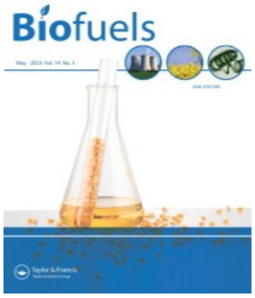
Taylor & Francis
Taylor & Francis Group



Biofuels

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/tbfu20

Hydroxy sulfonic acid catalyzed hydrolysis of cellulose

Ananda S. Amarasekara, Victor C. Nwankwo & Harshica Fernando

To cite this article: Ananda S. Amarasekara, Victor C. Nwankwo & Harshica Fernando (2023): Hydroxy sulfonic acid catalyzed hydrolysis of cellulose, Biofuels, DOI: 10.1080/17597269.2023.2221969

To link to this article: https://doi.org/10.1080/17597269.2023.2221969

BIOFUELS
https://doi.org/10.1080/17597269.2023.2221969

Taylor & Francis
Taylor & Francis Group

Hydroxy sulfonic acid catalyzed hydrolysis of cellulose

Ananda S. Amarasekara[a,b], Victor C. Nwankwo[a] and Harshica Fernando[a]

[a]Department of Chemistry, Prairie View A&M University, Prairie View, TX, USA; [b]Center for Energy and Environmental Sustainability, Prairie View A&M University, Prairie View, TX, USA

ABSTRACT

Development of efficient catalytic methods for the hydrolysis of cellulose is a major research challenge in sustainable biofuel and polymer areas. In this study five hydroxy sulfonic acids were studied as simple model compounds for cellulase enzyme for the hydrolysis of cellulose. The catalytic activities were measured by analysis of total reducing sugar (TRS) yields produced in a series of reactions carried out at 150–190 C using 0.050 M aqueous hydroxy sulfonic acid solutions. The highest catalytic activity was observed with isethionic acid, producing 62.7% TRS yield at 180 C after 4 hr. In the second phase of the work, Density Functional Theory (DFT) calculations were used to study the interactions between hydroxy sulfonic acids and cellulose model compound D-cellobiose to supplement the experimental results. The D-cellobiose – hydroxy sulfonic binding energies and the distance between glycosidic oxygen and -SO_3H acidic H were evaluated and the -SO_3H to glycosidic oxygen distance was identified as the more important parameter co-related to the catalytic activity. The isethionic acid with highest cellulose hydrolysis activity showed the short-est -SO_3H to glycosidic oxygen distance of 1.744 Å.

ARTICLE HISTORY
Received 11 March 2023
Accepted 1 June 2023

KEYWORDS
Cellulose; sulfonic acids; hydrolysis; acid catalyst; glucose; cellobiose

Introduction

Efficient hydrolysis of the most abundant biopolymer cellulose for processing to biofuels and feedstocks is one of the main challenges in utilization of renewable biomass in achieving a sustainable carbon-based future. At present three fundamental approaches based on biochemical, chemocatalytic and pyrolysis techniques are investigated for processing cellulosic biomass and generally all these routes have their inherent limits and challenges such as: meager yields, coke or char formation, poor catalyst efficiencies or inability to recycle catalysts as well as high energy costs [1,2]. As in any large scale chemical process, catalysis is the clear choice for processing cellulosic biomass; and the use of concentrated and diluted mineral acids [3,4], Lewis acids [5–7], ionic liquids in combination with diverse acids [8], Brønsted acidic ionic liquids [9,10], transition metal ions as co-catalysts in Brønsted acidic ionic liquids [11] as well as immobilized Brønsted acidic ionic liquids [12,13] are well known. Then there are several innovative approaches such as: acidic ionic liquids or organic acids in place of traditional mineral acids [14,15], solid acids [16], silica supported acidic ionic liquids [17], mechanical activation methods like ball milling [18] and also the integration of a co-catalyst to an acid catalyst [19–21] tested in recent years in attempts to improve the acid-catalyzed biomass processing. The enzymatic process is exceptionally energy efficient and high yielding on its own; however, cellulase enzyme catalyzed degradation method invariably requires an energy intensive pretreatment, and also the inability to recycle the labile enzymes is a certain disadvantage. Therefore, an inexpensive, recyclable chemocatalytic process, mimicking the enzymatic hydrolysis is the ideal and most sought-after route for cellulosic biomass hydrolysis.

Heterogeneous catalysts with -CO_2H or -SO_3H groups immobilized on a solid surfaces are excellent catalysts for cellulose hydrolysis and in these examples, superior catalytic activities are explained as a result of proximity of these active groups [22–26]. For instance, Kobayashi and Fukuoka have reported a remarkable glucose yield of 88% in depolymerization of cellulose at comparatively gentle reaction environments, while using a functionalized graphene catalyst with -COOH and -OH groups immobilized on the surface [23,27]. In sulfonated carbon catalysts, the use of a gas-liquid interfacial plasma method for the preparation of the catalyst is a notable example where high -SO_3H group densities of 3.47 3.63 mmol g^1 are reported [28]. By using this heterogeneous catalyst, Qin et al. has achieved 34.2 38.3% cellulose conversions for hydrolysis at 150 C for 15 h [28]. In another instance Van de Vyver et al. utilized a sulfonated silica/carbon nano-composite as the catalyst for cellulose hydrolysis in 60.7% conversion with 50.4% glucose yield for a reaction carried out at 150 C [29]. Additionally, exceptionally high cellulose hydrolysis yields are reported with application of cellulose nanocrystals as the catalyst support with di and tricarb-oxylic acid groups anchored on cellulose catalyzing the reaction [30]. As several studies are demonstrating the syn-ergistic effect of multiple -COOH or -SO_3H and -OH groups close to each other in enhancing the cellulose hydrolysis, this effect was interpreted as a consequence of multiple dipolar interactions and also hydrogen bonds linking the acid catalyst and the polysaccharide -OH groups [23,27].

