Lignocellulosics conversion in a molten salt hydrate media.

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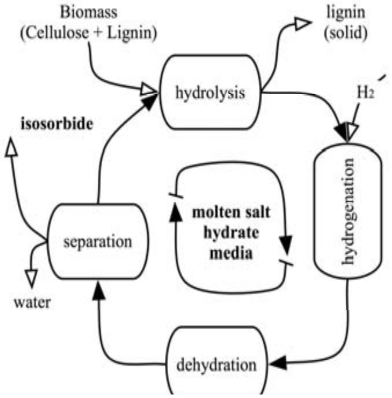
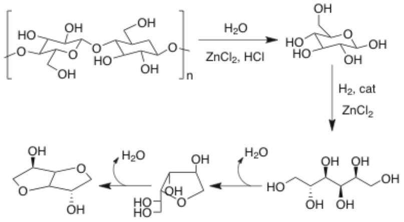
Introduction

An effective way to convert lignocellulosic biomass is a matter of universal interest.[1, 2] Main problems of existing processes arise from the lack of accessibility to cellulose (crystalline nature due to hydrogen bonding in glucosidic moieties)[3] and the reactivity of monosaccharides at higher temperatures,[1-2,4] leading to several dehydration and decarboxylation products.[5]

It is possible to turn the cellulosic portion of biomass soluble in a molten salt hydrate media, such as 65-75 wt% $ZnCl_2$. [6] Literature shows that hydrolysis is fast and complete with additional acid, but the separation of glucose product from the salt is difficult, being necessary expensive chromatographic methods or electrodialysis. [7]



Scheme 1. Proposed scheme for biomass conversion with molten salt hydrate media



Scheme 2 Main reactions: hydrolysis of cellulose to D-glucose, hydrogenation to D-glucitol, dehydration to sorbitan (pictured the 1,4-D-anhydroglucitol) and final dehydration to isosorbide..

We proposed the further conversion of glucose in the same molten salt hydrate media, to obtain products that can be more easily separated. As glucose is unstable, hydrogenation in molten salt hydrate media was effected to result in sorbitol. Sorbitol in the molten salt hydrate $ZnCl_2$ media is finally double dehydrated at higher temperature to 1,4:3,6-dianhydro-D-glucitol, or isosorbide. Isosorbide is considered a platform chemical with uses such as a renewable monomer[8]. At this stage, isosorbide can be separated by solubility in hydrocarbons, or other suitable method such as distillation or stripping as illustrated in Scheme 1. Main reactions are presented in Scheme 2.

Experimental

As feedstocks, long fibers cellulose, glucose and sorbitol were used. $ZnCl_2$ solutions were separately prepared. Reactions were held at batch 15 mL volume reactors system with previously heated temperature-controlled block. The products were analyzed by HPLC with refractive index detector, sugar column (calcium) with a $Ca(NO_3)_2$ 0.025 M mobile phase.

Results and discussion

Hydrolysis. Dissolution of cellulose in $ZnCl_2$ 70 wt% was fast and complete in salt hydrate / cellulose ratios higher than 9. Attempts were made also to dissolve cellulose in ionic liquid 1-Butyl-3-methylimidazolium chloride (BMIMCl) or mixtures of BMIMCl and $ZnCl_2$, but the dissolution is much slower than in the $ZnCl_2$ 70 wt% solution, and incomplete.

Hydrogenation. The hydrogenation of glucose to sorbitol in the molten salt hydrate $ZnCl_2$ media is possible. In a temperature of 100˚C, 50 bar and molten salt hydrate to glucose ratio of 12 wt/wt and a Ruthenium 5 wt%/Carbon catalyst (0.5 of catalyst to each g of glucose), the reaction is inhibited to circa 4 times lower reaction rate in comparison to the same concentration aqueous solution.

Dehydration. A first attempt was made to do further hydrogenolysis of sorbitol in the molten salt media and Ru/C cat, but an increase in $ZnCl_2$ concentration lead to the disappearance of hydrogenation/isomerization products and increase of just dehydration products.

Conclusions

The proposed combination of the steps of dissolution and hydrolysis of cellulose, glucose hydrogenation and sorbitol dehydration in the same molten salt hydrate media results in a process of isosorbide production with enhanced yield and selectivity.

The dissolution of cellulose allows a fast acid hydrolysis with easy acid separation and delignification. Although inhibited, hydrogenation in the molten salt hydrate media is possible. Higher temperatures are necessary to effect dehydration, and some additional salts other than $ZnCl_2$ enhance the reaction. Energy demanding steps of distillation before hydrogenation or dehydration or end product removal should not be necessary.

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