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Aryl sulfonic acid catalyzed hydrolysis of cellulose in water

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ABSTRACT

Catalytic activities of eight alkyl/aryl sulfonic acids in water were compared with sulfuric acid of the same acid strength (0.0321 mol H^+ ion/L) for hydrolysis of Sigmacell cellulose (DP ~ 450) in the 140–190 °C temperature range by measuring total reducing sugar (TRS), and glucose produced. Cellulose samples hydrolyzed at 160 °C for 3 h, in aqueous *p*-toluenesulfonic acid, 2-naphthalenesulfonic acid, and 4-biphenylsulfonic acid mediums produced TRS yields of 28.0, 25.4, and 30.3% respectively, when compared to 21.7% TRS produced in aqueous sulfuric acid medium. The first order rate constants at 160 °C in different acid mediums correlated with octanol/water distribution coefficient log *D* of these acids, except in the case of highly hydrophobic 4-dodceylbenzenesulfonic acid. In the series of sulfonic acids studied, 4-biphenylsulfonic acid appears to be the best cellulose hydrolysis catalyst.

1. Introduction

Efficient and economical hydrolysis of lignocellulosic biomass to fermentable sugars is the major hurdle for the realization of cellulosic ethanol, as well as the unsolved problem for the efficient generation of fuels and feed stock chemicals from abundant biomass [1–5]. For instance, cellulase enzyme technologies currently being tested in about a dozen of cellulosic ethanol pilot plants in US, are confronting enormous challenges in bringing the production cost competitive with gasoline [6]. This is due to a number of deficiencies in the current technology, firstly energy consuming high pressure, high temperature pretreatment [7–9] is required before the enzymatic saccharification process, and secondly the prohibitive cost and inability to recycle the enzyme adds to the cost of the enzyme [10]. Other alternative technology of gasification of biomass and then the use of microorganisms to convert the syngas to ethanol generally suffers from poor efficiency due to the inherent insolubility of these gases in water [11].

Saccharification using dilute aqueous sulfuric acid at high temperature and pressure is the oldest method used in the cellulosic ethanol process, which was replaced by enzyme methods developed in the last two decades. The main disadvantage of this dilute aqueous sulfuric acid hydrolysis of cellulosic biomass is the poor sugar yields, resulting in low ethanol yield, and secondly the high energy cost associated with operating at temperatures above 250 °C at high pressures [12,13]. Although, this direct dilute aqueous acid saccharification gives low sugar yields, several research groups have taken an interest in recent times [12–16] taking a second look at this classical method due to its lower cost, and simplicity, compared to enzymatic saccharification, which however requires an energy intense pretreatment.

Ionic liquids are well known [17–19] for their ability to dissolve cellulose and our interest in the search for efficient catalytic methods for saccharification of cellulose has led us to develop Brönsted acidic ionic liquids as solvents as well as catalysts for the degradation of cellulose [20,21]. Later we found that these acidic ionic liquids can be used in aqueous phase as well, where a dilute aqueous solution of acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride was shown to be a better catalyst than aq. sulfuric acid of the same H^+ ion concentration for the degradation of cellulose at moderate temperatures and pressures [22]. During these studies we have observed that *p*-toluenesulfonic acid used for comparison of the catalytic activity could also show activities similar to acidic ionic liquids with imidazolium cation. Surprisingly, dilute acid catalyzed aqueous phase cellulose hydrolysis has been studied only with mineral acids H_2SO_4 [12–16], H_3PO_4 [23,24], HCl [25] and small organic acids like formic [26], succinic [27], acetic [27], maleic [27], and oxalic [28,29] acids.

