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**Production of solubilized carbohydrate from cellulose using non-catalytic, supercritical  
depolymerization in polar aprotic solvents**

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**Abstract**

We report yields of solubilized and depolymerized carbohydrate from solvent processing of cellulose as high as 94% without use of catalysts. Cellulose was converted using a variety of polar aprotic solvents at supercritical conditions, including 1,4-dioxane, ethyl acetate, tetrahydrofuran, methyl iso-butyl ketone, acetone, acetonitrile, and gamma-valerolactone. Maximum yield of solubilized products from cellulose, defined as both depolymerized carbohydrate and products of carbohydrate dehydration, was 72 to 98% at 350 °C for reaction times of 8-16 min. In all cases solvents were recovered with high efficiency. Levoglucosan was the most prevalent solubilized carbohydrate product with yields reaching 41% and 34% in acetonitrile and gamma-valerolactone, respectively. Levoglucosan yields increased with increasing polar solubility parameter, corresponding to decreasing activation energy for cellulose depolymerization.

## Introduction

Development of alternative technologies based on renewable energy resources has proliferated in recent times to displace fossil fuels and petroleum-based chemicals. Lignocellulosic biomass has drawn attention as a sustainable feedstock for producing biobased renewable fuels and biochemicals.<sup>1</sup> Cellulose, the most abundant component of lignocellulosic biomass, is a good source of fermentable sugars.<sup>2</sup> Currently, the most prominent pathway to depolymerize cellulose to sugars is enzymatic hydrolysis. Although this biochemical route has high selectivity for final products, the process has several drawbacks such as slow conversion rates, high cost of enzyme, and end-product inhibitions.<sup>3,4</sup> Biomass depolymerization is slowed by the innate structural recalcitrance of cellulose. Cellulose is a three-dimensional cross-linked biopolymer of D-glucose units joined by  $\beta$ -1,4 glycosidic bonds, which is intrinsically rigid.<sup>5</sup> Additionally, the intensive inter- and intra-molecular hydrogen bonding in cellulose gives rise to a rigid crystalline structure, which is highly resistant to enzymatic hydrolysis.<sup>6</sup>

Alternatively, it is possible to produce fermentable sugars through thermochemical conversion pathways, such as pyrolysis and solvent liquefaction (also known as solvolysis).<sup>7</sup> If optimized, these technologies could be rapid, robust and economical approaches to convert biomass into solubilized carbohydrate at high yields. While glucose can be directly produced from cellulose in the presence of water, thermal depolymerization of cellulose in the absence of water usually produces levoglucosan (LG) as the main sugar monomer along with other anhydro monosaccharides and oligosaccharides. These anhydro sugars can be hydrolyzed to glucose and then fermented to ethanol or the anhydro monosaccharides can be directly fermented to ethanol.<sup>8</sup> <sup>9</sup> Levoglucosan is an important precursor chemical in its own right, which can be used to synthesize pharmaceuticals and biodegradable plastics.<sup>10</sup>

Solvent liquefaction is the depolymerization of biomass in the presence of a solvent. Reaction temperatures are normally in the range of 150 – 400 °C with system pressure elevated to keep the solvent from boiling.<sup>11</sup> Solvent liquefaction of cellulose can be very selective depending upon the choice of the solvent and/or catalyst. Solvents can dissolve some of the indigenous mineral matter in biomass that suppresses sugar yields during thermal depolymerization of lignocellulose.<sup>12</sup> Moreover, unlike pyrolysis, solvent liquefaction is able to recover non-volatile sugars (i.e., solubilized poly- or oligosaccharides) as products. The dilution of sugar products in the solvent can also potentially reduce secondary reactions that decompose sugars. Solvent phase conversion makes processing of wet biomass possible, thus eliminating energy intensive drying of raw feedstock.

Hydrolysis with highly concentrated acid could facilitate depolymerization of cellulose, but scaling up is challenging due to associated corrosive effects, handling hazards and complexity of acid recovery.<sup>13, 14</sup> Ionic liquids combined with homogenous or heterogeneous catalysts have also been explored because their exquisite solvation properties promote faster hydrolysis of cellulose.<sup>15, 16</sup> Nevertheless, the progress of this technology has been hindered because quantitative recovery and reuse (at least 98%) of these expensive solvents has not been solved.<sup>17</sup> Conversion of cellulose to solubilized carbohydrates also has been studied using hot and pressurized protic solvents.<sup>18-20</sup> Combinations of processing in supercritical and subcritical water has been employed to produce a hydrolyzed product.<sup>21</sup> Nevertheless, it has been reported that the presence of water may lower the activity of acid catalyst and also favor formation of undesired degradation products compared to other polar solvents.<sup>22-24</sup> The use of methanol leads to the formation of methylated oligosaccharides.<sup>25</sup>

Solvolytic biomass in polar aprotic solvents results in more desirable product distributions. For example, up to 38% of LG was produced when cellulose was treated with acetone,<sup>26</sup> sulfolane<sup>27</sup> or 1, 4-dioxane.<sup>28</sup> However, no information about other products was reported in these studies.

Luterbacher et al.<sup>29</sup> recently demonstrated high yields of solubilized carbohydrate from lignocellulosic biomass using gamma-valerolactone in the presence of acid catalyst. In their study, biomass was converted in a continuous flow reactor at 157 – 217 °C. Yield of solubilized carbohydrate from cellulose was as high as 80%, but required times as long as 2 h because of the low reaction temperatures. Only 90% of GVL was recovered after the reaction since some of the solvent was consumed during the process.