CONTACT Ananda S. Amarasekara asamarasekara@pvamu.edu Department of Chemistry, Prairie View A&M University, Prairie View, TX, USA.

Supplemental data for this article can be accessed online at https://doi.org/10.1080/17597269.2023.2221969.

This type of collective effects is possible in aqueous medium homogeneous cellulose depolymerization reactions as well and prominent in catalysts with -OH and -COOH groups adjacent to the active -COOH group. This unique case in point was recently demonstrated by Kobayashi's group; where they investigated the cellulose hydrolysis by using a set of aromatic carboxylic acids with halogens, phenolic -OH and secondary -COOH functions attached to an aromatic ring system as catalysts and observed that o-hydroxybenzoic and o-phthalic acids exhibit enhanced catalytic activities in comparison to other substituted aromatic carboxylic acids [31]. In addition, our recent experimental and computational work on homogeneous phase poly-carboxylic acid catalysts have also shown the importance of secondary interactions between carboxylic acid catalyst and the carbohydrate [32,33].

Even though cellulosic ethanol plants in 1940s used sulfuric acid as the catalyst, studies on use of sulfonic acid catalysts are rare in the literature [2,34]. However, we have previously evaluated the effect of hydrophobic nature of a group of sulfonic acids in cellulose depolymerization at 140–190 C by determining sugars produced [14]. For instance, hydrolysis of DP 450 cellulose in 2-naphthalenesulfonic acid, p-toluenesulfonic acid and 4-biphenylsulfonic acid aqueous solutions produced total reducing sugar yields of 25.4, 28.0 and 30.3% respectively for reactions carried out for 3 h at 160 C. Whereas, aqueous H_2SO_4 of simi-lar acid strength produced only 21.7% TRS yield under identical conditions [14].

Since 2009 we have studied a wide range of cellulose binding catalysts, including the use of -SO_3H functionalized Brnsted acidic ionic liquids [9,35,36], acidic ionic liquids with a metal ion co-catalysts as well as polycarboxylic acids as simple cellulase enzyme mimics in depolymerization of cellulose and lignocellulosic biomass for biofuel applications. Guided by previous work on hydroxy-carboxylic acids and polycarboxylic acids as cellulose hydrolysis catalysts we hypothesized that substitution of the carboxylic acid group by a strongly acidic sulfonic acid group in previously studied hydroxy-carboxylic acid systems may produce even higher sugar yields. In addition, as far as we are aware there are no reports on the influence of a hydroxyl group or groups in proximity to a highly acidic sulfonic acid group in homogeneous phase cellulose hydrolysis reaction. In an attempt to fill this void, we have undertaken a study on cellulose depolymerization using a series of hydroxy sul-fonic acids as catalysts in hot-compressed water as shown in Figure 1. Structures of the series of acids used in the study are shown in Figure 2. Furthermore, in this research article we present the co-relation between hydroxy sulfonic acid structure and the catalytic activity based on cellulose hydrolysis yield data, as well as a mechanistic interpretation based on a Density Functional Theory (DFT) study on cellulose model compound D-cellobiose.

Experimental

Materials and instrumentation

Cellulose from cotton linters (DP 450), 3,4-dinitrosalicylic acid (> 99%), sulfuric acid (98%), hydrochloric acid (37%), sodium isethionate (98.0þ%), sodium 4-hydroxybenzenesulfonate (98.0þ%), potassium hydroquinonesulfonate (98.0þ%), 3,5-dichloro-2-hydroxybenzenesulfonic acid sodium salt (98%), and 1,2-dihydroxybenzene-3,5-disulfonic acid disodium salt monohydrate (97%) were used. Stainless steel solvothermal reaction kettles with Teflon inner sleeves and internal volumes of 25 mL were used for cellulose depolymerization experiments. The high pressure reactors were heated in a temperature regulated oven with an accuracy ±1 C. Total reducing sugars (TRS) in aqueous solutions were measured by 3,4-dinitrosalicylic acid (DNS) assay [37,38]. This colorimetric assays were carried out using a GENESYS 150 UV-Vis spectrophotometer and 1.0 cm polystyrene cuvets.

General procedure for the hydrolysis of cellulose using hydroxy sulfonic acids and sulfuric acid as catalysts in water

Isethionic acid (ISE), 4-hydroxybenzene sulfonic acid (HBS), hydroquinone sulfonic acid (HQS), 3,5-dichloro-2-hydroxybenzene sulfonic acid (DCS), 1,2-dihydroxybenzene-3,5-disulfonic acid (DHS) stock solutions were prepared by dissolving appropriate amounts of their sodium or potassium salts in 50.00 mL of deionized water with the addition of an equivalent amounts of 0.100 mol/L of aqueous hydrochloric acid to produce of 0.050 mol H^{þ}/L acid concentration. Sigmacell cellulose (DP 450) (0.030 g) was suspended in 2.00 mL 0.050 mol H^{þ}/L acid solution in a high pressure reactor and heated in a temperature controlled oven for 4.00 h. At the end of the reaction time high pressure reactor was removed from the oven and immediately cooled in a crushed ice bath. Then the reaction products were diluted with deionized water, transferred into a glass centrifuge tube and, neutralized with 0.10 mol/L aqueous NaOH, total volume was adjusted to 10.00 mL and centrifuged at 3500 rpm for 10 min. The solids were separated by withdrawing the clear supernatant liquid using a pipette and used for the total reducing sugar measurement as shown below.