In these studies Ladisch and co-workers have shown [27] that maleic acid hydrolyzes microcrystalline cellulose Avicel as effectively as dilute sulfuric acid but with minimal glucose degradation. Furthermore, maleic acid was found to be superior to other carboxylic acids like succinic and acetic acid reported in this paper, and gives higher yields of glucose, that is more easily fermented

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as a result of lower concentrations of degradation products [27]. The only kind of sulfonic acid group containing catalyst that has been tested for the cellulose hydrolysis in water is a heterogeneous catalyst, bearing $-SO_3H$, —COOH and —OH groups on amorphous carbon surface. This catalyst is known to give low glucose yields under thermal [30] and microwave [31] conditions.

The effects of relatively large carbon groups attached to a Brönsted acid function like sulfonic acid groups in the catalysis of cellulose hydrolysis process in aqueous phase are not known. As far as we are aware the effects of large carbon groups, and their hydrophobicities in sulfonic acid catalysis have been studied only in the case of alkyl/aryl sulfonic acid functionalized hybrid mesoporous silica materials in the catalysis of an actylation reaction [32]. Therefore, in an attempt to develop a recyclable, efficient acid catalyst, and as an extension of our earlier work [20–22] on sulfonic acid substituted imidazolium ionic liquid catalysts, we have studied a series of alkyl/aryl sulfonic acids for the hydrolysis of cellulose in water at moderate temperatures and pressures.

2. Experimental

2.1. Materials and instrumentation

Sigmacell cellulose – type 101 (DP ~ 450, from cotton linters), sulfuric acid, and alkyl/aryl sulfonic acids were purchased from Aldrich Chemical Co. Cellulose hydrolysis experiments were carried out in 25 mL stainless steel solvothermal reaction kettles with Teflon inner sleeves, purchased from Lonsino Medical Products Co. Ltd., Jingsu, China. These reaction kettles were heated in a preheated Cole-Palmer WU-52402-91 microprocessor controlled convention oven with ±1 °C accuracy. Total reducing sugars (TRS, total of glucose and glucose oligomers with reducing groups) and glucose concentrations in aqueous solutions were determined using a Carey 50 UV–vis spectrophotometer and 1 cm quartz cells.

2.2. General experimental procedures for hydrolysis of cellulose samples in aqueous acid solutions

Stock solutions of the alkyl/aryl sulfonic acids and sulfuric acid were prepared by dissolving appropriate amounts of these acids in deionized water to give acid concentration of 0.0321 mol H^+/L in each solution. The accuracy of the concentration was checked by titration with standardized aq. NaOH solution using phenolphthalein as the indicator. Sigmacell cellulose-type 101 (DP ~ 450) (0.030 g, 0.185 mmol of glucose unit of cellulose) was suspended in 2.00 mL of aqueous acid solution in a 25 mL high pressure stainless steel reaction kettle with Teflon inner sleeve. The reaction kettle was firmly closed and heated in a thermostated oven maintained at the desired temperature for 3.0 h. Then reaction kettle was removed from the oven and immediately cooled under running cold water to quench the reaction. The contents were transferred into a centrifuge tube and diluted to 10.0 mL with deionized water, neutralized by drop wise addition of 0.5 M aq. NaOH, and centrifuged at 3500 rpm for 6 min to precipitate the solids before TRS determination using 3,4-dinitrosalicylic acid (DNS) method [29]. The glucose formed was measured using glucose oxidase/peroxidase enzymatic assay.

2.3. Analysis of hydrolyzate

2.3.1. TRS assay

A 1.00 mL portion of the clear hydrolyzate solution from the centrifuge tube was transferred into a vial and 2.50 mL of deionized water was added. To this, was added 0.50 mL of DNS reagent [33] and the mixture was incubated in a water bath maintained at 90 °C for 5 min. The reagent blank sample was prepared with 3.50 mL of deionized water and 0.50 mL of DNS reagent and heated similar to the samples. Then the absorbance was measured at 540 nm, against the reagent blank, and TRS concentrations in solutions were calculated by employing a standard curve prepared using glucose.

