

**Effects of  $\gamma$ -Valerolactone in Hydrolysis of Lignocellulosic Biomass to Monosaccharides**

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## COMMUNICATION

## Effects of $\gamma$ -Valerolactone in Hydrolysis of Lignocellulosic Biomass to Monosaccharides

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**The use of  $\gamma$ -valerolactone as solvent for acid-catalyzed biomass hydrolysis reactions increases reaction rates compared to reactions carried out in water. In addition, a low apparent activation energy for biomass hydrolysis and a higher value for monosaccharide conversion are displayed using GVL as solvent, leading to favourable energetics for monosaccharide production from biomass.**

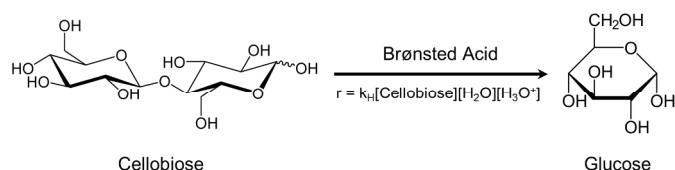
The current transition to a sustainable source of chemicals and energy is being driven by political, economic, and environmental concerns associated with petroleum-derived feed stocks. In this context, the conversion of lignocellulosic biomass, a renewable resource, into platform molecules and fuels has received increasing interest. In order for biomass to effectively contribute to reducing our dependence on petroleum, its efficient utilization is vital. Thus, major importance is being placed on the conversion of the hemicellulose (C<sub>5</sub> sugars) and cellulose (C<sub>6</sub> sugars) fractions of biomass into platform molecules, which then can, in turn, be further upgraded into chemicals and fuels.

Recently, the use of organic solvents has been shown to be beneficial in the chemical conversion of lignocellulosic biomass.<sup>1</sup> One such solvent is  $\gamma$ -valerolactone (GVL), which can be obtained from biomass and displays significant improvements in reaction performance for biomass conversion reactions compared to conversion in aqueous media, such as increased catalytic activity and higher selectivity to desired reaction products.<sup>2-6</sup> For example, high yields of levulinic acid (~70%) from cellulose using GVL as solvent have been achieved compared to yields as low as 20% obtained in water.<sup>2</sup> In addition, significant selectivity increases have been shown using GVL as solvent compared to reactions in water for the conversion of C<sub>5</sub> sugars<sup>3</sup> and C<sub>6</sub> sugars<sup>4</sup> to their corresponding furanic components furfural and 5-hydroxymethylfurfural (HMF), respectively, which are valuable platform molecules.

Previously, the production of monosaccharides from biomass in aqueous media has proven to be difficult due to the subsequent conversion of these sugars to their corresponding furanic components or degradation products, and therefore, current methods of monosaccharide production from biomass are cost prohibitive.<sup>7</sup> However, we have recently developed a processing strategy to produce concentrated streams of C<sub>5</sub> and C<sub>6</sub> sugars (e.g., 130 g/L) from the cellulose and hemicellulose fractions of lignocellulosic biomass in GVL-H<sub>2</sub>O solvent mixtures using dilute concentrations

of mineral acids (e.g., 0.005 M) at mild temperatures (e.g., 430-490 K) without using enzymes or ionic liquids.<sup>6</sup> After separation, the resulting aqueous stream of soluble sugars offer a versatile platform for subsequent upgrading by chemical or biological processes.

These results indicate that GVL is a promising solvent for biomass processing reactions; however, the fundamental scientific basis for solvent effects in biomass conversion reactions is limited at present. In the present study, we quantify the effects of GVL as a solvent with respect to changes in rates for acid-catalyzed biomass hydrolysis reactions compared to reactions carried out in water. Furthermore, we compare apparent activation energies for acid-catalyzed biomass hydrolysis and monosaccharide conversion reactions using both water and GVL as solvent. In particular, the liquid phase hydrolysis of cellobiose (i.e., a disaccharide of glucose units connected via a  $\beta(1\rightarrow4)$  glycosidic bond) is catalyzed by acid and serves as a probe reaction in the present study (Scheme 1). This reaction produces glucose, which is a valuable biomass-derived intermediate that can be subsequently transformed into high-value chemicals as well as potential biofuel components by both enzymatic and chemical approaches.<sup>8</sup>



Scheme 1. Acid-catalyzed hydrolysis of cellobiose to glucose.

