Universidade do Porto
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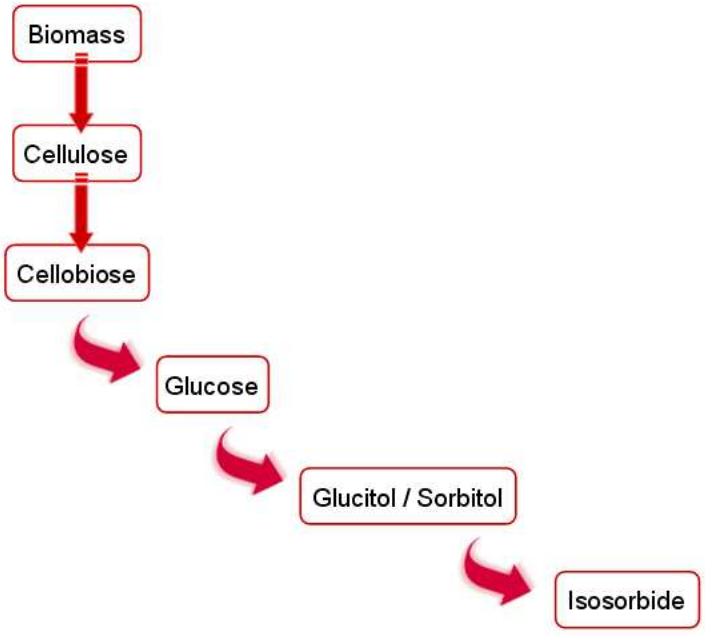
Catalysis Engineering

Biomass conversion:

Cellobiose and Methylcellobiose conversion

Master Thesis



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Abstract

The objective of this project was studied the conversion of biomass, organic materials with a particular interest for fuel and chemicals. Cellobiose conversion has been studied. This is a simple model component for Cellulose. With this molecule it is expecting an easier conversion than Cellulose, i.e., faster and with high yields rates, besides the analysis of products should be more simple.

Cellobiose can be converted in different steps. The first product could be Glucose and can be obtained for hydrolysis. Then, Glucitol is expected. It is a sugar alcohol with an open chain. In order to open the Glucose ring, the second step should be hydrogenation. Isosorbide could be the main component in fuel as used as an addictive in chemical. The third step should be Glucitol dehydration. However, all of these reactions are very complex and it was only possible to compare hydrolysis and hydrogenation of Cellobiose and Methylcellobiose.

During the hydrolysis different temperature conditions, different reaction times and also different hydrate molten salts as a solvent at constant pressure (30 bar) were tested, in order to improve the rate of Glucose and the selectivity to Glucose (main component from Cellobiose hydrolysis). After some reactions, was concluded that $ZnCl_2.4H_2O$ is the best hydrolysis solvent at 80ºC during more than two hours. In those conditions was possible to avoid secondary steps, some other sugars were not formed. Acidic conditions increased the rate but separation issues are created.

Hydrogenation reactions have formed two different kinds of products. On one hand, in $ZnCl_2.4H_2O$ some Glucitol (or Sorbitol) were formed but also a great number of Glucose molecules were in the system. On the other hand, in H_2O, Glucose-Sorbitol were formed. Once hydrogenation required a catalyst, Ruthenium supported on Carbon (Ru/C) was chosen. This is the most active catalyst in carbohydrate hydrogenations, not only in homogeneous but also in heterogeneous catalysis. Different rates of Sorbitol and Glucose-Sorbitol could be obtained between 0 and 100%, it only depends on hydrogenation conditions: amount of catalyst, reaction time and temperature.

A slightly more complex model component of Cellulose, Methylcellobiose has also been studied. Methylcellobiose derived from a condensation of two molecule of Glucose, one of them with a methyl ($-CH_3$) group that represents a long chain of Glucose molecules in the Cellulose chain. This component was studied because it could have similar reactions than Cellobiose. However, we have concluded that Methylcellobiose is a less reactive and more stable component than Cellobiose.

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1 Introduction

Fuels and platform chemicals are materials of great importance nowadays. The production of these materials from biomass is of an increasing interest. Attention has been focused on identifying suitable biomass species that cannot only provide high-energy fuels to replace conventional fossil fuel energy sources [1], [2], [3]. The goal of this project is to convert biomass to fuel/chemicals feedstock for industry. In order to answer this goal, the reaction networks for biomass conversion will be studied and their related kinetics measured.

Biomass is a very complex organic material that is composed of polymers that have extensive chains of carbon atoms linked into macro network of molecules. It consists of Cellulose, Hemi-cellulose, and Lignin. In order to gain insight on the potential of biomass, Cellulose might be selected. Cellulose consists of numerous molecules of D-glucose that condense through β-(1-4)-glycosidic bonds. The hydrolysis product of Cellulose is Glucose [1], [2], [3], [4].

For chemical conversion Cellulose is still very complex. More simple model components representing Cellulose, are Cellobiose (1-4 dimer of glucose) and Methylcellobiose [5]. The methyl group of the Methylcellobiose presents the polymeric behavior of the Cellulose. Therefore, Cellobiose and Methylcellobiose, both Cellulose derivatives, were used as biomass representatives.

1.1 Biomass

Biomass is all biologically produced matter. It is an organic material that is composed of polymers with long chains of glucose molecules (glucose is the main building block in nature and is called a carbohydrate), linked into macro-molecules. In the world, the production of biomass is around 146 billion metric tons per year. This material has major advantage over fossil derived mass as a feedstock for industry because it is a renewable resource [1], [2], [3], [4].

Biomass can have two different features. Firstly, as energy resource, biomass is the biological material that comes from a living organism and can be used as fuel or in industrial production of chemicals. Secondly, it can have an ecological feature. In this way, biomass is the total source of living matter in an ecosystem, a plant or an animal. For industrial production the biomass derives from different types of plants and trees, so it can be

considered a natural resource to fuel production. However, the particular plant used is of great importance in the end products [2].

Biomass conversion can be conducted on two different ways: biological digestion or chemical conversion [1].

The main process in biological digestion is fermentation. However, this process is expensive. It uses a great amount of water and for the separation of product from the fermentation solution an enormous amounts of energies are required. On the other hand, it is costly in terms of cultivated land use [1], [6].

Pyrolysis and hydrolysis are the chemical processes to convert biomass in useful material to produce fuel and chemicals. Pyrolysis is a thermo-chemical technique. It produces energy fuels with very low efficiency. However, it is a very endothermic process that uses a lot of energy for this pyrolysis conversion in the absence of oxygen or in reduced air. Another disadvantage of this process is the formation of unstable products. An alternative for pyrolysis is a hydrolysis process. This hydrolysis is cheaper since it needs less energy and water and does not form unstable products [1].

Plant biomass has three main components: Hemi-cellulose, Lignin and Cellulose. These components contribute to the mechanical strength to the cell wall [1-3], [7-9]. In this work we are interested in studying Cellulose since it has a particular interest for fuels and chemicals. It is a biological resource that does not use large amounts of energy and water, and has its origins in nature.

1.2 Cellulose, Cellobiose, and Methylcellobiose

Cellulose is the most abundant polymer on earth and it can be obtained from wood, jute, and cotton. The main resource for Cellulose production is pulpwood [10].

Cellulose exists in two different forms: crystalline or amorphous, the amorphous form is easier to reduce [10].

Cellulose is a polysaccharide consisting of long linear chains with the formula $[HOCH_2CHO(CHOH)_3]_nO_{n-1}$ (figure 1). The repetitive unit is Glucose and/or Cellobiose so it could be considered as the building block and could be used as a model component [5].

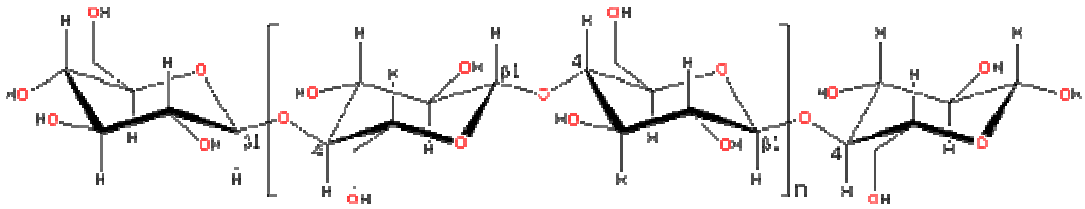

Figure 1 – Molecular structure of Cellulose.

In this work we used Cellobiose as a model component because it is expected that the conversion will be easier than for Cellulose, while the chemical pathway will probably be very similar. Moreover, analysis might be much easier. Cellobiose is a disaccharide with the formula $[HOCH_2CHO(CHOH)_3]_2O$ (figure 2) which cannot be digested by humans neither fermented by yeast. It can be formed by the condensation of two molecules of Glucose or by partial hydrolysis of Cellulose [5].

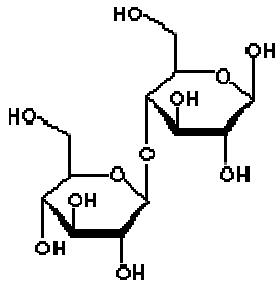

Figure 2 – Molecular structure of Cellobiose.

Cellobiose can be converted in three different kinds of technologies. It can be converted by fermentation, pyrolysis or hydrolysis like Cellulose. In this work we only will study the hydrolysis. This kind of reaction uses less amount of water and spends less energy than fermentation and does not form unstable products like in pyrolysis [1], [11].

Another raw material is Methylcellobiose (figure 3). This is a slightly more complex model component of Cellulose. Like Cellobiose, it is a polymer and also a disaccharide. However, this component can be obtained by condensation of two molecules of Glucose, one of them with a methyl group that represents a long chain of Glucose molecules in the Cellulose chain. So, Methylcellobiose is also used as model for the conversion of Cellulose.

Glucose can be formed in two different ways: on one hand, the C-O bond between the two rings breaks and it can form two molecules of Glucose: one is a normal molecule of Glucose and another molecule with a methyl group. On the other hand, the bond between O-CH_3 can be cleaved and can form two molecules of Glucose and Methanol.

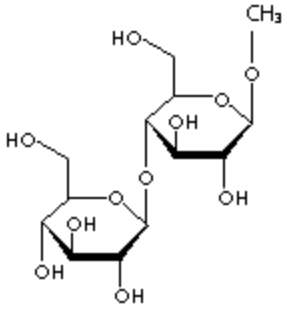

Figure 3 – Molecular structure of Methylglucose.

1.3 Cellobiose and Methylcellobiose reactions

The production of fuels or chemicals from Cellobiose and Methylcellobiose involves different steps. The first one is hydrolysis (figures 4 and 5).

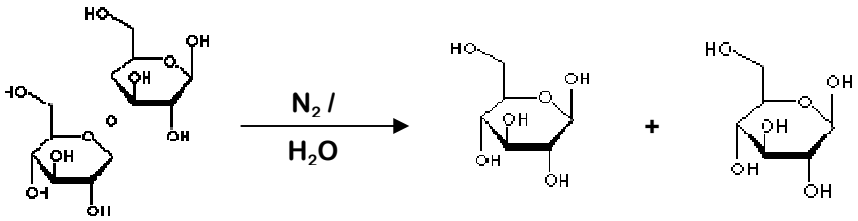

Figure 4 – Cellobiose hydrolysis.

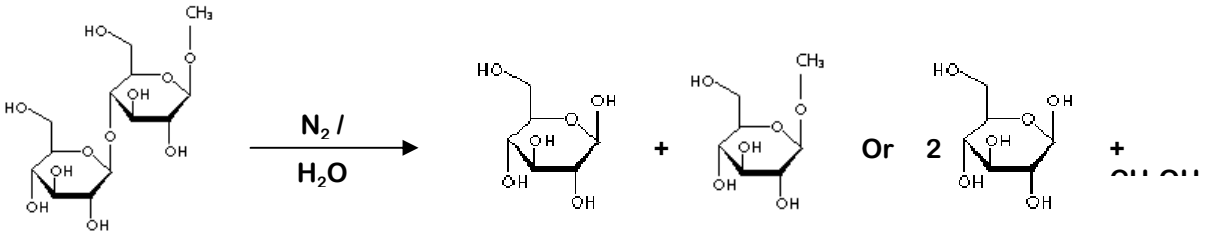

Figure 5 – Methylcellobiose hydrolysis.

Looking at the figures above, we can conclude that in Cellobiose hydrolysis (figure 4) per each molecule of Cellobiose, two molecules of Glucose can be formed (the C-O bond between the two rings breaks). However, in Methylcellobiose hydrolysis is different. Per each molecule of Methylcellobiose two different reactions can occur: if the C-O between two rings breaks it can form one molecule of Glucose and one molecule of Glucose with a methyl group; if the O-CH_3 bond then it can form two molecules of Glucose and one molecule of Methanol, as is shown in figure 5.

We can also obtain Glucose in Cellobiose or Methylcellobiose hydrogenation. In that kind of reaction, other types of products are anticipated. We can obtain typical hydrogenation products, i.e., reduce or saturate organic compounds with addition of pairs of hydrogen atoms to a molecule, or hydrolysis products. In figures 6 and 7 are shown hydrogenation reactions of both compounds.

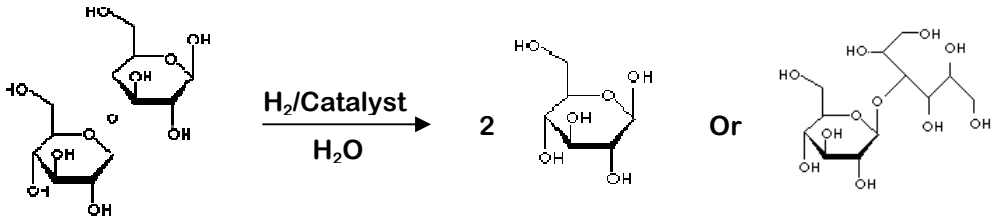

Figure 6 – Cellobiose hydrogenation.

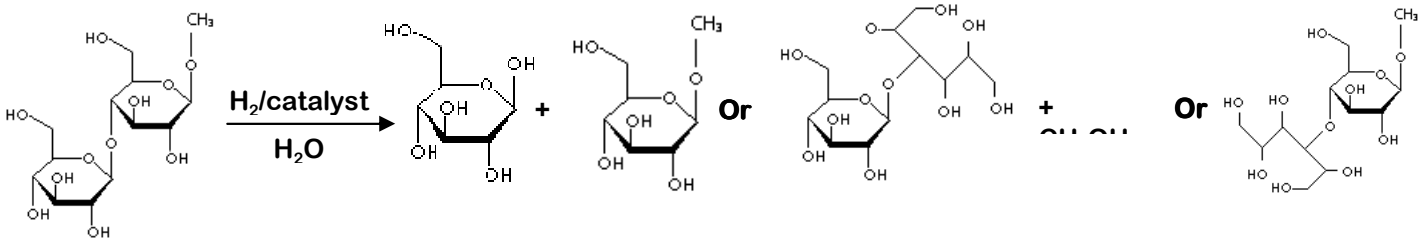

Figure 7 – Methylcellobiose hydrogenation.

At temperatures below 480ºC all the hydrogenations between organic compounds and H_2 need a metal catalyst from group VIII of the Periodic Table [12].

In Cellobiose hydrogenation (figure 6) we can obtain two different products. First two molecules of Glucose can be formed if the C-O bond between two rings breaks, although this is a more difficult reaction. Secondly, if the C-O bond in one of the rings breaks we can obtain Sorbitol connecting with the Glucose ring by the C-O bond, like a complex Glucose-Sorbitol (main component).

The same can happens in Methylcellobiose hydrogenation (figure 7). If the C-O bond between two rings breaks we can obtain typical hydrolysis products (one molecule of Glucose and one molecule of Glucose with a methyl group); on the other hand, if the C-O bond in one of the rings breaks we can obtain two kinds of complexes: Glucose-Sorbitol and Methanol or Methylglucose-Sorbitol (hydrogenation products).

Glucose is a monosaccharide that contains six carbon atoms ($C_6H_{12}O_6$) and can exist in two forms: an open-chain (acyclic) and like a ring (cyclic) [13]. Methylglucose is a

Glucose molecule that has substituted one of the -OH group in an O-CH_3 group. This molecule can exist only in cyclic and acyclic form.

The next step is Glucose hydrogenation (figure 8). It means that per each molecule of Glucose we can obtain one molecule of Glucitol.

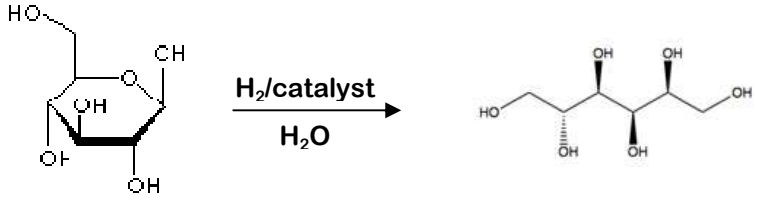

Figure 8 – Glucose hydrogenation.

Like in Cellobiose and Methylcellobiose hydrogenation, this reaction also needs a metal catalyst [12].

Glucitol is a sugar alcohol. It can be formed during Glucose hydrogenation when the molecule of Glucose is reduced, which happens when the aldehyde group in glucose is changed to an additional hydroxyl group [14].

The last step in biomass conversion for fuels or chemical platforms is Glucitol dehydration (figure 9). A double dehydration of Glucitol gives Isosorbide, a heterocyclic compound [15].

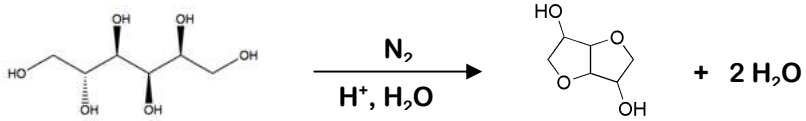

Figure 9 – Glucitol dehydration.

As is said before, the goal of this project is to convert biomass to fuel/chemicals feedstock for industry. Reaction networks for biomass conversion and their related kinetics measured will be studied.

2 Experiments

2.1 Mini auto-claves setup

In this work our goal was to study Cellobiose and Methylcellobiose conversion. For these reactions we have used the mini-autoclaves that are shown in figure 10.

The mini-autoclaves setup has six stirrer reactors (figure 11) of stainless steel with magnetically stirrers. To study different conditions in these reactors we also used a heated block. In each mini-autoclave we can also have different environment with nitrogen or hydrogen, at different pressures.

The conditions of our reactions were: 0,5g of Cellobiose or Methylcellobiose, 6,0g of solvent (molten salts hydrates or water) and 30 bar for hydrolysis or 40 bar for hydrogenation. Once in hydrogenation reactions we also needed a catalyst, we had used Ru/C at different amounts.

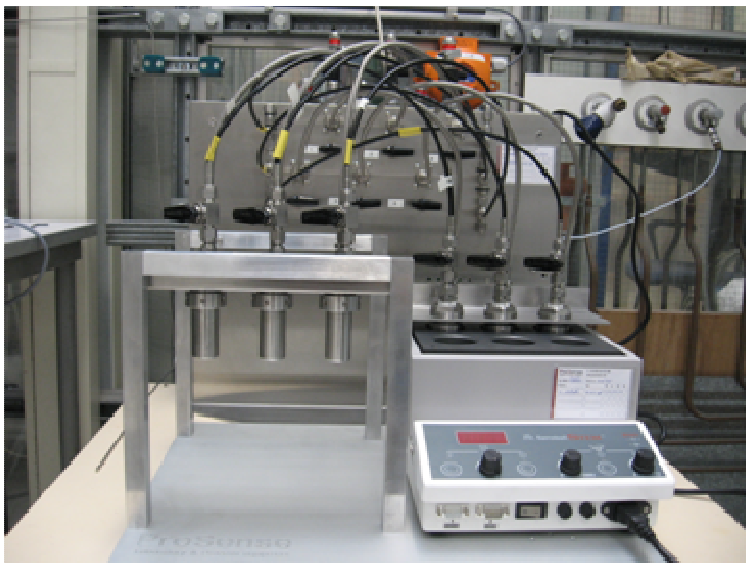

Figure 10 – Mini multi-autoclaves setup.

Figure 11 – Mini-autoclave (reactor) of stainless steel.

2.2 High Performance Liquid Chromatography (HPLC) setup

In order to analyze our results we used a High Performance Liquid Chromatography (HPLC) – figure 12. Modern HPLC has different applications. It can be used to separate, identify, purify and quantify various compounds.

Figure 12 – High Performance Liquid Chromatography (HPLC) setup.

This chromatograph works with a refractive index detector (RI).It is very sensitive to changes in ambient temperature, pressure and flow-rates. So, we need to be very carefully with those conditions.

The HPLC conditions are: 0,600 mL/min of flow-rate, at 85ºC and with Calcium Nitrate Tetrahydrate ($Ca(NO_3)_2.4H_2O$) as mobile phase (≈ 6g/L of $Ca(NO_3)_2$ in water).

3 Results

3.1 Hydrolysis solvents

Hydrolysis reactions need water solvents. They should follow some requirements: they should be a liquid at STP (Standard Temperature and Pressure) and do not need reactions with pre-treatment or activation of Cellobiose and/or Methylcellobiose. With this proposal we have chosen molten salts hydrates [16]. They can also be applied as reaction medium for derivatization of Cellulose [17].