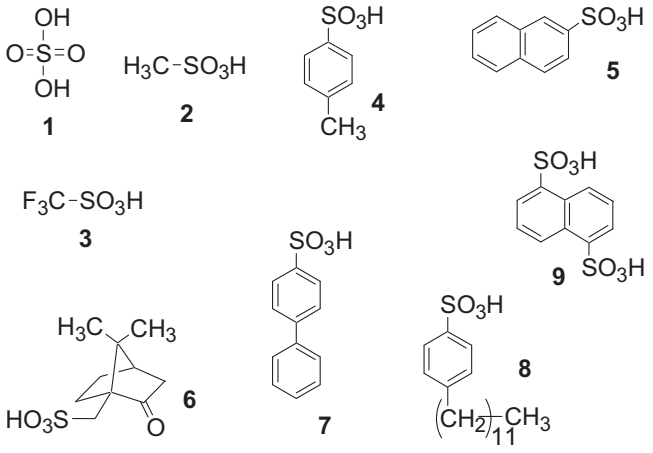

Fig. 1. Sulfuric acid (**SA**, **1**), methanesulfonic acid (**MSA**, **2**), trifluromethanesulfonic acid (**TFMSA**, **3**), *p*-toluenesulfonic acid (**PTSA**, **4**), 2-naphthalenesulfonic acid (**2-NSA**, **5**), 10-champhorsulfonic acid (**10-CSA**, **6**), 4-biphenylsulfonic acid (**4-BPSA**, **7**), 4-dodecylbenzenesulfonic acid (**4-DBSA**, **8**), and 1,5-naphthalenedisulfonic acid (**1,5-NDSA**, **9**) used in the cellulose hydrolysis.

2.3.2. Glucose assay

A 0.20 mL portion of the clear hydrolyzate solution from the centrifuge tube was transferred into a vial, and diluted with 1.80 mL deionized water. At zero time, reaction was started by adding 2.00 mL of glucose oxidase–peroxidase assay reagent [34,35] to the vial and mixing thoroughly, and the vial was incubated in a water bath at 37 °C for 30 min. Then reaction was quenched by adding 2.00 mL of 6 M HCl to give a pink solution. The reagent blank was prepared by mixing 2.00 mL of deionized water and 2.00 mL of assay reagent, and was treated similarly. Then the absorbance was immediately measured at 540 nm against the reagent blank and glucose concentration in the solution was calculated by employing a standard curve prepared using glucose.

3. Results and discussion

In this study, eight alkyl/aryl sulfonic acids (**2**–**9**) shown in Fig. 1 were compared with aqueous sulfuric acid (**1**) of the same H^+ concentration of 0.0321mol H^+ ion/L for the hydrolysis of Sigmacell cellulose type 101 (DP ~ 450) samples. Alkyl/aryl sulfonic acids used are thermally stable [36] in the temperature range used in this study, and all aqueous acid mediums used in the study were of the same H^+ ion concentration. According to Oscarson and Izatt's expression on temperature dependence of the first and second dissociation constants of sulfuric acid in aqueous medium, it is assumed that H_2SO_4 completely dissociates to give two H^+ ions in the 140–190 °C temperature range [26,37].

The average TRS and glucose yields produced in a series of experiments conducted in nine acid mediums, at 140–190 °C temperature range are shown in Figs. 2 and 3 respectively. These results show that cellulose samples heated in aqueous *p*-toluenesulfonic acid (**4**), 2-naphthalenesulfonic acid (**5**), and 4-biphenylsulfonic acid (**7**) at 160–170 °C temperature range produces significantly higher total reducing sugar yields compared to the sample heated in aqueous sulfuric acid solution of the same molar H^+ ion concentration (Fig. 2). These three acid mediums produced their maximum TRS yields at relatively lower temperatures; *p*-toluenesulfonic acid, 33.3% (170 ± 1 °C), 2-naphthalenesulfonic acid 31.5% (172 ± 1 °C),

