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Effects of γ-valerolactone in hydrolysis of lignocellulosic biomass to monosaccharides†

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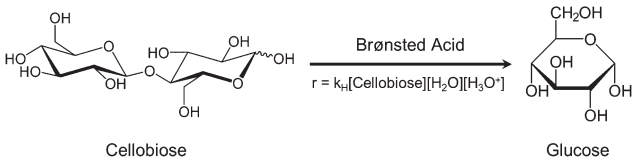
The use of γ-valerolactone as solvent for acid-catalyzed biomass hydrolysis reactions increases reaction rates compared to reactions carried out in water. In addition, a low apparent activation energy for biomass hydrolysis and a higher value for monosaccharide conversion are displayed using GVL as solvent, leading to favorable 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_5 sugars) and cellulose (C_6 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.[1] One such solvent is γ-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.[2–6] For example, high yields of levulinic acid (~70%) from cellulose using GVL as solvent have been achieved using Amberlyst 70 as catalyst compared to yields as low as 20% obtained in water.[2] In addition, significant selectivity increases have been shown using GVL as solvent compared to reactions in water for the conversion of C_5 sugars[3] and C_6 sugars[4] 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.[7] However, we have recently developed a processing strategy to produce concentrated streams of C_5 and C_6 sugars (*e.g.*, 130 g L^{-1}) from the cellulose and hemicellulose fractions of lignocellulosic biomass in GVL–H_2O 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.[6] 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 β(1→4) 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-



Scheme 1 Acid-catalyzed hydrolysis of cellobiose to glucose.

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derived intermediate that can be subsequently transformed into high-value chemicals as well as potential biofuel components by both enzymatic and chemical approaches.[8]

Reaction kinetics modeling was employed to quantify the effects of GVL on the reaction rates of biomass hydrolysis reactions. Reaction kinetics data (see ESI†) for acid-catalyzed hydrolysis of cellobiose to glucose were obtained in H_2O and various GVL–H_2O mixtures at typical biomass hydrolysis conditions using sulfuric acid (SA), a common catalyst for biomass deconstruction pretreatments.[9] GVL–H_2O 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_2O). The rate of cellobiose conversion was modeled as a function of a rate constant (k_H), cellobiose concentration, water concentration, and acid concentration (see ESI†). The estimated hydrolysis rate constants (k_H) using H_2O and organic–water mixtures as solvents with SA as catalyst at various temperatures are shown in Table 1.

Fig. 1 (left axis) shows the values of the rate constants for cellobiose hydrolysis plotted against the composition of GVL–H_2O 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_2O (4 : 1) shows a significant increase in the value of the rate constant of 31 times compared to the value in H_2O 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 β(1→4) 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_2O (4 : 1) and dioxane–H_2O (4 : 1) solvent compared to using H_2O 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.

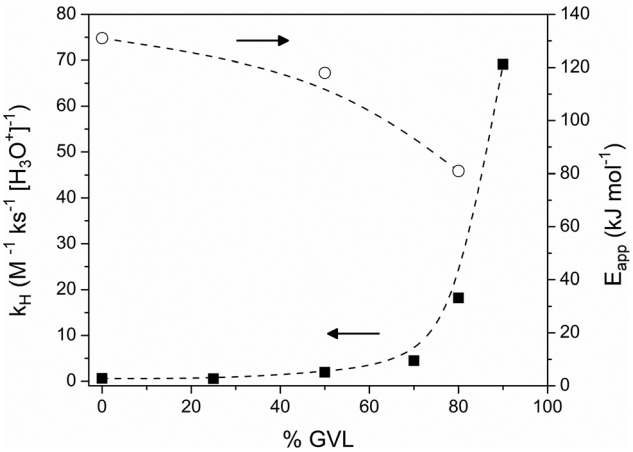

Fig. 1 Cellobiose hydrolysis rate constants (■; left axis) and apparent activation energies (○; right axis) *versus* GVL content in GVL–H_2O solvent mixtures.

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.[10] 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_2O. 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.[10]

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 β(1→4) 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 α(1→4) 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_2O (4 : 1) as solvent is 23 times greater than using H_2O at the same reaction conditions. This rate constant value increase in GVL–H_2O (4 : 1) is similar for cellobiose hydrolysis compared to using H_2O as solvent. Thus, the use of GVL as solvent also improves other acid-catalyzed hydrolysis reactions in addition to β(1→4) bond hydrolysis, showing that the

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^{-1} ks^{-1} $[H_3O^+]^{-1}$)
GVL–H_2O (4 : 1)	Cellobiose	393	8.9 ± 0.41
H_2O	Cellobiose	403	0.61 ± 0.051
H_2O	Maltose	403	0.81 ± 0.069
GVL–H_2O (1 : 3)	Cellobiose	403	0.54 ± 0.029
GVL–H_2O (1 : 1)	Cellobiose	403	2.0 ± 0.055
GVL–H_2O (2.33 : 1)	Cellobiose	403	4.5 ± 1.1
GVL–H_2O (4 : 1)	Cellobiose	403	18 ± 1.9
GVL–H_2O (4 : 1)	Maltose	403	19 ± 3.1
THF–H_2O (4 : 1)	Cellobiose	403	22 ± 3.3
Dioxane–H_2O (4 : 1)	Cellobiose	403	9.1 ± 1.5
GVL–H_2O (9 : 1)	Cellobiose	403	69 ± 9
GVL–H_2O (4 : 1)	Cellobiose	413	29 ± 6.1
H_2O	Cellobiose	418	2.2 ± 0.17
GVL–H_2O (1 : 1)	Cellobiose	418	8.6 ± 1.4
H_2O	Cellobiose	433	9.1 ± 1.5
GVL–H_2O (1 : 1)	Cellobiose	433	22 ± 3.4