Total reducing sugar (TRS) analysis of hydrolyzate

1.00 mL of cellulose hydrolyzate supernatant from previous experiment was diluted with 2.50 mL of deionized water in a 20 mL glass vial. Then 0.50 mL of 3,4-dinitrosalicylic acid (DNS) reagent was added to the diluted hydrolyzate and incubated at 90 C, for 5 min using a water bath [37,38]. The reagent blank sample was prepared by mixing 0.50 mL of 3,4-dinitrosalicylic acid (DNS) reagent and 3.50 mL of deionized water and was incubated as the test samples. The orange-brown color developed in test samples were measured against the blank solution at 540 nm using Fisherbrand 1.0 cm polystyrene cuvets. Total reducing sugar amounts in test samples were determined by utilizing a standard plot prepared by using a series of six glucose concentrations.

Computational methods

Computational study was carried out on cellulose model compound with two D-glucose units: D-cellobiose, which occurs as two anomers a and b; both anomers were considered. The geometries a and b D-cellobiose anomers and

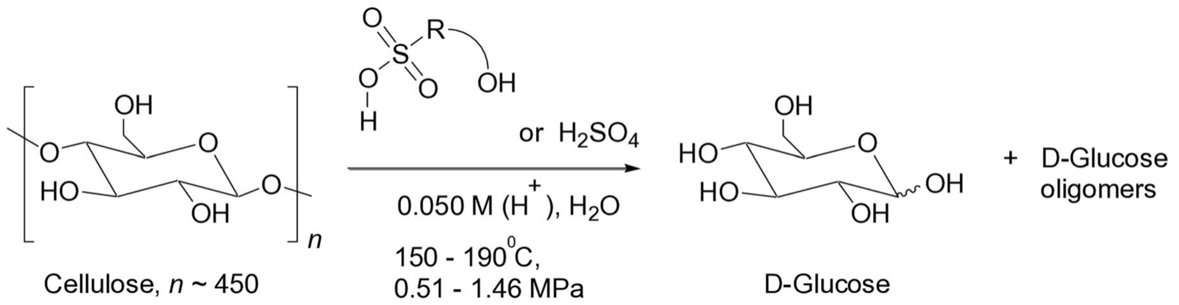


Figure 1. Hydrolysis of cellulose (DP 450) to D-glucose and D-glucose oligomers using hydroxy sulfonic acids and sulfuric acid in water.

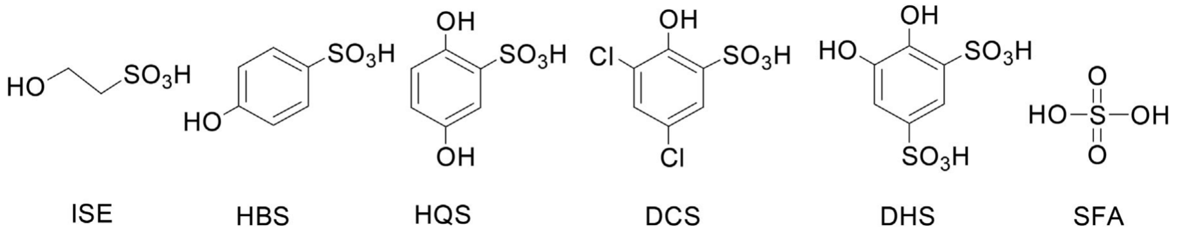


Figure 2. Acids used in the cellulose hydrolysis study: isethionic acid (ISE), 4-hydroxybenzene sulfonic acid (HBS), hydroquinone sulfonic acid (HQS), 3,5-dichloro-2-hydroxybenzene sulfonic acid (DCS), 1,2-dihydroxybenzene-3,5-disulfonic acid (DHS), and sulfuric acid (SFA).

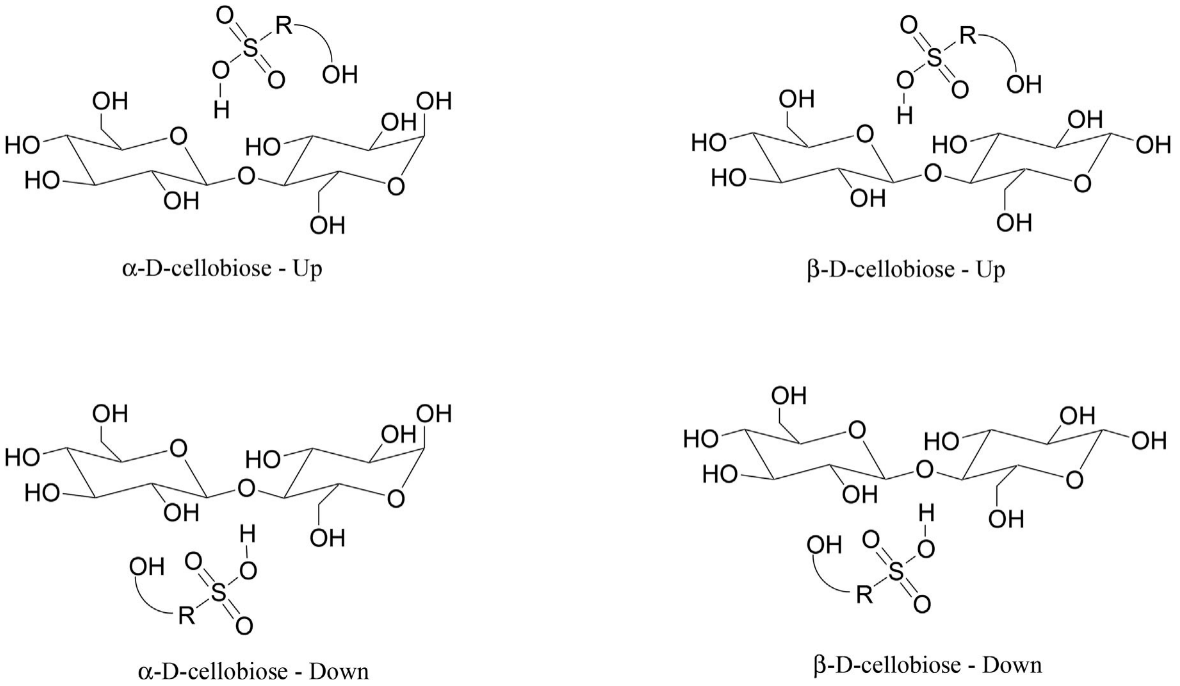


Figure 3. The Up and Down approaches of hydroxy sulfonic acids towards cellulose model anomers: a-D-cellobiose and b-D-cellobiose. R ¼ alkyl/aryl.