Table 1 – Results in the test to select the hydrolysis solvents: which one form a single phase based in a visual inspection.

x	$ZnCl_2.xH_2O$	$LiCl.xH_2O$	$CaCl_2.xH_2O$
1	heterogeneous	heterogeneous	heterogeneous
1,5			
2	**homogeneous**		
4		**homogeneous**	

As it is shown in table 1 the molten salts that were studied are: Zinc Chloride, Lithium Chloride and Calcium Chloride. Based on a visual inspection we can found which one can form a single phase (homogeneous solution) with different amounts of water.

Zinc Chloride only forms a homogeneous mixture with two or four molecules of water ($ZnCl_2.2H_2O$ or $ZnCl_2.4H_2O$) – figure 13. On the other hand, for Lithium Chloride this is only possible with four molecules of water ($LiCl.4H_2O$) – figure 14. However, for Calcium Chloride is not possible to have a homogeneous mixture with low amount of water. This is only possible with twenty molecules of water per molecule of Calcium Chloride – figure 15.

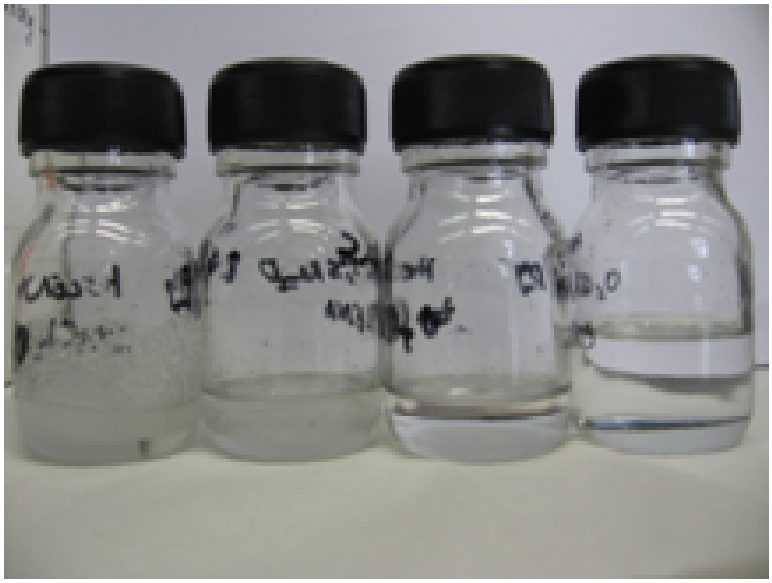

Figure 13 – Bottles with different concentrations of zinc chloride ($ZnCl_2$): $ZnCl_2$.,$1H_2O$ (10g), $ZnCl_2$.$1,5H_2O$ (10g), $ZnCl_2$.$2H_2O$ (10g) and $ZnCl_2$.$4H_2O$ (100g).

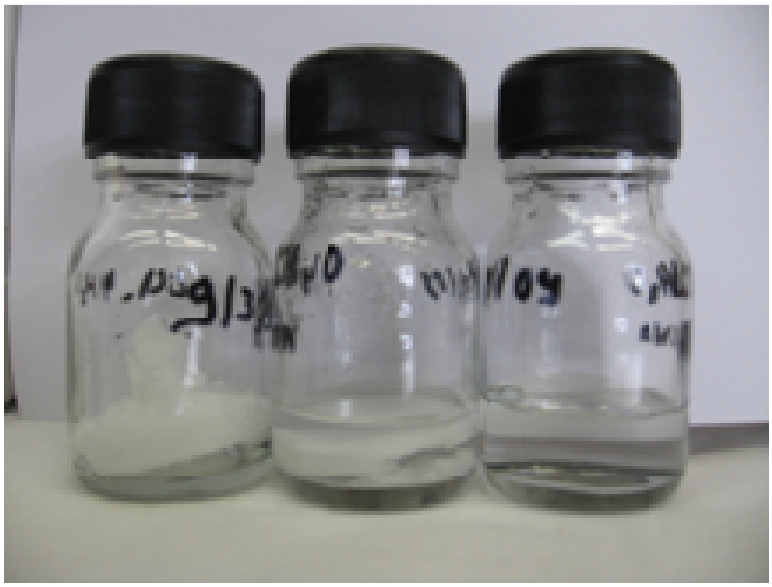

Figure 14 - Bottles with different concentrations of lithium chloride (LiCl): LiCl.$1H_2O$ (10g), LiCl.$2H_2O$ (10g) and LiCl.$4H_2O$ (10g).

Figure 15 - Bottles with different concentrations of calcium chloride ($CaCl_2$) : $CaCl_2.1H_2O$ (10g), $CaCl_2.4H_2O$ (10g) and $CaCl_2.20H_2O$ (10g).

3.2 Hydrolysis reactions

Different conditions (temperature and reaction times) and different molten salts hydrates at 30 bar was used in hydrolysis reactions. The end solutions were analyzed in the HPLC and with those pictures was possible to calculate not only the yields of Glucose, Methylglucose, Fructose and other isomers, but also the selectivity to Glucose and/or Methylglucose.

$$Yield\ of\ sugar\,(\%) = \left[\frac{PA_{sugar}}{\left(\frac{PA_{ZnCl_2}}{PA_{ZnCl\,2-blank}} \right)} \times PA_{glu\cos e-blank} \right] \times 100 \qquad (1)$$

$$Selectivity\ to\ sugar\,(\%) = \frac{Yield\ of\ sugar}{\sum Yield\ of\ products} \times 100 \qquad (2)$$

With:

PA_{sugar} – Peak area of Glucose, Methylglucose, Fructose and other isomers in the end solution

PA_{ZnCl2} – Peak area of Zinc Chloride hydrate in the end solution

$PA_{ZnCl2\text{-}blank}$ – Peak area of Zinc Chloride hydrate in the blank solution (Glucose dissolved in Zinc Chloride hydrate)

$PA_{glucose\text{-}blank}$ – Peak area of Glucose in the blank solution (Glucose dissolved in Zinc Chloride hydrate)

3.2.1 Cellobiose hydrolysis

Different temperatures and reaction times made different colors in the final solutions. Figures 16, 17 and 18 present the final solutions of Cellobiose hydrolysis in $ZnCl_2.4H_2O$ at 80, 100 and 130ºC and different reaction times.

Figure 16 - Final solutions from Cellobiose hydrolysis in $ZnCl_2.4H_2O$ at 80ºC after 30, 90, 120, and 240 minutes of reaction.

Figure 17 – Final solutions from Cellobiose hydrolysis in $ZnCl_2.4H_2O$ at 100ºC after 30, 60, and 120 minutes.

Figure 18 - Final solutions from Cellobiose hydrolysis in $ZnCl_2.4H_2O$ at 130ºC after 10, 30, and 60 minutes.

The main product in Cellobiose hydrolysis is Glucose. The yield of Glucose and the other by-products (fructose and other isomers) are presented in table 2 as well as the selectivity to Glucose.

Table 2 – Results from Cellobiose hydrolysis in $ZnCl_2.4H_2O$: Cellobiose conversion, yields of Glucose, Fructose and other isomers, and selectivity of Glucose.

Cellobiose hydrolysis in $ZnCl_2.4H_2O$					
80ºC and 30 bar N_2 *0,5g Cellobiose + 6,0g $ZnCl_2.4H_2O$*					
Reaction time (min)	Cellobiose conversion (%)	Yield of Glucose (%)	Yield of Fructose (%)	Yield of isomers (%)	Selectivity to Glucose (%)
0	-	0	0	0	-
30	4	3,6	0	0	100
90	7	6,6	0	0	100
120	9	8,5	0	0	100
240	9	9,2	0	0	100
100ºC and 30 bar N_2 *0,5g Cellobiose + 6,0g $ZnCl_2.4H_2O$*					
0	-	0	0	0	-
30	5	4,2	0,2	0,3	90
60	21	20,0	0,7	0,6	94
120	25	22,5	1,1	1,6	89
130ºC and 30 bar N_2 *0,5g Cellobiose + 6,0g $ZnCl_2.4H_2O$*					
0	-	0	0	0	-
10	43	36,9	1,8	4,3	86
30	34	25,2	1,3	7,3	75
60	21	11,5	3,5	5,8	55

At 80 and 100ºC the Glucose yield increases with the time until 120 minutes. At this time is possible to find a plateau at low Glucose rates. On the other hand, for high temperatures (130ºC), the rate of Glucose is decreasing with the time (figure 19).

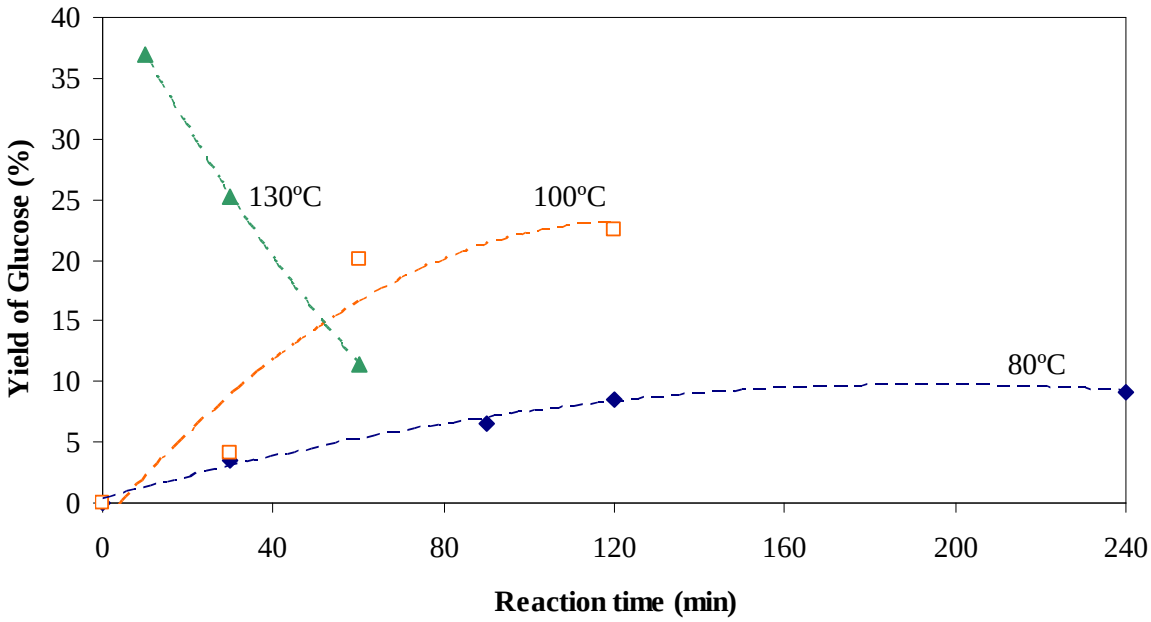

Figure 19 – Cellobiose hydrolysis in $ZnCl_2.4H_2O$: yield of Glucose.

For high concentrations of Zinc Chloride the number of by-products, mostly isomers, increased. This means that the final solution is darker and more viscous (figure 20 and 21).

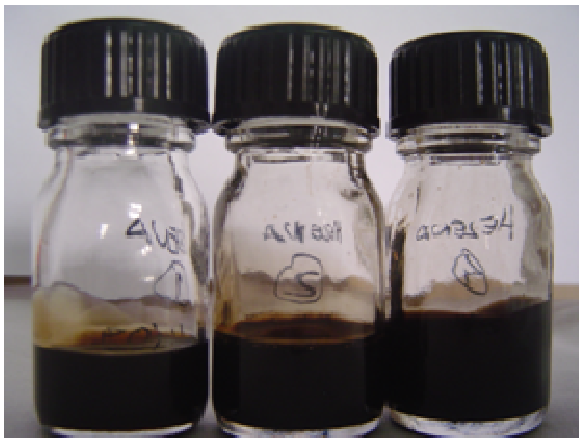

Figure 20 - Final solution from Cellobiose hydrolysis in $ZnCl_2.2H_2O$ at 100ºC after 30, 60, and 120 minutes.

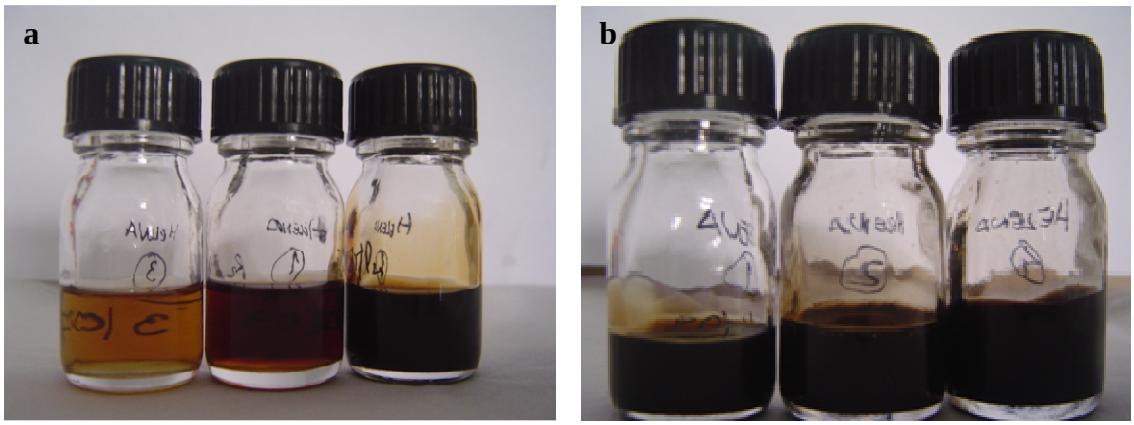

Figure 21 – Final solutions from Cellobiose hydrolysis in (a) $ZnCl_2.4H_2O$ and (b) $ZnCl_2.2H_2O$ at 100ºC after 30, 60, and 120 minutes.

So, it is expecting that at same conditions (100ºC, 30 bar N_2 and same reaction times) the selectivity to Glucose decreases (table 3).

Table 3 - Results from Cellobiose hydrolysis in $ZnCl_2.2H_2O$ at 100ºC: Cellobiose conversion, yields of Glucose, Fructose and other isomers, and selectivity of Glucose.

Cellobiose hydrolysis in $ZnCl_2.2H_2O$					
100ºC and 30 bar N_2					
0,5g Cellobiose + 6,0g $ZnCl_2.4H_2O$					
Reaction time (min)	Cellobiose conversion (%)	Yield of Glucose (%)	Yield of Fructose (%)	Yield of isomers (%)	Selectivity to Glucose (%)
0	-	0	0	0	-
30	13	9,1	1,1	2,7	71
60	17	10,5	1,6	4,8	62
120	24	17,0	1,4	5,5	71

Figure 22 presents the rate of Glucose at Cellobiose hydrolysis in $ZnCl_2.2H_2O$ at 100ºC and 30 bar N_2 during the time.

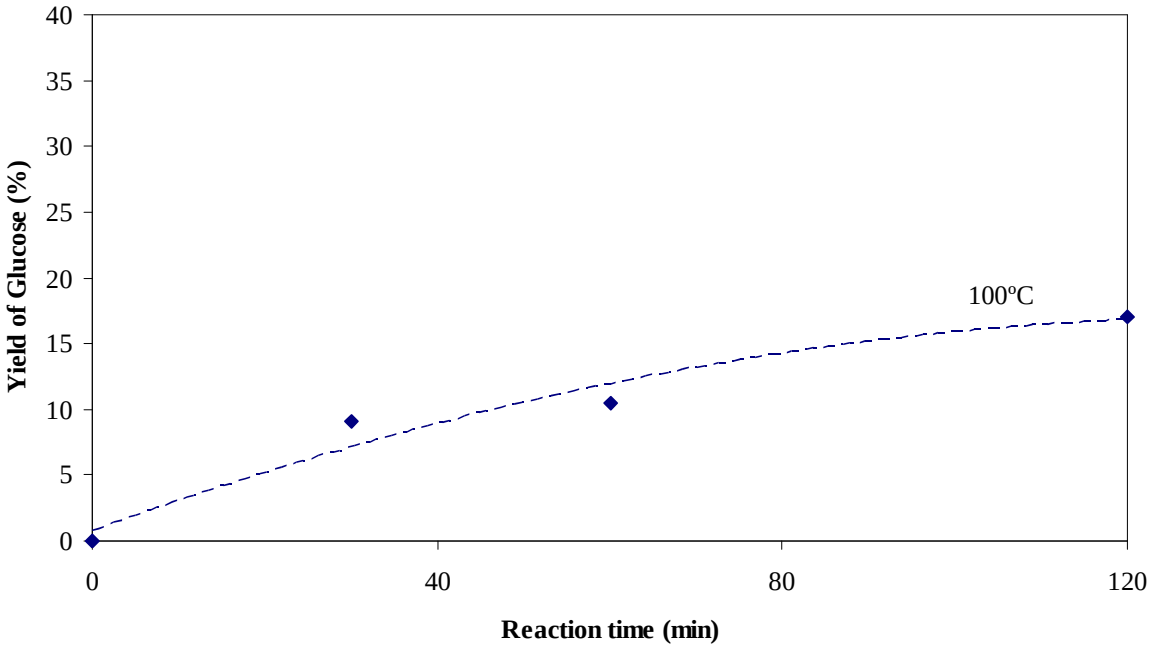

Figure 22 - Cellobiose hydrolysis in $ZnCl_2.2H_2O$ at 100ºC and 30 bar N_2: yield of Glucose

However, in low concentrations of zinc chloride did not have reactions (figure 23).

Figure 23 - Final solutions from Cellobiose hydrolysis at 100ºC, 30 bar N2 and after 60 minutes, in: H_2O, 1% $ZnCl_2$, $ZnCl_2.4H_2O$, and $ZnCl_2.2H_2O$.

As what was expected the samples for low concentrations of Zinc Chloride the rate of Glucose and other by-products are smaller or could not exist. This means that the final solution should be transparent, as is shown in figure 23. Table 4 also presents the results from Cellobiose hydrolysis in different concentrations of Zinc Chloride: Cellobiose conversion and the yield of each product.

Table 4 – Comparing results for Cellobiose hydrolysis in different concentrations of zinc chloride and at 100ºC and 30 bar N_2: Cellobiose conversion, yields of Glucose, Fructose and other isomers, and selectivity to Glucose.

Cellobiose hydrolysis					
100ºC, 60 minutes and 30 bar N_2 *0,5g Cellobiose + 6,0g solvent*					
Solvent	Cellobiose conversion (%)	Yield of Glucose (%)	Yield of Fructose (%)	Yield of isomers (%)	Selectivity to Glucose (%)
$ZnCl_2.4H_2O$	21	20,0	0,7	0,6	94
$ZnCl_2.2H_2O$	17	10,5	1,6	4,8	62
1% $ZnCl_2$	-	0	0	0	-
H_2O	-	0	0	0	-

Once the Glucose rates are less significant (< 10%) when secondary steps are inhibited, some tests with HCl were done. With some acid (H^+) in the system, the reaction can be faster: it not only accelerates the Cellobiose conversion, but also stabilizes the Glucose at the hydrolysis conditions [10].

Cellobiose hydrolysis in $ZnCl_2.4H_2O$ at 80ºC is the conditions with large selectivity (100%). This is the best hydrolysis conditions for Cellobiose conversion. 0,4 mol of HCl were added in this system (figure 24).

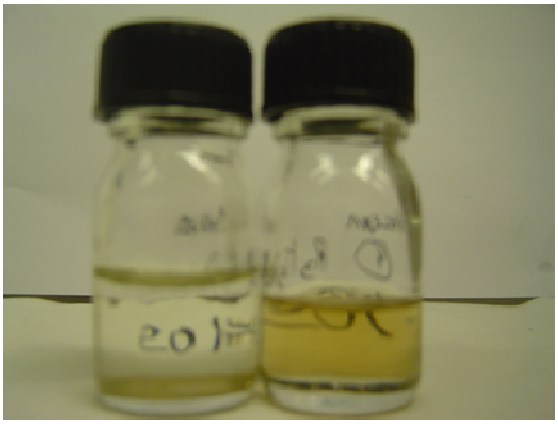

Figure 24 - Final solutions from Cellobiose hydrolysis in $ZnCl_2.4H_2O$ at 80ºC during 240 minutes: without and with 0,4 mol of HCl.

Figure 24 shows the colour of the final solution when HCl is absent or present. When it is present, the sample is less transparent and more yellow. So, the Glucose rate increases. This means that the reaction is faster (table 5).

Table 5 - Comparing results for Cellobiose hydrolysis in $ZnCl_2.4H_2O$ with and without HCl at 80ºC during 240 minutes: Cellobiose conversion, yields of Glucose and selectivity to Glucose.

