Biobased Chemistry and Technology

Thesis Biobased Chemistry and Technology

Hydrothermal conversion of cellulose using Raney Ni catalyst under alkaline conditions

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31-3-2016

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Name course	:	Thesis project Biobased Chemistry and Technology
Number	:	YEI-80324
Study load	:	24 ects
Date	:	September 2015 – March 2016

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Study programme	:	BBT
Report number	:	034 BCT

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Contents

Summary

The hydrothermal conversion of cellulose under alkaline conditions with a Raney nickel catalyst was investigated in this thesis. The goal was to investigate if high selectivity and conversion rate for the hydrolysis and/or gasification of cellulose with the use of a non-noble metal catalyst in alkaline media could be obtained. This was done in an one-pot reaction to improve the efficiency of cellulose conversion. Furthermore, the possibility of converting cellulose to organic acids through polyol intermediates by using hydrogen produced during the reaction was investigated. Through varying all the reaction conditions involved, optimisation of the cellulose conversion was investigated.

Since the proposed cellulose conversion consists of a complex network of different reactions all the reaction conditions were investigated separately. The following factors were investigated: Reaction temperature, reaction time, Raney nickel loading, base type and base concentration.

It was found that the optimal reaction temperature was 220 °C. At this temperature, almost all cellulose was converted and a high selectivity towards lactic acid was found. The reaction time was found optimal at ± seven hours as after this time about 90% of the cellulose was converted. The optimum for the amount of Raney Nickel was found to be 50 mg. The KOH concentration was found to be optimal at 1.5M as this resulted in the highest yield of lactic acid and complete cellulose conversion. The best base for the cellulose conversion was found to be $Ca(OH)_2$ as a 25% yield (g product/ g cellulose) on lactic acid was achieved. The gas phase composition consists vastly of hydrogen.

Besides lactic acid production, a lot of unknown minor by-products were formed and a lot of mass remains to be investigated as 68% is still unknown. In order to apply this in large-scale industry, the selectivity has to be improved. Furthermore, the reaction has to be tested on real ligno-cellulosic biomass in order to see if large-scale application is viable.

Improvement could be possible by investigating the effect of temperatures beyond 220 °C. This could potentially increase the selectivity towards lactic acid and will result in a higher cellulose conversion. The use of a higher KOH concentration is also recommended as this also increases the selectivity towards lactic acid.

Introduction

Currently, the world is heavily dependent on fossil fuel sources for the production of fuels and chemicals. To create a sustainable world economy and become independent of fossil fuels a lot of research is being done on the conversion of non-edible lignocellulosic biomass from plant-based materials into not only biofuel but also chemicals[1]. Since the main component in lignocellulose is cellulose (40-50%) the main focus is therefore cellulose conversion.

There are different ways to process lignocellulosic biomass, however, due to the high content in water of biomass, the hydrothermal route is preferred. Cellulose can be converted to many different useful chemicals including both aqueous and gaseous products. This hydrothermal process has two steps: the first step is the hydrolysis of cellulose to form glucose and in a second step glucose is converted to different carboxylic acids. Under alkaline conditions and at temperatures between 20 and 200°C, the main reaction products are: formic acid (100°C), acetic acid (170-190°C), DL-lactic acid (100°C, 240-320°C), 2-methyl-DL-glyceric acid, 3-deoxytetronic acids (25-45°C), D-glucoisosaccharino-1,4-lactone (19-23°C), α-D-glucoisosaccharinic acid (19-60°C and 100°C), β-D-glucoisosaccharinic acid (19-25°C, 100°C, 170-190°C)[7]. If the temperature is high enough and/or if a catalyst is present there is gas formation (hydrothermal gasification reaction) and the main gases obtained are H_2, CO_2 and CH_4. Among these three gases, H_2 is the most desired as it is a very clean source of energy. Table 1 shows a literature overview on cellulose conversion.

Ref.	Substrate	Products	Base	Catalyst*	Temperature (K)	Pressure (bar)	Reaction time (min)
3	Cellulose	73% conversion to gas (H_2, CO_2, CH_4)	-	40%wt Ni	593	30	30
12	Cellulose	27% lactic acid	2.5M NaOH	-	574	-	1
4	Cellulose	6.7% ethylene glycol 8.0% 1,2-propanediol 1.8% 1,2,5-pentanetriol	0.07M Ca(OH)$_2$	2%wt Ru	473	60 H_2	30
15	Cellulose	39.5% H_2 55.5% CO_2 1.9% CH_4 C_2-C_6 hydrocarbons	-	20-50%wt Pt/C	533	autogenous	360
5	Cellulose	3.9% H_2 43.2 % CH_4 47.8% CO_2	-	Ni	653	-	15
13	Cellulose	34.07% lactic acid	2.5M NaOH	100%wt Ni	573	-	4
14	Cellulose	42.15% lactic acid	2.5M NaOH	20%wt C, 5.7%wt Zn, 8.6%wt Ni	573	-	5
11	Ethylene glycol	90.8% H_2 4.9% alkanes	2.0M KOH	Raney Ni WHSV = 0.36 h^{-1}	498	25.8	-
6	Ethylene glycol	31% glycolic acid 27% formic acid	-	20%wt Ni/CNF	423	-	900

Table 1 : Literature overview on hydrothermal cellulose conversion.
* %wt based on the amount of substrate

The current issue with cellulose conversion is that it is vastly done at supercritical water conditions and this costs a lot of energy. Furthermore, it also harms the formation of hydrogen because hydrogen is thermodynamically more stable at lower reaction temperatures[2].

Both non-noble and noble metals are known to catalyse this reaction at low temperatures[3][4]. However, fast deactivation of metal catalysts is also a known problem. Noble metals suffer less from this[2] but they are much more expensive. When acids are used to catalyse the hydrolysis of cellulose, the activity of the metal catalyst (used for the gasification step) drops rapidly[5]. It is therefore preferred to use alkaline conditions for the cellulose hydrolysis step. When alkaline media combined with a metal catalyst are used to convert polyols or cellulose the following is known about the reactions conditions based on literature[6] **Figure 1**.
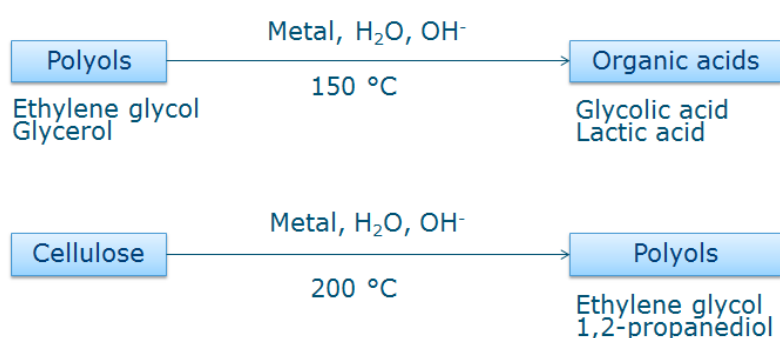

Figure 1 : Conversion of polyols and cellulose with a metal catalyst under alkaline conditions

Since the conversions mentioned in **Figure 1** occur under very similar reaction conditions, the possibility of combining both reactions into a single one-pot reaction was investigated. By combining these reactions the conversion of cellulose could potentially be very efficient as cellulose is then directly converted to high value chemicals in a single reaction. The proposed reaction is shown in **Figure 2**.
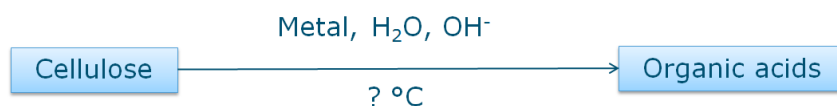

Figure 2 : Conversion of cellulose in a one-pot reaction with a metal catalyst under alkaline conditions

The goal of this study was to investigate if high selectivity and conversion rate for the hydrolysis and/or gasification of cellulose with the use of a non-noble metal catalyst in alkaline media could be obtained. The reaction was set up as an one-pot in order to improve the efficiency of the cellulose conversion. Furthermore, the possibility of converting cellulose to organic acids through polyol intermediates by using hydrogen produced during the reaction was investigated. In Figure 3 a schematic overview is given of the complete proposed reaction.
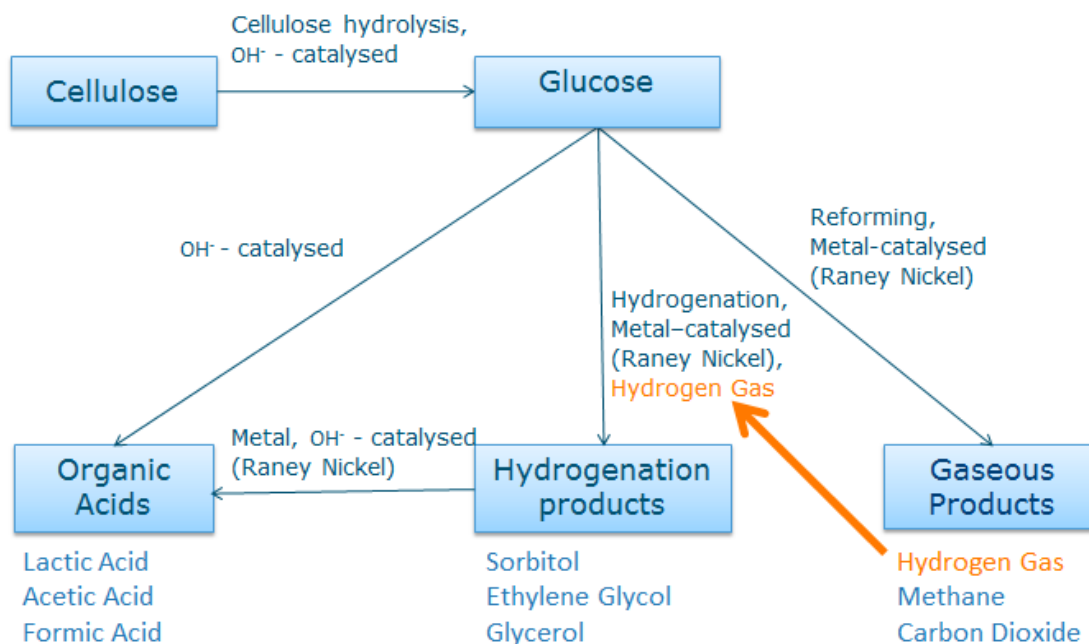
Figure 3 : One-pot reaction scheme for cellulose conversion with non-noble metal catalyser under alkaline conditions