four possible up and down face approaches of hydroxy sulfonic acids or sulfuric acid are shown in Figure 3. Avogadro software was used in drawing structures for initial optimizations. The same software was used in obtaining the preliminary Z-matrix coordinates and these data were further optimized using Gaussian 16. The final Gaussian 16 optimizations were carried out on computational cluster at Tennessee State University – Department of Physics, Nashville, Tennessee, USA. These structure optimizations were performed by Density Functional Theory (DFT) calculations using the B3LYP exchange-correlation function method [39–41]. The basis set 6–31 g with polarization functions was used and applied for every atom [42,43]. The self-consistent reaction field method (SCRF) with a polarized continuum model was used to incorporate solvation effects in all calculations [44]. The optimized structures of a/b D-cellobiose, acids and complexes are included under the supplementary information of this article. Mulliken population analysis method was used to obtain the charge distributions of the atoms.

Binding energies of the cellobiose-catalyst complexes were calculated using the equations shown below:

$$\mathrm{DE}\ ¼\ E_{\mathrm{cellobiosecatalyst}}–½E_{\mathrm{cellobiose}}\ þ\ \ E_{\mathrm{catalyst}}$$

and

$$E_{\mathrm{bind}}\ ¼\ \ \mathrm{DE}$$

Aqueous environments were used in all structure optimizations and calculations. Both up and down approaches of acids were considered in the analysis of a and b D-

Table 1. Calculated binding energies (E_{bind}) in kJ/mol for a/b D-cellobiose-acid complexes when hydroxy sulfonic acids and sulfuric acid are approaching a/b D-cellobiose from up (U) and down (D) faces. Arbitrarily selected binding energies > 57.00 kJ/mol are highlighted.

Anomer – approach	ISE	HBS	HQS	DCS	DHS	SFA
a-U	58.5591	62.7731	70.0864	61.5821	70.925	95.0069 a-
D	57.4562	38.8826	58.0566	49.3289	81.8003	81.1111 b-
U	33.3775	62.0734	31.8673	52.3527	66.0854	94.0202 b-
D	47.3422	38.9532	60.9066	60.9413	94.2423	54.6159

cellobiose glycosidic oxygen to closest catalyst acidic hydrogen distances, as illustrated in Figure 3. Calculated binding energies (E_{bind}) in kJ/mol for a/b D-cellobiose-acid complexes when hydroxy sulfonic acids and sulfuric acid are approaching a/b D-cellobiose from up (U) and down (D) faces are shown in Table 1. The -SO_3H to D-cellobiose glycosidic -O- atom distances (Å) for a/b D-cellobiose-acid complexes when hydroxy sulfonic acids and sulfuric acid are approaching a/b D-cellobiose from up (U) and down (D) faces are shown in Table 2.

Results and discussion

Five commercially available aliphatic and aromatic hydroxy sulfonic acids were selected for the current study. The concentrations of acid solutions, cellulose loading, temperatures and reaction times were selected based on our prior experiments on acid catalyzed depolymerization of DP 450 Sigmacell cellulose in hot compressed water [45,46]. The changes in % yields of total reducing sugar (TRS) pro-duced during the hydrolysis of Sigmacell cellulose (DP 450) using the five hydroxy sulfonic acids are shown in the plot in Figure 4. Isethionic acid catalyzed reaction produced the highest TRS yield of 62.7% at 180 C after 4.00 h as shown in Figure 4. In comparison to sulfuric acid, all hydroxy acids except 1,2-dihydroxybenzene-3,5-disulfonic acid (DHS) showed higher TRS yields for experiments car-ried out at 150–170 C range. For instance, at 170 C, isethi-onic (ISE), hydroquinone sulfonic (HQS), 4-hydroxybenzene sulfonic (HBS) and 3,5-dichloro-2-hydroxybenzene sulfonic acid (DCS) produced 59.3, 54.4, 52.9 and 47.7% TRS yields in comparison to 41.5% yield of sulfuric acid. These are 34.4, 31.1, 27.5 and 14.9% enhancements in yields due to neighboring group effects when compared to sulfuric acid. Most importantly, all hydroxy sulfonic acids show their peak TRS % yields at temperatures lower than the peak performance temperature of sulfuric acid of equivalent $H^þ$ concentration. This is most likely due to lowering of the activation energy of the reaction as a consequence of a binding or hydrogen bonding group of dipolar interactions between the polysaccharide and hydroxy sulfonic acid catalysts.

Next, Density Functional Theory (DFT) calculations were used to further explore the interactions and structural effects of hydroxy sulfonic acid catalysts on cellulose hydrolysis reaction. D-cellobiose was chosen as the model compound for cellulose as it is the simplest cellulose model with two glucose units connected through a b-glycosidic bond [47]. D-cellobiose exists as a mixture of a and b anomers. These anomers undergo an isomerization and b form is the major anomer in water; though this a/b ratio can be perturbed due to the pH value of the solvent and the acid catalyzed hydrolysis may take place in both a and b forms of the glucose dimer [32]. Additionally, the hydroxy sulfonic acid or sulfuric acid can approach the a and b anomers from up and down faces of D-cellobiose molecule during the critical glycosidic oxygen protonation step in the hydrolysis reaction as illustrated in Figure 3.

