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Conversion of Cellulose to Value Added-Chemicals

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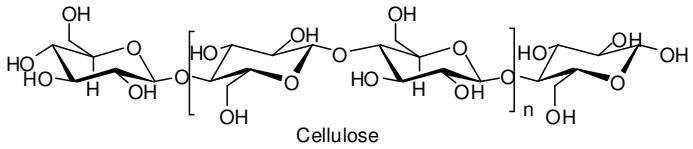
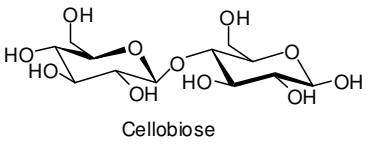
Abstract

Biomass-derived feedstock is of growing importance in the development of new synthetic pathways for commodity and specialty chemicals. Utilizing basic catalytic concepts such as hydrolysis, dehydration, isomerisation, and other common transformations of sugar in biomass conversion has already produced significant advances in the fundamental understanding of biomass conversion.

Despite the progress that has already been made, very few studies are dedicated to understanding the fundamentals of cellulose conversion under heterogeneous catalytic conditions. This is due to the complexity of both the catalytic steps at the metal/support interface and the structure of cellulose itself, being a highly functionalized homopolymer, characterized by hydrophilicity, chirality, and biodegrability. Difficulties in cellulose conversion stem from it's robust structure filled with intramolecular hydrogen bonding.





Our focus is on Cellobiose, a two-glucose unit dimer. It is ideal as a simplified model for cellulose because of the presence of a single ether-linkage per molecule and its solubility in water. This study aims to refine the fundamentals of Cellobiose conversion under conditions

near the critical point of water. Results have shown that, in the presence of a Ru/C catalyst, cellobiose offers high conversion with the primary products being Sorbitol or Mannitol polyols with shorter chain polyols such as xylitol, erythreitol, threitol, and glycerol also present in the reaction mixture.

1. Introduction

In light of current world affairs, finding sources of alternative energy options as well as a drive towards more sustainable means of production in the industrial sector is of paramount importance. Being a global warming believer or not, it is easy to see the importance or relevance that a fully renewable fuel from natural and available materials that is produced in a green fashion. The search for renewable and easily obtained starting materials for green chemical processes' has lead us to look around ourselves in a literal sense, and realize the abundant and carbon neutral resources that we have long taken for granted: biomass.

Biomass is one of the world's greatest untapped resources. Utilizing this carbon-neutral resource in a green fashion is the goal of this work. The implications of work with biomass derived cellulose could be far reaching and relevant on an industrial scale. Recycled paper, waste pulp from paper mills, and other paper waste all contains valuable cellulose that could be converted into a number of useful chemicals. Previous studies have shown that highly functionalized sugars such as glucose as well as other building block chemicals, like glycerol, are readily converted to high value products in catalytic environments [1,2]. It has been shown that utilizing cellulose in green reaction conditions can potentially produce Sorbitol, de-oxy hexitols, and other polyols [3,4]. Ruthenium metal catalysts are reported as a favorable candidate for this conversion from cellulose to industrially and commercially relevant products. Supercritical or near-supercritical water has been reported as having a dual purpose in this reaction as a generator

of free protons to promote hydrolysis of the ether linkages binding together the individual glucose units in cellulose, as well as giving a soluble medium for the robust and insoluble in water cellulose [3].

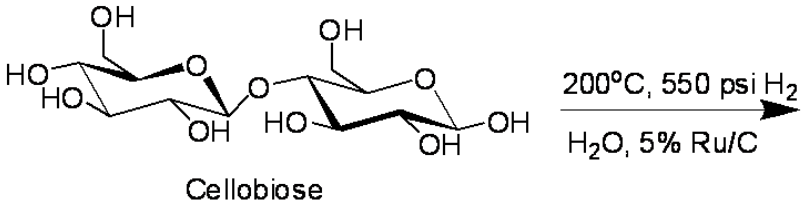


Figure 1 – General Reaction Scheme

Herein we present a study of cellobiose, a model system of cellulose comprised of two glucose units bound via an ether linkage in a heterogeneous Ru/C catalytic system. The heterogeneous catalytic system offers a of couple benefits over homogenous catalysts and enzyme digestion. Overhead cost is much lower than in enzymatic conversion; the catalyst is easily washed and recycled, and there is no need for harmful solvents to recover the catalyst as it can be obtained through simply gravity filtration.