In **Figure 3** the main idea is illustrated. First, cellulose is converted to glucose monomers via base-catalysed hydrolysis. The glucose can then be converted to either organic acids via base-catalysis, gaseous products via metal-catalysed reforming or polyols by using hydrogen formed during the reformation of the glucose. The polyols can then be converted to organic acids through base- and metal-catalysis. The approach of investigating the optimisation of the cellulose conversion in an one-pot reaction was varying all the reaction conditions involved and then use found optimum conditions in subsequent experiments.

Materials and methods

Chemicals

The following bases were used in the experiments: KOH reagent-grade (90% flakes, Sigma-Aldrich), K_2CO_3 (≥99.0%, Sigma-Aldrich), Na_2CO_3 (anhydrous 99.95-100.05% dry basis, Sigma-Aldrich), $Ca(OH)_2$ (≥95%, Sigma-Aldrich), $CaCO_3$ (≥99.0%, Sigma-Aldrich), NaOH (≥97.0% pellets, Fisher Scientific UK) and NH_3 (25% solution, Merck). The catalyst used was Raney Nickel 2800 catalyst (≥89% slurry, Sigma-Aldrich).

The chemicals used to make the HPLC standards were DL-lactic acid (≥85%), formic acid (≥95%), acetic acid (≥99.7%) and sorbitol (≥98%), all from Sigma-Aldrich. Microcrystalline cellulose (~50 μm particle size, Avicel PH-101) was used as feedstock.

Experimental Procedure

The reactions were conducted in a 6 Parr series 5000 parallel autoclave system. The reactor vessels were made of Hastelloy, with an inner diameter of 38.1 mm. The volume of the reactors was 75 mL (92.7 mL including headspace).

In a typical experiment feedstock, base, catalyst and water were mixed according to the following steps:

a) First, the base and the cellulose were weighed and added to the reactor vessels. The reactor vessels were then transported to a glove box where they were flushed 3 times with nitrogen in an airlock.

b) Next the Raney Nickel catalyst was weighed and added to the reactor vessels. The commercial Raney Nickel catalyst used was in slurry. Thus, before weighing the exact amount of catalyst needed for each experiment, the slurry was dried in a pure nitrogen environment. This was done under inert atmosphere inside a glove box to avoid the oxidation of the catalyst (Raney Nickel catalyst is pyrophoric).

c) After the addition of the catalyst, 30 mL of deoxygenized (by nitrogen flow) demi water were added. The reactors were then retrieved from the glove box and magnetic stirrer bars were added before sealing them off airtight. To prevent oxygen from dissolving into the water, the reactors were quickly transported to the parallel autoclave system, connected, and purged 3 times with nitrogen. After making all the connections (pressure and temperature sensor, water cooling system and gas inlet), the parameters (temperature, time, stirring speed) for the experiment were inserted into the computer software and the reaction was started. Note that the reactors were stirred continuously during the reaction.

d) After the set reaction time had expired, the stirring was stopped and the reactors were cooled down. Next, products on the liquid phase were collected and analysed by HPLC.

Below in **Figure 4** the experimental procedure is presented schematically. In **Figure 5** the Multi Reactor System that was used during the experiments is shown. In **Figure 6** a single reactor vessel is shown.
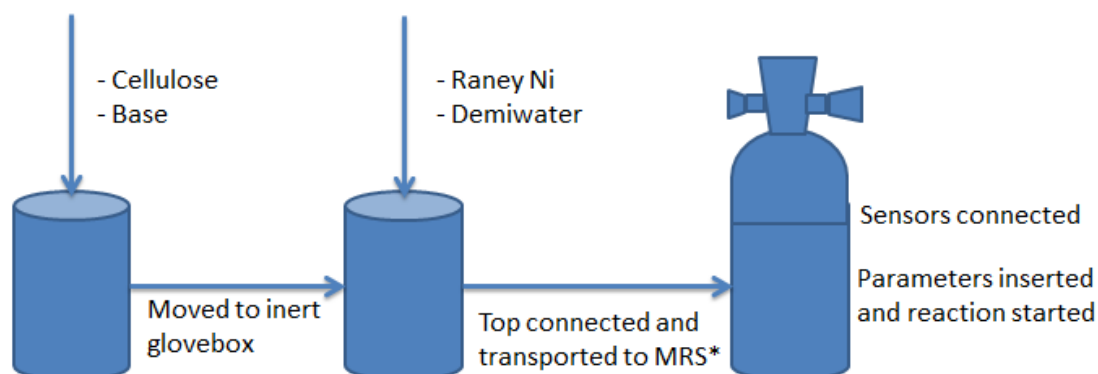

Figure 4 : Schematic representation of the experimental procedure
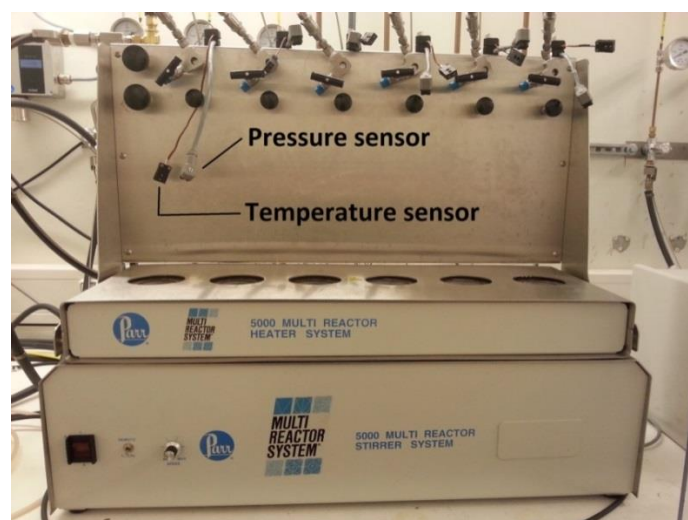

Figure 5 : Parr multi reactor system with indication on the pressure and temperature sensor
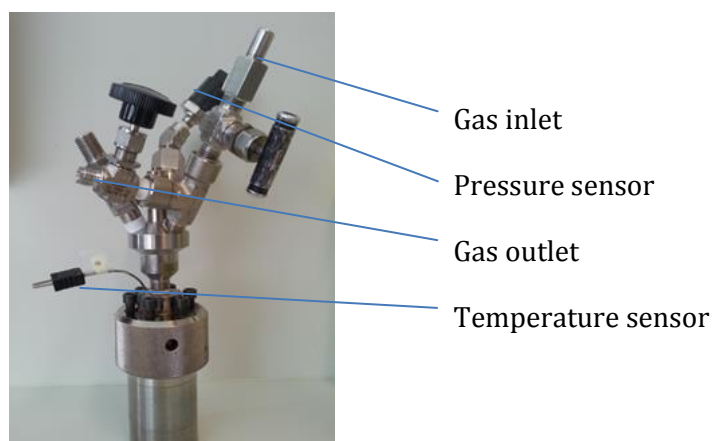

Figure 6 : Single reactor vessel with top part

The liquid phase products were collected by vacuum filtration with a Buchner funnel. This allowed the remaining cellulose and catalyst to be separated from the liquid products in a short time. The filter paper with the non-converted cellulose and the catalyst was dried overnight in an oven set at 130°C to evaporate all the water. After that, the dry cellulose was weighed. The cellulose weight measurement was adjusted for the catalyst that was also present on the filter paper. Since the catalyst remains intact during the reaction the weight was assumed to be identical to that of the added catalyst at the beginning of the reaction.

The liquid phase was collected in a 100 mL flask and diluted to 100 mL with demi water. The dilution to 100 mL was done to make sure that calculations based on sample volumes were accurate. The samples were diluted 10 times before being sampled into 2 mL vials and injected into the HPLC machine. Afterwards the pH of the 100 mL samples was determined and corrected by the dilution factor.

In some of the experiments the gas phase of the reactors fraction was collected and analysed. This was done with a gas bag (Tedlar, 1L) when the reactors had cooled down to room temperature. A sample was then taken with a syringe from the gas bag and injected into a GC machine.