We have recently produced soluble sugar monomers by depolymerizing acid pretreated switchgrass in 1, 4-dioxane solution.<sup>12</sup> Despite relatively high reaction temperatures (300 – 350 °C), the sugars were stable. Over 98% of the 1, 4-dioxane solvent was recovered after reaction. Yields of levoglucosan from cellulose were as high as 50% and oligosaccharides were not quantified. Other studies also showed that acid catalyzed aprotic solvents could produce dehydration products of cellulose such as 5-hydroxymethylfurfural, furfural and levoglucosenone at high yields.<sup>30, 31</sup>

While previous studies using various polar aprotic solvents suggest solvent liquefaction as an alternative to enzymatic hydrolysis for production of carbohydrates from lignocellulosic biomass, they either employed acid catalysts, heterogeneous catalysts or very long reaction times to achieve high yields of solubilized carbohydrates. Neither does the literature contain much information on the role of solvent properties on cellulose conversion. The choice of solvent not only determines product distributions and yields, but also influences the thermal stability of products and the ease of recycling the solvent. In general, solvents with low boiling points and high thermal and chemical stability are preferred.

The present work focuses on non-catalytic conversion of cellulose in polar aprotic solvents to produce solubilized carbohydrates, which are defined as the sum of monosaccharide, oligosaccharide and polysaccharide products that dissolve in the processing solvent. Although the

absence of acid simplifies the process, reaction rates and product yields are expected to decrease, thus requiring operation at higher temperatures and pressures to avoid long reaction times. In the present study, cellulose was depolymerized in seven different polar aprotic solvents to understand the effect of solvent properties on the yields and distribution of the cellulose depolymerization products.

## 2. Experimental section

### 2.1 Materials

Microcrystalline cellulose with average particle size of 50  $\mu\text{m}$  was purchased from Sigma-Aldrich. Levoglucosan (purity > 99.6%), cellobiosan (purity > 98.6%) were obtained from Carbosynth, UK and 5-hydroxymethylfurfural (5-HMF, purity > 99%) and furfural (purity > 99%) from Sigma Aldrich. Glucose (purity > 99%) from Fisher Scientific, cellobiose (purity > 98%) from Acros Organics, and maltotriose, maltotetraose and maltohexaose were obtained from MP Biomedicals. HPLC grade (submicron filtered) 1,4-dioxane, ethyl acetate, tetrahydrofuran (THF), methyl iso-butyl ketone (MIBK), acetone, acetonitrile, and gamma-valerolactone (GVL) were purchased from Fisher Scientific.

### 2.2 Solvent processing methodology

Solvolysis experiments were performed in mini-reactors from Swagelok (316 SS) assemblies each consisting of one male connector (NPT type) and two sealed 3/8 inch caps. These reactors had total capacity of 2.5 mL. Microcrystalline cellulose in the amount of 10-100 mg was placed in a mini-reactor with 1.2 mL of aprotic solvent. The mini-reactors were tightly sealed and shaken for 1 h prior to reaction. A fluidized sand bath (Techne Industrial Bed 51) was used as the heating source. The heating bath was operated at 325 to 375  $^{\circ}\text{C}$  and reaction times were up to 20 min. Experiments were performed with 1,4-dioxane, ethyl acetate, tetrahydrofuran (THF), methyl iso-

butyl ketone (MIBK), acetone, acetonitrile, and gamma-valerolactone (GVL) as solvent with each experiment performed two or three times with average results reported. The standard deviation was within 5% error from the mean for most of the solvents tested except for 1,4-dioxane, ethyl acetate and acetone (error slightly over 10%) probably because of evaporation of solvent during extraction process due to their high volatility or remaining solvent in solid residue. The heating rate of the reactor was  $7\text{ }^{\circ}\text{C s}^{-1}$  and the reaction time measured from the time the reactor entered the preheated sand bath to the time it was removed and immersed in cold water. After one hour, the cooled reactor was opened for extraction of the liquid and solids contents of the reactor at room temperature. The liquid contents were transferred from the reactor using a pipette (Fisher Scientific) and the solids were collected at the bottom. Liquid fraction contained both the original solvent and solubilized products from cellulose depolymerization. This liquid fraction was filtered using syringe-filters of pore size  $0.45\text{ }\mu\text{m}$ . Solid residues were dried in an oven at  $50\text{ }^{\circ}\text{C}$  overnight and weighed. Gas production was determined by weighing a reactor before and after venting non-condensable gases from the cooled reactor.

The following definition was used to calculate the yield of solubilized products:

$$\text{Solubilized products yield (\%)} = \left(1 - \frac{\text{mass of solid residue} + \text{mass of gas produced}}{\text{initial mass of cellulose}}\right) \times 100 \quad (1)$$

### ***2.3 Analytical methods***

A Gas Chromatograph with Mass Spectrometer and Flame Ionization Detector (Agilent 7890B GC-MS/FID) was used to analyze the liquid fraction. The products in liquid fraction were first identified by MS and then quantified by FID. The gas chromatograph was equipped with two identical Phenomenex ZB 1701 (60 m x 0.250 mm and 0.250  $\mu\text{m}$  film thickness) capillary columns for separation of the products. One of these columns was connected to the MS while the other was connected to the FID. The injection port and FID back detector in the GC were held at



250 and 300 °C, respectively. Helium carrier gas flow was 1 mL min<sup>-1</sup>. Injection volume for analysis was 1 µL. The oven temperature of GC was ramped from 40 (3 min hold time) to 240 °C (4 min hold time) at a heating rate of 3 °C min<sup>-1</sup>. The instrument was quantitatively calibrated with LG, 5-HMF and furfural. 1,6-anhydro-β-D-glucofuranose (AGF) was quantified using LG as the standard.