Cellobiose hydrolysis in $ZnCl_2.4H_2O$					
80ºC, 120 minutes and 30 bar N_2 *0,5g Cellobiose + 6,0g $ZnCl_2.4H_2O$ + 215 µL HCl 37%*					
HCl	Cellobiose conversion (%)	Yield of Glucose (%)	Yield of Fructose (%)	Yield of isomers (%)	Selectivity to Glucose (%)
absent	9	8,5	0	0	100
present	53	52,8	0	0	100

Cellobiose hydrolysis in Lithium Chloride Tetrahydrate ($LiCl.4H_2O$) never reacted in different reaction conditions (table 6).

Table 6 - Results for Cellobiose hydrolysis in $LiCl.4H_2O$ at 80ºC and 100ºC: Cellobiose conversion, yields of Glucose, Fructose and other isomers, and selectivity of Glucose.

Cellobiose hydrolysis with $LiCl.4H_2O$					
80ºC and 30 bar N_2 *0,5g Cellobiose + 6,0g $LiCl.4H_2O$*					
Reaction time (min)	Cellobiose conversion (%)	Yield of Glucose (%)	Yield of Fructose (%)	Yield of isomers (%)	Selectivity to Glucose (%)
120	0,00	0,00	0,00	0,00	-
100ºC and 30 bar					
60	0,00	0,00	0,00	0,00	-

In appendix are presented the chromatograms of each reaction and some pictures of the final solutions.

3.2.2 Methylcellobiose hydrolysis

The same reactions of Cellobiose were done in Methylcellobiose. This is a slightly more complex model component of Cellulose. It is a disaccharide with two molecules of Glucose, one of them that substitute one of the –OH group for $–OCH_3$. However, the same reactions are expected to occur than Cellobiose.

Figures 25, 26 and 27 presented the final solution of Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ and 30 bar N_2 at different conditions.

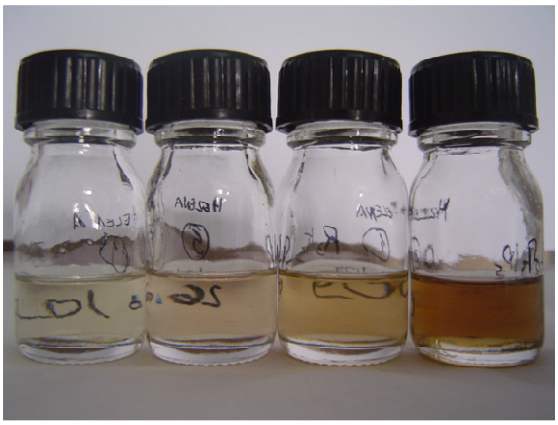

Figure 25 - Final solutions from Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ at 80ºC after 30, 90, 120, and 240 minutes of reaction.

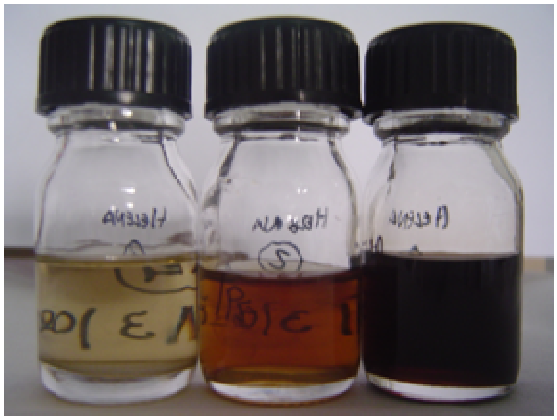

Figure 26 - Final solutions from Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ at 100ºC after 30, 60, and 120 minutes of reaction.

Figure 27 - Final solutions from Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ at 130ºC after 10, 30, and 60 minutes of reaction.

Methylcellobiose has two different main products in hydrolysis: Glucose and Methylglucose. This means that the selectivity should be to Glucose and Methylglucose and not only to Glucose. Equations 1 and 2 were used and once Methylglucose is not so different

than Glucose the blank peak to calculate the yields were the same (Glucose peak in $ZnCl_2.4H_2O$) – table 7.

Table 7 - Results after Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$: Methylcellobiose conversion, yields of Glucose, Methylglucose, Fructose and other isomers, and selectivity to Glucose and Methylglucose.

Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$						
80ºC and 30 bar N_2 *0,5g Methycellobiose + 6,0g $ZnCl_2.4H_2O$*						
Reaction time (min)	Methylcellobiose conversion (%)	Yield of Glucose (%)	Yield of Methylglucose (%)	Yield of fructose (%)	Yield of isomers (%)	Selectivity to glucose and methylglucose (%)
0	-	0	0	0	0	-
30	0,13	0,03	0,1	0	0	100
90	0,34	0,04	0,3	0	0	100
120	0,5	0,1	0,4	0	0	100
240	0,9	0,5	0,4	0	0	100
100ºC and 30 bar N_2 *0,5g Methylcellobiose + 6,0g $ZnCl_2.4H_2O$*						
0	-	0	0	0	0	-
30	1,78	0,8	1	0	0	100
60	3,3	1,7	0,7	0,3	0,6	73
120	9,2	5,8	0,2	1,0	2,2	66
130ºC and 30 bar N_2 *0,5g Methylcellobiose + 6,0g $ZnCl_2.4H_2O$*						
0	-	0	0	0	0	-
10	33	3,2	23,1	1,6	4,8	80
30	31	0,2	22,0	0,9	7,9	72
60	15	1,9	4,9	0,5	8,1	44

In figures 28 and 29 are possible to see the aspect of the curve from Glucose and Methylglucose yields (main components from Methylcellobiose hydrolysis).

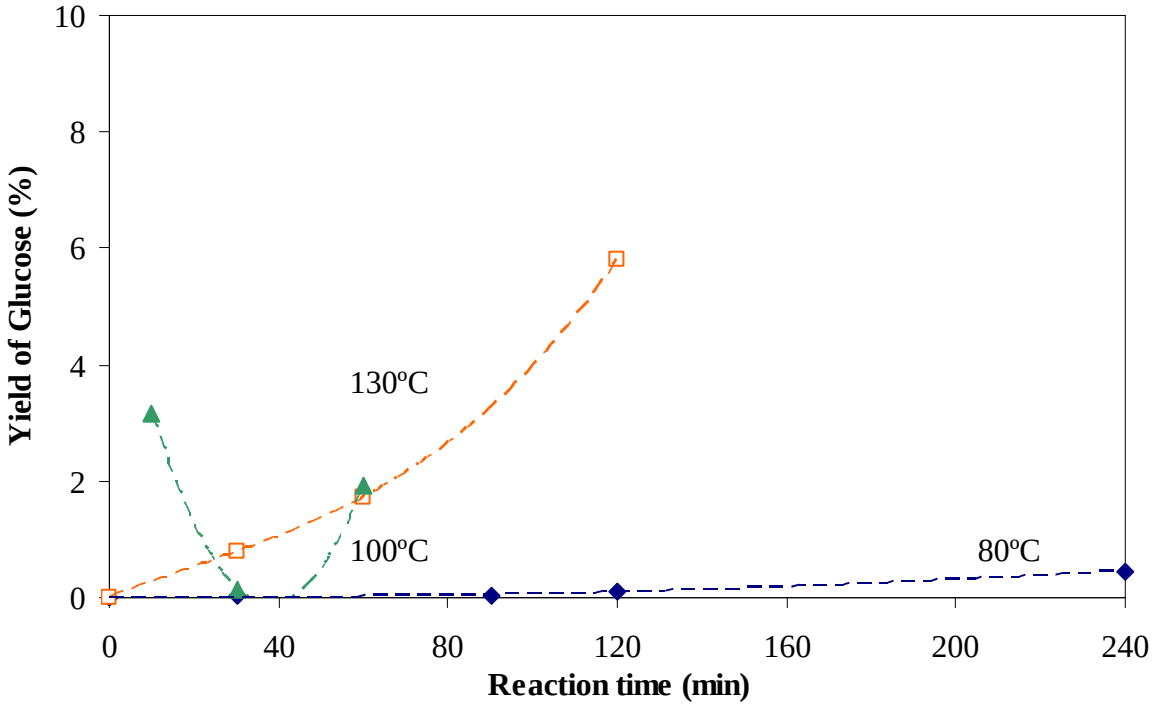

Figure 28 –Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$: yield of Glucose.

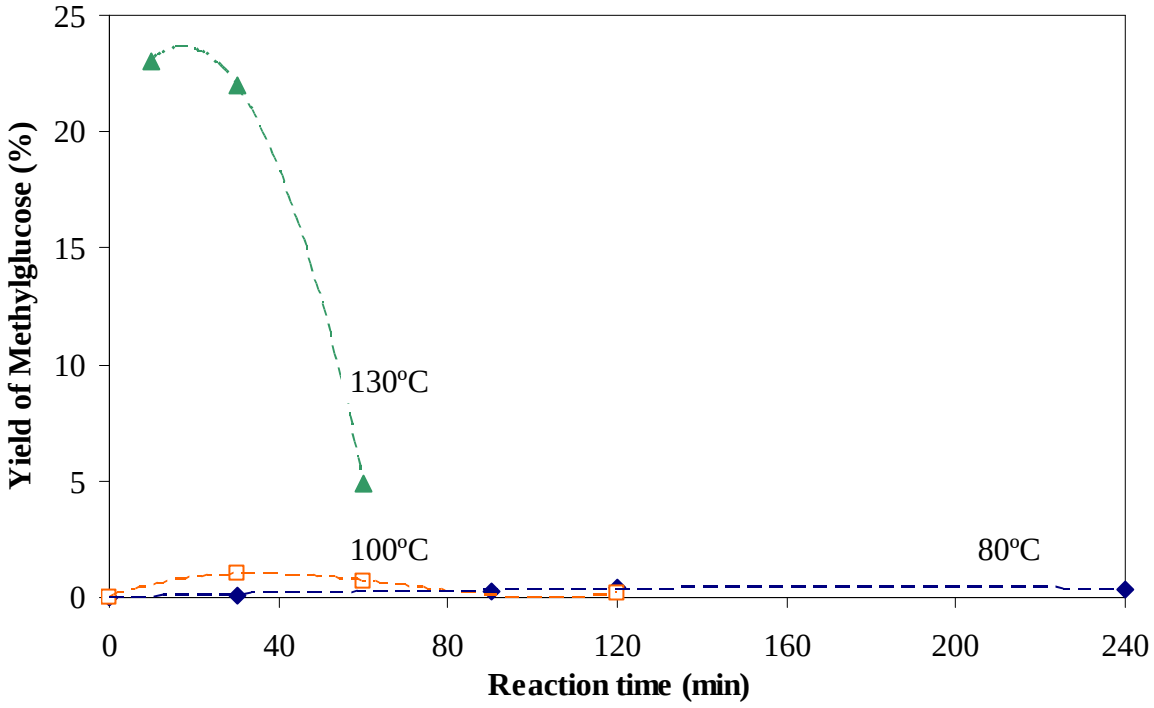

Figure 29 –Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$: yield of Methylglucose.

Once Methylcellobiose did not dissolve in $ZnCl_2.2H_2O$, it was only possible studied the Methylcellobiose hydrolysis in low concentrations of Zinc Chloride. It is expected that in

low concentrations of Zinc Chloride Methylcellobiose should not react once it is more complex component than Cellobiose (figure 30 and table 8).

Figure 30 - Final solutions from Methylcellobiose hydrolysis at 100ºC and 30 bar N_2 after 60 minutes in: H_2O, 1% $ZnCl_2$, $ZnCl_2.4H_2O$.

Table 8 - Comparing results for Methylcellobiose hydrolysis in different concentrations of zinc chloride at 100ºC and 30 bar N_2: Methylcellobiose conversion, yields of Glucose, Methylglucose, Fructose and other isomers, and selectivity to Glucose and Methylglucose.

Methylcellobiose hydrolysis						
100ºC, 60 minutes and 30 bar N_2 *0,5g Methylcellobiose + 6,0g solvent*						
Solvent	Methylcellobiose conversion (%)	Yield of Glucose (%)	Yield of Methylglucose (%)	Yield of Fructose (%)	Yield of isomers (%)	Selectivity to Glucose and Methylglucose (%)
$ZnCl_2.4H_2O$	3	1,7	0,7	0,3	0,6	73
1% $ZnCl_2$	-	0	0	0	0	-
H_2O	-	0	0	0	0	-

Methylcellobiose conversion could be faster if some acid was added into the system. Once only in $ZnCl_2.4H_2O$ Methylcellobiose was reacted, some HCl was added into the system (0,4 mol) – figure 31 and table 9.

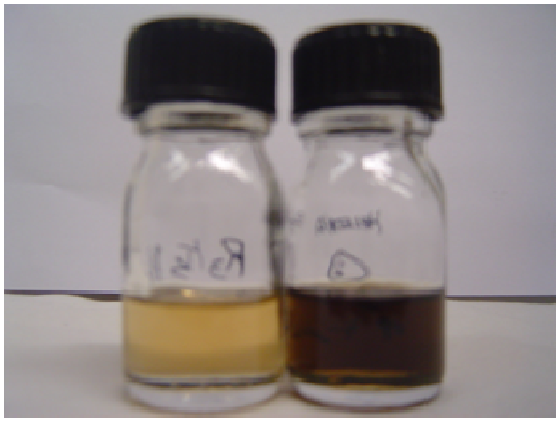

Figure 31 – Final solutions from Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ at 80ºC during 120 minutes without and with HCl.

Table 9 - Comparing results for Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ with and without HCl at 80ºC during 240 minutes: Methylcellobiose conversion, yields of Glucose, Methylglucose, Fructose and other isomers, and selectivity to Glucose and Methylglucose.

Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$						
80ºC, 120 minutes and 30 bar N_2 *0,5g Methylcellobiose + 6,0g solvent+ 215 µL HCl 37%*						
HCl	Methylcellobiose conversion (%)	Yield of Glucose (%)	Yield of Methylglucose (%)	Yield of Fructose (%)	Yield of isomers (%)	Selectivity to Glucose and Methylglucose (%)
absent	0,5	0,1	0,4	0	0	100
present	28	6,0	21,5	0	0	100

Lithium Chloride Tetrahydrate is a bad solvent for hydrolysis. In this hydrate molten salt, Methylcellobiose did not react apart temperature and reaction time conditions (table 10).

Table 10 - Results for Methylcellobiose hydrolysis in $LiCl.4H_2O$ at 80ºC and 100ºC: Methylcellobiose conversion, yields of Glucose, Methylglucose, Fructose and other isomers, and selectivity to Glucose and Methylglucose.

Methylcellobiose hydrolysis with $LiCl.4H_2O$						
80ºC and 30 bar N_2 *0,5g Methylcellobiose + 6,0g $LiCl.4H_2O$*						
Reaction time (min)	Methylcellobiose conversion (%)	Yield of Glucose (%)	Yield of Methylglucose (%)	Yield of Fructose (%)	Yield of isomers (%)	Selectivity to Glucose and Methylglucose (%)
120	0,00	0,00	0,00	0,00	0,00	0,0
100ºC						
60	0,00	0,00	0,00	0,00	0,00	0,0

In appendix are presented the chromatograms of each reaction and some pictures of the final solutions.

3.3 Hydrogenation reactions

Different conditions (temperature and reaction times), different amount of catalyst and different solvents at 40 bar were used during hydrogenation. Equations (3) and (4) were used to calculate the yields of Glucose, Methylglucose, Fructose and other isomers, and the selectivity to Glucose and/or Methylglucose.

$$Yield\ of\ sugar\,(\%)=\left[\frac{PA_{sugar}}{\left(\frac{PA_{ZnCl_2}}{PA_{ZnCl2-blank}}\right)}\times PA_{glucoseorsorbitol-blank}\right]\times 100 \qquad (3)$$

$$Selectivity\ to\ sugar\,(\%)=\frac{Yield\ of\ sugar}{\sum Yield\ of\ products}\times 100 \qquad (4)$$

With:

PA_{sugar} – Peak area of Glucose, Methylglucose, Fructose and other isomers in the end solution

PA_{ZnCl2} – Peak area of Zinc Chloride Tetrahydrate in the end solution

$PA_{ZnCl2\text{-}blank}$ – Peak area of Zinc Chloride hydrate in the blank solution (Glucose dissolved in Zinc Chloride tetrahydrate)

$PA_{glucose\ or\ sorbitol\ blank}$ – Peak area of Glucose or Sorbitol in the blank solution (Glucose or Sorbitol dissolved in Zinc Chloride tetrahydrate)

Some catalyst was required to have hydrogenation, Ru/C (Ruthenium catalyst supported on Carbon) was chosen. This is the most active catalyst in carbohydrate hydrogenations, not only in homogeneous but also in heterogeneous catalysis [18].

3.3.1 Cellobiose hydrogenation

Glucose is the first product in Cellobiose hydrogenation in $ZnCl_2.4H_2O$. This means that in this solvent some hydrolysis started and when some Glucose was formed, hydrogenation occurs. So, Glucose (hydrolysis product) and Sorbitol (hydrogenation product) are the main components in Cellobiose hydrogenation reaction.

Table 11 presents the effect of the amount of catalyst (Ru/C) in Cellobiose hydrogenation.

Table 11 - Results after Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC during 1 hour: Cellobiose conversion, yields of Glucose, Sorbitol and isomers, and selectivity to Sorbitol.

Cellobiose hydrogenation in $ZnCl_2.4H_2O$					
100ºC, 60 minutes and 40 bar H_2					
0,5g Cellobiose + 6,0g $ZnCl_2.4H_2O$ + catalyst (Ru/C)					
amount of catalyst (g)	Cellobiose conversion (%)	Yield of Glucose (%)	Yield of Sorbitol (%)	yield of isomers (%)	Selectivity to Sorbitol (%)
0	-	0	0	0	-
0,025	23	19,3	2,3	1,2	10
0,05	32	27,0	4,4	0,6	14
0,125	74	56,1	17,5	0,4	24
0,25	87	71,3	15,0	0,4	17

Figure 32 presents the curves from the yields of Glucose and Sorbitol with different amounts of Ru/C during Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC during 1 hour. For high amounts of Ru/C (bigger than 0,2 g), the yields of Glucose and Sorbitol do not increase so much, a plateau was formed.

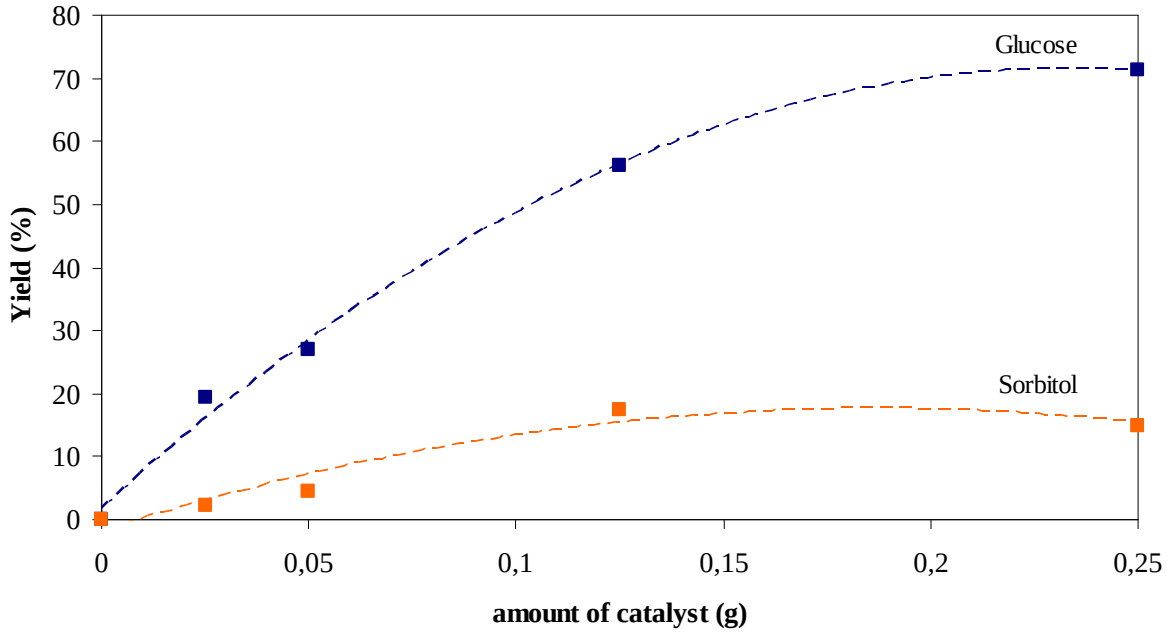

Figure 32 - Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC during 60 minutes: yields of Glucose and Sorbitol.

Temperature and reaction time also have some influence during Cellobiose hydrogenation. For lower temperatures (80ºC) only Glucose was formed. This means that

hydrogenation only occurs at high temperatures. On the other hand, at 130ºC some sorbitol was formed into the system and this amount increase for high reaction times. In the same time, the amount of Glucose started decreasing. This means that for high temperatures and big reaction times, the hydrolysis stops and only has hydrogenation (table 12 and 13).

Table 12 - Results after Cellobiose hydrogenation in Cellobiose in $ZnCl_2.4H_2O$ with 0,025g Ru/C at 80ºC during 120 minutes: Cellobiose conversion, yields of Glucose, Sorbitol and isomers, and selectivity to Sorbitol.