After each reaction the reactors were cleaned by hand with soap, acetone and water.

Analytical methods

The amounts of DL-lactic acid, formic acid, acetic acid and sorbitol that were present in the final reaction mixtures were quantified using a Dionex UltiMate 3000 HPLC. The HPLC was equipped with a RS autosampler, Biorad Aminex HPX-87H 300 x 7.8 mm organic acid column, a Shodex RI-101 refractive index detector and RS Variable Wavelength Detector. The eluent used was 5 mM H_2SO_4 diluted with MQ water set at a flow rate of 0.5 mL/min at 35°C. Each sample ran for 60 min. The products were determined by comparing with standard solutions prepared by dissolving the commercial acids (mentioned in chemical section) in demi water.

The pH of the final reaction mixtures was measured with an Oakton pH 6 Acorn series pH/mV/°C meter.

Thesis Results & Discussion

Approach

In this section, experimental results relevant for investigating the effect of different reaction conditions on the proposed one-pot reaction of this thesis are presented and discussed. The lines presented in the figures in this section are not fitted, they are there to guide the eye to the trends observed.

Since the proposed cellulose conversion consists of a complex network of different reactions all the reaction conditions were investigated separately. The initial reaction conditions are based previous studies that are known to successfully catalyse similar reactions. The amount of cellulose used for the reactions was 1.58 g. This was about 5% of the total reactor content weight. The amount of catalyst used was about 10% of the cellulose weight, this is quite a lot. However, to make sure it's active an abundant amount was used. The base used was KOH at a concentration of 0.5M.

Effect of the reaction temperature

The effect of the reaction temperature on the catalytic decomposition of cellulose with a Raney Nickel catalyst under alkaline conditions was investigated. This was the first parameter to analyse as it shows how the reaction progresses and displays which is the most suitable temperature for this reaction. In literature, high temperatures (>300 °C) are frequently used to do this conversion[5]. This is because the gasification step has a high activation energy so a lot of energy in form of heat is needed to overcome the activation energy barrier. However, from literature it is also known that cellulose starts to decompose under alkaline conditions at 170°C[9]. Therefore the temperature range chosen in this experiment is between 140°C and 220°C in steps of 20°C. The concentrations of base and catalyst used were the ones mentioned in the approach section.

In **Figure 7** and **Figure 8** the results of the above mentioned experiment are shown.

Figure 7 shows how the reaction temperature influences the gaseous product formation during the cellulose conversion. As it can be seen, an increase in temperature results in a higher cellulose conversion. At 220°C the conversion is 20% higher than at 200°C. The high final pressure in the reactor at 220- °C indicates that more gaseous products are formed. From this experiment it was concluded that almost full conversion of cellulose took place at 220°C. Thus, further experiments were conducted at this temperature. According to literature, lower reaction temperatures yield a higher fraction of hydrogen in the gas phase[5]. As our aim is to reduce glucose to polyols with hydrogen formed during the reaction, it was therefore chosen not to test higher temperatures as this would have negative effects on the glucose reduction. Besides that, almost all the cellulose is converted at 220°C so working at higher temperatures will have a very small effect on the cellulose conversion.
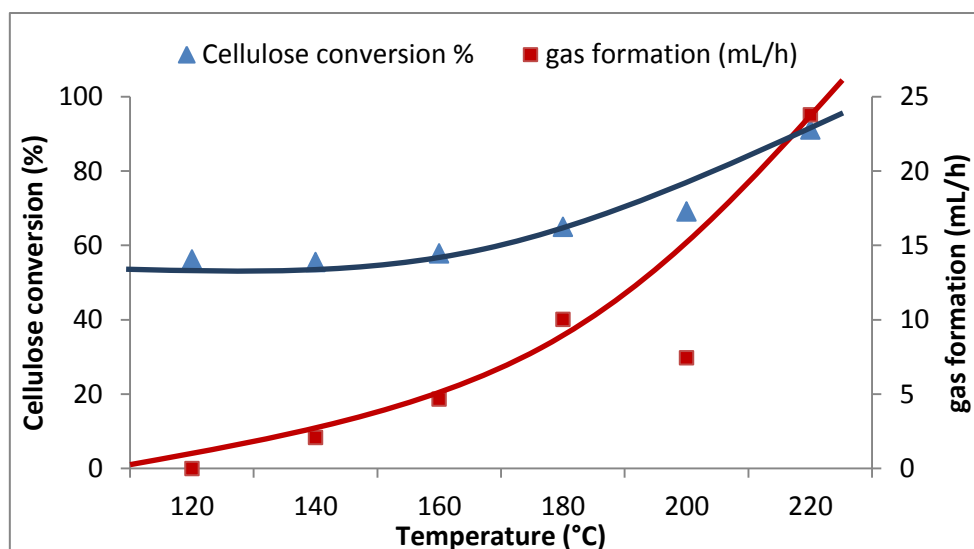
Figure 7 : Effect of temperature on cellulose conversion and gas formation
Reaction conditions: t = 8.25 hrs, 0.5M KOH, 50 mg Raney Ni, 1.58 g cellulose

Figure 8 shows the concentration of the main liquid phase reaction products of the cellulose conversion. As it can be seen, the main products detected were lactic acid, formic acid and acetic acid. No polyols were found in significant concentrations. As the temperature increases, the amount of lactic acid present in the final mixture also increases. The amount of formic acid decreases when the temperature increases, leaving a final mixture that is more selective towards lactic acid. The third most abundant compound, acetic acid, is present at 140°C – 220°C, Its concentration is relatively constant in this temperature range and lays between 0.01g – 0.02g per gram of cellulose. From literature it is known that formic acid is more abundant at 100°C, so the observation that the formic acid yield decreases at higher temperature supports this[9]. The opposite is true for lactic acid, According to literature lactic acid is more abundant when cellulose is converted under basic conditions between 240°C – 320°C[9]. Since a higher temperature leads to a higher selectivity the experiments were continued with 220 °C. Higher temperatures were not investigated because it would have a negative effect on the formation of hydrogen in the gas phase.
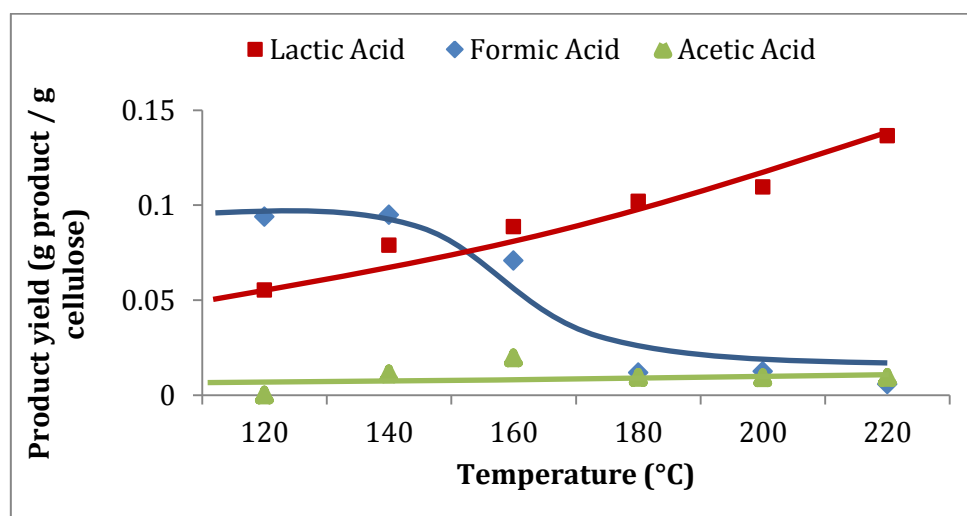

Figure 8 : Effect of temperature on the liquid phase product distribution
Reaction conditions: t=8.25 hrs, 0.5M KOH, 50 mg Ni, 1.58 g cellulose

Effect of the reaction time

Besides the temperature of the reaction, the reaction time is very important because it has a large impact on the selectivity of the cellulose conversion. Besides that, if a shorter reaction time can be used this would save energy as a shorter heating time is required. From an experiment not mentioned here, the reaction time was tested from 1 hour up to 16 hours with steps of 3 hours in between. However, after 1 hour more than 70% of the cellulose was already converted. In an attempt to find out at what time most cellulose is converted, reaction times were tested below 1 hour (0, 5, 10, 15, 30 and 60 min). Note that a reaction time of 0 means that the reaction mixture was heated up to 220°C and then immediately cooled down. The results of that experiment are shown below in **Figure 9** and **Figure 10**.

The end product yields of the cellulose conversion under standard conditions are shown in **Figure 9**. It can be seen that over time, the product selectivity goes towards lactic acid as the presence of formic acid drops. As was mentioned before, formic acid is mostly formed at 100°C. As the reaction temperature is 220°C, this means that formic acid is formed during the heating up of the reaction and further decomposed to gaseous products in the first hour of the reaction. The amount of acetic acid remains relatively constant over time.