The yield and selectivity of a particular solubilized product were calculated on carbon molar basis as:

$$\text{Yield (\%)} = \frac{\text{moles of carbon in the solubilized product}}{\text{moles of carbon in initial feedstock}} \times 100 \quad (2)$$

$$\text{Selectivity (\%)} = \frac{\text{moles of carbon in the solubilized product}}{\text{total moles of carbon in all solubilized products}} \times 100 \quad (3)$$

GC/MS non-detectable solubilized products, such as solubilized carbohydrates with degree of polymerization (DP) higher than 1, were characterized by molecular weight using Gel Filtration Chromatography (GFC). GFC analysis was conducted with a Dionex Ultimate 3000 series HPLC system using water as the eluent. The organic liquid fraction from solvolysis was diluted to 90% water content and then tested for GFC. Two columns of the type PL-aquagel-OH-20 5 µm were connected in series at 25 °C and DI water passed through as the mobile phase at 0.8 mL min<sup>-1</sup>. Refractive index was the basis of detection. Polyethylene glycol (PEG) was used as a standard to generate a calibration curve of the molecular weight distribution of the solubilized products relative to PEG. Identification of some of the solubilized products was done by comparing retention times of individual standards of LG, glucose, cellobiosan and cellobiose. To obtain more accurate molecular weight distributions and DP of the products, a calibration system was developed between the known molecular weights of the carbohydrates LG, cellobiosan, maltotriose, maltotetraose and maltohexaose and their relative molecular weights determined by PEG standard in GFC. Although malto-oligosaccharides from cellulose are not expected as

products, these compounds show similar DP to their analogous cello-oligosaccharides, thus justifying this molecular weight estimation for carbohydrates produced from cellulose. The DP for the oligo- or polysaccharides was then determined by dividing this molecular weight by 162. The yield of solubilized carbohydrates was calculated according to:

$$Y_{SC} = Y_{SP} - Y_F \quad (4)$$

where  $Y_{SC}$ ,  $Y_{SP}$ , and  $Y_{SF}$  are the yields of solubilized carbohydrates, solubilized products, and furans (5-HMF and furfural), respectively.

### 3. Results and Discussion

#### 3.1. Effect of different polar aprotic solvents on cellulose depolymerization

##### 3.1.1 Solubilized carbohydrate production and conversion efficiency

The evolution of solubilized monomeric products from cellulose is presented in Figure 1 for different solvents at 350 °C. For all solvents LG was the major solubilized monomeric product, achieving maximum yield within 8-16 min of reaction. The highest LG yield of 38% was achieved in acetonitrile followed by 34% in GVL. The lowest yield was 15% in 1,4-dioxane. For all solvents, the maximum yield of 5-HMF, the second most dominant solubilized monomeric product, reached maximum yield at nearly the same time as LG. The maximum yield of 5-HMF occurred in THF (9%) while the minimum yield occurred in acetonitrile (1%). Other solubilized co-products, furfural and 1,6-anhydro-β-D-glucofuranose (AGF), showed a combined yield of less than 3% in all the solvents.

Table 1 shows that all the polar aprotic solvents produced relatively high yields of solubilized products from cellulose in relatively short times. Overall, the yields of solubilized products at 350 °C at the reaction time that achieved maximum LG yield were in the range of 72-98% depending

upon the solvent. Although treating cellulose in MIBK produced the highest solubilized products yield (98%), the same process in THF, acetone, GVL and acetonitrile also achieved impressive yields of solubilized products, exceeding 90%. Even 1,4-dioxane and ethyl acetate, which had the lowest optimum LG yields, resulted in yields of solubilized products above 72%. The order of solubilized products yield in various solvents from low to high was 1,4-dioxane » THF < acetone < Ethyl acetate < GVL » acetonitrile < MIBK. Conversion rate of cellulose was estimated as the initial rate at which the unreacted cellulose decomposed. The order of conversion rate of cellulose from low to high was 1,4-dioxane < THF < acetone < ethyl acetate < acetonitrile < GVL < MIBK and ranged from 2.07 to 3.53 mol min<sup>-1</sup> (Figure S4).

The total mass balance of cellulose conversion at the condition of maximum LG yield is summarized in Figure 2 where solubilized products include solubilized carbohydrates (LG, AGF and solubilized carbohydrates with DP > 1) and other dehydration products (5-HMF and furfural). The solubilized products contained significant amounts of solubilized carbohydrates with DP > 1, confirmed by GFC analysis, in addition to monomeric carbohydrates (the analysis will be discussed in detail in a later section). As shown in Table 2, solubilized carbohydrate yield from processing in acetonitrile and GVL reached 94 and 86%, respectively, compared to 63% for 1,4-dioxane. Furthermore, the selectivity of LG among the solubilized products was found to be in the range of 16-40%, depending upon the solvent.

Stability of LG in different solvents is also compared in Table 2 using a degradation rate, defined as the slope of the LG yield curve with time after the point of its maximum yield. The order of decreasing LG stability is: 1,4-dioxane > MIBK > THF > acetone > acetonitrile > ethyl acetate > GVL. Although GVL and acetonitrile had comparable high yield of LG, GVL had degradation rate that was three times higher than acetonitrile.

### **3.1.2 Solvent recovery**

The recovery of solvent was quantified for acetonitrile, GVL and THF. For processing at 350 °C solvent recovery was very high: 97% for acetonitrile, 98% for THF and 99% for GVL. Except for ethyl acetate and MIBK, other solvents also had high solvent recovery, as estimated by GC/MS peak areas for solvent decomposition products.