Cellobiose hydrogenation in $ZnCl_2.4H_2O$					
80ºC and 40 bar H_2 *0,5g Cellobiose + 6,0g $ZnCl_2.4H_2O$ + 0,025g Ru/C*					
Reaction time (min)	Cellobiose conversion (%)	Yield of Glucose (%)	Yield of Sorbitol (%)	Yield of isomers (%)	Selectivity to Sorbitol (%)
120	7	7,2	0	0	0

Table 13 - Results after Cellobiose hydrogenation in Cellobiose in $ZnCl_2.4H_2O$ with 0,025g Ru/C at 130ºC and different reaction times: Cellobiose conversion, yields of Glucose, Sorbitol and isomers, and selectivity to Sorbitol.

Cellobiose hydrogenation in $ZnCl_2.4H_2O$					
130ºC and 40 bar H_2 *0,5g Cellobiose + 6,0g $ZnCl_2.4H_2O$ + 0,025g Ru/C*					
Reaction time (min)	Cellobiose conversion (%)	Yield of Glucose (%)	Yield of Sorbitol (%)	Yield of isomers (%)	Selectivity to Sorbitol (%)
0	-	0,00	0,00	0,00	-
30	32	22,2	3,2	6,8	10
60	26	10,6	8,5	6,6	33

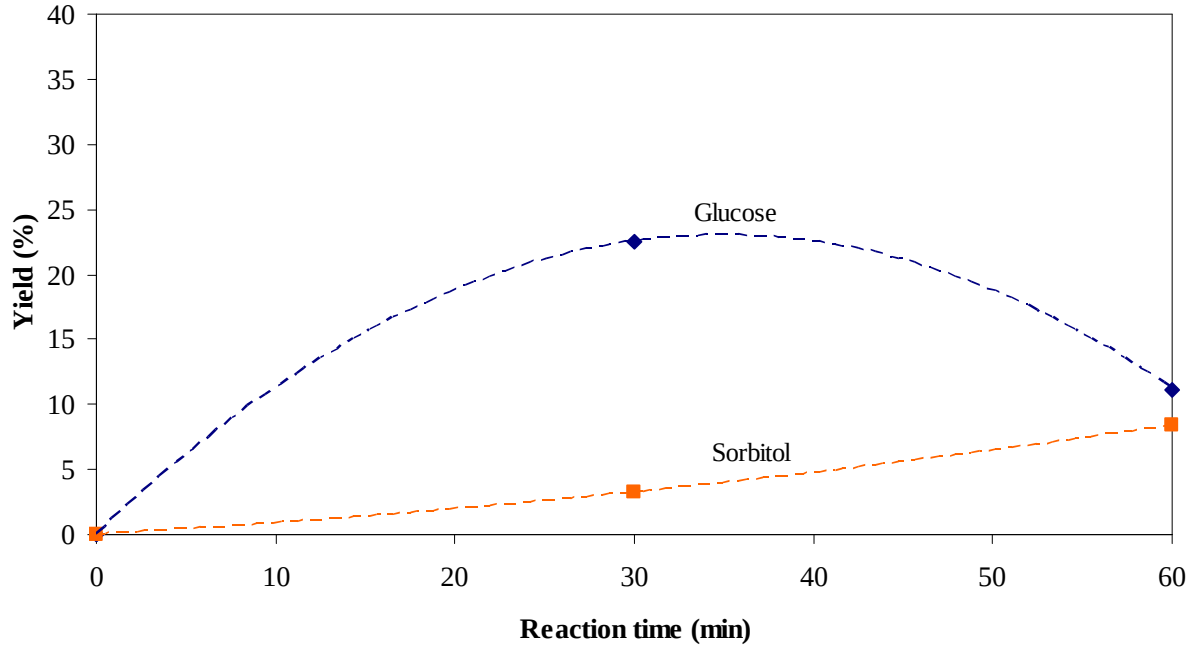

Figure 33 - Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 130ºC with 0,025g Ru/C: yields of Glucose and Sorbitol.

Figure 33 presents Glucose and Sorbitol yields during Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 130ºC. As was said before, at 130ºC after 30 minutes of reaction only hydrogenation occurred into the system. This means that the yield of Glucose starts decreasing but the yield of Sorbitol only increase. However, three reaction times is not enough to analyze the yield's growth.

The influence of the reaction times was analyzed at 100ºC (minimum of temperature to have hydrogenation) – table 14 and figure 34.

Table 14 - Results after Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC with 0,025g Ru/C and different reaction times: Cellobiose conversion, yields of Glucose, Sorbitol and isomers, and the selectivity to Sorbitol.

Cellobiose hydrogenation in $ZnCl_2.4H_2O$					
100ºC and 40 bar H_2					
0,5g Cellobiose + 6,0g $ZnCl_2.4H_2O$ + 0,025g Ru/C					
Reaction time (min)	Cellobiose conversion (%)	Yield of Glucose (%)	Yield of Sorbitol (%)	Yield of isomers (%)	Selectivity to Sorbitol (%)
0	-	0	0	0	-
30	19	17,1	1,6	0	8
60	23	19,3	2,3	1,2	10
120	38	27,0	3,7	7,4	10
240	41	23,4	5,3	12,5	13

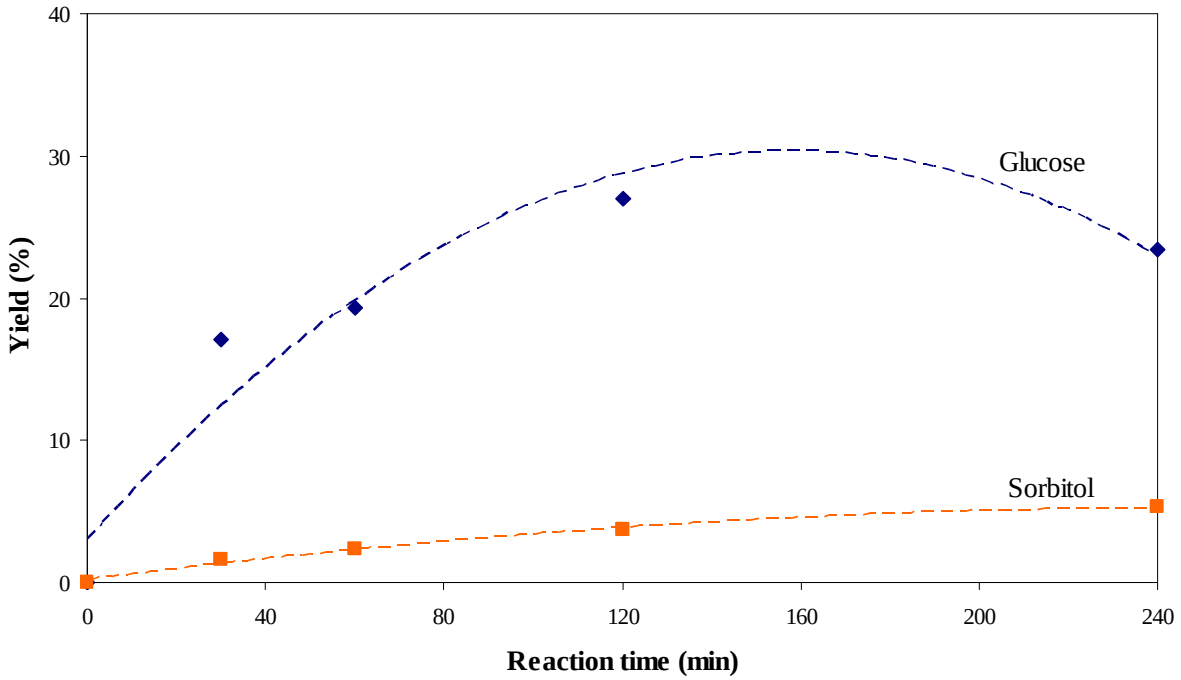

Figure 34 - Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC with 0,025g Ru/C: yields of Glucose and Sorbitol.

When Zinc Chloride was changed for Water as a hydrogenation solvent, the results were so different. With water we did not only have Sorbitol or Glucose has a product a mixture of these two components. This means that some Glucose-Sorbitol was formed. This is a single product of Cellobiose hydrogenation in Water. So, Cellobiose was not hydrolyzed in water, i.e., Glucose was not a product. Although, Glucose-Sorbitol has the same retention time than Glucose so, some Glucose molecules may exist into the system.

Table 15 shown an approximation to the yield of Glucose-Sorbitol when different amounts of catalyst was tested. Those results are approximated because they were compared with Cellobiose blank peak. This is possible once only have two peaks in the chromatograms, so is possible to compare with the completely conversion.

Table 15 - Results after Cellobiose hydrogenation in H_2O at 100ºC during 60 minutes and different amounts of catalyst: Cellobiose conversion and the yield of Glucose-Sorbitol.

Cellobiose hydrogenation in H_2O		
100ºC, 60 minutes and 40 bar H_2 *0,5g Cellobiose + 6,0g H_2O + catalyst*		
Amount of catalyst (g)	Cellobiose conversion (%)	Yield of glucose-sorbitol (%)
0	-	0
0,025	86,6	86,6
0,05	86,3	86,3
0,125	92,5	92,5
0,25	93,1	93,1

Table 16 presents the influence of the temperature in Cellobiose hydrogenation in H_2O.

Table 16 - Results after Cellobiose hydrogenation in H_2O at 80 and 130ºC with different reaction times: Cellobiose conversion and the yield of Glucose-Sorbitol.

Cellobiose hydrogenation in H_2O		
80ºC and 40 bar H_2 *0,5g Cellobiose + 6,0g H_2O + 0,025g Ru/C*		
Reaction time (min)	Cellobiose conversion (%)	Yield of glucose-sorbitol (%)
120	39,9	39,9
130ºC and 40 bar H_2 *0,5g Cellobiose + 6,0g H_2O + 0,025g Ru/C*		
0	-	0
30	63,0	63,0
60	84,7	84,7

In Cellobiose hydrogenation in H_2O, some Glucose-Sorbitol was formed at low temperatures. However, for high temperature this amount is bigger. And for big reaction times it also increased.

The influence of reaction times was also studied in Cellobiose hydrogenation in Water (table 17 and figure 35).

Table 17 - Results after Cellobiose hydrogenation in H_2O at 100ºC with different reaction times: Cellobiose conversion and the yield of Glucose-Sorbitol.

Cellobiose hydrogenation in H_2O		
100ºC and 40 bar H_2 *0,5g Cellobiose + 6,0g H_2O + 0,025g Ru/C*		
Reaction time (min)	Cellobiose conversion (%)	Yield of Glucose-Sorbitol (%)
0	-	0
30	74,1	74,1
60	86,6	86,6
120	$\approx 90^{(*)}$	$\approx 90^{(*)}$
240	$\approx 100^{(*)}$	$\approx 100^{(*)}$

(*) this is an aproximation once the chromatogram did not have a Cellobiose peak and we could not compare the peak area of glucose sorbitol.

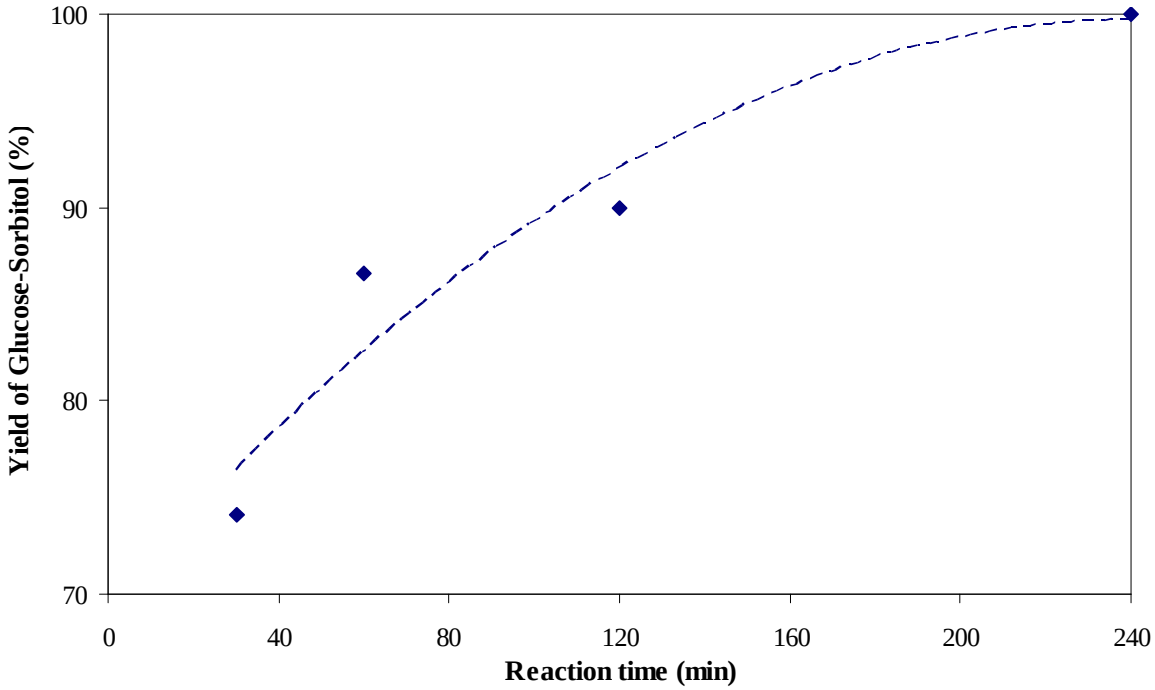

Figure 35 – Cellobiose hydrogenation in H_2O at 100ºC with 0,025g Ru/C: yield of Glucose-Sorbitol.

In appendix is shown the chromatograms of each hydrogenation reaction of Cellobiose.

3.3.2 Methylcellobiose hydrogenation

As what was done in hydrolysis, in hydrogenation some reactions with Methylcellobiose has also been done. Once this is a more complex model component of Cellulose in respect of Cellobiose, it is expected difficult conversion and different products. However, the same reactions of Cellobiose should occur.

Starting with the influence of the catalyst (Ru/C) in Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$, the results are presented in table 18.

Table 18 - Results for the effect of the amount of catalyst in Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC during 60 minutes: Methylcellobiose conversion, yields of Glucose, Methylglucose, Sorbitol and isomers, and selectivity to Sorbitol.

Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$						
100ºC, 60 minutes and 40 bar H_2						
0,5g Methylcellobiose + 6,0g $ZnCl_2.4H_2O$ + catalyst						
Amount of catalyst (g)	Methylcellobiose conversion (%)	Yield of Methylglucose (%)	Yield of Glucose (%)	Yield of Sorbitol (%)	Yield of isomers (%)	Selectivity to Sorbitol (%)
0	-	0	0	0	0	-
0,025	6	1,8	2,8	0,5	1,1	8
0,05	5	1,7	1,5	1,6	0,2	32
0,125	22	2,3	7,2	12,0	0,5	54
0,25	21	2,9	7,6	10,0	0,3	48

Figure 36 presents the curves for Glucose, Methylglucose and Sorbitol yields, main products in Methylcellobiose hydrogenation. As what was said, Methylcellobiose is more difficult to convert than Cellobiose. The yields of Methylglucose, Glucose and Sorbitol have a less increasing.

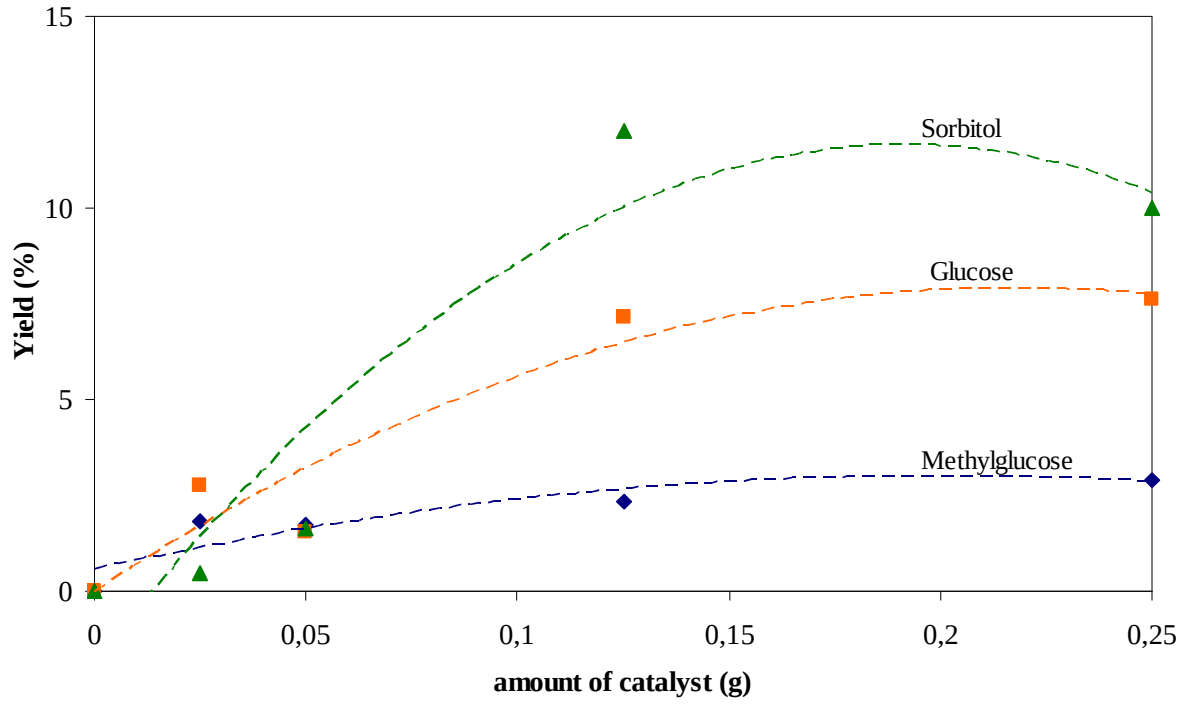

Figure 36 –Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC during 60 minutes: yields of Methylglucose, Glucose and Sorbitol.

In Methylcellobiose hydrogenation was also tested the influence of temperature and reaction time (table 19).

Table 19 - Results after Methylcellobiose hydrogenation reaction in $ZnCl_2.4H_2O$ at 80 and 130ºC, during different reaction times: Methylcellobiose conversion, yields of Methylglucose, Glucose, Sorbitol and isomers, and selectivity to Sorbitol.

Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$						
80ºC and 40 bar H_2 *0,5g Methylcellobiose + 6,0g $ZnCl_2.4H_2O$ + 0,025g Ru/C*						
Reaction time (min)	Methylcellobiose conversion (%)	Yield of Methylglucose (%)	Yield of Glucose (%)	Yield of Sorbitol (%)	Yield of isomers (%)	Selectivity to Sorbitol (%)
120	2,39	1,07	1,32	0,00	0	0
130ºC and 40 bar H_2 *0,5g Methylcellobiose + 6,0g $ZnCl_2.4H_2O$ + 0,025g Ru/C*						
0	-	0,0	0,0	0,0	0,0	-
30	21,6	8,77	7,75	1,28	3,79	5,9
60	19,8	4,17	4,13	3,36	8,13	17,0

For low temperatures (80ºC), only hydrolysis occurred, Sorbitol did not form. On the other way, for high temperatures and big reaction times (60 minutes), hydrolysis stop and some hydrogenation of Glucose and Methylglucose start.

However, three points is not enough to study the influence of the reaction times. So, some tests were done at 100ºC (table 20 and figure 37).

Table 20 - Results for Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC with 0,025g Ru/C and different reaction times: Methylcellobiose conversion, yields of Glucose, Methylglucose, Sorbitol and isomers, and the selectivity to Sorbitol.

Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$						
100ºC and 40 bar H_2 *0,5g Methylcellobiose + 6,0g $ZnCl_2.4H_2O$ + 0,025g Ru/C*						
Reaction time (min)	Methylcellobiose conversion (%)	Yield of Methylglucose (%)	yield of Glucose (%)	yield of Sorbitol (%)	Yield of isomers (%)	Selectivity to Sorbitol (%)
0	-	0	0	0	0	-
30	4	1,7	1,4	0,9	0	23
60	6	1,6	3,3	0,4	1,1	6
120	32	0,4	13,1	14,5	3,7	46
240	30	0,4	12,6	14,1	3,4	46

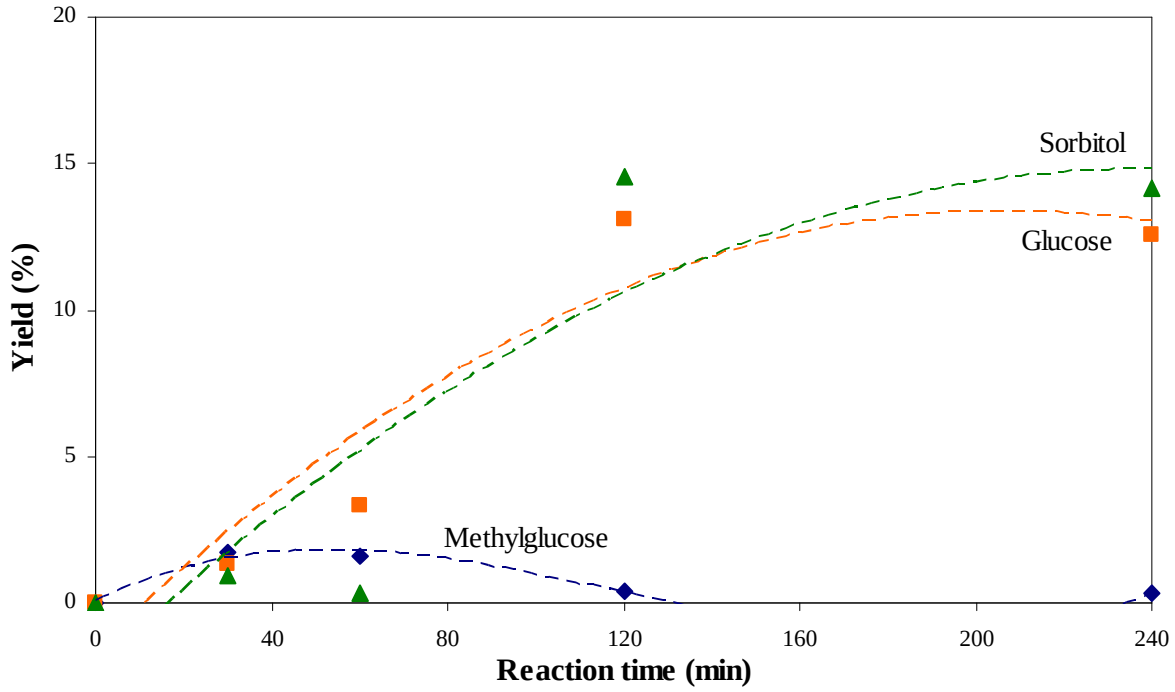

Figure 37 – Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC with 0,025g Ru/C: yields of Methylglucose, Glucose and Sorbitol.

When the solvent was changed for Water, Methylcellobiose only react at high temperatures. Figure 38 is the example of Methylcellobiose hydrogenation at 100ºC during 60 minutes and different amounts of catalyst and only has one peak (from Methylcellobiose). As what was expected, at 100ºC and different reaction times was also not possible to have reaction (figure 39).

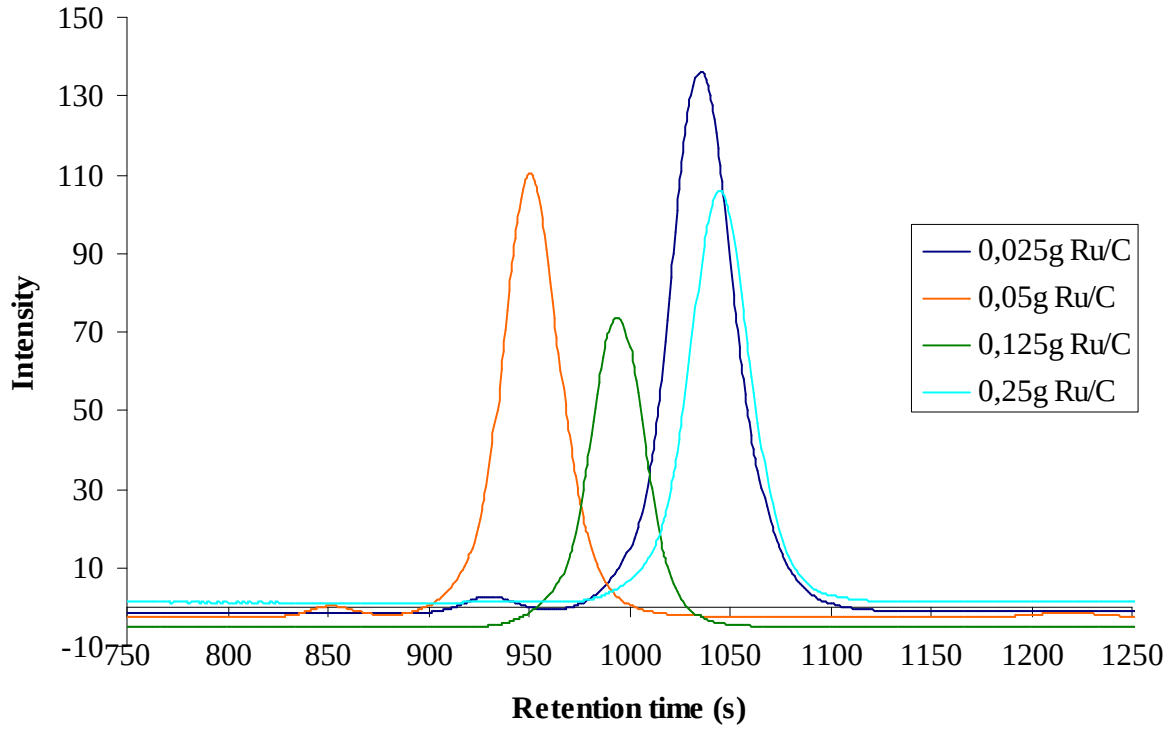

Figure 38 – HPLC analyzes of Methylcellobiose hydrogenation in H_2O at 100ºC during 60 minutes with different amounts of catalyst.

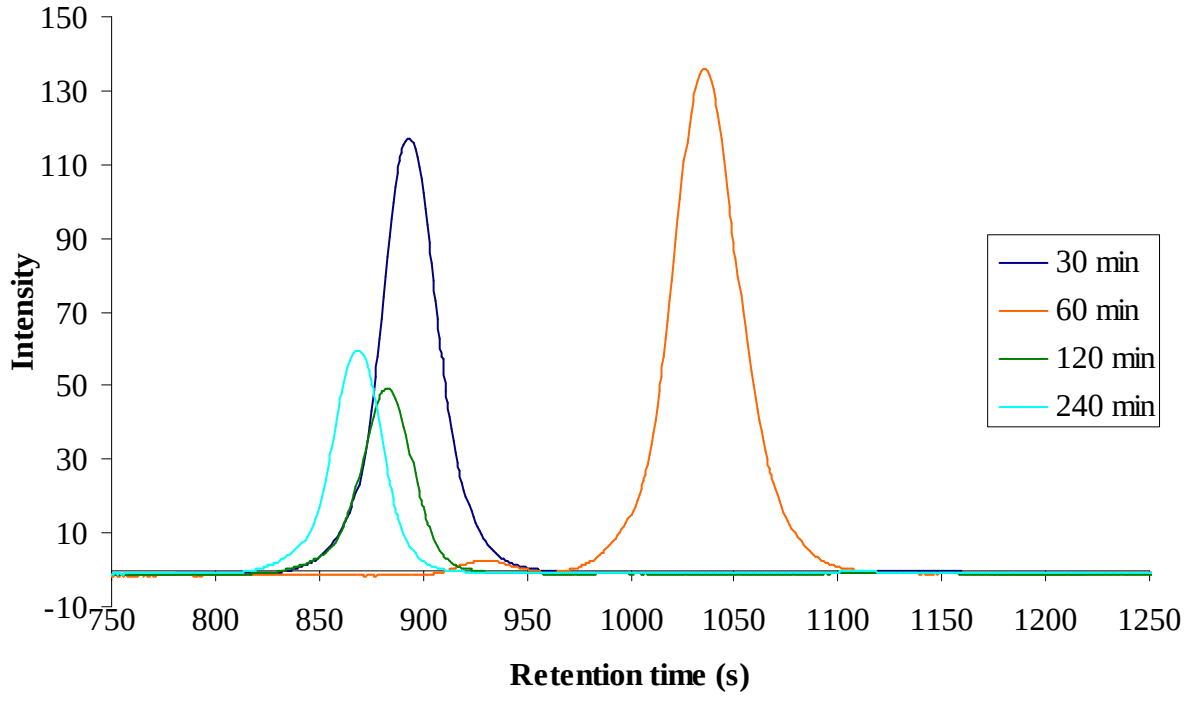

Figure 39 – HPLC chromatogram of Methylcellobiose hydrogenation in H_2O at 100ºC with 0,025g Ru/C and different reaction times.

At high temperatures, some Glucose, Methylglucose and Sorbitol were found into the system (table 21). This means that Methylcellobiose need strongest conditions to react than Cellobiose.

Table 21 - Results for Methylcellobiose hydrogenation in H_2O at 130ºC with 0,025g Ru/C and different reaction times: Methylcellobiose conversion, yields of Glucose, Methylglucose and Sorbitol, and the selectivity to Sorbitol.

Methylcellobiose hydrogenation in H_2O					
130ºC 40 bar H_2 *0,5g Methylcellobiose + 6,0g H_2O + 0,025g Ru/C*					
Reaction time (min)	Methylcellobiose conversion (%)	Yield of Methylglucose (%)	Yield of Glucose (%)	Yield of Sorbitol (%)	Selectivity to Sorbitol (%)
0	0	0	0	0	0,0
30	6,6	1,6	3	2	30,3
60	9,9	3,7	2,3	3,9	39,4

In appendix is shown the chromatograms of each hydrogenation reaction of Methylcellobiose.

4 Discussion

4.1 Hydrolysis solvents

Hydrolysis reactions use water solvents. Molten salts were chosen because they are a liquid at STP (Standard Temperature and Pressure), Cellobiose and/or Methylcellobiose do not need pre-treatment or activation and they can be applied as reaction medium for derivatization of Cellulose [17].

To select which is the amount of water that should be used to dissolve each molten salt, different concentrations were studied at room temperature (table 1). After a visual inspection, if the molten salt have dissolved and did a homogeneous mixture (single phase), the solvent can be used in hydrolysis reactions. On the other hand, if it did not completely dissolve and a heterogeneous mixture was formed, the solvent can not be used in hydrolysis (figures 13, 14 and 15). So, Zinc Chloride Tetrahydrate ($ZnCl_2.4H_2O$), Zinc Chloride Dehydrate ($ZnCl_2.2H_2O$) and Lithium Chloride Tetrahydrate ($LiCl.4H_2O$) can be used like a hydrolysis solvent once they formed a single phase. On the other hand, Calcium Chloride did not form a homogeneous solution with 1; 1,5; 2; or 4 molecules of water per molecule of $CaCl_2$. A single phase was only possible for twenty molecules of water per molecule of calcium chloride. However, when it was done in industrial scale, a large amount of water is required and it will be so expensive.

4.2 Hydrolysis reactions

Optimal conditions for hydrolysis were chosen in that section: best hydrolysis solvent, optimal temperature and the reaction time to avoid secondary steps such as degradation or isomerisation of Glucose. The hydrolysis mechanism of Cellobiose and/or Methylcellobiose was written too.

4.2.1 Cellobiose hydrolysis

Selectivity is a measure of the tendency to occur one reaction and is influenced both by the solvent, temperature and reaction time. So, selectivity was chosen as a parameter to decide which the best hydrolysis solvent is between the different molten salts hydrates that were already studied. However, that parameter is only respecting to the hydrolysis products

Tables 4 and 6 shows which is the solvent with high selectivity and Zinc Chloride Tetrahydrate ($ZnCl_2.4H_2O$) was chosen.

Table 2 presents hydrolysis reactions at different temperatures and reaction times. At 80ºC did not have isomers into the system, this means that degradation and/or isomerisation of Glucose were suppressed. However, the rate of Glucose is small. On the other hand, at 100 and 130ºC greater hydrolysis rates occurs but some by-products appeared. So, the best hydrolysis temperature should be chosen after analyzing the investment to remove by-products from the system or to have less yields of Glucose

If 80ºC is the best temperature for hydrolysis reactions, is also possible to conclude that that between 120 and 240 minutes the Glucose rate do not have great differences (8,49 to 9,20%). So, in these conditions was not necessary to spend more energy because the rates will never be to much bigger than ≈ 10%. This means that to have higher conversion, different environmental conditions should be used. Once the selectivity is 100% during 120 and 240 minutes of reaction, at 80ºC and 30 bar N_2, 120 minutes is enough for that reaction.

Cellobiose did not react in low concentrations of Zinc Chloride neither in water but for high amounts of $ZnCl_2$ ($ZnCl_2.2H_2O$), a lot of Cellobiose and Glucose isomers were formed. This means that Cellobiose is more stable in water or low concentrations of zinc chloride (1% $ZnCl_2$) and start to be unstable when the amount of zinc chloride increases because the solvent start to be more viscous and secondary steps was improved (table 4). $LiCl.4H_2O$ is a weak solvent as 1% $ZnCl_2$ or H_2O and Cellobiose did not react (table 6).

Once Cellobiose hydrolysis was so slow, some HCl was added into the system. As what is expected, the yield of Glucose increase too much (from 8,5% to 52,8%). However, acidic conditions should not have into the system because is very difficult to remove HCl from the system and separation issues are created (table 5).

Figures 16-24 show the colour of the final solutions. When secondary steps were available the final sample started to be darker and became to be solid. To analyze where the by-products are from, some reactions were done. Glucose stability at high temperatures (100ºC) was done and a lot of isomers and degradation products were found into the system. So, high temperatures improve secondary steps and some degradation and/or isomerisation occurs.

4.2.2 Methylcellobiose hydrolysis

Zinc Chloride Tetrahydrate is also the best hydrolysis solvent for Methylcellobiose. With this solvent, highest selectivity to Glucose and Methylglucose (100%) was possible. However, Methylcellobiose did not dissolve in high concentrations of $ZnCl_2$ ($ZnCl_2.2H_2O$) because it has a high viscosity. So, Methylcellobiose should be more stable and less reactive than Cellobiose (tables 8 and 10). On the other hand, in low concentrations of $ZnCl_2$ and in water, Methylcellobiose also did not react. So, they are not enough strong solvents to hydrolysis reactions.

Methylcellobiose is more stable than Cellobiose so, the reaction time should be bigger. Table 7 present this affirmation. Between 120 and 240 minutes, have a big increasing in the yield of Glucose (from 0,1% to 0,5%). This means that Methylcellobiose hydrolysis did not finish after four hours of reaction at 80ºC.

Some HCl was added into the system because fast reactions are interested. However, in Methylcellobiose acidic conditions did not have a large effect in Glucose. The yield of Glucose only increased from 0,1 to 6% but for Methylglucose had more effect: from 0,4 to 21% (table 9). This ratio should be 1:1 but some deconvolution occurs because both peaks are together in the chromatogram and was so difficult to split them. Some separation issues are also created when HCl are present into the system. It is very difficult to remove from a mixture.

In the pictures from the bottles of the final solutions, the same conclusion can be done. So, for high amounts of by-products into the system, the sample is darker and become to have some solids (figures 25-31).

During Methylcellobiose hydrolysis, the rates of Methylglucose and Glucose should be the same once per each molecule of Methylcellobiose have one molecule of Glucose and one molecule of Methylglucose. Tables 7-10 show that these yields are different. Some deconvolution occurs because some times the peaks of Glucose and Methylglucose were jointly and is difficult to separate it. Some approximations were done.

The way that the hydrolysis occurs in each compound (Cellobiose and Methylcellobiose) is a strong point in this project. After analyzing all the last results, hydrolysis mechanism is known. This means that hydrolysis breaks the oxygen bond between the two Glucose rings in Cellobiose and Methylcellobiose.

4.3 Hydrogenation reactions

Different products of hydrolysis were expecting once Glucitol/Sorbitol should be the main product. This means that the break bond should not be the oxygen bond between the two molecules of glucose of each disaccharide. With this goal, different solvents were tested ($ZnCl_2.4H_2O$ and H_2O) and different products were formed.

4.3.1 Cellobiose hydrogenation

Cellobiose hydrogenation in $ZnCl_2.4H_2O$ has two different products. This reaction started with a hydrolysis and some Glucose was formed. Later, some hydrogenation of Glucose occurred and Sorbitol was found into the system. Different amounts of catalyst, different reaction times and different temperatures were studied to analyze the influence of these conditions in the rate of Sorbitol.

Table 11 presents an increasing in the amount of catalyst that was used. Big amounts of catalyst improved the reaction and more Sorbitol was formed. But between 0,125g and 0,25g of Ru/C this consideration did not occur. In spite of Cellobiose conversion had increased, the yield of Sorbitol started decreasing. It can have four different reasons. First is the amount of catalyst. 0,25g is a large amount and some Ru/C was deposited in the bottom of the reactor and not only did not react but also adsorb some sugar in its surface. Secondly, some sugar can be remained in the filter during the filtration. The amount of catalyst is bigger and the filter could be full of catalyst and some sugar could be remained there. The third reason can be some poisoning of the catalyst because a lot of by-products were formed. The forth reason, and maybe the strongest one, is some errors during the yields calculation. That measure was calculated based in a relation between peak areas of Zinc Chloride and Sorbitol in the solution and in the blank. This is an approximation that can introduce some errors.

Figure 33 presents the yields of Glucose and Sorbitol during the time in Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC with 0,025g Ru/C. The yield of sorbitol is always increasing during the time (orange line) but the yield of Glucose starts decreasing after two hours and a half (blue line). This means that after that time, hydrolysis reaction stopped and only had hydrogenation of Glucose.

Cellobiose hydrogenation in H_2O has different products than in $ZnCl_2.4H_2O$. Some Glucose-Sorbitol was formed and only one product was found.

Tables 15 and 17 present the influence of the amount of catalyst and the reaction time in Cellobiose hydrogenation in H_2O. As what was expected, the rate of Glucose-Sorbitol was increasing and high yields of this product were formed.

4.3.2. Methylcellobiose hydrogenation

Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$ results in Glucose, Methylglucose, Methanol and Sorbitol. Glucose and Methylglucose are products from the first part of the reaction: hydrolysis. Methanol and Sorbitol are typical hydrogenation products and are formed in the second part of the reaction: Glucose hydrogenation forms Sorbitol and Methylglucose hydrogenation forms Sorbitol and Methanol.

For big amounts of catalyst was expected big conversion and great amounts of Sorbitol. Although the same problem than in Cellobiose hydrogenation occurred. This means that not only the yield of Sorbitol decrease but also the conversion of Methylcellobiose decrease (table 18). This can have for the same four reasons that were already explained: deposit of some catalyst, some sugar can be remained in the filter, poisoning of the catalyst and/or wrong approximations during the yields calculates.

For big reaction times, Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$ also has a problem. Table 20 presents the influence of the reaction time in that hydrogenation and after two hours of reaction the yield of Sorbitol and Methylcellobiose conversion start decreasing. It can happen for two different reasons: first, the catalyst could be poisoning because a lot of by-products were formed. Secondly, mistakes in the yields calculate once they have a lot of approximations.

Methylcellobiose hydrogenation in water requires high temperatures. This means that did not have reaction for fewer temperatures than 130ºC (figures 38 and 39) even with big amounts of catalyst or big reaction times. Figures 38 and 39 only have one peak and when some Methylcellobiose was injected into this system, it as increasing. So, this is a Methylcellobiose peak. Methylcellobiose needs strong conditions to react. At 130ºC, some Methylglucose, Glucose and Sorbitol were found (table 21). This has a very complex chemistry explanation. The –OH group from Cellobiose instead of $–OCH_3$ group from Methylcellobiose can have two positions: α and β. These two forms give less stability into the molecule and hydrogenation is easier.

The way that Cellobiose and Methylcellobiose hydrogenation occurs can answer the goal of this project. So, after analyzing all the last results, hydrogenation mechanism is known. However, the hydrogenation mechanism is different between $ZnCl_2.4H_2O$ and H_2O. For Cellobiose and Methylcellobiose in $ZnCl_2.4H_2O$ the reaction starts with a hydrolysis of each compound and the oxygen bond between the two rings broke. For Cellobiose, two molecules of Glucose were formed, or, for Methylcellobiose, one molecule of Glucose and one molecule of Methylglucose were created. Then, the hydrogenation attacks the oxygen bond in each ring (Glucose and/or Methylglucose) and some Sorbitol is formed. For Cellobiose and Methylcellobiose in H_2O, the reaction has different answer in both compounds. In Cellobiose, the oxygen bond in one of the rings breaks and Glucose-Sorbitol was formed. In Methylcellobiose, only at high temperatures have reaction and the same products than in $ZnCl_2.4H_2O$ were formed: Glucose and Methylglucose in the first step and Sorbitol when some Glucose and Methylglucose exist into the system.

5 Conclusions

Biomass conversion process has been worked over time. This is a very complex system that has several conversion options. During this project only a part of Cellulose (one of the three main components of biomass) has been studied. I have used a simpler model component of Cellulose, called Cellobiose, and I was expecting that the same conversion reactions could be possible. I was interesting in study if these reactions were faster and if conversion was easier. However, it was only possible to analyze if the same reactions could be done. Cellobiose could be converted with the same reactions than Cellulose. To analyze the speed of the reactions and the ease of that, more reactions should be done in the future. The results were not enough to conclude this affirmation.

Methylcellobiose is less reactive than Cellobiose. It is more difficult to hydrolyzed and hydrogenated, and besides did not completely dissolve in high concentrations of zinc chloride ($ZnCl_2.2H_2O$), had a slowly dissolutions in the other solvents in respect to Cellobiose.