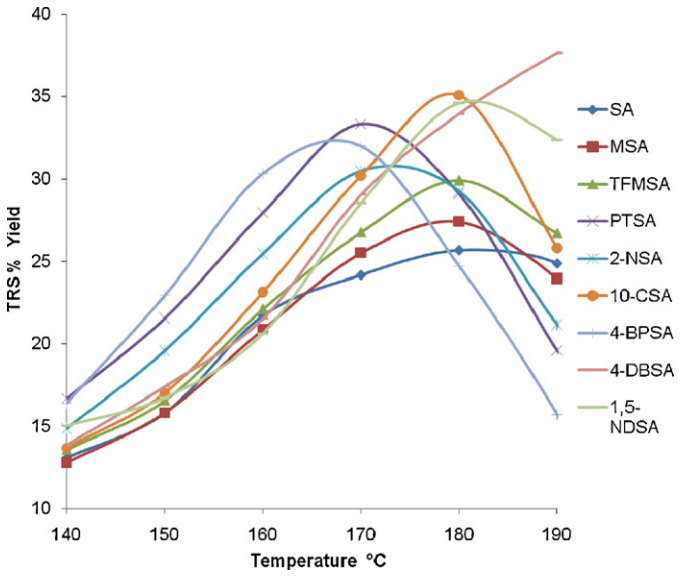

Fig. 2. The changes in % yields of total reducing sugar (TRS) produced during the hydrolysis of Sigmacell cellulose (DP ~ 450) in aq. sulfuric acid and eight alkyl/aryl sulfonic acids at different temperatures. All acid solutions are 0.0321 mol H^+/L, reaction time: 3.0 h 0.030 g of Sigmacell cellulose in 2.00 mL of aq. acid was used in all experiments. Averages of duplicate experiments.

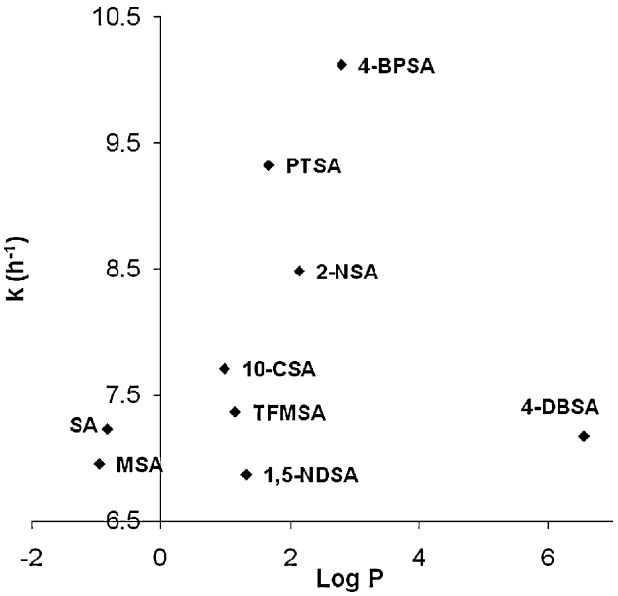

Fig. 4. The plot of first order rate constant k (h^{-1}) at 160 °C versus the octanol/water partition coefficient of sulfonic acids log P.

and 4-biphenylsulfonic acid 32.6% (165 ± 1 °C), compared to sulfuric acid 25.6% (180 ± 1 °C). Two other acid mediums, 10-camphorosulfonic acid 35.1%, and 1,5-naphthalenedisulfonic acid 34.6% reached their maximum TRS yields around 180 ± 1 °C, whereas the 4-dodeylbenzenesulfonic acid produced the highest TRS yield of 37.6% at 190 ± 1 °C. The one carbon small sulfonic acids, methanesulfonic acid and trifluromethanesulfonic acid showed curves similar to the sulfuric acid curve, indicating that their catalytic activities are similar to the sulfuric acid throughout the 140–170 °C range. This is a clear indication of the enhancement of catalytic activity by the large hydrophobic group attached to the sulfonic acid function. Furthermore, when we compare the TRS yields of the three aryl sulfonic acids,