### *3.1.3 Effect of reaction conditions*

The influence of reaction conditions was further evaluated for THF and acetonitrile as solvents. Acetonitrile and THF were chosen because they produced the highest LG and 5-HMF yields, respectively. Both of the solvents have low boiling points, easing their recovery. As shown in Figure 3 (a) and (b), higher temperatures facilitated the rate of reaction as evidenced by the shorter time to reach maximum LG yield. Increasing temperature from 325 to 350 °C significantly enhanced the maximum LG yield for both acetonitrile and THF, but no further increase in LG yield was seen for temperature above 350 °C. The yield of 5-HMF in THF at 350 °C was marginally higher than at 325 °C. Further increases in temperature significantly reduced the yield of 5-HMF (Figure 3 (c)).

The effect of mass loading on the yields of major monomeric products was also studied for acetonitrile and THF. The optimal mass loadings were strongly dependent on the choice of solvent as well as the reaction products studied. As shown in Figure 4 (a), maximum LG yield of 41% was obtained at 10 mg mass loading of cellulose in acetonitrile at 350 °C. An increase in mass loading of cellulose from 20 mg to 50 mg caused a reduction in LG yield from 38 to 12%. On the other hand, the optimum mass loading in THF to achieve maximum LG yield (24%) at 350 °C was 50 mg cellulose (Figure 4 (b)). The increase in LG yield was accompanied by a decrease in 5-HMF yield from 9 to 7% for THF (Fig. 4 (c)).

It was further noted that optimal mass loading of cellulose varied by product. For example, the maximum LG yield for solvolysis in THF at 350 °C occurred at mass loading of 20 mg while maximum 5-HMF yield occurred at mass loading of 50 mg. Increasing the mass loading of cellulose up to 100 mg was detrimental to the production of both LG and 5-HMF possibly due to mass transfer limitation in the conversion process of cellulose.

### ***3.2 Understanding cellulose depolymerization in polar aprotic solvents***

#### ***3.2.1 Role of solubility parameter of the solvents on carbohydrate yields and selectivity***

In order to maximize the production of solubilized carbohydrates, it is important to identify solvent properties that play a role in enhancing the depolymerization of cellulose. High solubility or degree of interaction of cellulose with a solvent may contribute to faster reaction and higher degree of depolymerization.<sup>32</sup> The solubility parameter of a solvent compared to that of cellulose is potentially a good indicator of the degree of interaction between the two.<sup>33-35</sup> However, for the solvents evaluated in this study, the solubility parameters at ambient conditions were in the range of 17-26.3 MPa<sup>1/2</sup>, significantly lower than the solubility parameter for cellulose (39.3 MPa<sup>1/2</sup>) (see  $\delta_{ref}$  in Table S3).<sup>33</sup> Despite these differences, the solvents showed excellent conversion of cellulose to solubilized products, ranging from 72 to 98% at 350 °C. At all reaction conditions tested, the aprotic polar solvents were operated above their critical points with the possible exception of GVL, for which critical point data is not available in the literature (see Table S1 and S2 in the supplemental data for details). The solubility parameter, which is a function of temperature and pressure, was estimated for the reaction conditions based on thermophysical properties of the solvents described in the supplementary material (Table S4). At reaction conditions, the solubility parameters for all solvents investigated were estimated to be in the range of 25.7-33.8 MPa<sup>1/2</sup>, which approaches the solubility parameter of cellulose (Table S5).

This similarity is likely responsible for the high level of cellulose conversion to solubilized products even in the absence of catalyst.

The three major components of solubility parameter are the dispersive solubility parameter, the polar solubility parameter and the hydrogen bonding solubility parameter.<sup>36</sup> Of these, only the polar solubility parameter,  $\delta_p$ , exhibited a wide variability among the solvents tested (Table S5). As shown in Figure 5 (a) and (b), the maximum yield of LG and its selectivity among solubilized products increased linearly with increasing solvent  $\delta_p$ . Although the maximum yields of 5-HMF did not correlate with the polar interaction parameter of the solvents, the ratio of 5-HMF to LG maximum yields decreased linearly with solvent polar solubility parameter (Figure 5 (c)), indicating that polarity of the solvent indirectly influences the selectivity of 5-HMF. These observations suggest that  $\delta_p$  could be an important parameter in solvent selection.

### ***3.2.2 Activation energy for cellulose solvolysis in different solvents***

The activation energies of cellulose decomposition were calculated and compared for several of the solvents (see Table S6, Figure S1, S2, S3). The activation energies for solvolysis in GVL, acetonitrile, and THF were 19.7, 20.23 and 26.53 kcal mol<sup>-1</sup>, respectively. Activation energy for cellulose decomposition during pyrolysis above 300 °C was previously reported to be 45-60 kcal mol<sup>-1</sup>.<sup>37-39</sup> Clearly, solvolysis in polar aprotic solvents substantially reduces the activation energy of cellulose depolymerization. Thus, it seems likely that the higher polar solubility parameters of acetonitrile and GVL compared to THF (Table S5) contribute to their lower activation energies for cellulose depolymerization and, hence, enhanced LG yields.

### ***3.2.3 Formation of solubilized carbohydrate as a function of solvent polarity***

Evolution of solubilized carbohydrate with DP > 1 was investigated using GFC analysis. Figure 6 (a) and (b) show GFC chromatograms of solubilized products from solvent processing of

cellulose in acetonitrile and THF, respectively, for selected reaction times. It can be seen that solubilized products gradually shifted to lower molecular weight with increasing reaction time. These high molecular weight species are undoubtedly anhydro oligo- and polysaccharides. In fact, the complete absence of monosaccharides and disaccharides (glucose and cellobiose) and the prevalence of anhydro monosaccharides and disaccharides (LG and cellobiosan) support this supposition. As reaction progressed, the molecular weight of the anhydro polysaccharides (defined as  $DP > 10$ ) decreased accompanied by an increase in LG and anhydro oligosaccharides (defined as  $2 \leq DP \leq 10$ ). For both acetonitrile and THF solvent, LG and anhydro oligosaccharides (defined as  $2 \leq DP \leq 10$ ) were the major solubilized carbohydrates when LG yield reached maximum (Figure 6 (c)).