Figure 9 : Effect of reaction time on the yield of the main liquid phase products.
Reaction conditions: 0.5M KOH, T=220°C, 50 mg Ni, 1.58 g cellulose

In **Figure 9** the pressure build up and the total amount of cellulose that was converted during the reaction is presented. From this information it can be seen that gas production is fast at the beginning of the reaction as after 5 minutes there is already 0.6 bar of gas. After 60 minutes the pressure of the reactor is 1.3 bar, a little bit more than 2 times 0.6 bar. This indicates a higher gas formation rate at the beginning of the reaction.

In **Figure 10** the conversion and gas formation are shown. As can be seen the conversion of cellulose slightly increases over time. Most of the cellulose (70%) is already converted during the heating up of the vessel (before reaching the set reaction temperature). However, for a more complete conversion, up to at least 90%, more time is required. For the gas formation more time is required as well. The pressure steadily increases over time. Thus, if the reaction is prolonged more gas will be produced. In further experiments the difference in gas formation for other factors (type of base, amount of Ni etc...) was researched. It was therefore useful to continue the reactions for a longer period of time. Over a longer period of time the difference in gas pressure build up is larger and allows finer analysis. For these reasons, reaction times were set to 5.5 hours up until 7.5 hours for the further experiments.

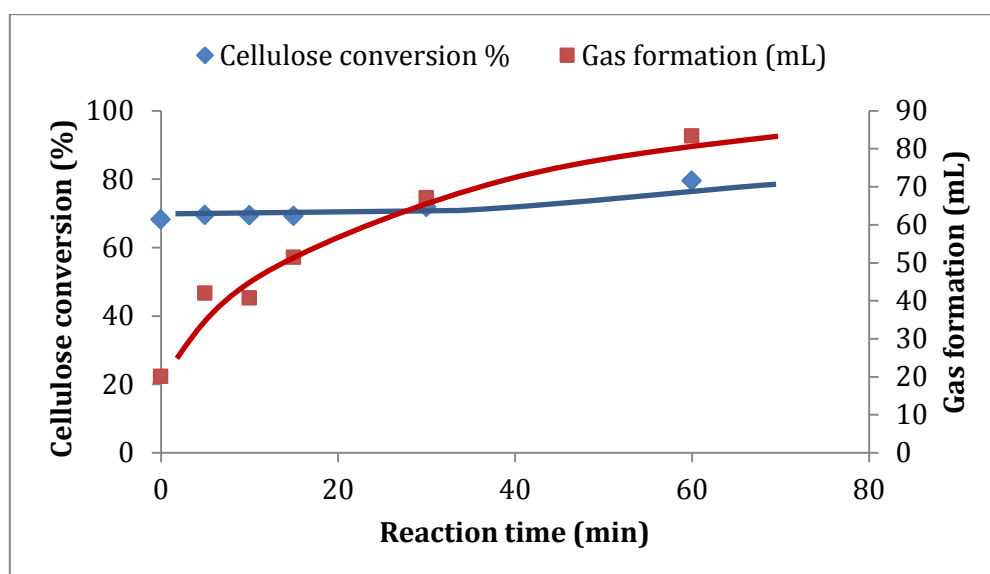**Figure 10** : Effect of reaction time on the gas formation
Reaction conditions: 0.5M KOH, T=220°C, 50 mg Ni, 1.58 g cellulose

Gas phase composition and mass distribution

In order to investigate the selectivity of the gaseous products, the gas phase of a reaction containing 0.5M KOH, 50mg Raney Nickel and 1.58g cellulose. The reaction was performed at 220°C for 0 and 6 h and it was done *in triplo* to account for reproducibility of the experiments. In **Figure 11** the gas phase composition is shown.

The most important fact observed in **Figure 11** is the large increase in hydrogen gas when the reaction is continued for 6 hours, which matches with previous experiments (see fig 5). Based on this it can be stated that under the reaction conditions mentioned above the conversion has a favourable selectivity towards hydrogen in the gas phase. Very little methane is formed during the reaction. This is due to the relatively low reaction temperature as the selectivity towards methane will most likely increase with a higher reaction temperature[5]. Carbon dioxide is formed in significant amount as by-product during the catalytic cellulose gasification. As expected, the amount of carbon dioxide increases over time as more cellulose is converted more by-product is formed. The amount of carbon dioxide formed is correlated with the amount of hydrogen produced.
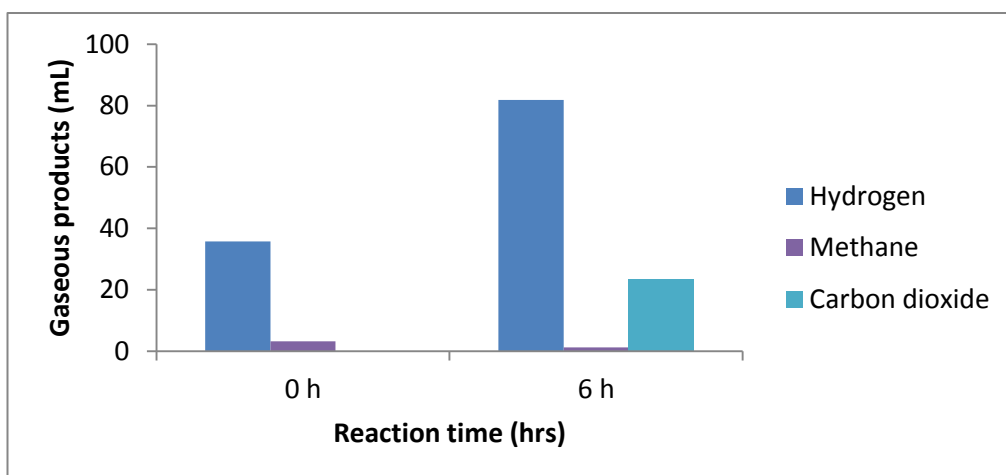
13

Figure 11 : Effect of time on gaseous phase product composition of the cellulose conversion
Reaction conditions: 0.5M KOH, T=220°C, 50 mg Ni, 1.58 g cellulose

In **Figure 12** the mass distribution of the reaction after 0 h and 6 h is shown. This concerns the same *in triplo* reaction of which the gas phase composition was determined.

Figure 12 : Effect of time on product mass distribution
Reaction conditions: 0.5M KOH, T=220°C, 50 mg Ni, 1.58 g cellulose

Figure 12 shows that a large amount of mass after the reactions remains unidentified. A part of this fraction consists of minor liquid products. However, this does not account for all the missing mass. Some of it could also be carbonates undetected by the HPLC. It could also be high molecular weight products that are undetected by the HPLC. To check if any glucose oligomers (high molecular weight) were formed, an experiment with cellulase was done. This enzyme breaks the glycosidic bond that links glucose in cellulose molecules together. The experiment showed no increase in glucose, this means glucose oligomers cannot account for the unidentified product mass. This experiment is described in the Annex. However, from the known fraction, the yield on lactic acid was the highest. The fraction became larger when a longer reaction time is used. This is because of a more complete cellulose conversion as it goes up from 70% to 85%.

Effect of the Raney Nickel loading

The catalyst used in this project was a commercial Raney Nickel catalyst. As a non-noble metal, Raney Nickel is cheaper than the noble metals that are often used for these kind of reactions[5]. Besides that, this catalyst is known to effectively catalyse ethylene glycol under similar reaction conditions[8]. Based on this, it was expected that the catalyst could effectively convert cellulose into useful gaseous and liquid products. To test whether the presence of the catalyst changes the reaction rate and/or selectivity of the reaction, an experiment with different concentrations of Raney Nickel was set in.

The reaction time used was 6.5 hours, the KOH concentration 0.5M and the temperature 220°C while the Raney Nickel concentration was varied. Below in **Figure 13** and **Figure 14** the influence of Nickel on the gas formation rate and on the product selectivity is illustrated.

Figure 13 shows that when more Ni is used a higher final pressure is achieved. The blank (contains 0 mg of Nickel) illustrates that without Ni, only a small amount of cellulose is eventually converted to gas products. The cellulose conversion was not affected by the Ni variation nor by the absence of Ni. The change in gas formation rate is highest when going from 0 mg to 50 mg, from there on only slightly more gas is formed when adding 50 mg of Ni stepwise. Adding four times as much Ni only leads to a two times increase in gas formation rate. The effect of adding more than 50 mg of Ni is therefore minimal. After this, it was decided to continue with a concentration of 50 mg of Ni in further experiments. 50 mg of Ni is 3.1% of the cellulose weight as 1.58 g of cellulose is used during the reactions. Furthermore, since with and without catalyst almost full conversion is reached, the catalyst appears to only influence the selectivity of the consecutive step. This is because the first step of the cellulose conversion is the hydrolysis which is base-catalysed and is unaffected by the amount of Ni.

Figure 13 : Effect of the amount of catalyst on the gas formation rate
Reaction conditions: t=6.5hrs, 0.5M KOH, T=220°C, 1.58 g cellulose

In **Figure 14** the lactic acid yield is plotted versus the Raney Nickel loading in order to illustrate the effect of the catalyst on the lactic acid. It can be seen that the lactic acid yield decreases when

more Ni is added to the reaction. This suggests together with the results of **Figure 13** that lactic acid is converted to gaseous products when increasing the amount of Ni used. Because Ni catalyses reactions towards gas formation this is most likely happening. However, it can also mean that Ni increases selectivity toward other liquid products which results in a lower concentration of lactic and acetic acid. To test whether lactic acid is converted towards gaseous products an experiment with lactic acid, base and two different Ni concentrations was done. This experiment is shown in the Annex section of this report.