2. Experimental

2.1 Preparation of catalysts

5% Ru/C was reduced in a 100 mL Parr Autoclave. 0.083 grams of catalyst (5 mmol of Ru) was loaded into the reactor and heated to 100°C. The reactor was then flushed 3 times with H_2 gas to remove air from the reactor, and then pressurized to 100 psi of H_2. The catalyst was left to stir for 30 minutes, at these conditions, then cooled and the reaction mixture added to the reduced catalyst.

2.2 Reactions

A 0.1 M stock solution of cellobiose was prepared by adding 10 grams (.05 moles) of cellobiose to 500 mL of water in a volumetric flask. This solution was used as feed for all of the

subsequent reactions performed in this study. For each reaction, 40 mL of stock solution was added to the reduced catalyst (if catalyst was utilized) and the vessel sealed. The reactor was then heated to 200°C and flushed 3 times with H_2 gas. As the temperature approached 200°C, the reactor was fully pressurized to 550 psi of H_2 gas and allowed to proceed at this set of reaction conditions for different amounts of time. After the allotted time had passed the reactor was removed from heat, and cooled in an ice bath until the internal temperature and pressure had been reduced to near ambient conditions. Control experiments were also run with sorbitol, mannitol, and cellulose as starting materials. The molar concentration was held at a constant 0.1M. A constant mole ratio of eleven moles of starting material to one mole of catalyst.

2.3 Analysis

Samples were prepared directly from 1.5 mL of post reaction mixture, 10 µL aliquots were analyzed via HPLC. Reaction mixtures were analyzed on an Agilent 1100 series HPLC equipped with a Phenomenex Rezex Pb2+ resin column, RI, and UV detector. Quantitation was carried out through RI detection and the use of standard calibration curves for quantifiable standards. Qualitative results were obtained via Jeol 300 mHz HNMR, IR, and LC-MS. 100% HPLC grade water was used as mobile phase.

3. Results and Discussion

The yields and product distribution is outlined in table 1. Performing control experiments without a catalyst load aimed to identify the effect of temperature and pressure. Our results confirm that the ether linkage between the two glucose units is vulnerable to cleavage at high temperatures and pressure (entry 1,2,3), hence the appearance of glucose as the primary product as seen in figure 2.

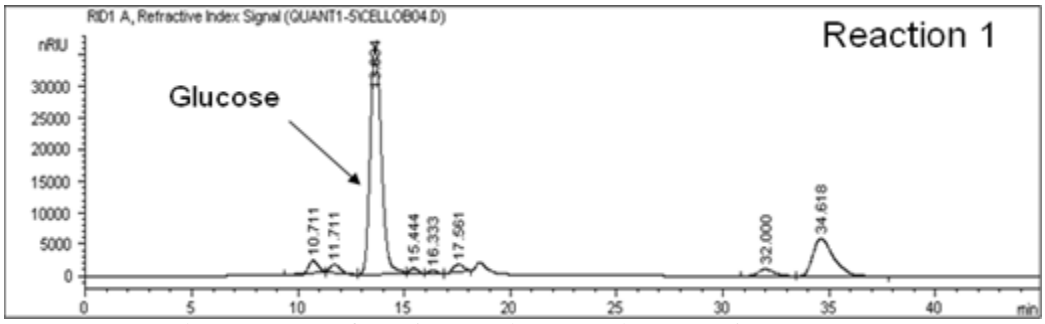


Figure 2 – HPLC chromatogram of reaction 1. Glucose peak at ~13 mins

These reactions without catalyst produced a dark brown colloidal suspension in every case. This tar like product could possibly be the results of aldol condensation processes between molecules of glucose formed over the course of the reaction. Utilization of a "false catalyst" of activated carbon showed no activity other than what we observed in the reactions with no activated carbon (entry 3). This finding confirmed that the support for our catalyst was not contributing or interfering in any way with our reaction condition. The addition of Ru/C catalyst had a visible effect on our product distribution. Post reaction, the mixtures went from being a dark, brown suspension to perfectly clear. Analysis revealed that the product mixture contained fully hydrogenated products and confirmed that Ru was active in the cleavage of C-C bonds (entry 4-10) through the presence of lower carbon polyols as observed in figure 3.