Despite the aforementioned similarities, the product distributions of solubilized carbohydrates for acetonitrile and THF were distinct. For acetonitrile, the concentration of solubilized anhydro polysaccharides was low during the entire course of reaction (Figure 6 (a)). As time progressed, the LG peak increased rapidly whereas anhydro oligosaccharides gradually decreased. On the other hand, the solubilized products in THF contained much higher concentrations of anhydro polysaccharides with higher average DPs. Furthermore, the concentration of both LG and anhydro oligosaccharides increased as anhydro polysaccharides decreased in THF as the reaction progressed (Figure 6 (b)). This suggests that depolymerization of anhydro poly- and oligosaccharides to LG proceeded more slowly in THF than in acetonitrile. This difference we attribute to the higher activation energy barrier for cellulose depolymerization when using a lower polarity solvent like THF compared to acetonitrile.

Solubilized products also include 5-HMF and furfural as minor products. As previously shown in Figure 1, 5-HMF and furfural increased along with LG and reached their maximum yields at the same time as LG. This suggests that LG, 5-HMF and furfural were simultaneously produced rather than 5-HMF and furfural being products of secondary decomposition of LG. In fact, neither

5-HMF nor furfural was produced when LG was reacted in THF and acetonitrile at 350 °C. These dehydration products could be produced from the reducing ends of anhydro poly- or oligosaccharides through well-known ring-opening<sup>40-42</sup> fragmentation and rearrangement mechanisms. Based on these observations, we propose Scheme 1 for the depolymerization of cellulose in aprotic solvents.

## Conclusions

We demonstrated that polar aprotic solvents at supercritical condition are capable of rapidly converting cellulose into solubilized and depolymerized carbohydrate without the use of catalysts. A wide range of polar aprotic solvents effectively deconstructed cellulose with maximum yields of solubilized products reaching 72-98% and maximum yields of solubilized carbohydrate reaching 63-94%. To our knowledge, this is the highest yield of solubilized carbohydrate reported for non-catalytic solvent processing of cellulose. These high yields are attributed to a close correspondence in solubility parameters for cellulose and the solvents at the elevated temperatures and pressures of the experiments. Levoglucosan was the major carbohydrate product with the highest maximum yield of 41% obtained using acetonitrile as solvent. Solvents with higher polar solubility parameters lowered the activation energies for cellulose depolymerization and promoted LG formation whereas anhydro polysaccharides and oligosaccharides were preferentially produced in solvents with lower polar solubility parameter.

## Acknowledgement

Financial support from the Iowa Energy Center is greatly acknowledged. The authors would like to thank Tanner C. Lewis for his assistance in performing experiments. The expertise of Patrick Johnston, Marjorie Rover and Patrick Hall in analyzing products is also greatly appreciated.



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Table 1. Solubilized products in different solvents (350 °C and 20 mg mass loading)

Solvent	Maximum LG yield (%)	Time to reach maximum LG yield (min)	Solubilized products yield at maximum LG yield (%)
1,4-dioxane	15	8	72
Ethyl acetate	21	8	81
THF	22	~12	91
MIBK	25	12	98
Acetone	25	10	95
GVL	34	8	93
Acetonitrile	38	16	95

Table 2. Yields of solubilized carbohydrate, and selectivity of LG in solubilized products, both at the optimum condition for LG production, and also thermal stability of LG in different solvents (350 °C and 20 mg mass loading)

Solvent	Solubilized carbohydrate in liquid (%)	Selectivity of LG in liquid (%)	Degradation rate of LG <sup>a</sup> (mol min <sup>-1</sup> )
1,4-dioxane	63	16	0.063
Ethyl acetate	72	26	0.250
THF	81	28	0.159
MIBK	91	25	0.098
Acetone	89	26	0.207
GVL	86	36	0.681
Acetonitrile	94	40	0.216