Figure 14: Effect of Ni on the lactic acid yield
Reaction conditions: t=6.5 hrs, 0.5M KOH, T=220°C, 1.58 g cellulose.

Effect of the KOH concentration

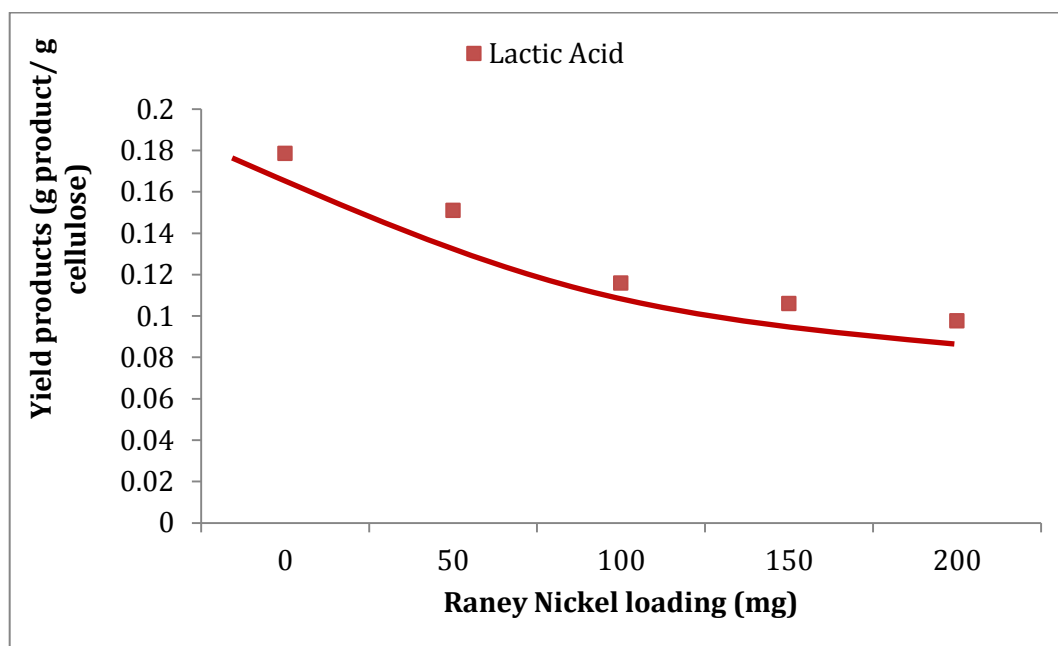After elucidating the effect of the Raney Ni concentration on the cellulose conversion, the effect of the basicity of the beginning reaction was investigated. Literature shows that basicity of the liquid medium determines the reaction pathway of the cellulose conversion as at a pH between 13 and 14 only carboxylic acids are formed[4]. To prevent the formation of unwanted products and to achieve a high selectivity towards these acids, a high pH should be maintained during the experiments. Thus, base molarities that result in a pH higher than 13 will be used, as if a lower pH is used at the beginning of the reaction, the mixture will turn acidic[4]. Furthermore, maintaining a high pH will also prevent the catalyst from being quickly oxidized[5]. To confirm the literature some experiments with a pH lower than 13 will be done as well.

To study the effect of basicity on the catalytic conversion of cellulose, different experiments were carried out using KOH as a base. The concentration of the base was increased from 0.1 to 1.5M in steps of 0.5M. The results are shown in **Figure 15**.

Figure 15 : Effect of basicity on the liquid phase product distribution.
Reaction conditions: t=6 hrs, T=220°C, 50 mg Ni, 1.58 g cellulose.

From **Figure 15** it can be seen that when a higher base concentration is used, more lactic acid is produced. Both formic acid and acetic acid remain relatively constant. The use of a higher base concentration also influences the conversion of cellulose. More cellulose is converted when more base is used. The increased base concentration leads to an abundancy of OH- and increases the reaction rate of the base-catalysed cellulose hydrolysis.

At the lowest KOH molarity (0.1M), the final reaction mixture became acidic. On the UV HPLC chromatogram formation of HMF (42.9 min) is visible, albeit in low concentration. This means that there was not enough base present to keep the reaction mixture basic after the formation of acids derived from the base-catalysed cellulose hydrolysis. This resulted in an acidic mixture

that allowed the formation of acid-catalysed products such as HMF. This is unwanted as it negatively affects the reaction selectivity towards base-catalysed products. This means that the reaction is more selective towards the base-catalysed products at higher base concentrations, favouring the use of high base concentration (≥1M) for the cellulose conversion.

Effect of the base type

After studying the effect of the catalyst and the basicity on the reaction, the influence of different bases on the catalytic decomposition of cellulose was investigated. The following bases were tested: KOH, NaOH, $Ca(OH)_2$, NH_4OH, Na_2CO_3, $Ca(HCO_3)_2$ and K_2CO_3. KOH and NaOH were expected to be the most interesting, as they are known to promote H_2 formation in biomass conversion[5][6]. However, since they are highly soluble in water, the reaction conditions are very basic when working with high molarities of these bases and such strong basic conditions might damage the reactor. $Ca(OH)_2$ is much less soluble and allows to maintain a high pH and mild reaction conditions. A comparison between hydroxides and carbonates was done as well as carbonate bases only dissolve when acidic products are formed and thus they could provide a solution to the problem of the pH decrease after the cellulose hydrolysis. Besides these common bases, NH_4OH was used as well. This base was chosen because it does not consist of a metal ion. Therefore it allows to study the effect of the metal ion on the cellulose conversion.

The effect of different types of bases on the liquid phase product distribution of the hydrolysis of cellulose are presented in **Figure 16**. For these reactions 150 mg of Ni has been used instead of 50 mg. This was done to make sure that gas would be produced in a significant amount and to make sure that the amount of Ni would not be limiting the gas formation.

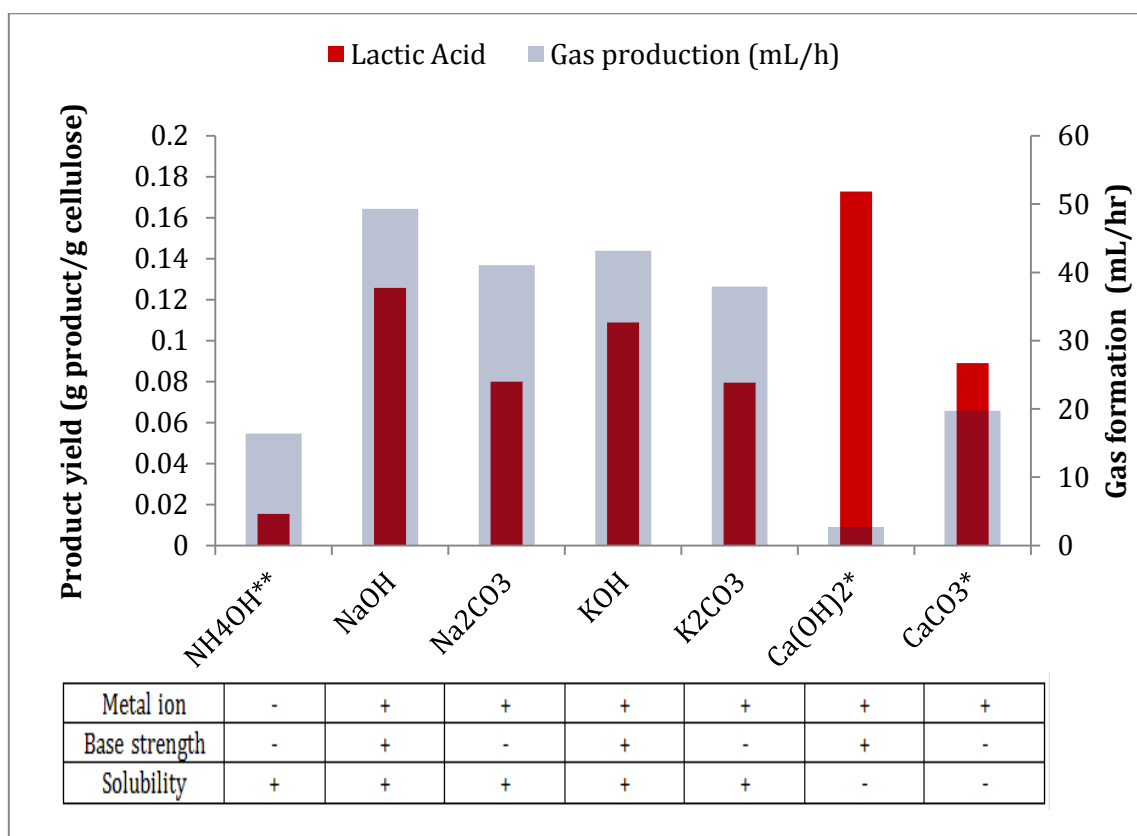**Figure 16**: Effect of different bases on the lactic acid yield and the gas formation.
Reaction conditions: 0.5M base, t=6 hrs, 150 mg Ni, T=220°C.
Note: the reaction time with $CaCO_3$ was 19 hrs.
**Note: NH_4OH had a lower cellulose conversion.

