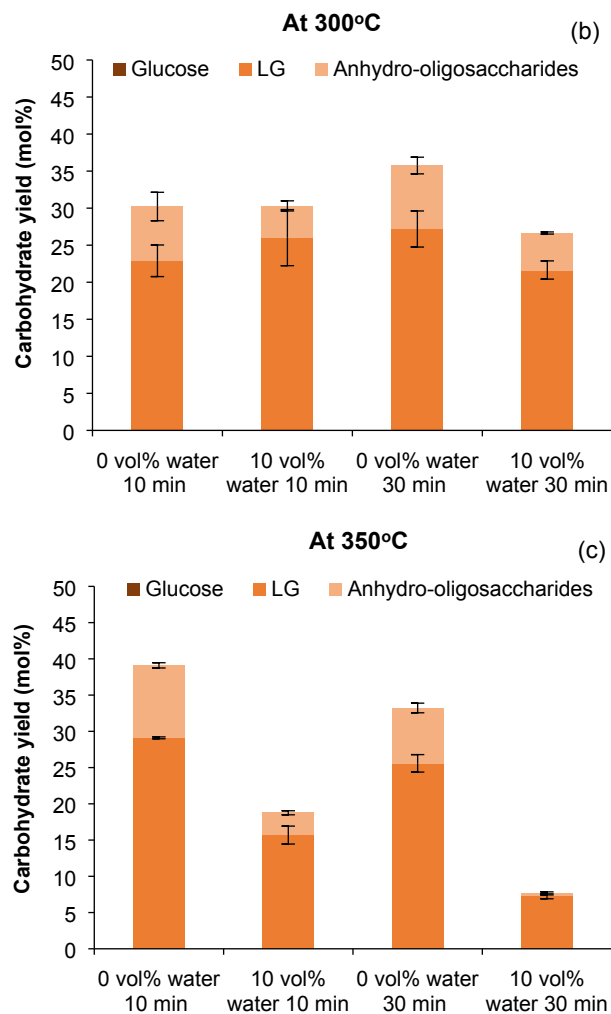


Figure 7. Yields of solubilized carbohydrates from acid-catalyzed solvent liquefaction in 1,4-dioxane and water as a function of water content, reaction time and temperature. (a) 250°C, (b) 300°C, (c) 350°C (0.25 mM H₂SO₄)

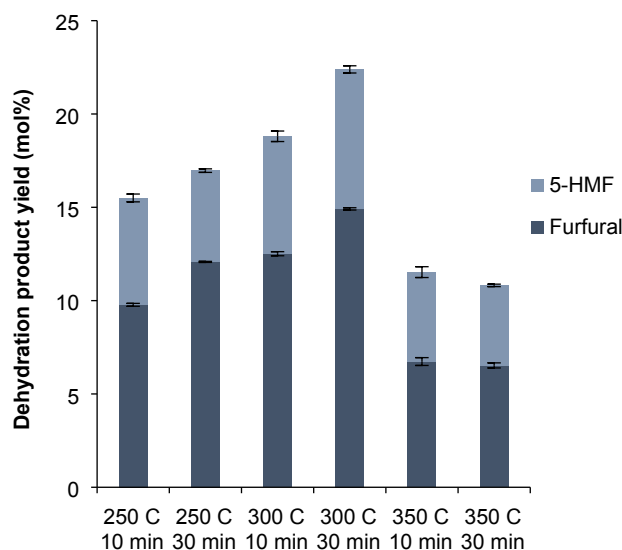


Figure 8. Yields of dehydration products from acid-catalyzed solvent liquefaction in 1,4-dioxane and water as a function of temperature and reaction time (0.25 mM H₂SO₄; 10 vol% water).

The effect of water on dehydration products as functions of reaction temperature and reaction time are illustrated in Figure 8. For both short (10 min) and long (30 min) reaction times, increasing temperature from 250 to 300°C increased both 5-HMF and furfural. Increasing reaction temperature to 350°C, however, dramatically reduced yields of dehydration products for both short and long reaction times. Considering that solubilized carbohydrate also disappeared at this temperature (Figure 7), presumably as the result of accelerated dehydration reactions, this result is a little surprising. A possible explanation is that at high temperatures water promoted the conversion of dehydration products to humins.^{36,55,60–64} To test this hypothesis, solid residue from solvent liquefaction was analyzed for elemental composition and the O/C and H/C ratios plotted in a Van Krevelen diagram (see Figure S8 in the Supplementary Material). The residues obtained from solvent liquefaction at temperatures below 300°C, plotted very close to cellulose, suggesting the residues were essentially unreacted cellulose. However, for long reaction times or in the presence of water, residue from solvent liquefaction at 300°C or higher plotted much closer to humins, suggesting substantial repolymerization of dehydration products to humins. Further, it is important to note that some gasification is also possible in addition to humin generation at severe

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3 reaction conditions (high temperature and long reaction time) via ring fragmentation of
4 intermediate reducing sugar and furanic products.⁵⁸ Nevertheless, this phenomenon seems less
5 likely to occur due to negligible gas yields observed at the above reaction conditions.
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10 **Conclusions**