a: Calculated after maximum in LG yield

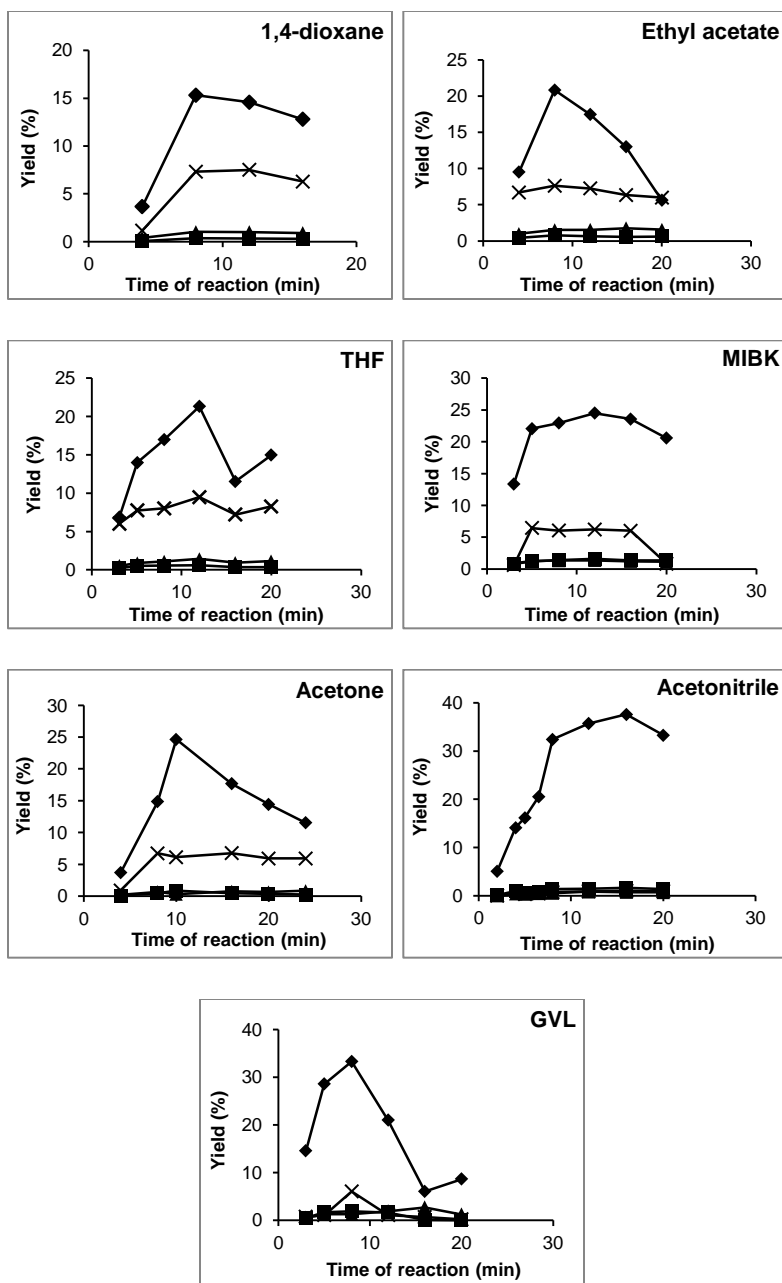


Figure 1. Carbon molar yields of GC/MS detectable solubilized products as a function of time for several polar aprotic solvents at 350 °C with 20 mg cellulose as feedstock (◆ LG; × 5-HMF; ▲ Furfural; ■ AGF).

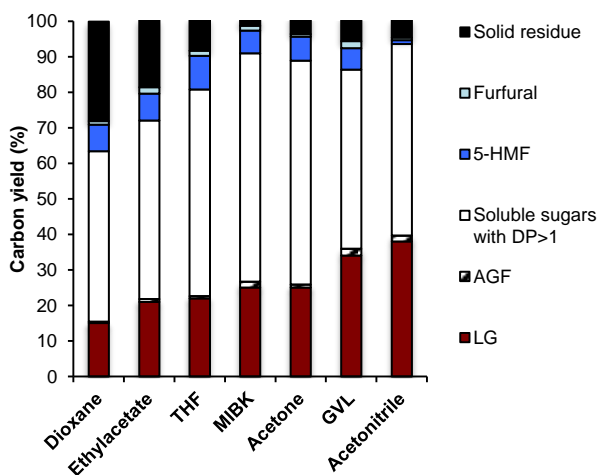


Figure 2. Product distribution of cellulose in different solvents reacted at 350 °C with 20 mg mass loading of cellulose. The reaction times are varied for solvents and depend on the time to reach the maximum LG yield in each solvent (see Table 1). The yield of solubilized carbohydrate with DP > 1 is determined by subtracting the yields of GC/MS detectable monomers (LG, 5-HMF, furfural and 1,6-anhydro- $\beta$ -D-glucofuranose (AGF)) from the yield of solubilized products.