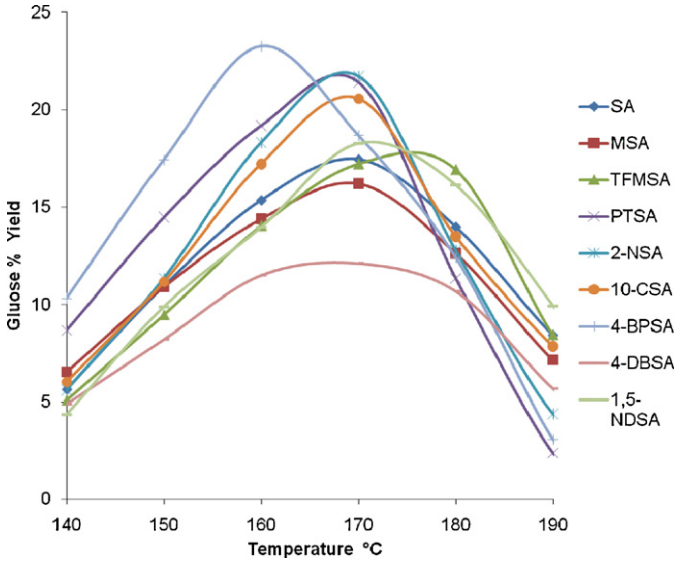

Fig. 3. The changes in % yields of glucose produced during the hydrolysis of Sigmacell cellulose (DP ~ 450) in aq. sulfuric acid and eight alkyl/aryl sulfonic acids at different temperatures. All acid solutions are 0.0321 mol H^+/L, reaction time: 3.0 h, 0.030 g of Sigmacell cellulose in 2.00 mL of aq. acid was used in all experiments. Averages of duplicate experiments.

p-toluenesulfonic acid (28.0%), 2-naphthalenesulfonic acid (25.4%), and 4-biphenylsulfonic acid (30.3%) with that of sulfuric acid (21.7%) medium at 160 °C, the relative catalytic activity enhancements are 29.0, 20.3, and 39.6% respectively for these three acids.

The variation of glucose % yields with temperature is shown in Fig. 3, and shows a pattern similar to the TRS % yields (Fig. 2) for most of the acid mediums. The glucose yields also reached higher maximum yields at relatively lower temperatures for *p*-toluenesulfonic acid 21.5% (166 ± 1 °C), 2-naphthalenesulfonic acid 21.4% (167 ± 1 °C), and 4-biphenylsulfonic acid 23.3% (160 ± 1 °C), compared to sulfuric acid 17.4% (170 ± 1 °C). Additionally, the glucose yield shows rapid decrease beyond 170–180 °C for all the acid mediums, and this is due to well known decomposition of glucose to various products like 5-hydroxymethulfurfural, 1,6-anhydroglucose, levulinic acid, and formic acid at high temperatures [38,39].

We have studied the correlation of catalytic efficiencies of these sulfonic acids with octanol/water partition coefficient log P and distribution coefficient log D of the sulfonic acids by plotting first order rate constants (k) with log P and log D. The partition coefficient is a ratio of concentrations of un-ionized compound between octanol and water. Whereas the distribution coefficient is the ratio of the sum of the concentrations of all forms of the compound (ionized plus un-ionized) in each of the two phases in octanol/water system [40]. The log P, and log D (at pH 1.49) values were calculated using software, ChemAxon™ log P/D calculator [41]. The plot of first order rate constants (k) for the degradation of cellulose to reducing sugars at 160 °C, versus log P is shown in Fig. 4, whereas the k versus log D is shown in Fig. 5. The first order rate constants (k) at 160 °C were used in the analysis, because at higher temperatures sugars produced tend to decompose into complex by-products, and we assume that at 160 °C, degradation of cellulose to glucose and glucose oligomers is the dominant reaction. The correlation plots, Figs. 4 and 5 shows that rate constants for degradation of cellulose correlate better with log D (Fig. 5) than log P (Fig. 4). It is well known that log D [42,43] is a better parameter than log P for ionizable compounds like sulfonic acids, and our results further support those observations. The rate constant (k)–log D plot (Fig. 5) clearly shows that sulfonic acids with similar hydrophobicities show similar catalytic efficiencies, and increasing hydrophobicity can produce an increase in cellulose degradation