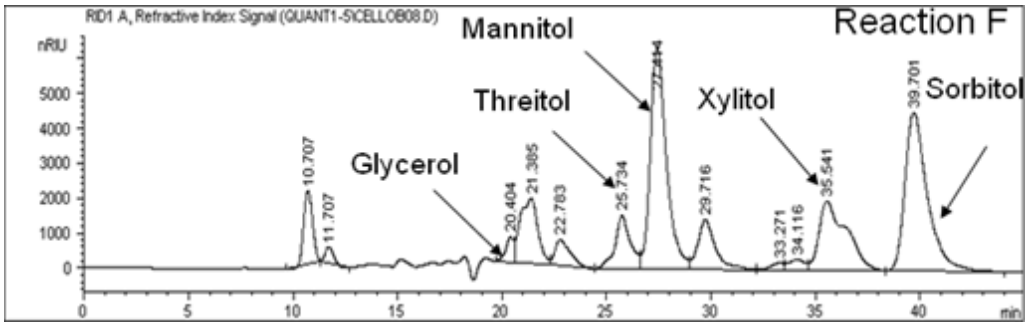


Figure 3 – Notice the lack of glucose and the appearance of fully hydrogenated products (Reaction F refers to entry 6 in table 1.)

Increasing the time scale of the reaction served to widen the product distribution and give rise to shorter chains. Under our conditions, we achieved the best selectivity towards hexitols

under a short time interval (entry 4). As time increased, the product distribution changed drastically to include higher quantities of shorter chain polyols as observed in figure 3.

Rxn #	Conditions	Time	Glycerol (%)	Threitol (%)	Xylitol (%)	Sorbitol (%)	Mannitol (%)	Glucose (%)
1	200˚C	30'	0.0	0.0	0.0	0.0	0.0	53.0
2	200˚C, 550 psi	30'	0.0	0.0	0.0	0.0	0.0	50.0
3	200˚C, 550 psi, C	30'	0.0	0.0	0.0	0.0	0.0	16.0
4	200˚C, 550 psi, C+Ru	5'	0.0	0.0	1.1	46.4	6.1	0.3
5		15'	0.6	2.3	4.2	23.3	13.7	0.4
6		30'	0.8	3.9	5.0	11.8	12.7	0.0
7		60'	1.8	4.7	5.7	5.0	8.5	0.6
8		90'	2.8	5.6	3.7	1.7	5.6	0.0
9		120'	3.1	5.3	2.2	0.7	3.4	0.0
10		150'	3.7	6.3	3.3	1.1	5.0	0.0