In **Figure 16**, the lactic acid yield has been combined with the gas formation to illustrate to selectivity of the cellulose conversion towards both liquid and gaseous products. The lactic acid yield is highest when $Ca(OH)_2$ is used as base catalyst. The two strongest bases, KOH and NaOH, also have high selectivity towards lactic acid. The carbonates of these two bases show very similar results. NH_4OH shows the least conversion, it has lactic acid nor gaseous products. All tested bases except $Ca(OH)_2$ show a significant amount of gas produced. This is explained when we see that $Ca(OH)_2$ clearly shows more selectivity towards liquid products but also because if CO_2 gas is formed, it is more likely to form CaCO3 instead of going to the gas phase. Thus we see that almost no gas was produced when used as $Ca(OH)_2$ as base catalyst. As lactic acid is the main liquid product formed during all the experiments the aim became to achieve a high yield for this product. Since $Ca(OH)_2$ gave the highest yield for lactic acid, a concentration range of this base was investigated and compared with KOH.

Effect of the $Ca(OH)_2$ concentration

The previous experiment with the comparison between different bases showed that when $Ca(OH)_2$ was used as a base catalyst, the higher lactic acid yield was obtained. To study the influence of the base concentration on the lactic acid yield and gas production an experiment varying the concentration of $Ca(OH)_2$ from 0.05 to 1.0 M was done. This was then compared with the KOH results for the lactic acid yield and the gas formation. The results of this comparison are shown in **Figure 17**.

Figure 17 : Effect of $Ca(OH)_2$ concentration on lactic acid yield and gas formation rate
Reaction conditions: t=6 hrs, T=220°C, 50 mg Ni

In **Figure 17** It can be seen that the lactic acid yield increases substantially throughout increasing the base concentration up to 1M of $Ca(OH)_2$, with a final yield of 25%. $Ca(OH)_2$ shows a higher selectivity towards lactic acid than KOH as over the whole concentration range all the lactic acid yields of KOH are lower than the lactic acid yields obtained by $Ca(OH)_2$. $Ca(OH)_2$ is

therefore the more preferred base for the reaction. When we compare the gas formation rate we observe the same as before in **Figure 16**, almost no gas is produced when $Ca(OH)_2$ is used whereas KOH actually promotes the conversion towards gaseous products. The lactic acid stabilizing effect of $Ca(OH)_2$ could be the reason for the higher lactic acid yield as the lactic acid stability experiment showed that under used conditions the lactic acid can be converted towards gaseous products.

Summary and conclusions

Cellulose was successfully converted to several liquid and gas phase products under alkaline conditions and using Raney Nickel as a non-noble metal catalyst. All reaction condition factors were successfully investigated. The optimal reaction temperature was found to be 220 °C. At this temperature, almost all cellulose was converted and a high selectivity towards lactic acid was found. The reaction time was found optimal at ± seven hours as after this time about 90% of the cellulose was converted. The liquid product selectivity of the reaction did not change anymore after one hour. The optimum for the amount of Raney Nickel was found to be 50 mg. When four times as much was used (200 mg) the amount of gas formed had only doubled. The KOH concentration was found to be optimal at 1.5M as this resulted in the highest yield of lactic acid and complete cellulose conversion. The best base for the cellulose conversion was found to be $Ca(OH)_2$ as a 25% yield (g product/ g cellulose) on lactic acid was achieved. In literature similar experiments found a comparable yield[15]. The gas phase composition looks promising as it vastly consists of hydrogen.

However, a lot of unknown minor by-products were formed and a lot of mass remains to be investigated as 68% is still unknown. In order to apply this in large-scale application, the selectivity has to be improved. Furthermore, the reaction has to be tested on real ligno-cellulosic biomass in order to see if large-scale application is viable.

The use of produced hydrogen during the cellulose conversion to reduce glucose to polyols was investigated but unsuccessful. It is assumed that not enough hydrogen was produced in order to reduce the glucose to polyols.

Recommendations

Temperature increase

The temperature investigation stopped at 220°C as almost full conversion was achieved and the selectivity in the gas phase is more favourable towards hydrogen at a lower reaction temperature. However, when focussing on lactic acid production a higher reaction temperature could be favourable as lactic acid is stable up to 220°C. Furthermore, when $Ca(OH)_2$ is used as base catalyst, the lactic acid may be stabilised promoting the selectivity. On the other hand, the amount of hydrogen produced in the gas phase will most likely decrease and the selectivity will shift towards methane, which is a less valuable product.

Hydrogen pressure experiment

During the experiments we were unable to use the produced hydrogen in the gas phase to reduce glucose towards polyols. It was assumed this was due to a too low concentration of hydrogen. To find out at what concentration of hydrogen reduction of glucose towards polyols takes place, an experiment with hydrogen pressure can be done. In this experiment, similar reaction conditions are used as throughout this thesis while adding hydrogen pressure up to the point where a significant amount of polyols are produced. This will give an idea of how much hydrogen you need to form in order to realise the glucose reduction.

Real biomass

In this thesis only microcrystalline cellulose has been used for the cellulose conversion. In order to give a realistic view of using this one-pot reaction in industrial application, experiments with real biomass have to be done. As non-edible lignocellulosic biomass consists of more than just cellulose (lignin and hemicellulose), some preparation steps may have to be taken in order to separate the cellulose from the other components in order to convert it towards valuable chemicals with an one-pot reaction.

Annex

Liner problem

During the first experiments liners were used. The liners were made from glass and did not fit quite well into the reactor. The main reason for using liners was to prevent the reactors from becoming dirty. However, it resulted in very dirty liners that proved to be impossible to clean completely and their reuse could influence the reactions results. Furthermore, because they did not fit well into the reactor some space was in between the reactor wall and the liner. This resulted in liquid getting in between the liner and the reactor wall, rendering the liner useless as the reactor still became dirty. This is shown in **Figure 18**.

Figure 18 : Reactor with liner, visualizing space between the reactor wall and the dirty liner.

To test whether the use of the liner affected the results the following experiment was set up. The same reaction (0.5M KOH, t=17 hrs, 50 mg Ni, T=220°C) was done *in triplo* with and without liner. The results of these experiments are shown below.

In **Figure 19** we can see that there is a significant difference when using a liner. The colour of the latter 3 vials (where a liner was used) is clearly darker than the first three.

Figure 19 : Final reaction mixture result of liner experiment, first three contained no liner, last three did.

In **Figure 20** we can see that about 10% less cellulose is converted when a liner is used. In **Figure 21** it becomes clear that the selectivity is also affected by using a liner. More lactic acid is produced compared to not using a liner. This may be caused by liquid sitting in between the liner and the reactor wall, this influences the reactant concentrations in the liner resulting in different ratios which positively influences lactic acid formation. However, the decision was made to continue without liners as this it required a lot less hand cleaning of the reactors and increases the consistency of the cellulose conversion.
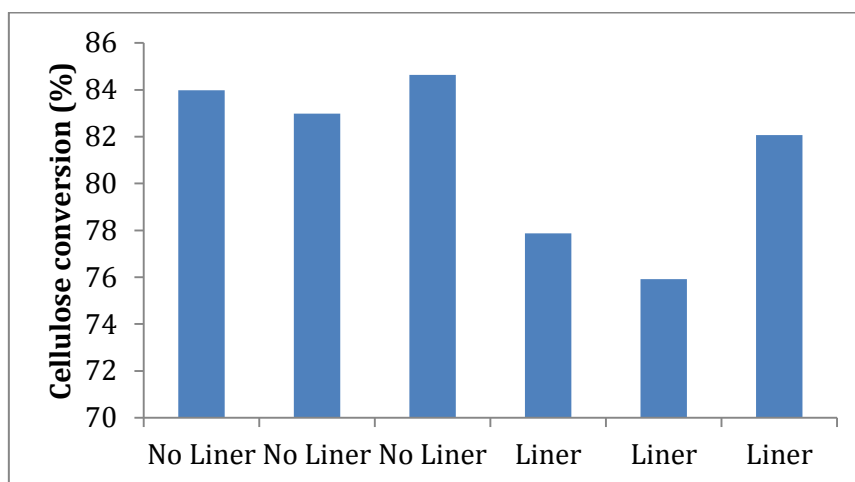

Figure 20 : Cellulose conversion from liner/no liner experiment.
Reaction conditions: 0.5M KOH, t=17 hrs, 50 mg Ni, T=220°C.

Figure 21 : Effect of using liner/no liner on the liquid phase product distribution.
Reaction conditions: 0.5M KOH, t=17 hrs, 50 mg Ni, T=220°C.

Cellulase experiment

During all the experiments the carbon balance was found to be incomplete (see example in 'Gas phase analysis and mass balance' section) . To try to account for the missing carbon, cellulase enzyme was added to the final reaction mixture of a typical (0.5M KOH, 220°C, 50 mg Ni) experiment. In this way, any dissolved glucose oligomers that were not completely hydrolysed by the reaction would be able to be hydrolysed by the enzyme. In this way, we would see an increase in the amount of glucose. The enzyme used for this experiment was Multifect GF Extra-PIS Cellulase. The experiment was conducted as follows: 25 mL of sample was taken and HCl was added to lower the pH of the sample to 5. An HPLC analysis was done to the sample before and after the acidification. After that 0.5 mL of cellulase was added and the reaction was incubated for 72 hours at 40°C. After 72 hours a new HPLC analysis was done to the sample. Below in the results of this experiment are shown.