Table 2. Calculated -SO_3H to D-cellobiose glycosidic -O- atom distances (Å) for a/b D-cellobiose-acid complexes when hydroxy sulfonic acids and sul-furic acid are approaching a/b D-cellobiose from up (U) and down (D) faces. Arbitrarily selected close distances < 3.00 Å are highlighted. Two distances each are shown for acids with two acidic hydrogens, DHS and SFA.

Anomer – approach	ISE	HBS	HQS	DCS	DHS	SFA
a-U	4.312	4.301	2.869	4.281	11.154, 4.235	4.568, 3.948
a-D	1.744	6.38	3.093	3.129	4.651, 6.977	3.895, 4.599
b-U	4.999	6.213	7.896	4.146	4.505, 8.318	4.514, 3.985
b-D	4.52	2.909	4.134	4.067	4.739, 6.267	2.664, 5.451

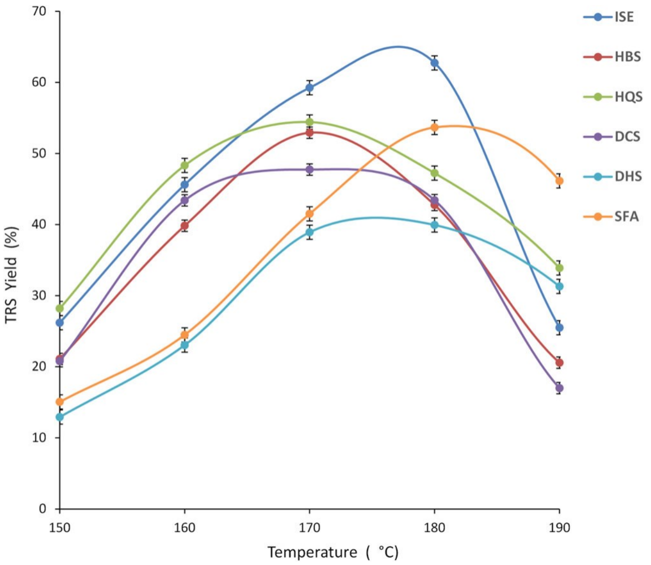


Figure 4. The changes in % yields of total reducing sugar (TRS) produced during the hydrolysis of Sigmacell cellulose (DP 450) using five hydroxy sulfonic acids: isethionic acid (ISE), 4-hydroxybenzene sulfonic acid (HBS), hydroquinone sulfonic acid (HQS), 3,5-dichloro-2-hydroxybenzene sulfonic acid (DCS), 1,2-dihydroxybenzene-3,5-disulfonic acid (DHS), and sulfuric acid (SFA) at 150–190 C. Acid concentration: 0.050 mol $H^þ$/L in all acid solutions, 0.030 g of Sigmacell cellulose in 2.00 mL of aq. acid and reaction time: 4.0 hr. in all experiments.

The series of sulfonic acids as well as sulfuric acid used in the study are strong acids, which are expected to ionize completely in aqueous phase and the acidic $H^þ$ can leave the acid function during the approach towards the glycosidic bond. In a leading study, Suzuki and co-workers have recently optimized the molecular structures of a series of -SO_3H functionalized Brønsted acidic ionic liquids with various anions and different alkyl chain lengths using B3LYP/6-311 Gþþ(d,p) methods. In their study Suzuki and co-workers have successfully interpreted experimental cellulose hydrolysis results by using DFT calculations and by optimizing Brønsted acidic ionic liquid structures with -SO_3H groups containing acidic protons for assessing geometries of these organic catalysts [48]. In our calculations we have adopted the Suzuki and co-workers DFT calculation approach used in -SO_3H functionalized Brønsted acidic ionic liquids for our catalyst system while considering the geometries of hydroxy sulfonic acids just before the ionization in approach to D-cellobiose [48]. Consequently, in our cellulose hydrolysis model we have considered the intermolecular interactions between D-cellobiose and the

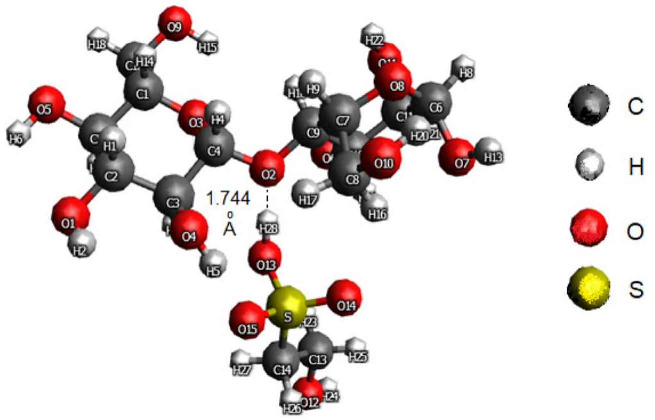


Figure 5. The DFT optimized geometry of isethionic acid (ISE) approaching a D-cellobiose anomer from down face.

hydroxy sulfonic or sulfuric acid in all four configurations as in Figure 3. The representative example of DFT optimized geometry of isethionic acid (ISE) approaching a D-cellobiose anomer from down face is shown in Figure 5. This view shows the approach of $-SO_3H$ acidic hydrogen towards the glycosidic oxygen with a proximity of 1.744 Å, which is the closest observed in all cases studied. All other DFT optimized geometries of a/b D-cellobiose anomers, acids and a/b D-cellobiose-acid complexes are included in the supplementary material.

