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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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