Table 1- Product breakdown by percent yield for cellobiose reactions

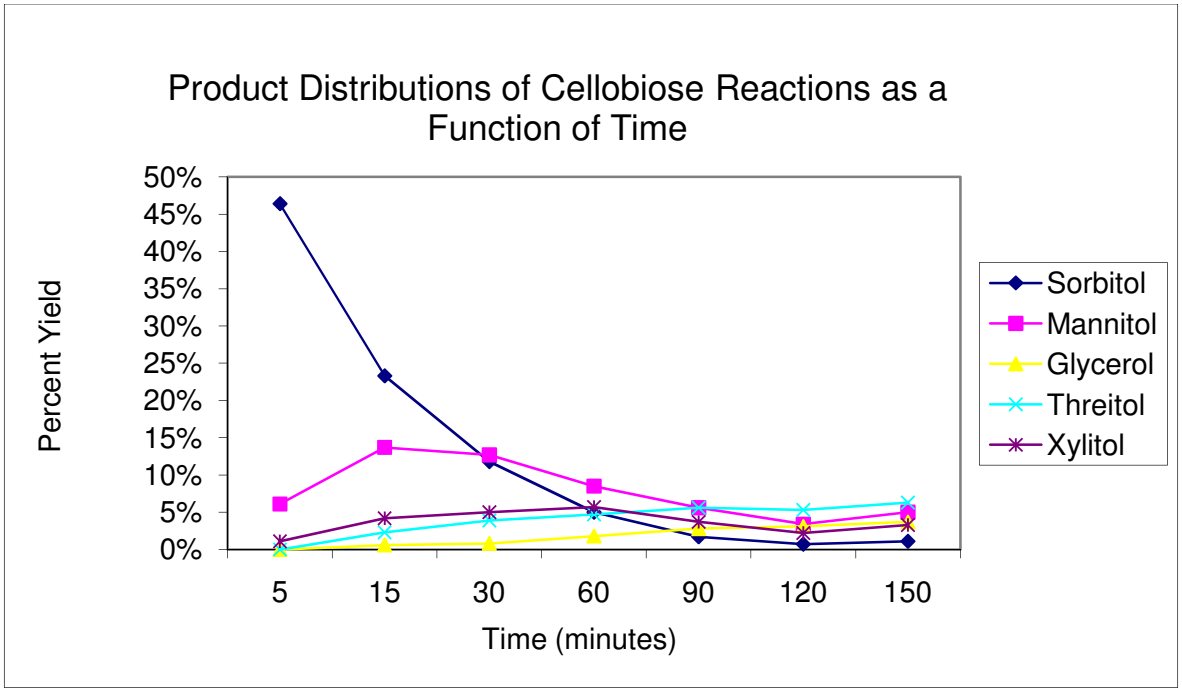


Figure 4- Cellobiose product distribution over time.

Observations from figure 4 lead us to the conclusion that shorter chain products are the result of subsequent reactions of Sorbitol and Mannitol. Our results indicate a two-step process. First the cellobiose units are cleaved apart via hydrolysis of the ether bond, and then the glucose units are hydrogenated to sorbitol.

Additional control experiments were carried out using sorbitol and mannitol as starting material for the reaction. Subjecting sorbitol and mannitol to same reaction conditions as cellobiose revealed two very interesting finds. First sorbitol and mannitol rapidly interconvert to one another in the presence of Ru, and second the product distributions were nearly qualitatively identical. The results of these experiments are shown in table 2. If this interconversion is a direct result of catalyst addition, it is reasonable to assume that the sugar molecules are being absorbed onto the surface of the catalyst in order for this reaction to take place, and from the surface of the catalyst the epimerization reaction takes place rapidly while the C-C bonds that make up the polyols are cleaved. Figures 5 and 6 show these changes over time and highlight the interconversion of sorbitol and mannitol.

Rxn #	Conditions	Time	Glycerol (%)	Threitol (%)	Xylitol (%)	Sorbitol (%)	Mannitol (%)	Glucose (%)
11	200˚C, 550 psi, C+Ru, Sorbitol	30'	0.7	2.3	4.7	24.8	14.5	0.0
12		60'	2.9	7.0	4.3	5.0	9.9	0.0
13	200˚C, 550 psi, C+Ru, Mannitol	30'	0.9	3.3	4.2	11.5	17.5	0.0
14		60'	3.5	7.1	3.7	3.1	8.9	0.0