Reaction kinetics modeling was employed to quantify the effects of GVL on the reaction rates of biomass hydrolysis reactions. Reaction kinetics data (see Supporting Information) for acid-catalyzed hydrolysis of cellobiose to glucose were obtained in H<sub>2</sub>O and various GVL-H<sub>2</sub>O mixtures at typical biomass hydrolysis conditions using sulfuric acid (SA), a common catalyst for biomass deconstruction pretreatments<sup>9</sup>. GVL-H<sub>2</sub>O mixtures were used, because water is necessary in hydrolysis reactions as it is a reactant. Furthermore, biomass contains inherent moisture, and the addition of water reflects real biomass processing conditions, and a fraction of water is needed to solubilize the disaccharide. It is important to note

that a lower SA catalyst concentration was used in the organic solvent compared to reaction in water to maintain similar kinetic profiles in these two solvent systems (e.g., in GVL, up to 5 times less SA was used than in H<sub>2</sub>O). The rate of cellobiose conversion was modeled as a function of a rate constant ( $k_H$ ), cellobiose concentration, water concentration, and acid concentration (see Supporting Information). The estimated hydrolysis rate constants ( $k_H$ ) using H<sub>2</sub>O and organic-water mixtures as solvents with SA as catalyst at various temperatures are shown in Table 1.

Table 1. Rate constants for acid-catalyzed hydrolysis of cellobiose and maltose in various solvent systems using SA as catalyst. Reaction conditions: 4 mL of solvent and stir rate of 700 rpm.

Solvent System	Reactant	Temp (K)	$k_H$ (M <sup>-1</sup> ks <sup>-1</sup> [H <sub>3</sub> O <sup>+</sup> ] <sup>-1</sup> )
GVL-H <sub>2</sub> O (4:1)	Cellobiose	393	8.9 ± 0.41
H <sub>2</sub> O	Cellobiose	403	0.61 ± 0.051
H <sub>2</sub> O	Maltose	403	0.81 ± 0.069
GVL-H <sub>2</sub> O (1:3)	Cellobiose	403	0.54 ± 0.029
GVL-H <sub>2</sub> O (1:1)	Cellobiose	403	2.0 ± 0.055
GVL-H <sub>2</sub> O (2.33:1)	Cellobiose	403	4.5 ± 1.1
GVL-H <sub>2</sub> O (4:1)	Cellobiose	403	18 ± 1.9
GVL-H <sub>2</sub> O (4:1)	Maltose	403	19 ± 3.1
THF-H <sub>2</sub> O (4:1)	Cellobiose	403	22 ± 3.3
Dioxane-H <sub>2</sub> O (4:1)	Cellobiose	403	9.1 ± 1.5
GVL-H <sub>2</sub> O (9:1)	Cellobiose	403	69 ± 9
GVL-H <sub>2</sub> O (4:1)	Cellobiose	413	29 ± 6.1
H <sub>2</sub> O	Cellobiose	418	2.2 ± 0.17
GVL-H <sub>2</sub> O (1:1)	Cellobiose	418	8.6 ± 1.4
H <sub>2</sub> O	Cellobiose	433	9.1 ± 1.5
GVL-H <sub>2</sub> O (1:1)	Cellobiose	433	22 ± 3.4

Figure 1 (left axis) shows the values of the rate constants for cellobiose hydrolysis plotted against the composition of GVL-H<sub>2</sub>O mixtures at 403 K using SA as catalyst. The rate constant exhibits an exponentially increasing trend with increasing concentrations of GVL. For instance, the hydrolysis rate constant for the conversion of cellobiose in GVL-H<sub>2</sub>O (4:1) shows a significant increase in the value of the rate constant of 31 times compared to the value in H<sub>2</sub>O at the same reaction conditions. Thus, it can be concluded that the rate of acid-catalyzed cellobiose hydrolysis is increased significantly using GVL as solvent, promoting the increasing rate of  $\beta(1\rightarrow4)$  bond cleavage.