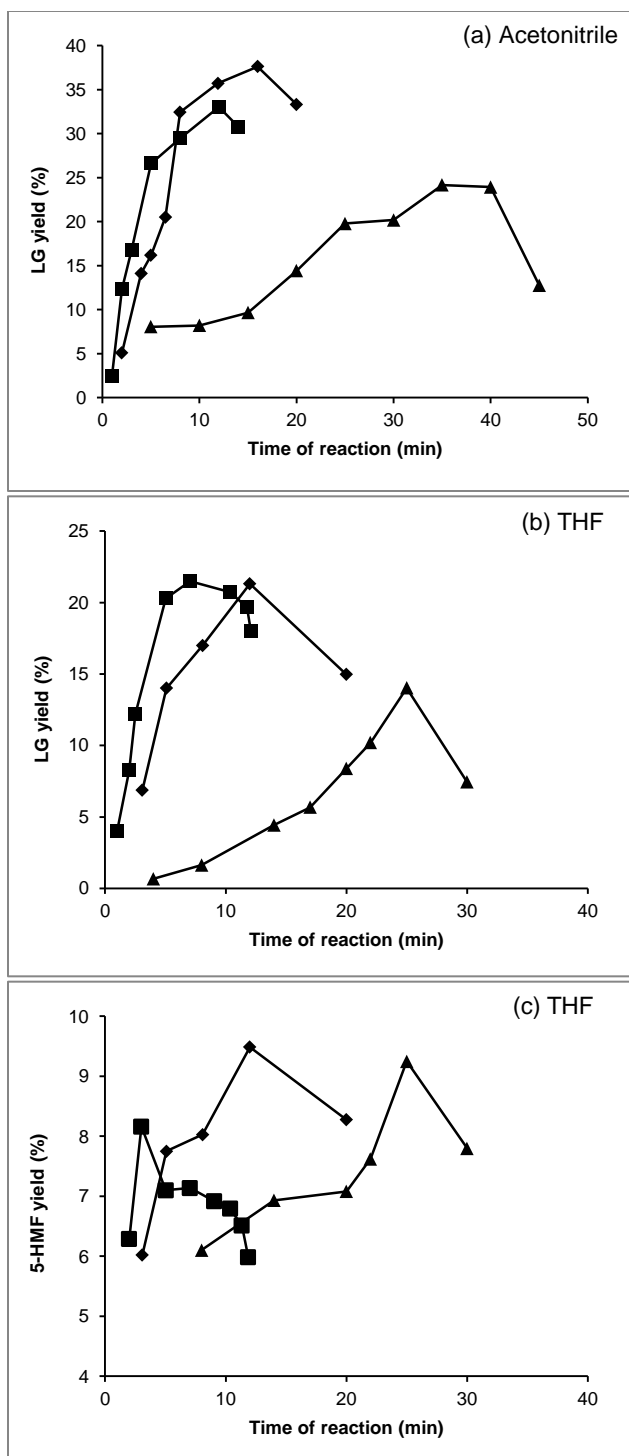


Figure 3. Effect of temperature on product yields as a function of time for cellulose solvolysis with 20 mg mass loading of cellulose; (a) LG in acetonitrile, (b) LG in THF, (c) 5-HMF in THF (▲ 325 °C; ◆ 350 °C; ■ 375 °C).

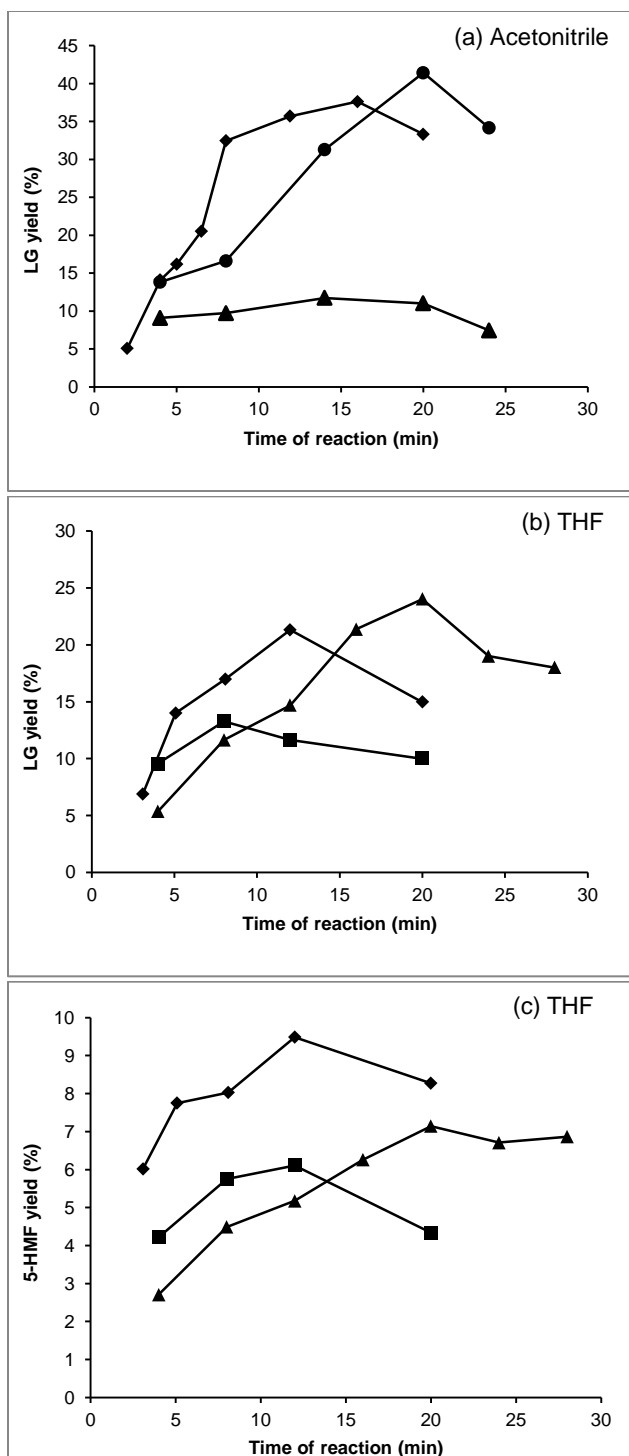


Figure 4. Effect of mass loading of cellulose on product yields as function of time for solvolysis at 350 °C (a) LG yield in acetonitrile; (b) LG yield in THF; (c) 5-HMF yield in THF (● 10 mg loading; ◆ 20 mg loading; ▲ 50 mg loading; ■ 100 mg loading).