The reaction network to produce Sorbitol (or Glucitol) is presented in figures 40 and 41:

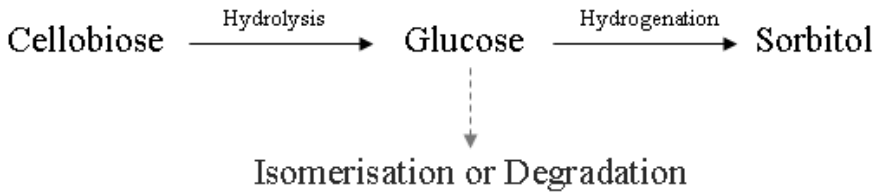

Figure 40 – Reaction network to form sorbitol.

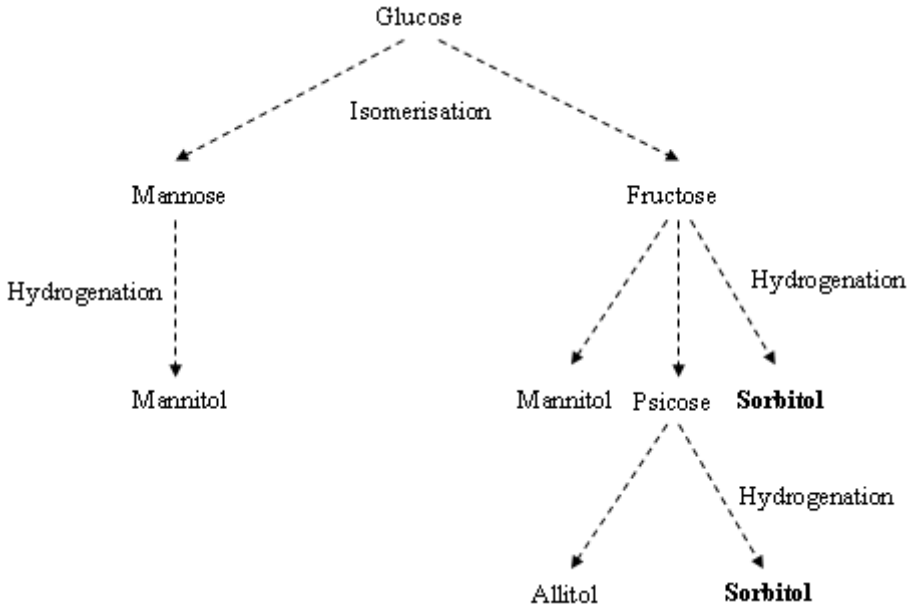

Figure 41 – Secondary step from reaction network: isomerisation and/or degradation reactions from Glucose.

Sorbitol can be produced from hydrogenation of Glucose or, when some Glucose degradation or isomerisation occurs, hydrogenation of Fructose and Psicose also form Sorbitol.

The mechanism of hydrolysis and hydrogenation reactions of Cellobiose and Methylcellobiose are also already known. During the hydrolysis, the mechanism is the same for both compounds. So, it breaks the oxygen bond between the two rings.

Hydrogenation mechanism is different between $ZnCl_2.4H_2O$ and H_2O. For Cellobiose and Methylcellobiose in $ZnCl_2.4H_2O$ the reaction starts with a hydrolysis of each compound and the oxygen bond between the two rings broke. For Cellobiose, two molecules of Glucose were formed, or, for Methylcellobiose, one molecule of Glucose and one molecule of Methylglucose were created. Then, the hydrogenation attacks the oxygen bond in each ring (Glucose and/or Methylglucose) and some Sorbitol is formed. In H_2O, the reactions have different answers in both compounds. In Cellobiose, the oxygen bond in one of the rings breaks and Glucose-Sorbitol (figure 42) was formed.

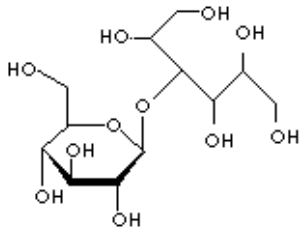

Figure 42 – Structural molecule of Glucose-Sorbitol.

In Methylcellobiose, only at high temperatures have reaction and the same products than in $ZnCl_2.4H_2O$ were formed: Glucose and Methylglucose in the first step and Sorbitol when some Glucose and Methylglucose exist into the system.

6 Recommendations

Biomass conversion is a very promise area and a lot of things are still under discovered. A lot of questions have no answered yet. So, in order to improve the work in that theme I would like to purpose some studies.

Different hydrogenations conditions can be studied than what was already done. More reactions with different amounts of catalyst (Ru/C) between the two limits (0,025g and 0,25g) should be study once we need more points to understand the evolution of the yield of sorbitol during the process.

Still in hydrogenation reactions, can be a good work try different catalysts, for example Cu/Cr. It could be a good catalyst once it was already used in some sugars hydrogenations.

Improve the studies of Cellobiose hydrogenation in Water could have good yields of Sorbitol if the C-O bond in Glucose-Sorbitol will be break. However, high amounts of catalyst and high reaction times were not enough to break this bond. This can form a lot of Sorbitol once the Cellobiose conversion is near one hundred percent.

During this work not only the influence of the temperature has been studied, but also the amount of catalyst and the reaction times. However, all the reactions were done at 40 bar H_2. So, it can have good results if some reactions with both solvents at different pressures can be done.

Once we did not finish all of purposed work, after improve hydrogenation conditions, the next reactions steps should be study: Isosorbide is a component with great importance for fuel or chemicals. So, a combination between hydrolysis and hydrogenation can be a good step and also Glucitol dehydration.

Acknowledgments

First of all, I would like to thank my supervisor Jianrong Li for all of her attention since my first day in Delft. I also would like to thank her for shared her knowledge with me and help me during my experimental and theoretical work everyday.

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I would like to thank some friends: Diogo Henriques for his help and availability during my project, especially when I worked with Matlab; João Martins for help me to improve my English; and Joana Carneiro for her help with my life in Delft and also with the structure of my report.

I cannot forget Harrie and Kevin that help me and Jianrong when we received the new setup.

I would like to share my satisfaction with all the students and workers in our group. They are really nice people with who I spent great moments.

Last but not the least, I would like to say thank you to my parents for their support during my life in Delft and for incentivise me to have this wonderful experience (ERASMUS).

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Appendix

A Calibration

For the calibration different concentrations of Cellobiose and Methylcellobiose in Water and 70% Zinc Chloride diluted in Water were used. Each solution had 5,0g with different amounts of raw material (Cellobiose or Methylcellobiose). However, the results only give information about the position of Cellobiose and Methylcellobiose in Water and in Zinc Chloride. They do not have a meaning in calibration.

Cellobiose and Methylcellobiose have a retention time near with Water and 70% Zinc Chloride but the peaks are asymmetric. For Cellobiose, they are not symmetric in the right side of the peak so, Cellobiose should have a bigger retention time than these solvents. On the other hand, for Methylcellobiose the peaks are not symmetric in the left side. Methylcellobiose should have a smaller retention time than Water and 70% Zinc Chloride.

As these results have no meaning to the calibration, some solutions were done with different dissolved solution. They were diluted in mobile phase ($Ca(NO_3)_2.4H_2O$) – figures 43-46. The calibration was done twice (in March and in June) because after two months of work the column was changed.

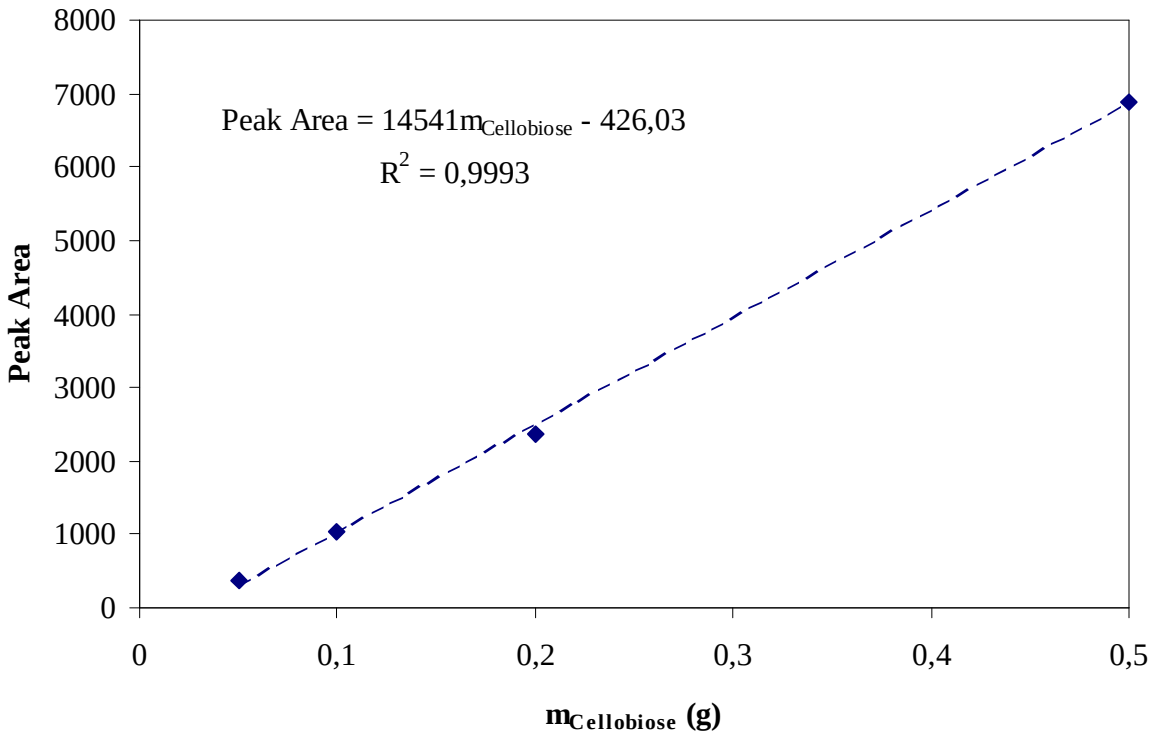

Figure 43 – Calibration of Cellobiose in water, diluted in mobile phase (March 2009).

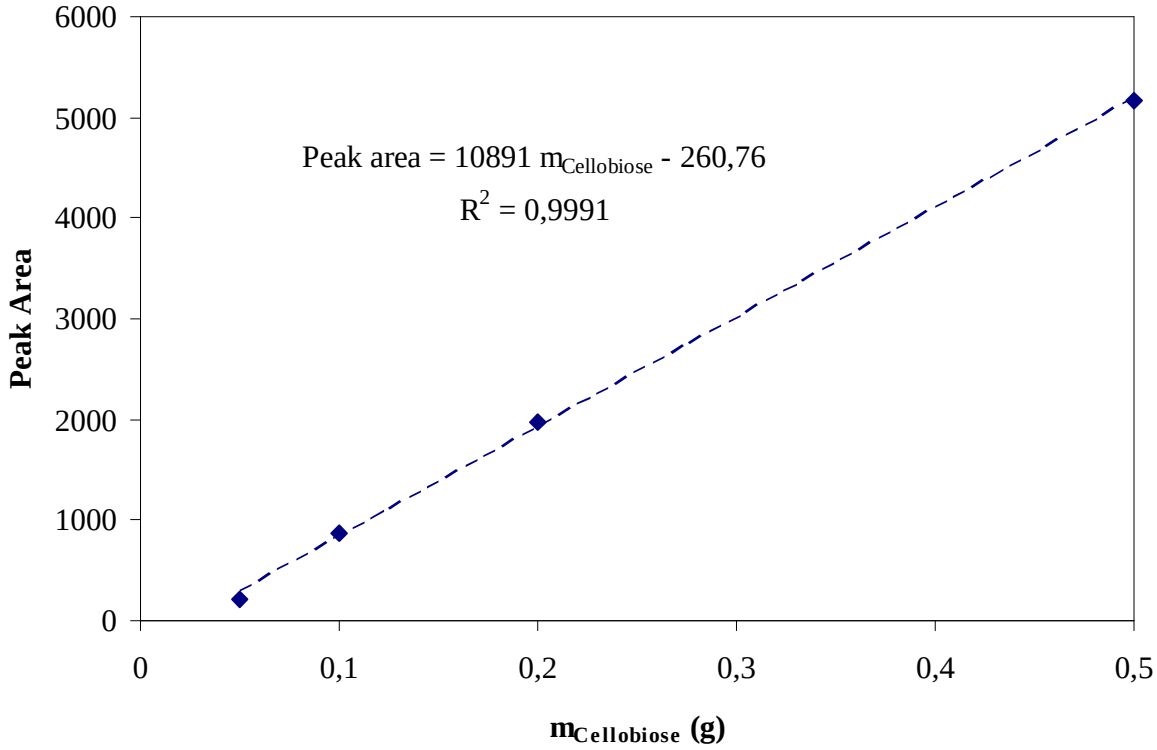

Figure 44 - Calibration of Cellobiose in water, diluted in mobile phase (June 2009).

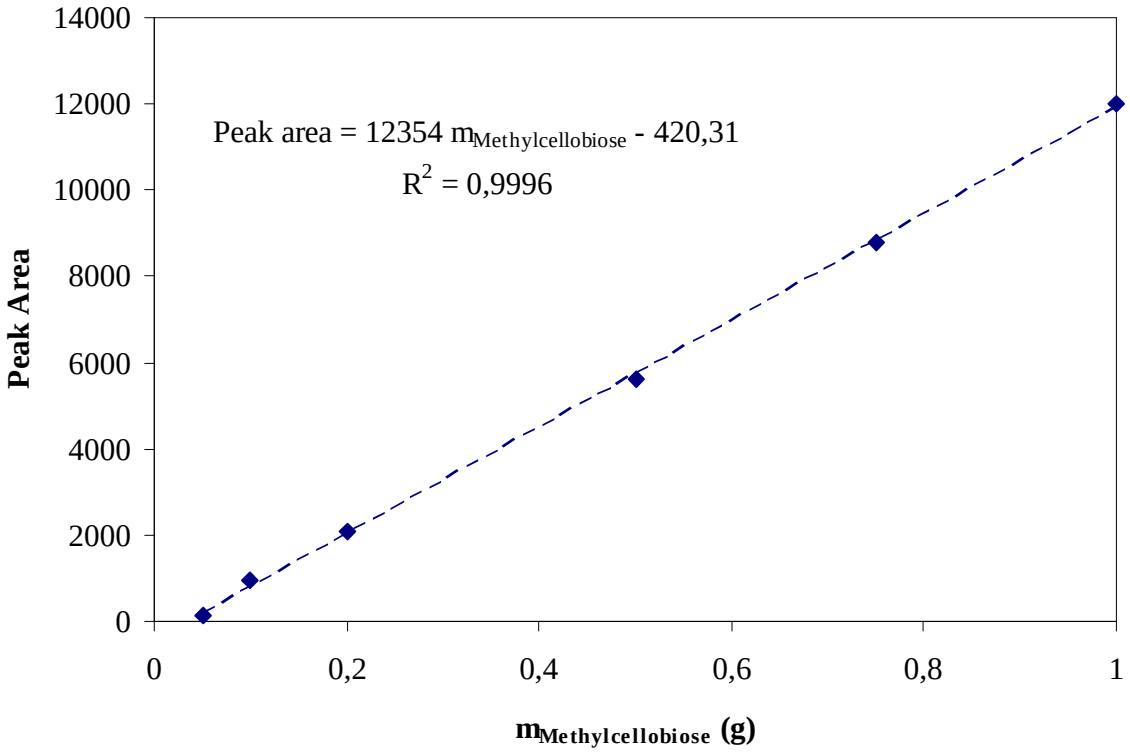

Figure 45 – Calibration of Methylcellobiose in water, diluted in mobile phase (March 2009).

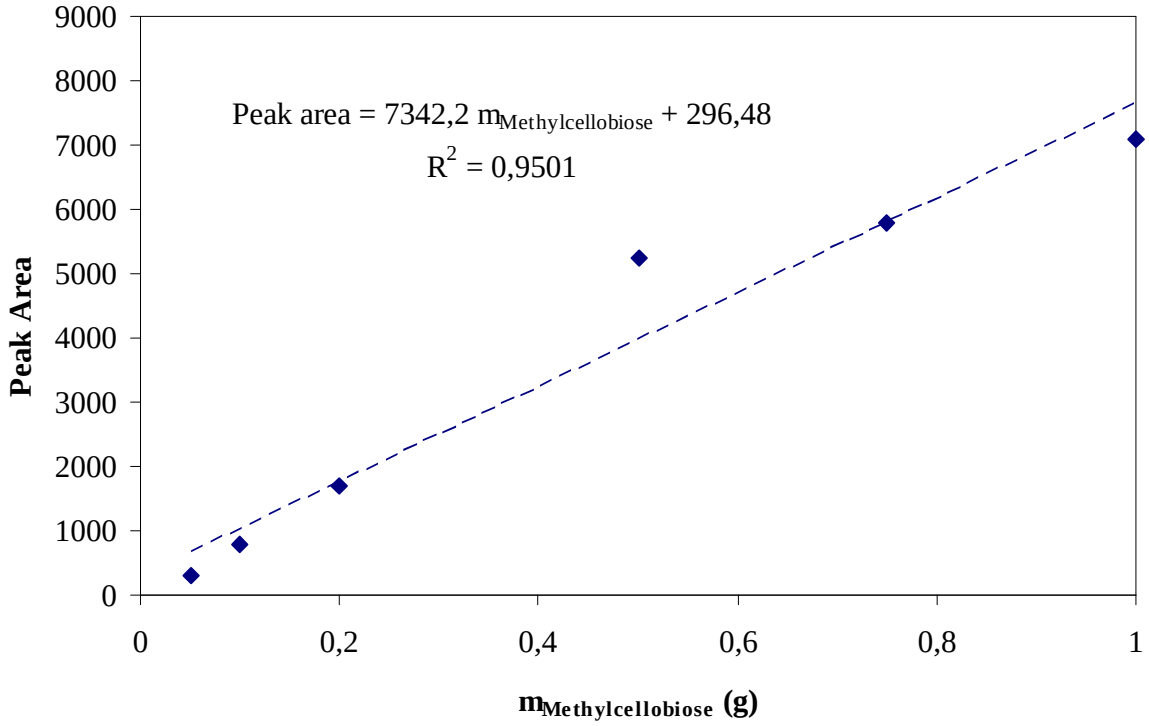

Figure 46 - Calibration of Methylcellobiose in water (June 2009).

B Hydrolysis reactions

Some chromatograms from hydrolysis reactions and some secondary are presented in this section.

Figures 47 and 48 are the HPLC chromatograms for Cellobiose and Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ at 80ºC.

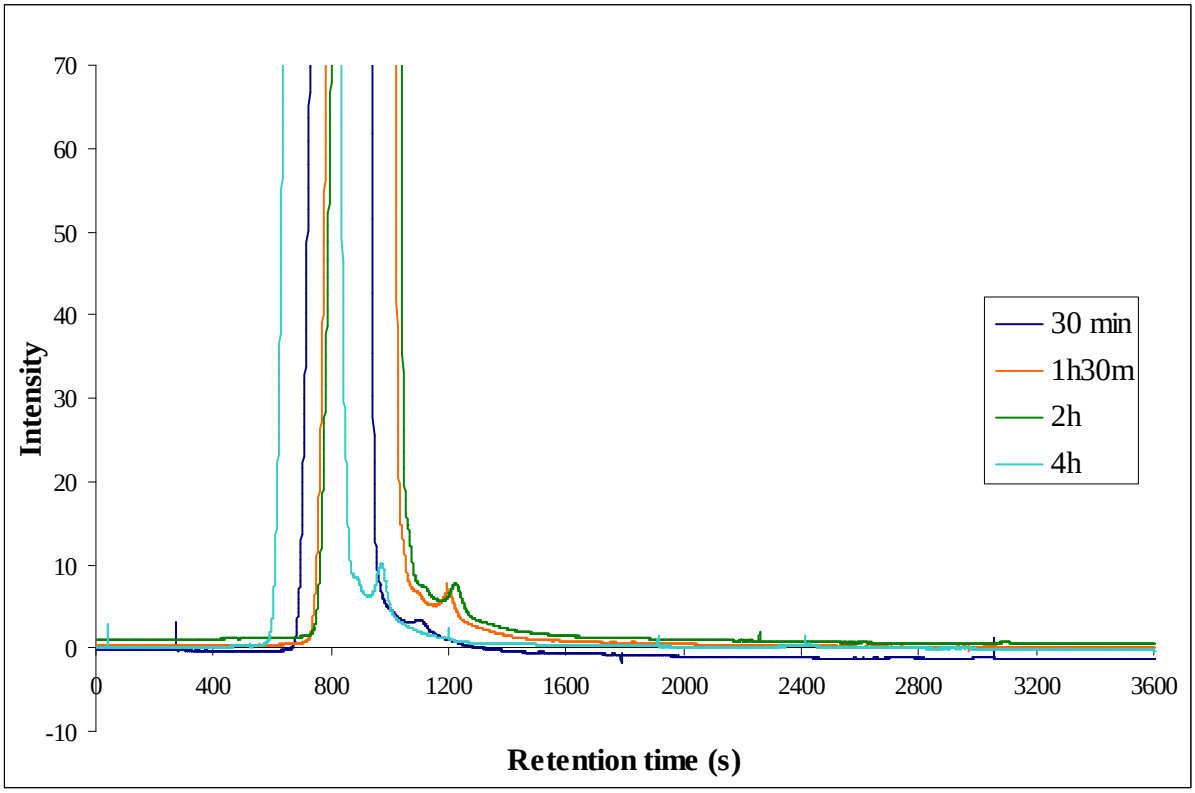

Figure 47 - Cellobiose hydrolysis in $ZnCl_2.4H_2O$ at 80ºC and 30 bar N_2.