We have found that increased rates of cellobiose hydrolysis are also observed for other polar aprotic solvents. For example, we have also studied cellobiose hydrolysis to glucose over SA using tetrahydrofuran (THF) and dioxane as solvent systems. The optimized rate constants ( $k_H$ ) derived from these measurements are reported in Table 1. The values observed for  $k_H$  increase by over an order of magnitude for both THF-H<sub>2</sub>O (4:1) and Dioxane-H<sub>2</sub>O (4:1) solvent compared to using H<sub>2</sub>O as a solvent using SA at the same reaction conditions. These results show that polar aprotic solvents such as dioxane and THF also display increased reaction rates similar to the GVL solvent for cellobiose hydrolysis to glucose.

This behavior of increased reaction rates for cellobiose hydrolysis in polar aprotic solvents compared to water is similar to that previously reported for the acid-catalyzed dehydration of xylose to furfural.<sup>10</sup> From these previous results, we have suggested that polar

aprotic solvents such as GVL affect the stabilization of the acidic proton relative to protonated transition states compared to reactions carried out in H<sub>2</sub>O. This stabilization effect for the proton and protonated transition states promotes favorable reaction energetics (i.e., lowers the activation free energy), leading to accelerated reaction rates for these acid-catalyzed biomass conversion reactions.<sup>10</sup>

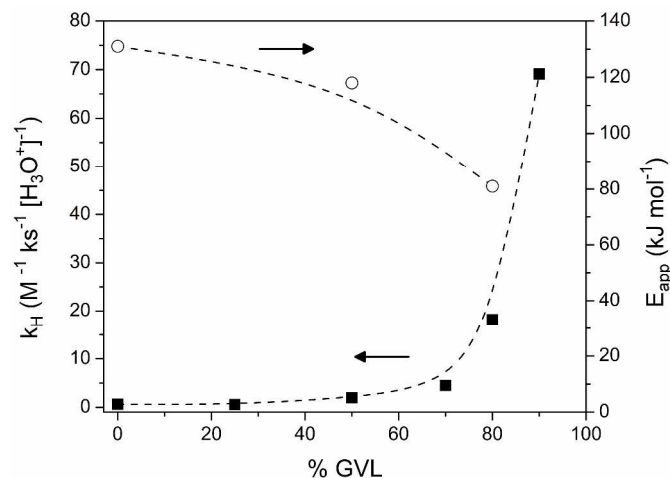


Figure 1. Cellobiose hydrolysis rate constants (■; left axis) and apparent activation energies (○; right axis) versus GVL content in GVL-H<sub>2</sub>O solvent mixtures.

We have investigated whether the increased rate of hydrolysis in polar aprotic compounds compared to reaction in water is specific to the case of cellobiose hydrolysis and  $\beta(1\rightarrow4)$  bond cleavage, or whether it is a more general phenomenon for other acid-catalyzed hydrolysis reactions. Accordingly, we studied the acid-catalyzed hydrolysis of maltose, which is disaccharide of glucose units connected via an  $\alpha(1\rightarrow4)$  bond using SA as catalyst. Reaction kinetics data were acquired and the values of the hydrolysis rate constants are reported in Table 1. The rate constant value for maltose using GVL-H<sub>2</sub>O (4:1) as solvent is 23 times greater than using H<sub>2</sub>O at the same reaction conditions. This rate constant value increase in GVL-H<sub>2</sub>O (4:1) is similar for cellobiose hydrolysis compared to using H<sub>2</sub>O as solvent. Thus, the use of GVL as solvent also improves other acid-catalyzed hydrolysis reactions in addition to  $\beta(1\rightarrow4)$  bond hydrolysis, showing that the increased reaction performance using GVL as solvent is not limited to cellobiose hydrolysis and  $\beta(1\rightarrow4)$  bond cleavage.

To probe more directly the kinetics of biomass conversion, we studied the acid-catalyzed hydrolysis of cellulose, a polymer of glucose, using GVL as a solvent. The conversion of cellulose was carried out in H<sub>2</sub>O and GVL-H<sub>2</sub>O (4:1) using 0.005 M and 0.0005 M SA, respectively at 448 K. Figure 2 shows the concentration profiles versus time for glucose production from cellulose in both H<sub>2</sub>O and GVL-H<sub>2</sub>O (4:1). The initial rate of glucose production in H<sub>2</sub>O is 0.26 mM min<sup>-1</sup> compared to a rate of 0.13 mM min<sup>-1</sup> in GVL-H<sub>2</sub>O (4:1). Accounting for the 10-fold decrease in catalyst concentration and the 5-fold decrease in H<sub>2</sub>O concentration (a reactant in hydrolysis) in GVL-H<sub>2</sub>O (4:1), an increase in the rate constant by a factor of 25 is observed for glucose production from cellulose in GVL-H<sub>2</sub>O (4:1). This increase in the rate constant is comparable with the increase observed above (a factor of 31) in the rate constant for cellobiose hydrolysis in the GVL-H<sub>2</sub>O (4:1) solvent system.