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14 1,4-Dioxane was used to demonstrate the utility of low polarity and low boiling point aprotic
15 solvents for acid-catalyzed depolymerization of cellulose into solubilized carbohydrates. These
16 solvents offer advantages in converting cellulose into solubilized carbohydrates at high yields with
17 the advantage over high polarity, high boiling solvent of ease in separating sugar products from the
18 solvent. Levoglucosan was the major carbohydrate product when using pure 1,4-dioxane while a
19 mixture of levoglucosan and glucose was produced in co-solvent mixtures of 1,4-dioxane and
20 water. High temperatures and low acid concentrations promoted high yields of levoglucosan as a
21 result of lower rates of anhydrosugar degradation by secondary reactions. A maximum
22 levoglucosan yield of 51% was achieved at 350°C using 0.25 mM sulfuric acid in pure 1,4-dioxane.
23
24 A mixture of 1,4-dioxane and water at 9:1 mass ratio increased yields of solubilized products to
25 62% and solubilized carbohydrates to 38%. Adding water as co-solvent to 1,4-dioxane enabled
26 effective conversion of cellulose into solubilized carbohydrates at low temperatures (e.g. 250°C)
27 which is more increases the feasibility of this process for large scale application. Larger amounts
28 of water and higher temperatures were detrimental to sugar yields due to increased rates of
29 dehydration of monosaccharides to furfural and 5-HMF, which could polymerize to humins at the
30 most severe reaction conditions.
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49 The results are useful in developing a solvent liquefaction process for converting lignocellulosic
50 biomass into sugars. Appropriate operating conditions are proposed in Table 1.
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Table 1. Proposed qualitative optimum regime for maximizing carbohydrate yields from cellulosic biomass in 1,4-dioxane

Reaction parameter	Proposed optimal regime
Reaction time	10 min
Reaction temperature	250 °C
Acid concentration	0.25 mM
Co-solvent water content	10 vol%

Acknowledgement

We acknowledge the financial support of the Iowa Energy Center. The authors would like to thank Tanner C. Lewis, Robert Dunteman and Yu Hui Lui for their help in conducting solvent liquefaction experiments. We also appreciate the contributions of Patrick Johnston, Marjorie Rover and Patrick Hall in analyzing the solubilized products.

Supplementary Information. Flow chart of experimental design, Boiling point and reactor pressure estimates, Optimization of analytical dilute acid-hydrolysis test, Molecular weight distribution of solubilized carbohydrates, Pre- and post-hydrolysis chromatograms of carbohydrate products, Effect of acid concentration on LG degradation products, Effect of acid concentration on rate of LG formation and degradation, Effect of water on solubilized carbohydrate yields in absence of acid catalyst, Relationship between 5-HMF and furfural yields and water content in 1,4-dioxane, Determination of extent of dehydration by O/C and H/C ratios, Gas production during acid-catalyzed cellulose depolymerization in 1,4-dioxane/water, Figure S1: Flow chart of experimental design for studying the effects of factors influencing cellulose solvent liquefaction in 1,4-dioxane, Table S1: Boiling points and reactor pressure estimates of polar aprotic solvents, Figure S2: Recovery of glucose versus acid concentration in analytical acid-hydrolysis test, Figure S3: Molecular weight distribution of solubilized carbohydrates from acid-catalyzed solvent liquefaction of cellulose in 1,4-dioxane, Figure S4: HPLC chromatograms of pre- and post-hydrolysis of the solubilized product from solvent liquefaction of cellulose in

1,4-dioxane and water, Figure S5: Maximum yields of degradation products from acid-catalyzed solvent liquefaction of cellulose in 1,4-dioxane, Figure S6: Initial reaction rates of acid-catalyzed solvent liquefaction of cellulose in 1,4-dioxane as a function of H₂SO₄ concentration (no water, 350 °C, Figure S7: Yields of furanic compounds from acid-catalyzed solvent liquefaction of cellulose in 1,4-dioxane and water as a function of water content, Figure S8: Van Krevelen diagram of cellulose and solid residues from acid-catalyzed solvent liquefaction of cellulose in 1,4-dioxane and water, Table S2: Gas production in 50 mg cellulose conversion in 90/10 vol% 1,4-dioxane/water with 0.25 mM sulfuric acid, References.

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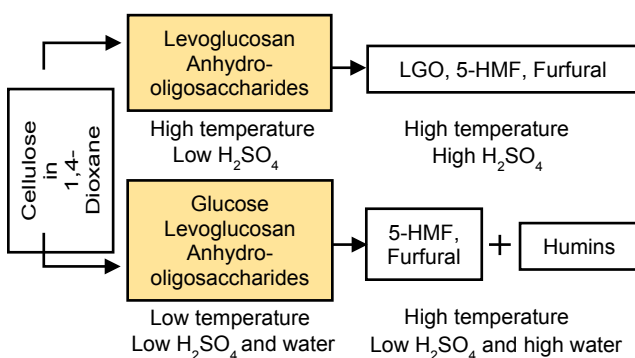
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Synopsis

Solvent liquefaction parameters of cellulose conversion in 1,4-dioxane could be tuned judiciously to produce high sugar yields without having to use severe reaction conditions.