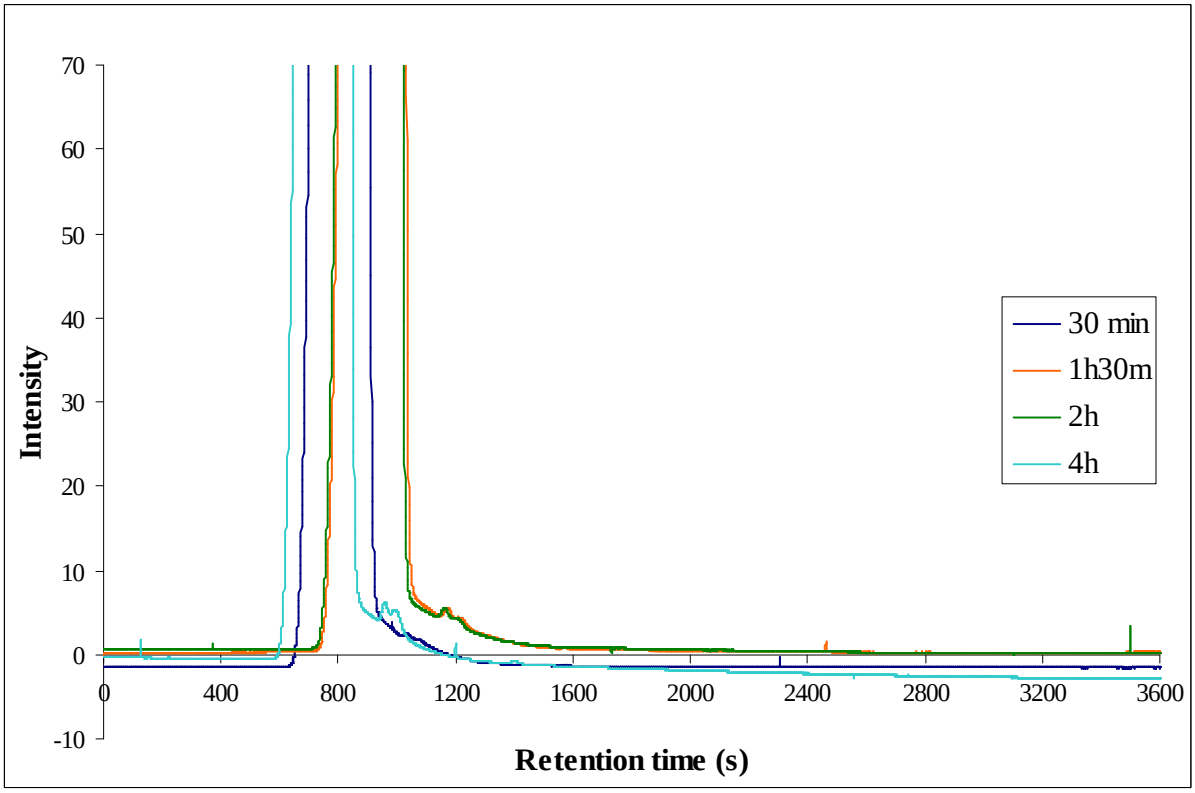

Figure 48 - Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ at 80ºC and 30 bar N_2.

The same reactions were done for 100ºC (figures 49 and 50).

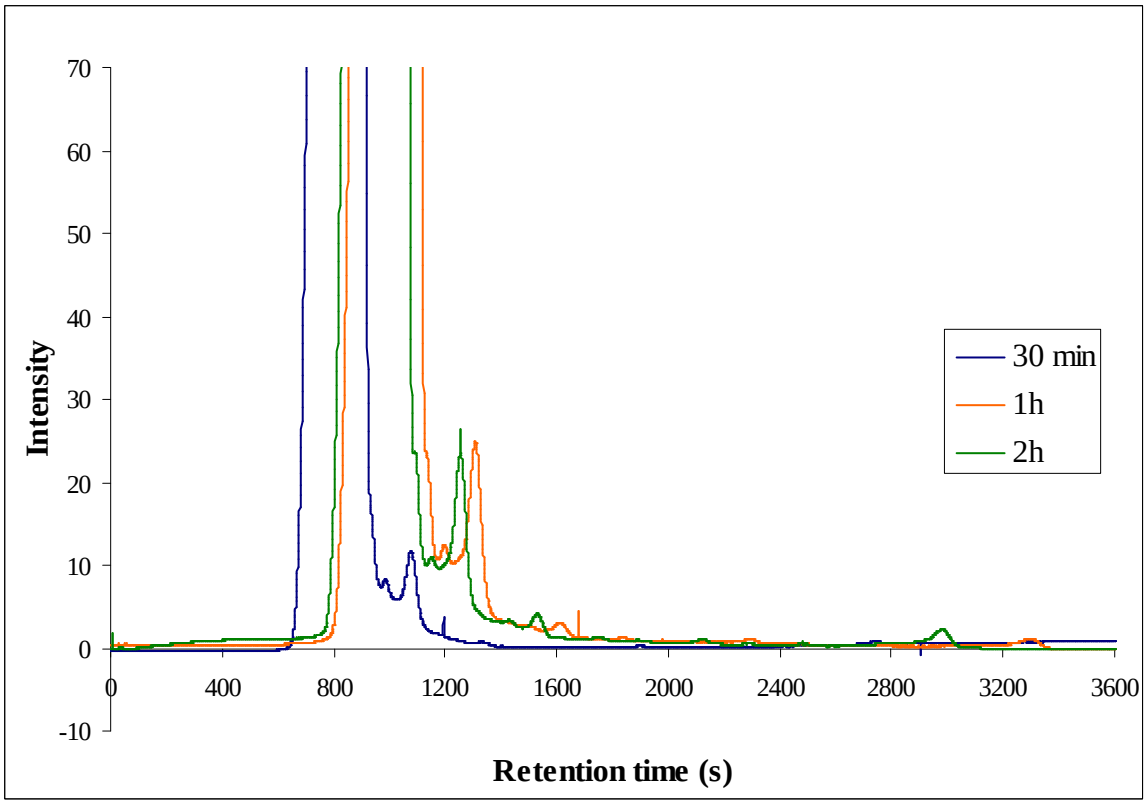

Figure 49 - Cellobiose hydrolysis in $ZnCl_2.4H_2O$ at 100ºC and 30 bar N_2.

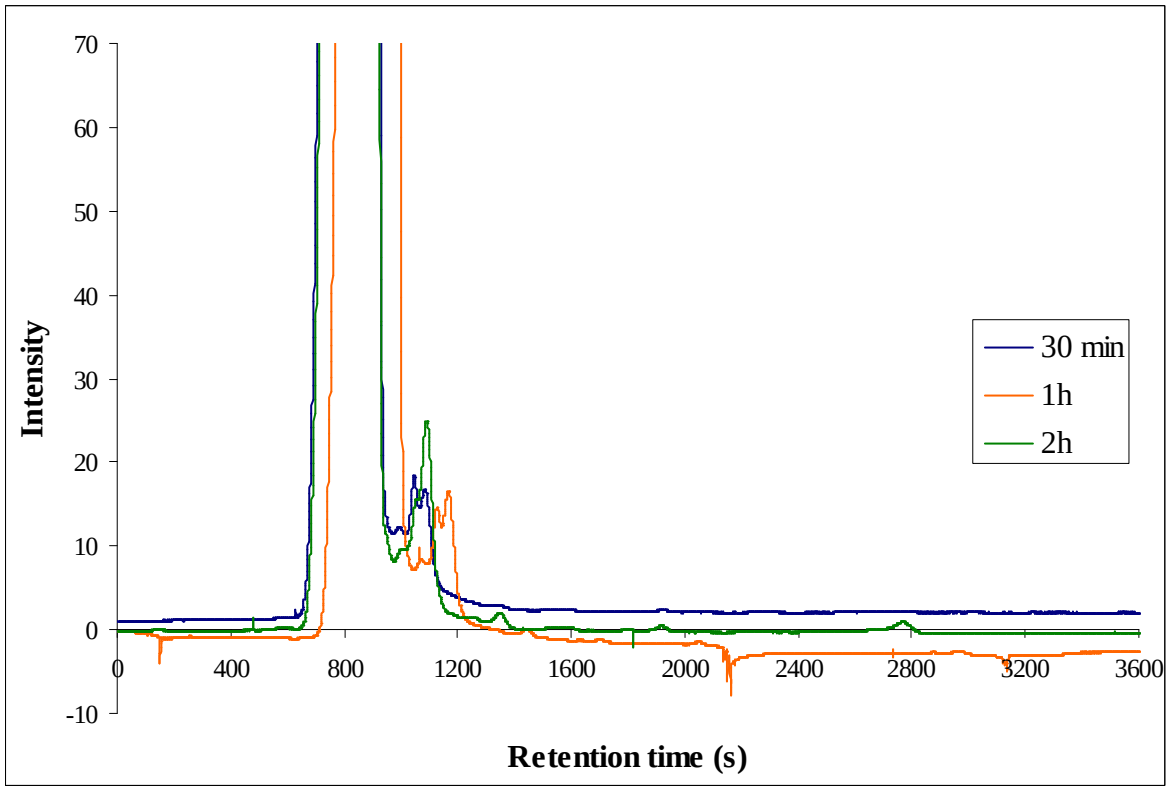

Figure 50 - Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ at 100ºC and 30 bar N_2.

At 130ºC, the results are presented in figures 51 and 52.

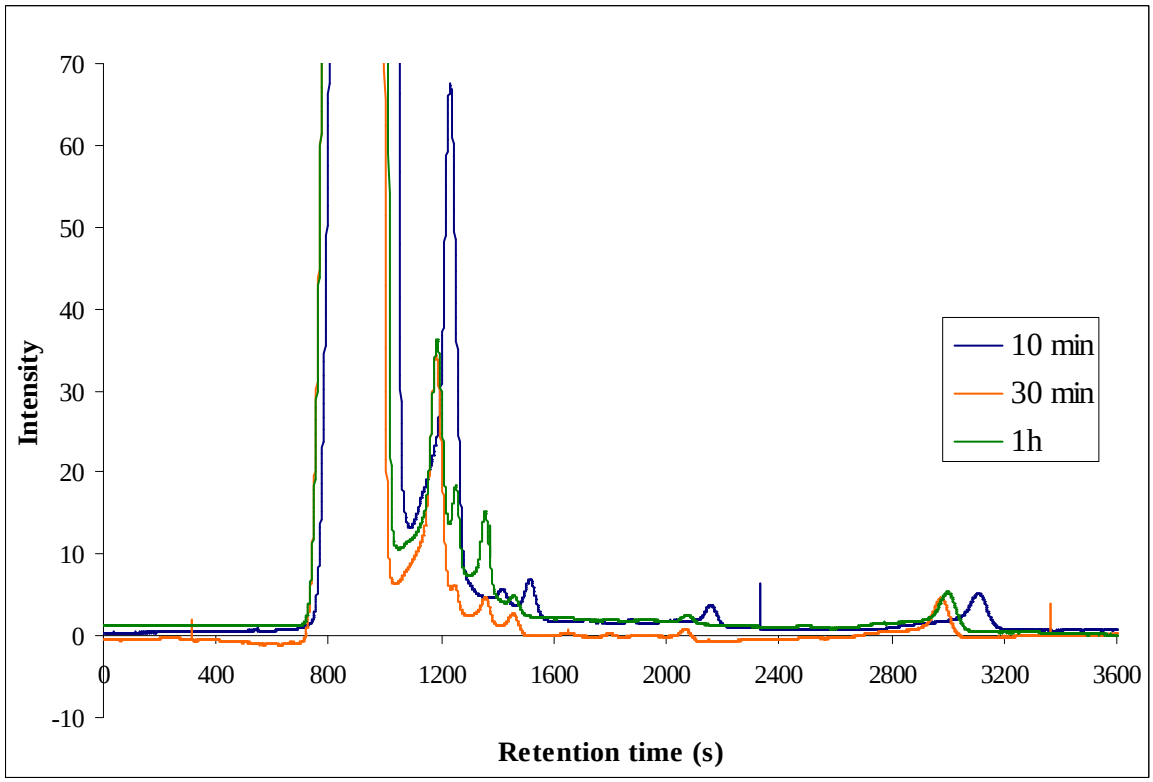

Figure 51 - Cellobiose hydrolysis in $ZnCl_2.4H_2O$ at 130ºC and 30 bar N_2.

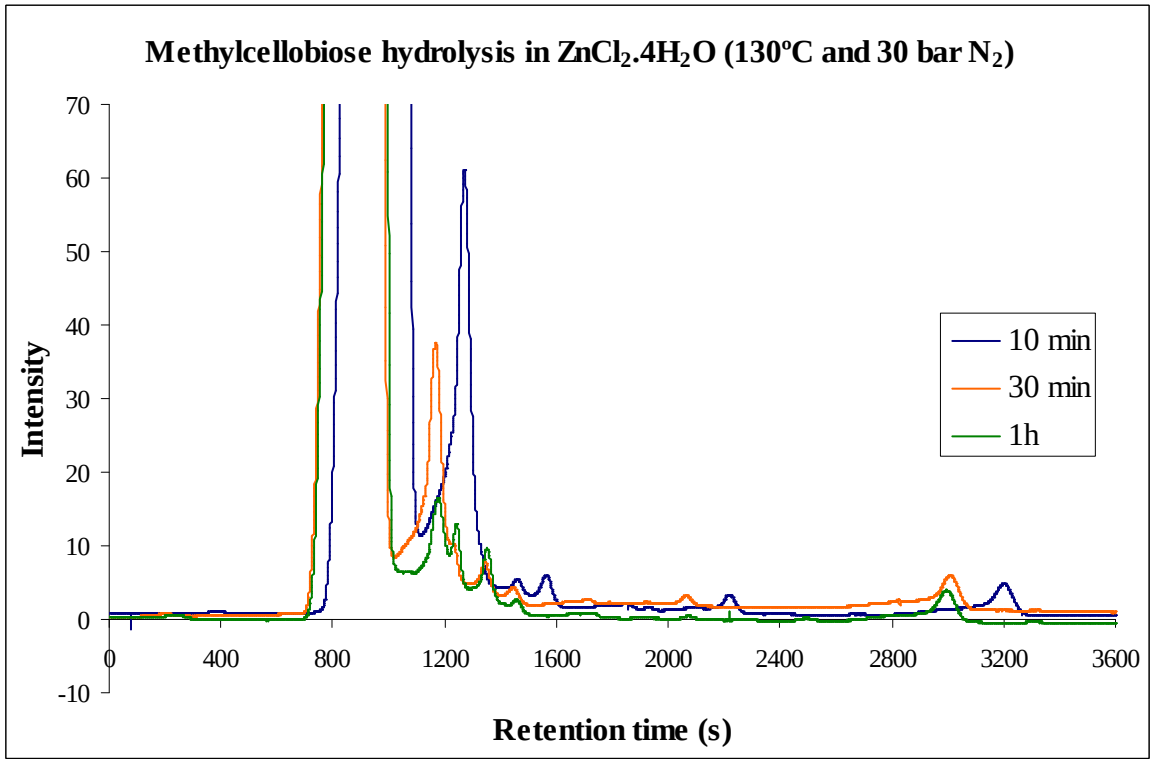

Figure 52 - Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ at 130ºC and 30 bar N_2.

At high temperatures (100 or 130ºC) more peaks than Glucose peak are found. For 80ºC only have Glucose peak. As between 80 and 100ºC have a big temperature gradient

(20ºC), Cellobiose and Methylcellobiose hydrolysis at 90ºC were done. This reaction gives information about the minimum temperature to start secondary reactions (figures 53 and 54).

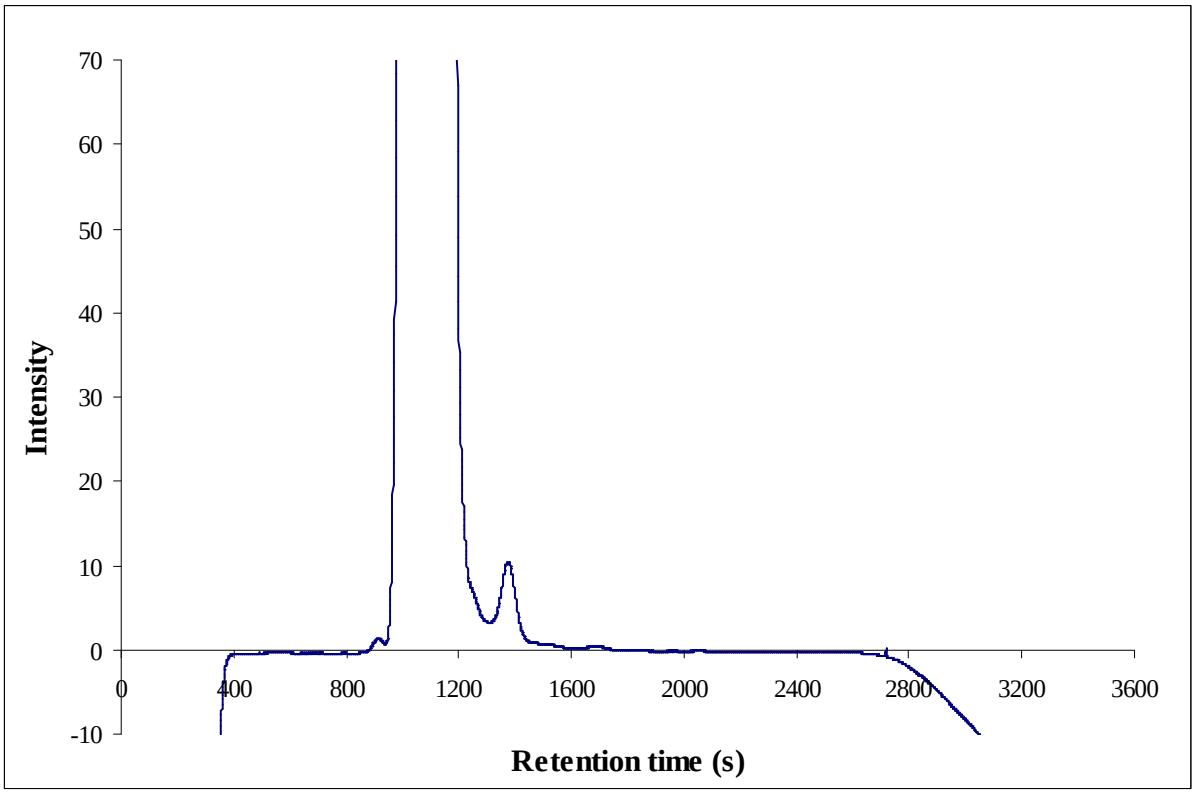

Figure 53 - Cellobiose hydrolysis in $ZnCl_2.4H_2O$ at 90ºC and 30 bar N_2..

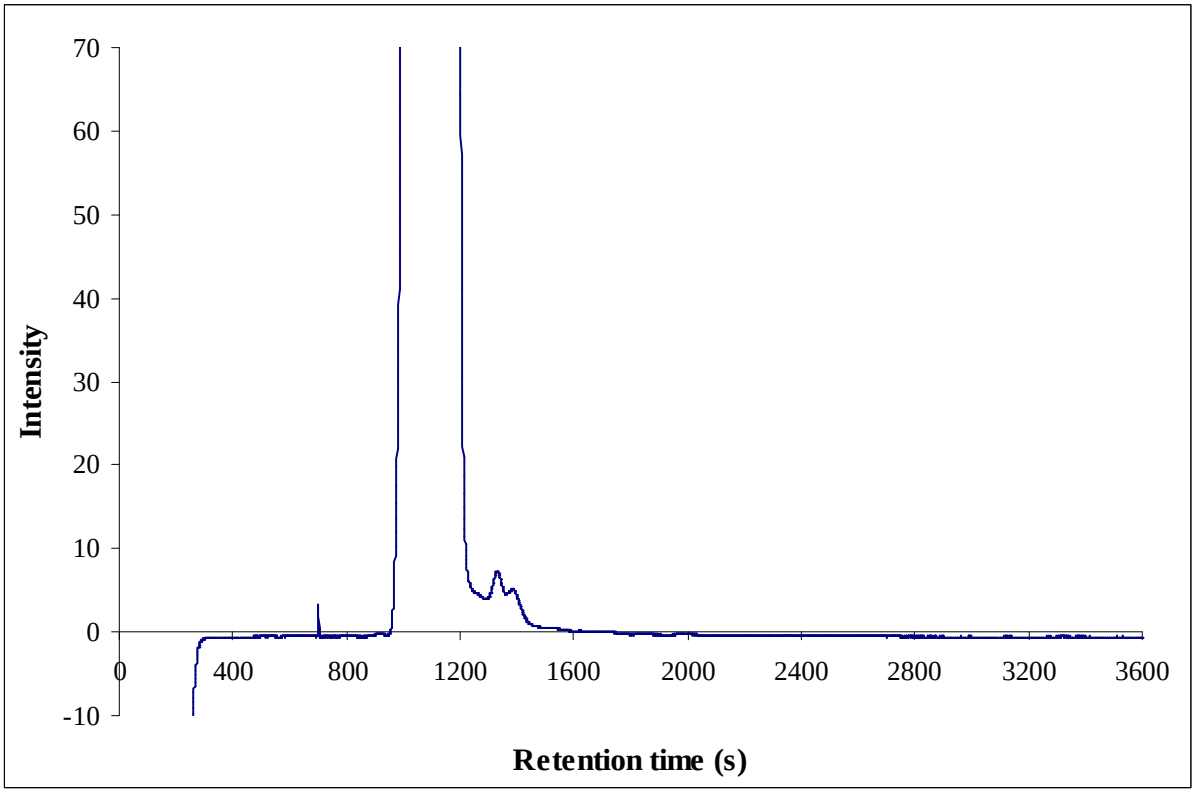

Figure 54 - Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ at 90ºC and 30 bar N_2.