Table 2- Product Breakdown by percent yield for control reactions

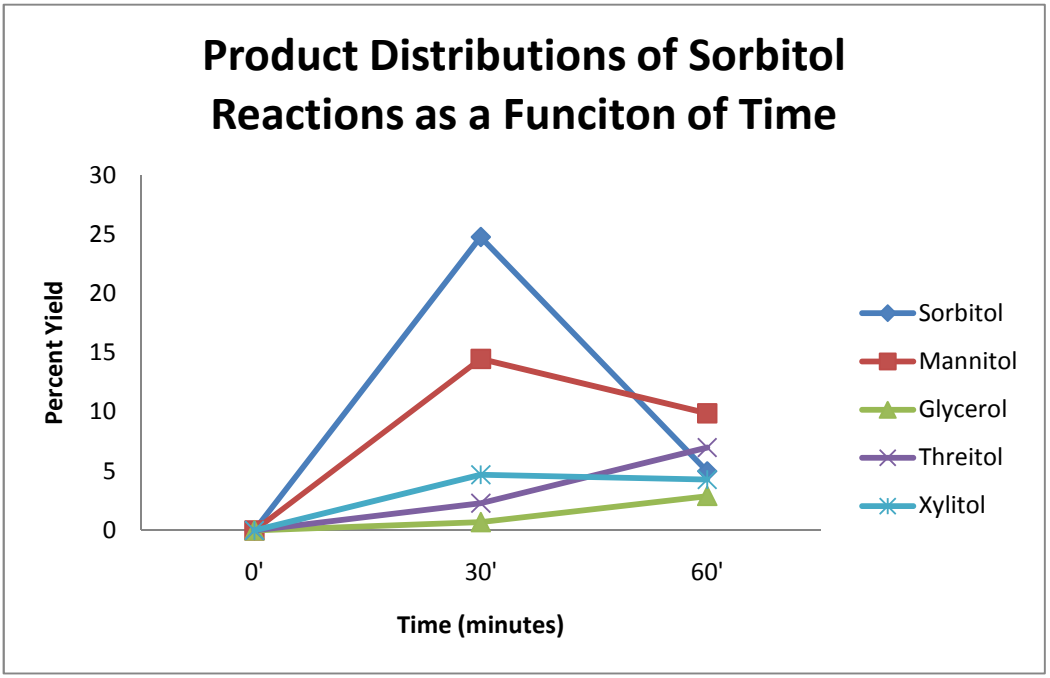


Figure 5 – Sorbitol product distribution over time.