Figure 22 : HPLC RI result cellulase reaction.
Reaction conditions: 0.5M KOH, 220°C, 50 mg Ni, 1.58 g cellulose.

It can be seen that after the cellulase experiment (green line) there is a huge peak around 12.5 minutes which is associated to sorbitol. This led us to think that maybe glucose oligomers were being reduced by the hydrogen produced during cellulose conversion. To check whether this was indeed the case the cellulase experiment was repeated on 6 other samples, including one that did not contain Raney Nickel. As Raney Nickel promotes the formation of hydrogen, the reaction mixture should not contain any reduced oligomers. However, they all contained sorbitol in the same amount. This means that the cellulase sample must be contaminated.

Lactic acid stability

During the experiments (**Figure 14**) lactic acid was found to decrease in concentration if the concentration of Raney Nickel was increased. This suggested that lactic acid was unstable. To prove this theory the following experiment was set up. Two reactors were filled with concentrations of lactic acid similar to the ones found in final reaction mixtures when 0.5M KOH, 1.58 g cellulose, 50 mg Raney Nickel was used, which was approximately 0.25 mg/mL and two different amounts of Raney Nickel catalyst were added (50 and 200 mg). The results are shown in table 2.

	50 mg Raney Ni		200 mg Raney Ni	
	Lactic acid (mg/mL)	Pressure (bar)	Lactic acid (mg/mL)	Pressure (bar)
Before reaction	0.28	0	0.22	0
After reaction	0.16	1.83	0	1.86

Table 2 : Results lactic acid experiment, 50/200 mg Raney Ni, 0.5M KOH, t=6 hrs, 0.25 mg/mL lactic acid.

From **table 2** it can be seen that lactic acid is indeed instable under our reaction conditions. When using 200 mg of Raney Ni the lactic acid is even completely gasified.

Figure 23 shows that when 50 mg of Raney Ni was used, not all lactic acid was converted to gas product. A lot of lactic acid was converted to an unknown compound and half of the lactic acid remained intact. It would have been interesting to do the same experiment with the base $Ca(OH)_2$ as this base is expected to stabilise the lactate that is formed during the cellulose conversion. If that is indeed the case, then almost no gas would be formed and the lactic acid would remain constant.

Figure 23 : HPLC UV Chromatogram 50 mg and 200 mg Raney Nickel.
Reaction conditions: 50/200 mg Ni, 0.5M KOH, t=6 hrs, 0.25 mg/mL lactic acid.

L or D-Lactic Acid

Lactic acid was the main liquid product produced during the catalytic conversion of cellulose. The final mixtures were expected to contain both D- and L-lactic acid. This means that the mixture has to be optically inactive as racemic mixtures nullify each other's optical activity. In order to prove this, a test with a polarimeter had to be done.

The optical activity measurement was done with a sodium lamp as light source in a Perkin Elmer 241 Polarimeter. The final reaction mixture that was measured came from a reaction conducted with 50 mg Raney Nickel, 0.5M KOH, 1.58 g cellulose at 220 °C. First demiwater was measured as a blank. Next, about a mL of sample was inserted. However, it turned out to be to concentrated as the energy that passed through was too low. The mixture was then diluted 10 times with demiwater. A demi water blank was measured again and the sample was inserted. Below the result of this measurement is shown.

Figure 24 shows that no optical activity was detected in the reaction mixture. This means that the products (most of which is lactic acid) are racemic and the reaction is not stereospecific. This was expected as stereospecific products are often only formed when enzymes are used to catalyse the reaction.

Figure 24 : Polarimeter measurement result

Calculations

Cellulose conversions

The cellulose conversions were calculated based on the amount of added cellulose in the reactor before the reaction minus the amount of cellulose that was left after the reaction. Besides the cellulose left on the filtrate after the reaction some other things were present as well, the nickel and the stirrer bar remained. After drying the filtrate to make sure that the weight of any left water could be ruled out, the filtrate was weighed together with the nickel and stirrer bar. The stirrer bar, nickel and filter paper were weighed beforehand. The cellulose recovery which includes compensation for the stirrer bar, nickel and filter paper was calculated as follows.

$Cellulose\ Recovery = Sample\ weight - Filter\ paper\ weight - Stirrer\ bar\ weight -$
$Nickel\ weight - Dry\ filter\ weight^*$

Dry filter weight* : This factor was included because after drying the filter paper it was a bit lighter than it would before the filtration.

After establishing the cellulose recovery the amount of converted cellulose can be calculated. This was done by subtracting the cellulose recovery from the amount of cellulose that was added before of the reaction.

$$Converted\ Cellulose = Cellulose\ weight - Cellulose\ recovery$$

After calculating the converted cellulose, the cellulose conversion could be calculated. This was done by dividing the cellulose recovery by the cellulose weight (which was added before the reaction).

$$Cellulose\ conversion = \frac{Converted\ Cellulose}{Cellulose\ weight} * 100$$

Below an example with numbers is given. In **Figure 13** this number is used for the cellulose conversion of 0 mg of Raney Nickel.

$$Cellulose\ Recovery = 2237.0\ mg - 196.7\ mg - 1832.2\ mg - 0\ mg - 11.8\ mg = 196.3\ mg$$

Then fill into converted cellulose formula.

$$Converted\ Cellulose = 1580.3\ mg - 196.3 = 1384\ mg$$

Then fill into cellulose conversion formula

$$Cellulose\ conversion = \frac{1384\ mg}{1580.3\ mg} * 100\% = 87.59\ \%$$

Yields

The yields were calculated based on the UV HPLC results. The yield was defined as gram product / gram cellulose. The HPLC gave results in mg/mL. The amount of product was calculated by multiplying the HPLC results by the amount of sample mL and accounting for the 10 times dilution that was used to make the HPLC sample. The calculation was done as follows

$$g\ Product\ formed = \frac{x\frac{mg}{mL} * 10(HPLC\ dilution) * 100(100\ mL\ sample\ flask)}{1000(mg\ to\ g)} =$$

After calculating the amount of product in grams the amount is divided by the amount of cellulose that was used in the reaction (which was always 1.58 grams).

$$Yield = \frac{x\ g\ (product)}{1.58\ g\ (cellulose)}$$

Below an example with numbers is given. The lactic acid production of the sample that contains 50 mg Raney is used here (**Figure 14**).

$$\frac{0.2837\frac{mg}{mL} * 10(HPLC\ dilution) * 100(100\ mL\ sample\ flask)}{1000(mg\ to\ g)} = 0.2837\ g$$

Then fill number into the yield formula.

$$Yield = \frac{0.2387\ g\ (product)}{1.58\ g\ (cellulose)} = 0.15\ g/g$$

Gas formation rate

The gas formation rate was calculated with the ideal gas law. First the amount of mL gas formed was calculated. This was done by comparing the initial pressure and temperature (always 1 bar and 21 °C) with the final pressure by using the ideal gas law. In this way the gas formation was obtained in mL/h.

By rewriting the ideal gas law we get.

$$\frac{P_1 * V_1}{T_1} = \frac{P_2 * V_2}{T_2}$$

Then, by dividing the gas formed by the amount of time it took to form, the gas formation rate is obtained in mL/h

$$Gas\ formation\ rate = \frac{mL}{hour} = \frac{mL\ of\ gas\ after\ the\ reaction\ has\ cooled\ down}{Reaction\ time}$$

Below an example with numbers is given. The example used can be found back in **Figure 13** where 100 mg of Raney Nickel was used. Initial pressure and temperature and final pressure are inserted into the ideal gas law.

$$Gas\ formed\ (V_2) = \frac{1*62.6}{21} = \frac{3.39*V_2}{21} = 212.6\ mL$$

After that the gas formation rate is calculated with the reaction time.

$$Gas\ formation\ rate = \frac{212.6}{5.5} = 38.7\ mL/h$$

Gas phase composition

The composition of the gas phase was determined with the GC results. From these GC results a certain volume percentage was obtained for each of different gas components that were present. The gas volume that was present after the reaction had cooled down was used. This was then multiplied by the volume percentage to obtain the amount of gas in mL.

$$gas\ produced = volume\ percentage * total\ gas\ volume\ after\ cooldown$$

The example calculation given below refers to one of the *in triplo* results described in **Figure 11**.

$$Hydrogen\ produced = 0.01 * 33.2\% * 249.1\ mL = 82.7\ mL\ hydrogen$$

Mass distribution

The mass distribution was determined by using the UV HPLC values (mg/mL) of known compounds together with the volume of the samples (100mL). This gives the mass of the liquid products. These were added up and then divided by the amount of cellulose that had been converted during the reaction. This gives that percentage of known mass. To determine the mass percentage of an individual component, the mass of that component was divided by the amount of cellulose that had been converted during the reaction.