The calculated binding energies (E_{bind}) in energy minimized structure for a/b D-cellobiose-acid complexes when hydroxy sulfonic acids and sulfuric acid are approaching a/b D-cellobiose from up (U) and down (D) faces are shown in Table 1. We have arbitrarily selected binding energies > 57.00 kJ/mol as relatively strong interaction between acid and the disaccharide and these values are highlighted in Table 1. The complexes from ISE, HBS and DCS show two possible strong interaction configurations. Whereas, DHS with two sulfonic acid groups and two hydroxyl groups show strong interactions in all possible configurations as expected. The sulfuric acid (SFA) with two acidic hydrogens and hydroquinone sulfonic acid (HQS) with two hydroxyl groups and one sulfonic acid group also strongly interacting in three modes each as shown in Table 1.

The calculated $-SO_3\underline{H}$ to D-cellobiose glycosidic -O- atom distances for a/b D-cellobiose-acid complexes when hydroxy sulfonic acids and sulfuric acid are approaching a/b D-cellobiose from up (U) and down (D) faces are shown in Table 2. We have arbitrarily selected < 3.00 Å as a close interaction between $-SO_3\underline{H}$ and D-cellobiose glycosidic -O- atom and these values are highlighted in Table 2. The hydroxy sulfonic acids ISE, HBS and HQS as well as sulfuric acid $-SO_3H$ acidic hydrogens shows at least one < 3.00 Å close approach towards the glycosidic oxygen in one configuration. Whereas 1,2-dihydroxybenzene-3,5-disulfonic acid (DHS) with two $-SO_3H$ groups and bulky 3,5-dichloro-2-hydroxybenzene sulfonic acid (DCS) failed to approach close in any of the configurations. This DFT result from cellulose model compound corroborate well with cellulose hydrolysis results shown in Figure 4; in particularly where DHS catalysis resulted the lowest reducing sugar yields for all experiments carried out below 180 C. Short $-SO_3H$ to glycosidic oxygen distances of 1.744 and 2.664 Å were predicted for interactions between a-cellobiose – ISE down (a-D) and b-cellobiose -SFA down (b-D) configurations respectively as shown in Table 2. This DFT prediction also support the experimental result shown in Figure 4; where small ISE and SFA approaches closer to glycosidic oxygen producing 62.7 and 53.7% high TRS yields at 180 C. Interestingly the shortest $-SO_3H$ to glycosidic oxygen distances of 1.744 Å predicted in a-cellobiose – ISE down (a-D, Table 2) by DFT calculations on model compound substantiate the highest cellulose hydrolysis TRS yield of 62.7% observed for 180 C experiment as shown in Figure 4.

Conclusion

Cellulose hydrolysis catalytic activities of a series hydroxy sulfonic acids were evaluated against H_2SO_4; and except 1,2-dihydroxybenzene-3,5-disulfonic acid, all acids studied showed higher activities than H_2SO_4 in 150–170 C temperature range. The most noticeable catalytic activity enhancements were observed for isethionic, hydroquinone sulfonic, and 4-hydroxybenzene sulfonic acids in experiments carried out at 170 C. In addition, the experimental study was supplemented by Density Functional Theory (DFT) study on D-cellobiose, which was used as the model compound for cellulose. Possible interactions between a/b D-cellobiose and acid catalysts were evaluated by calculating the binding energies as well as distances between acidic protons of the acid catalysts used and D-cellobiose glycosidic oxygen. Out of the six acids studied isethionic acid, 4-hydroxybenzene sulfonic acid and 3,5-dichloro-2-hydroxybenzene sulfonic acid showed two binding modes each with binding energies greater than 57.00 kJ/mole for the four configurations studied. The shortest $-SO_3H$ to glycosidic oxygen distance of 1.744 Å was observed for isethionic acid, supporting the experimental result of highest catalytic activity observed at 180 C. In conclusion, although the binding between the carbohydrate and sulfonic acid is an important factor in enzyme mimicking catalytic activity, the distance between $-SO_3H$ acidic hydrogen and the glycosidic oxygen in the polysaccharide is the more influencing factor in determining the cellulose hydrolysis yield in the set of five hydroxy sulfonic acids studied.

Authors' contributions

Ananda S. Amarasekara: writing the original draft and conceptualization. Victor C. Nwankwo: methodology and laboratory experiments. Harshica Fernando: computational study and data analysis

Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

Authors thank United States Department of Energy – National Nuclear Security Administration (DOE-NNSA) grant DE-NA0003947, Welch Foundation grant L0002 – 20181021, National Science Foundation (NSF) grants: CBET-1704144, HRD-1036593, and US Department of

Agriculture (USDA) grants AFRI 65209-31474, SUN-2-569230.PVAMU1 for financial support.

ORCID

Ananda S. Amarasekara http://orcid.org/0000-0002-2052-3947

References

[1] Saravanan A, Kumar PS, Jeevanantham S, et al. Recent advances and sustainable development of biofuels production from lignocellulosic biomass. Bioresour Technol. 2022;344(Pt B):126203. https://dx.doi.org/10.1016/j.biortech.2021.126203.

[2] Amarasekara AS. Handbook of cellulosic ethanol. NewYork: Wiley; 2013.

[3] Fan L-T, Gharpuray MM, Lee Y-H. Cellulose hydrolysis. Vol. 3. Berlin: Springer Science & Business Media; 2012.

[4] Camacho F, Gonzalez-Tello P, Jurado E, et al. Microcrystalline-cellulose hydrolysis with concentrated sulphuric acid. J Chem Technol Biotechnol. 1996;67(4):350–356. https://dx.doi.org/10.1002/(SICI)1097-4660(199612)67:4<350::AID-JCTB564>3.0.CO;2-9.