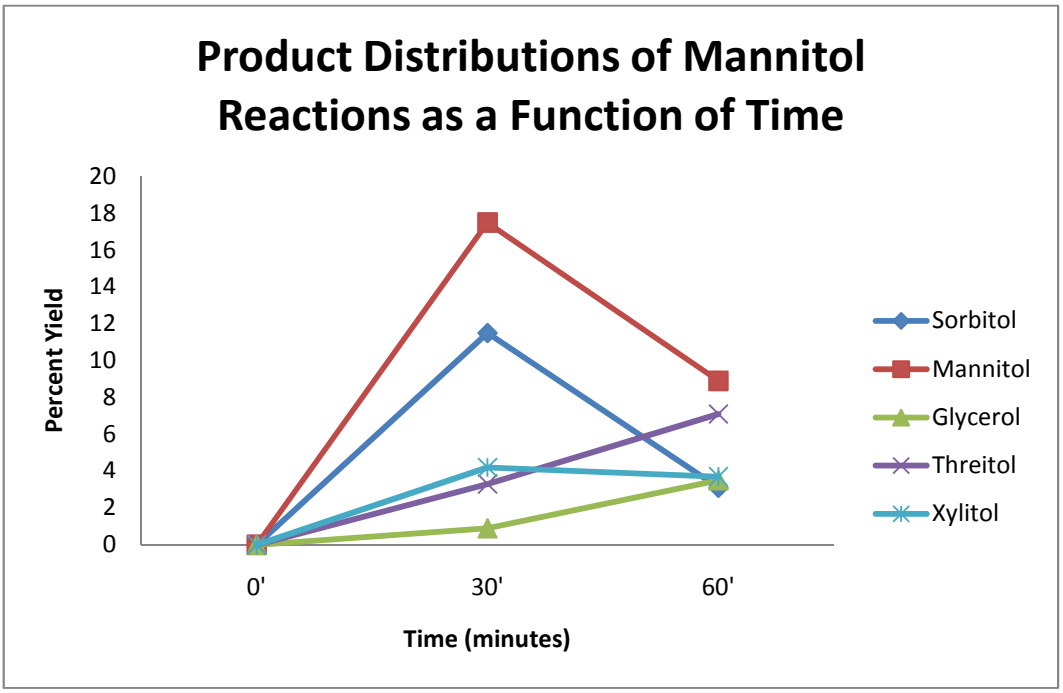


Figure 6 – Mannitol product distribution over time

Preliminary work done with microcrystalline-cellulose showed promising results. Conversions of cellulose (figure 5) were lower than the conversions of cellobiose, but that is to be expected[3,5,6]. The multiple unit chains that make up cellulose creates a far more robust structure that contains vast amounts of intermolecular hydrogen bonding. When we subject cellulose to conditions without Ru/C metal catalyst, we see low conversion of our starting material with good selectivity towards glucose. Analysis of product mixtures when using Ru/C catalyst revealed the same type of products, however they are only present in trace quantities. The carbon balance in the case of cellulose is incomplete. Our current set-up does not allow for us to analyze the gaseous phase head-space in our reactor where the lost carbon may be, the presence of possible small volatiles or traces of methane gas are still undetermined.

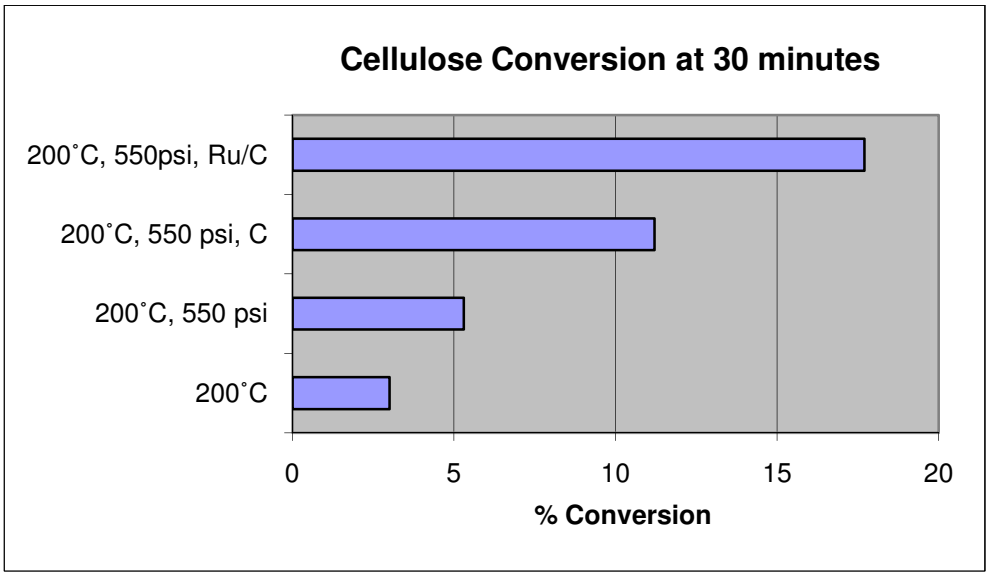


Figure 7: Cellulose Conversion

4. Conclusions

Cellulose's behavior in a heterogeneous catalytic system is modeled accurately by the glucose dimer, cellobiose. Through cellobiose we can see that in the presence of a Ru/C catalyst supported by carbon in a near-super critical water solvent system we can get high conversions in a one pot reaction towards industrially relevant products such as sorbitol, mannitol, glycerol, and many others.

In reactions with cellobiose, Ru/C catalyst shows high activity as a catalyst with a strong tendency towards cleavage of C-C bonds. Its activity lends itself to high conversions of the robust cellulose material but as far as selective conversions it is fairly hard to contain its activity and it lends itself to the formation of many hard to identify products.

Our results reported with cellobiose demonstrate a consistently high conversion of starting material (~99%), but, as the time scale increases, the product distribution widened and favored the formation of glycerol as opposed to higher carbon hexitols. The greater conversion to lower

carbon polyols can be attributed to the tendency of Ru to rapidly cleave C-C bonds[7]. Cellulose will require further investigation due to its inherently robust nature that is not easily cracked.

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