If GVL had a significant effect on cellulose crystallinity or cellulose solvation rather than just on cellulose bonds, as previously proposed<sup>6</sup>, we would expect to see a greater increase in the cellulose hydrolysis rate in the presence of GVL compared to the analogous increase in rate for cellobiose hydrolysis. Therefore, the promotion of cellulose hydrolysis in GVL, which allows for the production of sugars at low temperatures (<490 K), seems to be mainly due to the increase in the rate of the acid-catalyzed  $\beta(1\rightarrow4)$  bond hydrolysis rather than any effects on cellulose crystallinity.

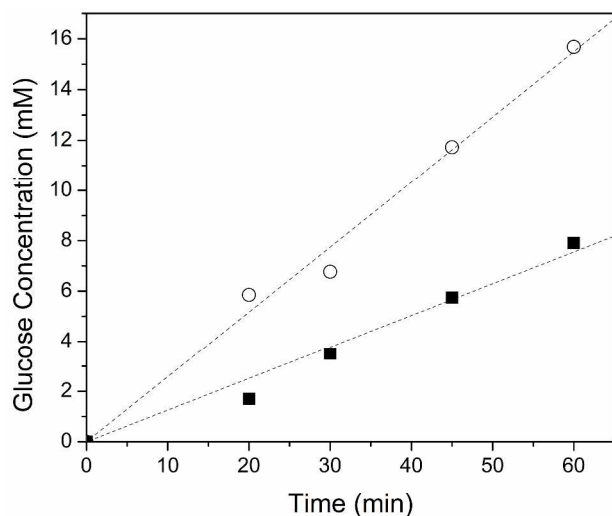


Figure 2. Glucose concentration versus time from cellulose conversion in H<sub>2</sub>O using 0.005 M SA (●) and GVL-H<sub>2</sub>O (4:1) using 0.0005 M SA (■) at 448 K.

The apparent activation energies for cellobiose hydrolysis were measured in H<sub>2</sub>O and GVL-H<sub>2</sub>O mixtures by collecting reaction kinetics data at different temperatures (Table 1), and the results are shown in Table 2. The measured apparent activation energy for cellobiose hydrolysis in water was 131 kJ mol<sup>-1</sup>, in good agreement with previous literature values using SA as catalyst.<sup>11</sup> The apparent activation energy for cellobiose hydrolysis decreases as the GVL to water ratio increases, changing by 50 kJ mol<sup>-1</sup> from H<sub>2</sub>O to GVL-H<sub>2</sub>O (4:1). Furthermore, the measured values of the apparent activation energies for cellobiose hydrolysis in solvents consisting of H<sub>2</sub>O, GVL-H<sub>2</sub>O (1:1), and GVL-H<sub>2</sub>O (4:1) are plotted versus the GVL concentration in Figure 1 (right axis), showing an exponentially decreasing trend with increasing concentration of GVL. Thus, the use of GVL as solvent significantly changes the energetics of the cellobiose hydrolysis reaction.

The apparent activation energies were measured for glucose and xylose conversion to their corresponding furanic components, HMF and furfural, respectively. Reaction kinetics data were collected at different temperatures in H<sub>2</sub>O and GVL-H<sub>2</sub>O (4:1) (see Supporting Information), and these activation energies are shown in Table 2. The apparent activation energy for glucose conversion in H<sub>2</sub>O was determined to be 135 kJ mol<sup>-1</sup>, in agreement with reported literature values.<sup>12,13</sup> Similarly, the apparent activation energy for xylose conversion in H<sub>2</sub>O was measured to be 138 kJ mol<sup>-1</sup>, also in agreement with reported literature values.<sup>13,14</sup> Importantly, the apparent activation energies are similar for cellobiose hydrolysis and glucose and xylose conversion in H<sub>2</sub>O, ranging from 131–138 kJ mol<sup>-1</sup>. Accordingly, low sugar yields from biomass have been obtained in aqueous media at these conditions due to the competition