Calculation for known mass

$$Percentage\ known\ mass$$
$$= \frac{\frac{mg}{mL}\ Lactic\ acid * 100 + \frac{mg}{mL}\ Acetic\ acid * 100 + \frac{mg}{mL}\ Formic\ acid * 100}{Amount\ of\ converted\ cellulose\ (mg)} * 100$$

Calculation for single component

$$Mass\ percentage\ indivudual\ compound = \frac{\frac{mg}{mL}\ Compound * 100}{Amount\ of\ converted\ cellulose} * 100$$

Below an example calculation is given. This calculation was used in the *in triplo* mass distribution shown in **Figure 11**.

$$Percentage\ known\ mass = \frac{0.3001 * 100 + 0.0319 * 100 + 0.0137 * 100}{1353.81} * 100 = 26\%$$

And for a single compound, e.g. lactic acid.

$$Mass\ percentage\ indivudual\ compound = \frac{0.3001 * 100}{1353.81} * 100 = 22\%$$

Sample list of all reactions

R_i=reaction number, LA=lactic acid (mg/mL), FA=Formic acid (mg/mL), AA=acetic acid (mg/mL), CC=Cellulose conversion %, Gas=Gas produced in bar

R1, reaction conditions: Liner, 0.5M KOH, 1.58g Cellulose, T=Variable, 150mg Ni, t=15h

R1	LA	FA	AA	CC	Gas	Note
A	0.16	0.22	-	95.37	1.72	Blank 240 °C
B	0	0.02	-	17.32	0.65	150 °C
C	0.03	0.01	-	60.65	6.54	180 °C
D	0.13	0.03	-	87.72	4.85	200 °C
E	0.11	0.03	-	74.97	4.33	220 °C
F	0.05	0.01	-	68.47	1.77	150 °C

R2, reaction conditions: Liner, 0.5M KOH, 1.58g Cellulose, T=220°C, Ni=Variable, t=15h

R2	LA	FA	AA	CC	Gas	Note
A	0.010	0.010	0.017	67.00	2.95	0mg Ni + No base
B	0.367	0.267	0.029	85.62	8.27	0mg Ni
C	0.242	0.069	0.029	91.40	9.94	50mg Ni
D	0.098	0.021	0.024	81.49	9.86	150mg Ni
E	0.081	0.023	0.023	89.04	9.12	300mg Ni
F	0.022	0.000	0.000	107.24	4.48	150mg Ni +0.05M KOH

R3, reaction conditions: Liner, 0.5M KOH, 1.58g Cellulose, T=220°C, Ni=150, t= Variable

R3	LA	FA	AA	CC	Gas	Note
A	0.209	0.035	0.012	73.21	9.94	t=1h
B	0.147	0.023	0.015	77.63	9.99	t=4h
C	0.170	0.028	0.018	82.33	9.60	t=7h
D	0.190	0.021	0.019	87.03	9.99	t=10h
E	0.189	0.023	0.022	93.03	9.87	t=13h
F	0.247	0.014	0.014	84.62	10.07	t=16h

R4, reaction conditions: Liner, KOH= Variable, 1.58g Cellulose, T=220°C, Ni=150, t=15h

R4	LA	FA	AA	CC	Gas	Note
A	0.018	0.002	0.020	97.46	2.87	0.01M KOH
B	0.037	0.003	0.024	100.8	4.55	0.1M KOH
C	0.074	0.005	0.019	83.21	3.06	0.25M KOH
D	0.150	0.210	0.054	95.81	4.78	0.5M KOH + No Ni
E	0.146	0.029	0.023	89.26	4.94	1M KOH
F	0.154	0.024	0.031	53.85	4.91	2.5M KOH

R5, reaction conditions: Liner, Base = Variable 0.5M, 1.58g Cellulose, T=220°C, Ni=150, t=15h

R5	LA	FA	AA	CC	Gas	Note
A	0.177	0.020	0	67.10	0.51	NH_4OH
B	0.177	0.020	0.034	81.55	4.78	NaOH
C	0.364	0.061	0.019	18.08	0.47	$Ca(OH)_2$
D	0.268	0.048	0.039	51.51	4.81	Na_2CO_3
E	0.120	0.056	0.038	75.90	5.14	K_2CO_3
F	0.028	0.043	0.041	96.91	4.71	No base

R6, reaction conditions: Liner + no liner, Base=0.5M KOH, 1.58g Cellulose, T=220°C, Ni=0mg, t=17h

R6	LA	FA	AA	CC	Gas	Note
A	0.179	0.028	0.028	83.98	2.31	No liner
B	0.228	0.064	0.043	82.98	1.91	No liner
C	0.191	0.061	0.038	84.64	2.48	No liner
D	0.308	0.068	0.040	77.87	2.9	Liner
E	0.310	0.070	0.031	75.92	2.31	Liner
F	0.348	0.110	0.049	82.07	1.39	Liner

R7, reaction conditions: Base=0.5M KOH, 1.58g Cellulose, T=Variable, Ni=50mg, t=7.25h

R7	LA	FA	AA	CC	Gas	Note
A	0.088	0.148	0.000	56.18	0	120 °C
B	0125	0.150	0.018	55.50	0.24	140 °C
C	0.140	0.112	0.031	57.79	0.54	160 °C
D	0.161	0.019	0.015	64.96	1.16	180 °C
E	0.173	0.020	0.014	69.11	0.86	200 °C
F	0.216	0.009	0.015	91.14	2.75	220 °C

R8, reaction conditions: Base=Variable, 1.58g Cellulose, T=220 °C, Ni=150mg, t=6h

R8	LA	FA	AA	CC	Gas	Note
A	0.024	0.000	0.021	54.55	1.57	NH_4OH
B	0.199	0.018	0.035	79.63	4.72	NaOH
C	0.273	0.069	0.047	26.91	0.26	$Ca(OH)_2$
D	0.126	0.015	0.028	80.74	3.93	Na_2CO_3
E	0.126	0.011	0.025	82.28	3.63	K_2CO_3
F	0.172	0.005	0.020	81.56	4.13	KOH

R9, reaction conditions: Base=0.5M KOH, 1.58g Cellulose, T=220 °C, Ni=Variable, t=5.5h

R9	LA	FA	AA	CC	Gas	Note
A	0.239	0.000	0.050	84.32	1.57	50mg Ni
B	0.183	0.018	0.052	83.37	4.72	100mg Ni
C	0.168	0.069	0.040	81.74	0.26	150mg Ni
D	0.154	0.015	0.037	84.25	3.93	200mg Ni
E	0.105	0.011	0.027	85.68	3.63	50mg Ni+1.0M KOH
F	0.279	0.005	0.058	97.72	4.13	50mg Ni+0.1M KOH

R10, reaction conditions: Base=0.5M KOH, 1.58g Cellulose, T=220 °C, Ni=50mg, t=Variable

R10	LA	FA	AA	CC	Gas	Note
A	0.117	0.133	0.038	68.18	0.32	0min
B	0.194	0.126	0.038	69.47	0.67	5min
C	0.152	0.132	0.039	69.46	0.65	10min
D	0.175	0.108	0.028	69.24	0.82	15min
E	0.178	0.089	0.051	71.81	1.07	30min
F	0.177	0.064	0.039	79.48	1.33	60min

R11, reaction conditions: Base=Variable, 1.58g Cellulose, T=220 °C, Ni=50mg, t=18h

R11	LA	FA	AA	CC	Gas	Note
A	0.141	-	-	32.88	5.66	0.5M CaCO$_3$
B	0.240	-	-	97.42	-	2.5M KOH
C	0.290	-	-	106.93	2.65	1M K$_2$CO$_3$
D	0.346	-	-	105.48	5.56	2.5M NaOH

R12, reaction conditions: Base=Variable, 1.58g Cellulose, T=220 °C, Ni=50mg, t=6h

R12	LA	FA	AA	CC	Gas	Note
A	0.326	0.000	0.045	83.29	2.86	0.5M KOH
B	0.230	0.033	0.033	97.17	2.6	0.05M Ca(OH)$_2$
C	0.239	0.000	0.128	64.84	1.09	0.1M Ca(OH)$_2$
D	0.351	0.067	0.024	57.95	0.3	0.25M Ca(OH)$_2$
E	0.308	0.048	0.031	37.57	0.49	0.5M Ca(OH)$_2$
F	0.381	0.051	0.029	39.71	0.76	1.0M Ca(OH)$_2$

R13, reaction conditions: Base=Variable, 1.58g Cellulose, T=220 °C, Ni=50mg, t=6h

R13	LA	FA	AA	CC	Gas	Note
A	0.094	0.133	0.110	76.27	0.65	No base + No Ni
B	0.282	0.228	0.000	90.03	0.2	0.5M KOH + No Ni
C	0.146	0.015	0.051	83.59	2.45	0.1M KOH
D	0.259	0.021	0.052	74.92	1.74	0.25M KOH
E	0.320	0.032	0.041	101.05	3.41	1.0M KOH
F	0.342	0.014	0.119	96.73	4.46	1.5M KOH

R14, reaction conditions: Base=0.5M, 1.58g Cellulose, T=220 °C, Ni=50mg, t=Variable

R13	LA	FA	AA	CC	Gas	Note
A	0.300	0.014	0.032	85.68	3.98	t=6h
B	0.291	0.025	0.028	85.14	3.93	t=6h
C	0.350	0.047	0.034	84.04	4.64	t=6h
D	0.305	0.130	0.032	70.16	1.93	t=0h
E	0.244	0.102	0.030	69.91	1.91	t=0h
F	0.262	0.112	0.035	70.16	1.92	t=0h

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