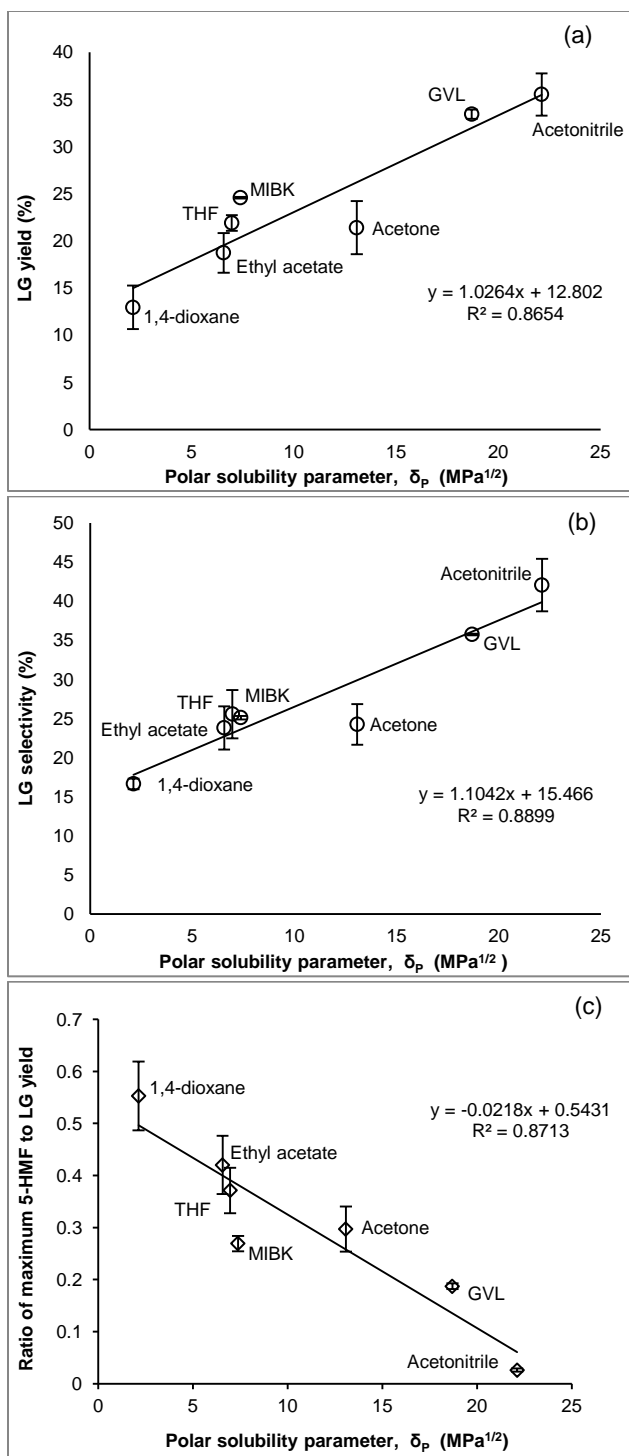


Figure 5. Correlation between the polar solubility parameter of the solvent and (a) maximum LG yield; (b) LG selectivity at maximum LG yield; and (c) yield ratio of 5-HMF to LG at maximum LG yield for cellulose depolymerization at 350 °C using 20 mg cellulose loading.



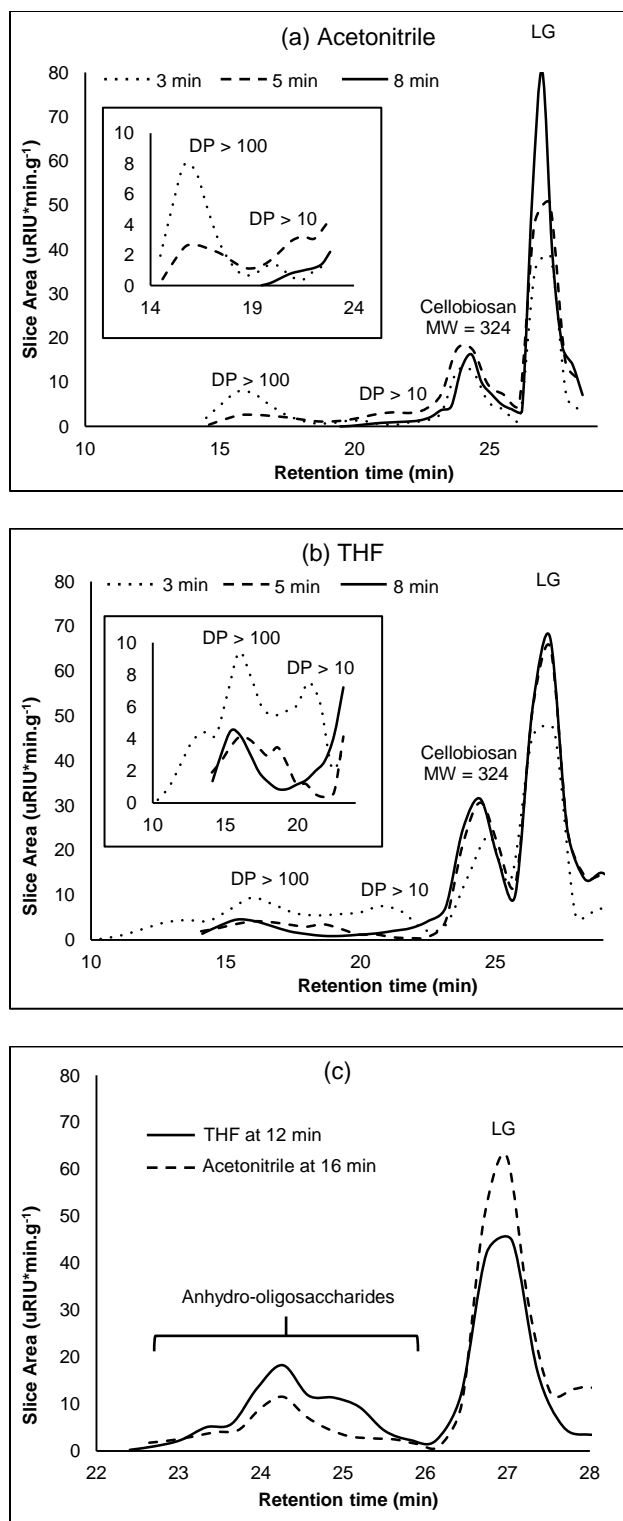


Figure 6. Molecular weight distribution of solubilized products from the solvolysis of cellulose at 350 °C for different reaction times in (a) Acetonitrile; (b) THF; (c) Comparison of acetonitrile and THF at 16 min and 12 min, respectively (Peak areas were normalized by the weight of solubilized products).

Scheme 1. Proposed depolymerization pathway of cellulose in aprotic polar solvents