between cellulose and hemicellulose hydrolysis and the subsequent sugar conversion reactions. However, the use of GVL as solvent increases the difference between the apparent activation energy values for cellobiose hydrolysis and glucose and xylose conversion. In the GVL-H<sub>2</sub>O (4:1) solvent, apparent activation energies of 138 and 135 kJ mol<sup>-1</sup> are observed for glucose and xylose conversion, respectively, whereas the apparent activation energy is significantly lower for the cellobiose hydrolysis reaction (81 kJ mol<sup>-1</sup>) comparatively, which makes sugar production favorable in the GVL solvent versus the subsequent dehydration of the sugars to furan compounds.

Table 2. Apparent activation energies for acid-catalyzed hydrolysis of cellobiose and conversion of glucose and xylose in H<sub>2</sub>O and GVL-H<sub>2</sub>O mixtures using SA as catalyst.

Solvent System	Reactant	E <sub>app</sub> (kJ mol <sup>-1</sup> )
H <sub>2</sub> O	Cellobiose	131
	Glucose	135
	Xylose	138
GVL-H <sub>2</sub> O (1:1)	Cellobiose	118
GVL-H <sub>2</sub> O (4:1)	Cellobiose	81
	Glucose	138
	Xylose	135

## Conclusions

The results of this study show that the apparent activation energy for cellobiose hydrolysis in the GVL solvent (81 kJ mol<sup>-1</sup>), and thus cellulose hydrolysis, is lower than the apparent activation energies of glucose conversion (138 kJ mol<sup>-1</sup>) and xylose conversion (135 kJ mol<sup>-1</sup>). This difference suggests that hydrolysis reactions of the hemicellulose and cellulose fractions of biomass are favored at lower temperatures compared to conversion reactions of the corresponding C<sub>5</sub> and C<sub>6</sub> sugar monomers. Thus, operation at lower temperatures is favorable for deconstruction of biomass in the GVL solvent to produce C<sub>5</sub> and C<sub>6</sub> sugars without conversion to the sugar products to the corresponding furanic components. Importantly, operation in the GVL solvent leads to higher rates of acid-catalyzed reactions compared to reactions in water, thus allowing for high rates of biomass conversion at the low temperatures that are favorable for the selective production of monosaccharides versus the subsequent formation of furan compounds. This predicted behavior explains results from our recent report<sup>6</sup> that high yields of sugars can be produced by deconstruction of biomass in GVL at mild temperatures (e.g., 430–490 K) using dilute concentrations of mineral acids (e.g., 0.005 M).

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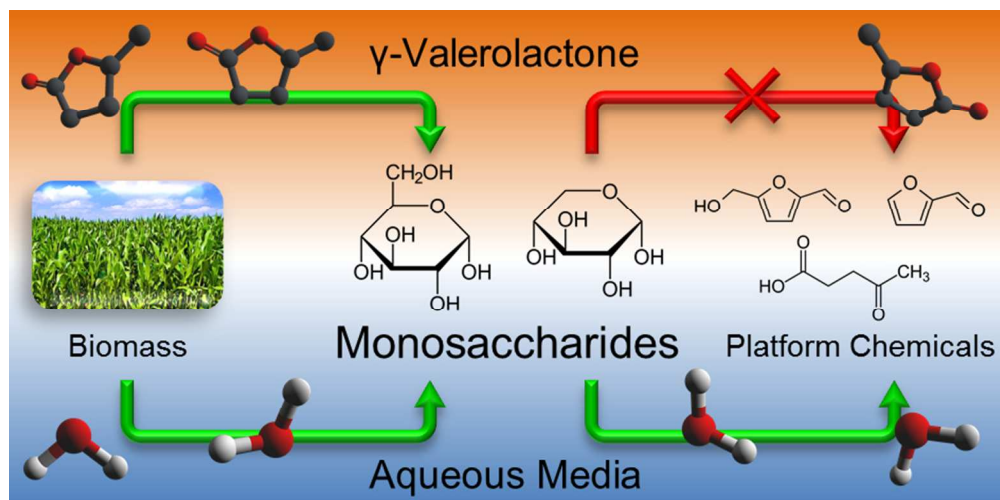
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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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