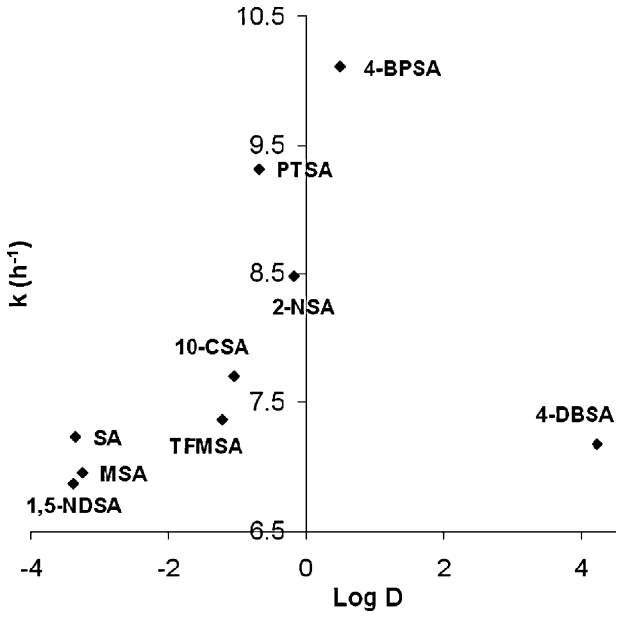

Fig. 5. The plot of first order rate constant k (h^{-1}) at 160 °C versus the octanol/water distribution coefficient of sulfonic acids log D.

up to a certain limit, as very large 4-dodecylbenzenesulfonic acid is completely out of the trend. Highly hydrophilic methanesulfonic acid (MSA), 1,5-naphthalenedisulfonic acid (1,5-NDSA) and sulfuric acid (SA) points were seen close together, where as the remaining acids follow an approximately linear correlation.

As seen in Figs. 2 and 3, very small sulfonic acids like strong acid trifluoromethanesulfonic acid (TFMSA) are not highly active as expected. Therefore, having a small alkyl group does not help to penetrate into the complex H-bonding network of cellulose. The activity enhancement can be explained as a result of an adsorption of alkyl/aryl sulfonic acids on to the cellulose surface, which is supported by the repulsion of the hydrophobic molecule from the bulk of the water phase, thereby pushing in to the cellulose structure, which causes the disruption of the cellulose H-bonding network. This repulsion from water, sustained by the hydrophobic group is not found in small acids like methanesulfonic acid and sulfuric acid. Therefore, MSA and H_2SO_4 showed relatively weaker activity. On the other extreme, water phase can exert a strong pushing towards the cellulose surface in the case of 4-dodecylbenzenesulfonic acid (4-DBSA) with very large hydrophobic group, but the bulkiness can make this molecule too big to penetrate into the H-bonding network in cellulose, especially at lower temperatures, making 4-DBSA a poor catalyst below 170 °C, however, a very effective catalyst above 180 °C (Fig. 2).

4. Conclusion

In the series of sulfonic acids studied, 4-biphenylsulfonic acid (**7**) appears to be the optimum size and shape to produce maximum catalytic activity with high TRS and glucose yields at relatively low temperatures, as seen in Figs. 2 and 3. This fundamental discovery is a lead for a small molecule that can efficiently penetrate and hydrolyze cellulose in the water phase at moderate temperatures and pressure. This type of system would work like a simple artificial cellulase, and with the use of thermally stable small aromatic hydrophobic compound, the catalyst is easily recyclable through solvent extraction from the resulting aqueous sugar solution, making an excellent economical catalyst in the industrial scale.

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