increased reaction performance using GVL as solvent is not limited to cellobiose hydrolysis and β(1→4) 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_2O and GVL–H_2O (4 : 1) using 0.005 M and 0.0005 M SA, respectively at 448 K. Fig. 2 shows the concentration profiles *versus* time for glucose production from cellulose in both H_2O and GVL–H_2O (4 : 1). The initial rate of glucose production in H_2O is 0.26 mM min^{-1} compared to a rate of 0.13 mM min^{-1} in GVL–H_2O (4 : 1). Accounting for the 10-fold decrease in catalyst concentration and the 5-fold decrease in H_2O concentration (a reactant in hydrolysis) in GVL–H_2O (4 : 1), an increase in the rate constant by a factor of 25 is observed for glucose production from cellulose in GVL–H_2O (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_2O (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,[6] 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 β(1→4) bond hydrolysis rather than any effects on cellulose crystallinity.

The apparent activation energies for cellobiose hydrolysis were measured in H_2O and GVL–H_2O 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^{-1}, in good agreement with previous literature values using SA as catalyst.[11] The apparent activation energy for cellobiose hydrolysis decreases as the GVL to water ratio increases, changing by 50 kJ mol^{-1} from H_2O to GVL–H_2O (4 : 1). Furthermore, the measured values of the apparent activation energies for cellobiose hydrolysis in solvents consisting of H_2O, GVL–H_2O (1 : 1), and GVL–H_2O (4 : 1) are plotted *versus* the GVL concentration in Fig. 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.

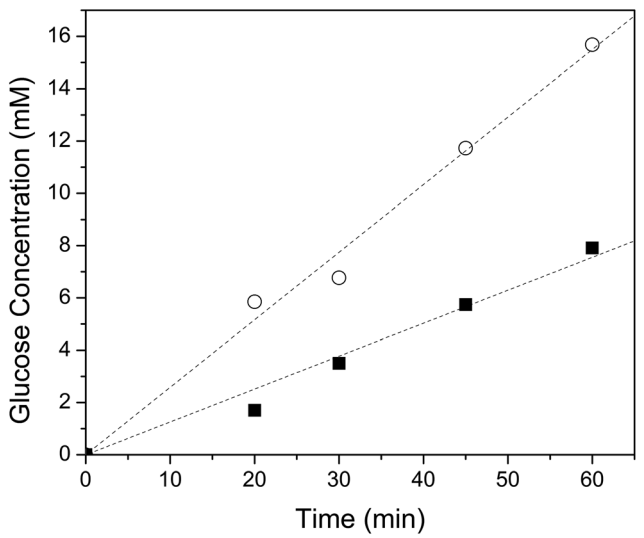

Fig. 2 Glucose concentration *versus* time from cellulose conversion in H_2O using 0.005 M SA (○) and GVL–H_2O (4 : 1) using 0.0005 M SA (■) at 448 K.

Table 2 Apparent activation energies for acid-catalyzed hydrolysis of cellobiose and conversion of glucose and xylose in H_2O and GVL–H_2O mixtures using SA as catalyst

Solvent system	Reactant	E_{app} (kJ mol^{-1})
H_2O	Cellobiose	131
H_2O	Glucose	135
H_2O	Xylose	138
GVL–H_2O (1 : 1)	Cellobiose	118
GVL–H_2O (4 : 1)	Cellobiose	81
GVL–H_2O (4 : 1)	Glucose	138
GVL–H_2O (4 : 1)	Xylose	135

The apparent activation energies were measured for glucose and xylose conversion, which leads to their corresponding furanic components, HMF and furfural, respectively, as well as degradation products. Reaction kinetics data were collected at different temperatures in H_2O and GVL–H_2O (4 : 1) (see ESI†), and these activation energies are shown in Table 2. The apparent activation energy for glucose conversion in H_2O was determined to be 135 kJ mol^{-1}, in agreement with reported literatures values.[12,13] Similarly, the apparent activation energy for xylose conversion in H_2O was measured to be 138 kJ mol^{-1}, also in agreement with reported literature values.[13,14] Importantly, the apparent activation energies are similar for cellobiose hydrolysis and glucose and xylose conversion in H_2O, ranging from 131–138 kJ mol^{-1}. 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_2O (4 : 1) solvent, apparent activation energies of 138 and 135 kJ mol^{-1} are observed for glucose and xylose conversion, respectively, whereas the apparent activation energy is significantly lower for the cellobiose hydrolysis reaction (81 kJ mol^{-1}) comparatively, which makes sugar production favorable in the GVL solvent *versus* the subsequent dehydration of the sugars to furan compounds.

Conclusions

The results of this study show that the apparent activation energy for cellobiose hydrolysis in the GVL solvent (81 kJ mol^{-1}), and thus cellulose hydrolysis, is lower than the apparent

activation energies of glucose conversion (138 kJ mol^{-1}) and xylose conversion (135 kJ mol^{-1}). 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_5 and C_6 sugar monomers. Thus, operation at lower temperatures is favorable for deconstruction of biomass in the GVL solvent to produce C_5 and C_6 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[6] 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).

Acknowledgements

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