[5] Hu L, Lin L, Wu Z, et al. Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts. Appl Catal B: Environ. 2015;174–175:225–243. https://dx.doi.org/10.1016/j.apcatb.2015.03.003.

[6] Huang YB, Fu Y. Hydrolysis of cellulose to glucose by solid acid catalysts. Green Chem. 2013;15(5):1095–1111. https://dx.doi.org/10.1039/c3gc40136g.

[7] Liu WY, Qi W, Zhou JS, et al. Research progress in cellulose hydrolysis by carbonaceous solid acid. Chem Ind Forest Product. 2015;35(1):138–144. https://dx.doi.org/10.3969/j.issn.0253-2417.2015.01.022.

[8] Li C, Wang Q, Zhao ZK. Acid in ionic liquid: an efficient system for hydrolysis of lignocellulose. Green Chem. 2008;10(2):177– 182. https://dx.doi.org/10.1039/B711512A.

[9] Amarasekara AS, Owereh OS. Hydrolysis and decomposition of cellulose in bronsted acidic ionic liquids under mild conditions. Ind Eng Chem Res. 2009;48(22):10152–10155. https://dx.doi.org/10.1021/ie901047u.

[10] Da Costa Lopes AM, Bogel-Lukasik R. Acidic ionic liquids as sustainable approach of cellulose and lignocellulosic biomass conversion without additional catalysts. ChemSusChem. 2015;8(6):947–965. https://dx.doi.org/10.1002/cssc.201402950.

[11] Amarasekara AS, Wiredu B. Chemocatalytic hydrolysis of cellulose at 37 C, 1 atm. Catal Sci Technol. 2016;6(2):426–429. https://dx.doi.org/10.1039/C5CY01677K.

[12] Amarasekara AS. Acidic ionic liquids. Chem Rev. 2016;116(10):6133–6183. https://dx.doi.org/10.1021/acs.chemrev.5b00763.

[13] Amarasekara AS. Ionic liquids in biomass processing. Isr J Chem. 2019;59(9):789–802. https://dx.doi.org/10.1002/ijch.201800140.

[14] Amarasekara AS, Wiredu B. Aryl sulfonic acid catalyzed hydrolysis of cellulose in water. Appl Catal A: Gen. 2012;417–418:259–262. https://dx.doi.org/10.1016/j.apcata.2011.12.048.

[15] Mosier NS, Sarikaya A, Ladisch CM, et al. Characterization of dicarboxylic acids for cellulose hydrolysis. Biotechnol Prog. 2001;17(3):474–480. https://dx.doi.org/10.1021/bp010028u.

[16] Zeng M, Pan X. Insights into solid acid catalysts for efficient cellulose hydrolysis to glucose: progress, challenges, and future opportunities. Catal Rev. 2022;64(3):445–490. https://dx.doi.org/10.1080/01614940.2020.1819936.

[17] Wiredu B, Amarasekara AS. Synthesis of a silica-immobilized broensted acidic ionic liquid catalyst and hydrolysis of cellulose in water under mild conditions. Catal Commun. 2014;48:41–44. https://dx.doi.org/10.1016/j.catcom.2014.01.021.

[18] Zhang Y, Li Q, Su J, et al. A green and efficient technology for the degradation of cellulosic materials: structure changes and enhanced enzymatic hydrolysis of natural cellulose pretreated by synergistic interaction of mechanical activation and metal salt. Bioresour Technol. 2015;177:176–181. https://dx.doi.org/10.1016/j.biortech.2014.11.085.

[19] Liu L, Sun J, Cai C, et al. Corn stover pretreatment by inorganic salts and its effects on hemicellulose and cellulose degradation. Bioresour Technol. 2009;100(23):5865–5871. https://dx.doi.org/10.1016/j.biortech.2009.06.048.

[20] Peng L, Lin L, Zhang J, et al. Catalytic conversion of cellulose to levulinic acid by metal chlorides. Molecules. 2010;15(8): 5258–5272. https://dx.doi.org/10.3390/molecules15085258.

[21] Kamireddy SR, Li J, Tucker M, et al. Effects and mechanism of metal chloride salts on pretreatment and enzymatic digestibility of corn stover. Ind Eng Chem Res. 2013;52(5):1775–1782. https://dx.doi.org/10.1021/ie3019609.

[22] Su J, Qiu M, Shen F, et al. Efficient hydrolysis of cellulose to glucose in water by agricultural residue-derived solid acid catalyst. Cellulose. 2018;25(1):17–22. https://dx.doi.org/10.1007/s10570-017-1603-4.

[23] Kobayashi H, Fukuoka A. Development of solid catalyst-solid substrate reactions for efficient utilization of biomass. BCSJ. 2018;91(1):29–43. https://dx.doi.org/10.1246/bcsj.20170263.

[24] To AT, Chung P-W, Katz A. Weak-acid sites catalyze the hydrolysis of crystalline cellulose to glucose in water: importance of post-synthetic functionalization of the carbon surface. Angew Chem Int Ed Engl. 2015;54(38):11050–11053. https://dx.doi.org/10.1002/anie.201504865.

[25] Vilcocq L, Castilho PC, Carvalheiro F, et al. Hydrolysis of oligosaccharides over solid acid catalysts: a review. ChemSusChem. 2014;7(4):1010–1019. https://dx.doi.org/10.1002/cssc.201300720.

[26] Pang J, Wang A, Zheng M, et al. Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures. Chem Commun (Camb). 2010;46(37):6935–6937. https://dx.doi.org/10.1039/c0cc02014a.

[27] Shrotri A, Kobayashi H, Fukuoka A. Cellulose depolymerization over heterogeneous catalysts. Acc Chem Res. 2018;51(3):761–768. https://dx.doi.org/10.1021/acs.accounts.7b00614.

[28] Qin L, Ishizaki T, Takeuchi N, et al. Green sulfonation of carbon catalysts via gas–liquid interfacial plasma for cellulose hydrolysis. ACS Sustainable Chem Eng. 2020;8(15):5837–5846. https://dx.doi.org/10.1021/acssuschemeng.9b07156.

[29] Van de Vyver S, Peng L, Geboers J, et al. Sulfonated silica/carbon nanocomposites as novel catalysts for hydrolysis of cellulose to glucose. Green Chem. 2010;12(9):1560–1563. https://dx.doi.org/10.1039/c0gc00235f.

[30] Spinella S, Maiorana A, Qian Q, et al. Concurrent cellulose hydrolysis and esterification to prepare a surface-modified cellulose nanocrystal decorated with carboxylic acid moieties. ACS Sustainable Chem Eng. 2016;4(3):1538–1550. https://dx.doi.org/10.1021/acssuschemeng.5b01489.

[31] Kobayashi H, Yabushita M, Hasegawa J-Y, et al. Synergy of vicinal oxygenated groups of catalysts for hydrolysis of cellulosic molecules. J Phys Chem C. 2015;119(36):20993–20999. https://dx.doi.org/10.1021/acs.jpcc.5b06476.

[32] Amarasekara AS, Wiredu B, Lawrence YM. Hydrolysis and interactions of D-cellobiose with polycarboxylic acids. Carbohydr Res. 2019;475:34–38. https://dx.doi.org/10.1016/j.carres.2019.02.002.

[33] Fernando H, Amarasekara SA. The effect of dicarboxylic acid catalyst structure on hydrolysis of cellulose model compound D-cellobiose in water. Curr Organocatal. 2021;8:1–1. https://dx.doi.org/10.2174/2213337208666211129090444.

[34] Badger P. Ethanol from cellulose: a general review. Trend New Crops New Uses. 2002;14:17–21.

[35] Amarasekara AS, Wiredu B. Degradation of cellulose in dilute aqueous solutions of acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride, and p-toluenesulfonic acid at moderate temperatures and pressures. Ind Eng Chem Res. 2011;50(21):12276–12280. https://dx.doi.org/10.1021/ie200938h.

[36] Amarasekara AS, Shanbhag P. Degradation of untreated switchgrass biomass into reducing sugars in 1-(alkylsulfonic)-3-methylimidazolium broensted acidic ionic liquid medium under mild conditions. Bioenerg Res. 2013;6(2):719–724. https://dx.doi.org/10.1007/s12155-012-9291-2.

[37] Li C, Zhao ZK. Efficient acid-catalyzed hydrolysis of cellulose in ionic liquid. Adv Synth Catal. 2007;349(11–12):1847–1850. https://dx.doi.org/10.1002/adsc.200700259.

[38] Breuil C, Saddler JN. Comparison of the 3,5-dinitrosalicylic acid and Nelson-Somogyi methods of assaying for reducing sugars and determining cellulase activity. Enzym Microb Technol. 1985;7(7):327–332. https://dx.doi.org/10.1016/0141-0229(85)90111-5.

[39] Becke A. Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys. 1993;98(7):5648–5652. https://dx.doi.org/10.1063/1.464913.

[40] Pople JA, Gill PM, Johnson BG. Kohn–Sham density-functional theory within a finite basis set. Chem Phys Lett. 1992;199(6):557–560. https://dx.doi.org/10.1016/0009-2614(92)85009-Y.

[41] Stephens PJ, Devlin FJ, Chabalowski CF, et al. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. J Phys Chem. 1994;98(45):11623–11627. https://dx.doi.org/10.1021/j100096a001.

[42] Montgomery JA, Jr Frisch MJ, Ochterski JW, et al. A complete basis set model chemistry. VI. Use of density functional geometries and frequencies. J Chem Phys. 1999;110(6):2822–2827. https://dx.doi.org/10.1063/1.477924.

[43] Montgomery JA, Jr Frisch MJ, Ochterski JW, et al. A complete basis set model chemistry. VII. Use of the minimum population localization method. J Chem Phys. 2000;112(15):6532–6542. https://dx.doi.org/10.1063/1.481224.

[44] Tomasi J, Mennucci B, Cammi R. Quantum mechanical continuum solvation models. Chem Rev. 2005;105(8):2999–3093. https://dx.doi.org/10.1021/cr9904009.

[45] Amarasekara AS, Wiredu B. Acidic ionic liquid catalyzed one-pot conversion of cellulose to ethyl levulinate and levulinic acid in ethanol-water solvent system. Bioenerg Res. 2014;7(4):1237–1243. https://dx.doi.org/10.1007/s12155-014-9459-z.

[46] Wiredu B, Dominguez JN, Amarasekara AS. The Co-catalyst effect of zeolites on acidic ionic liquid catalyzed one-pot conversion of cellulose to ethyl levulinate and levulinic acid in aqueous ethanol. CCAT. 2015;4(2):143–151. https://dx.doi.org/10.2174/2211544704666150727215943.

[47] Cao B, Du J, Du D, et al. Cellobiose as a model system to reveal cellulose dissolution mechanism in acetate-based ionic liquids: density functional theory study substantiated by NMR spectra. Carbohydr Polym. 2016;149:348–356. https://dx.doi.org/10.1016/j.carbpol.2016.04.128.

[48] Suzuki S, Takeoka Y, Rikukawa M, et al. Brønsted acidic ionic liquids for cellulose hydrolysis in an aqueous medium: structural effects on acidity and glucose yield. RSC Adv. 2018;8(26):14623–14632. https://dx.doi.org/10.1039/c8ra01950a.