For 90ºC, only one peak was found. This means that secondary steps occurred for high temperatures (upper than 100ºC) and some by-products could be formed. The secondary steps are from Glucose degradation or isomerisation (figures 55 and 56).

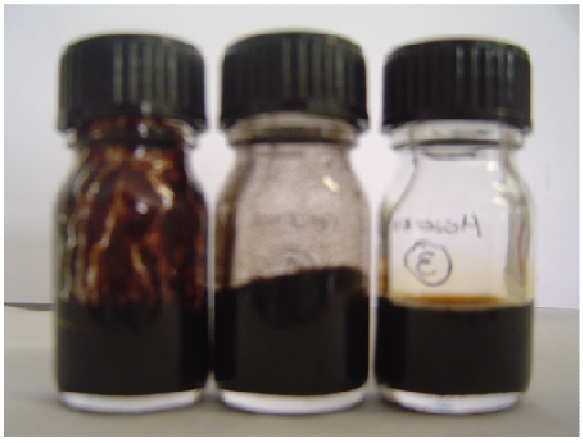

Figure 55 - Final solutions from Glucose stability in $ZnCl_2.4H_2O$ at 100ºC and 30 bar N_2.

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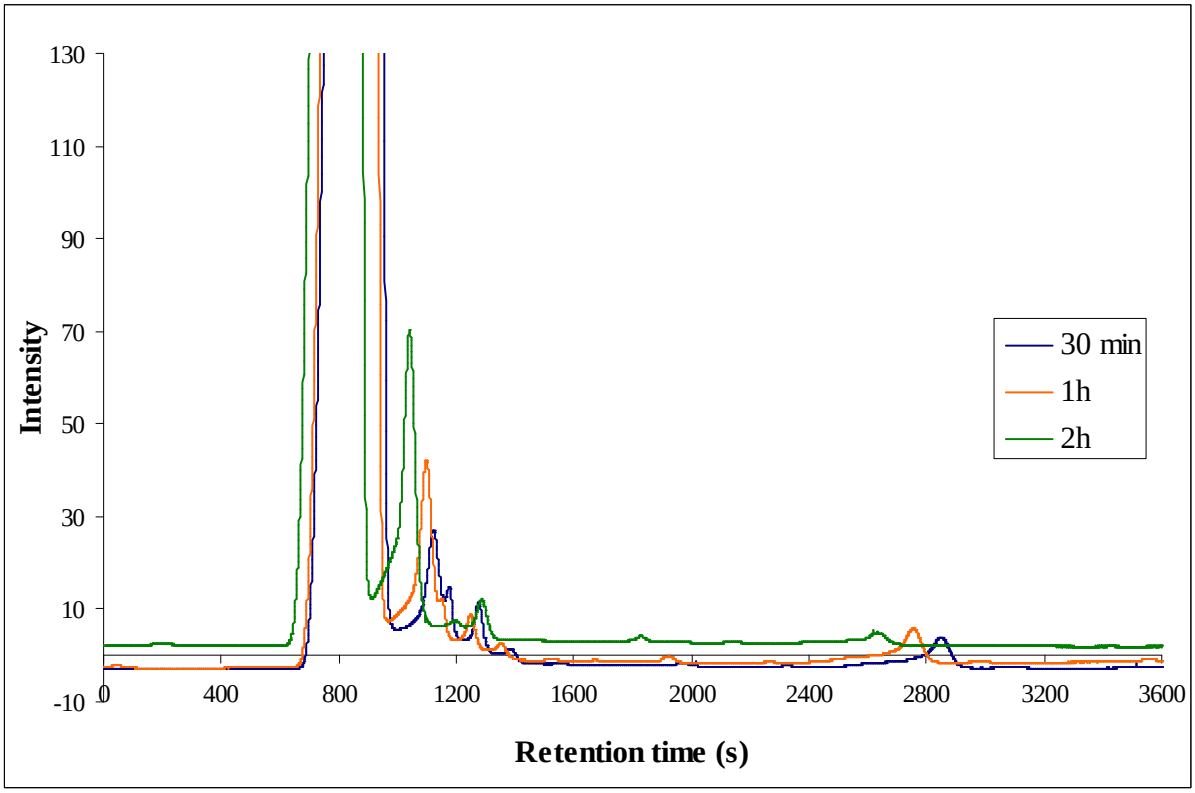


Figure 56 – Glucose stability in $ZnCl_2.4H_2O$ at 100ºC and 30 bar N_2.

At low temperatures (80ºC), Glucose did not have degradation or isomerisation (figures 57 and 58).

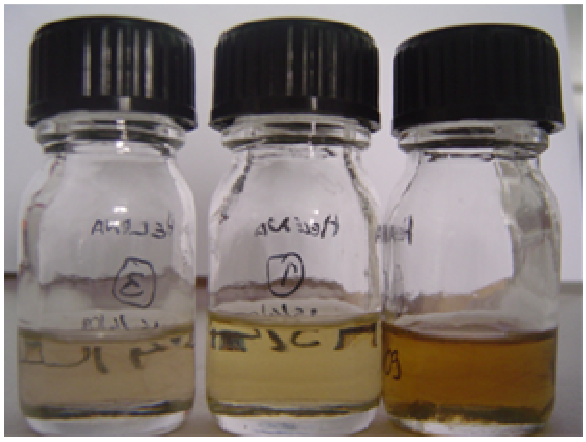
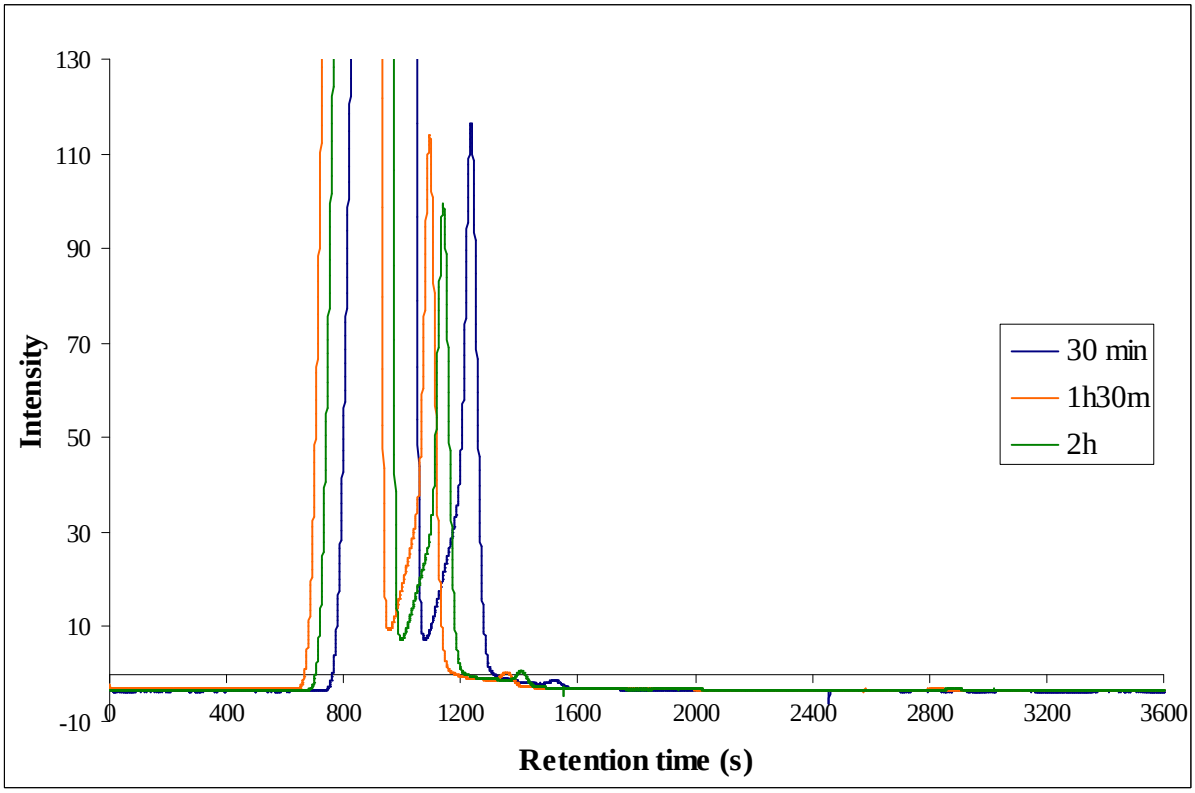


Figure 57 - Final solutions from Glucose stability in $ZnCl_2.4H_2O$ at 80ºC and 30 bar N_2.



.Figure 58 - Glucose stability in $ZnCl_2.4H_2O$ at 80ºC and 30 bar N_2.

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Different Zinc Chloride concentrations and Water as solvents were tested in Cellobiose and Methylcellobiose hydrolysis.

In low zinc chloride concentrations (1% $ZnCl_2$) and in Water both Cellobiose and Methylcellobiose are very stable, they did not react. On the other hand, in high zinc chloride concentrations ($ZnCl_2.2H_2O$), Cellobiose can form a lot of by-products but Methylcellobiose did not completely dissolve because this is a very viscous solvent (figures 59-62).

Figure 59 - Final solutions from Cellobiose hydrolysis at 100ºC in H_2O, 1% $ZnCl_2$, $ZnCl_2.4H_2O$ and $ZnCl_2.2H_2O$.

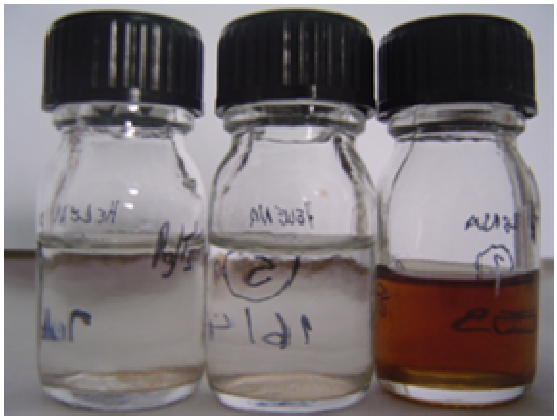

Figure 60 - Final solutions from Methylcellobiose hydrolysis at 100ºC in H_2O, 1% $ZnCl_2$, $ZnCl_2.4H_2O$.

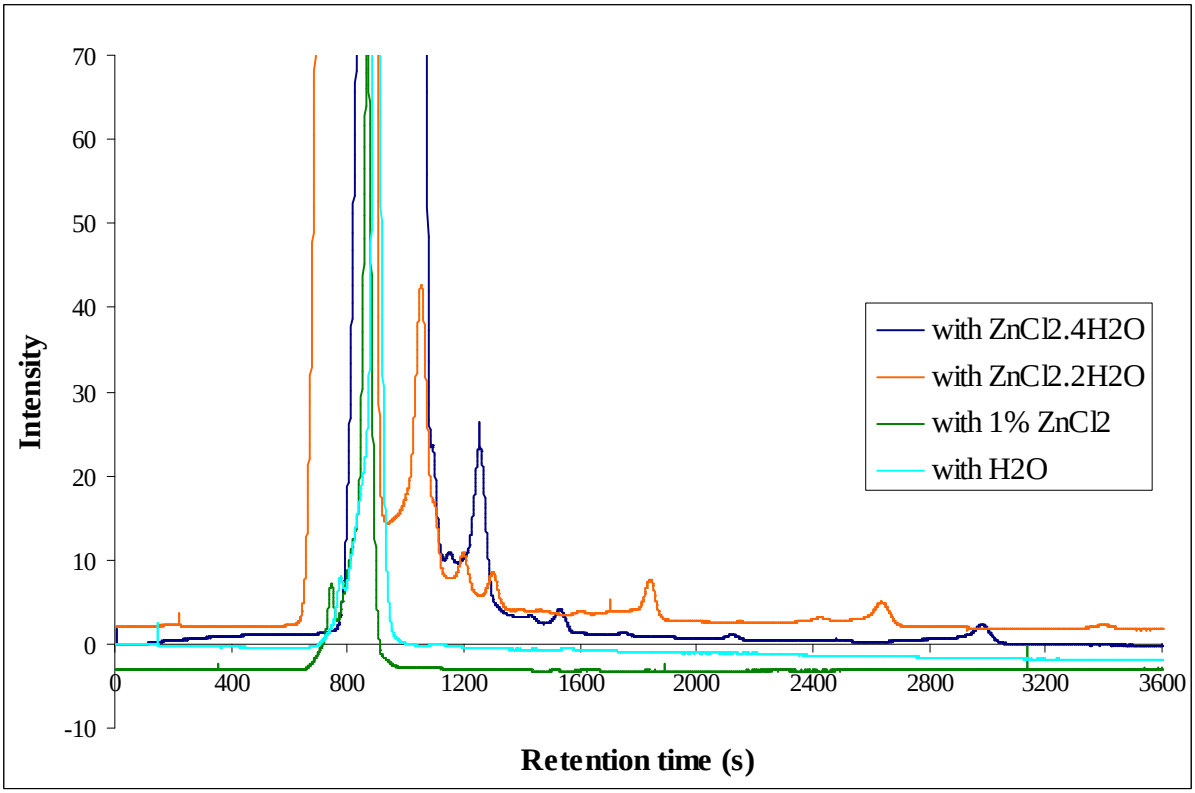

Figure 61 – Cellobiose hydrolysis at 100ºC during 60 minutes and 30 bar N_2. in $ZnCl_2.4H_2O$, $ZnCl_2.2H_2O$, 1% $ZnCl_2$ and H_2O.

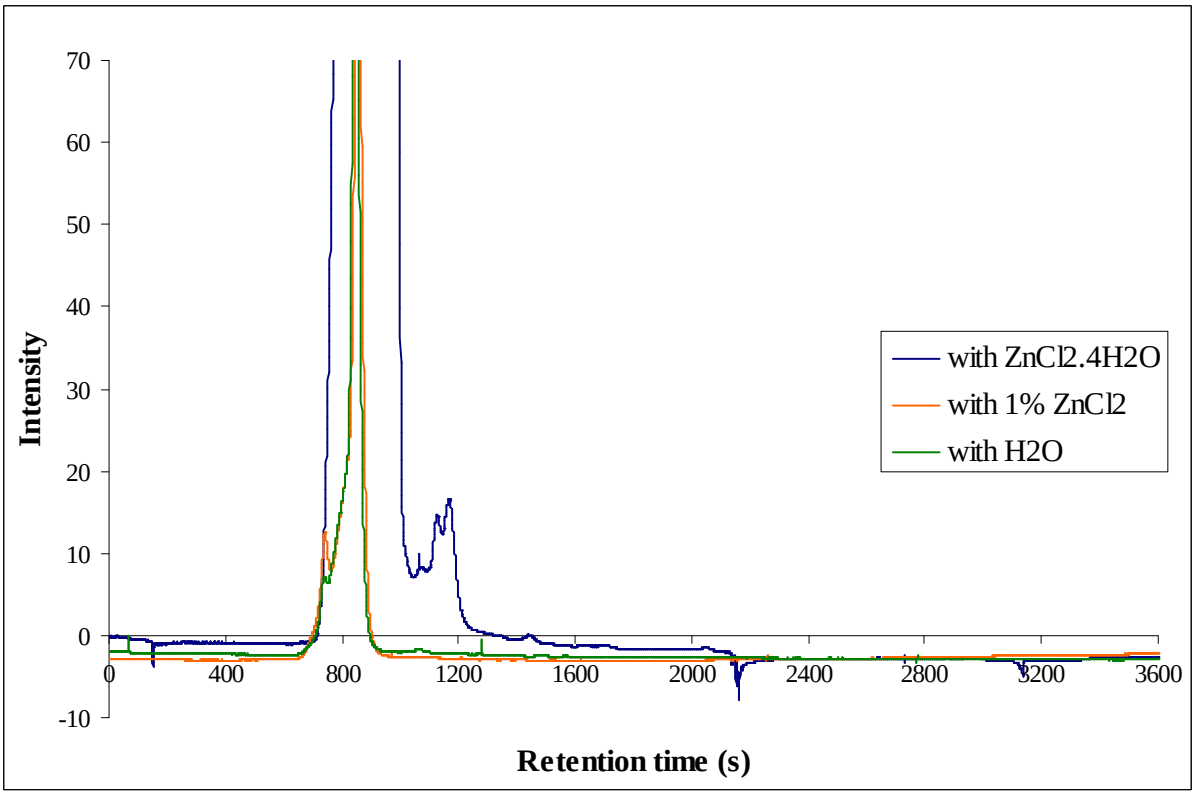

Figure 62 - Methylcellobiose hydrolysis at 100ºC during 60 minutes and 30 bar N_2 in $ZnCl_2.4H_2O$, 1% $ZnCl_2$ and H_2O.

Acidic conditions improve fast reactions and the yield of Glucose and/or Methylglucose have a big increasing (figures 63 and 64).

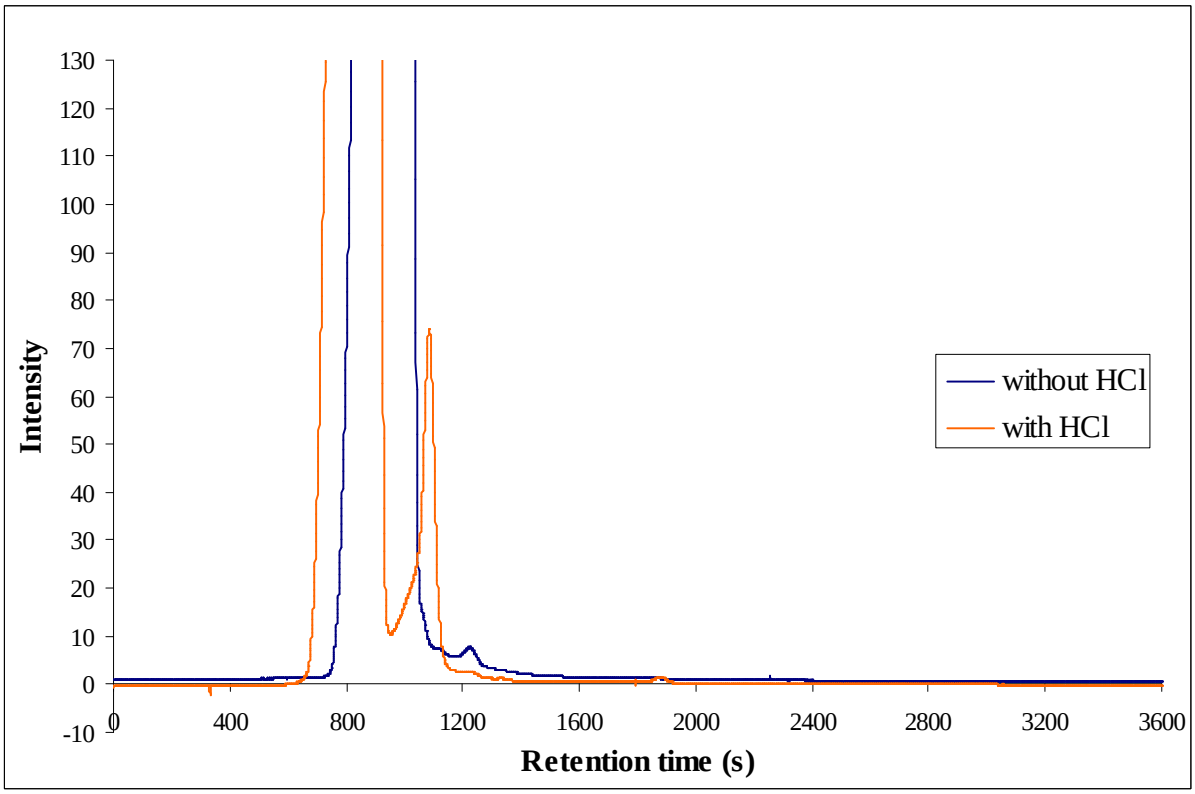

Figure 63 – Influence of acidic conditions in Cellobiose hydrolysis in $ZnCl_2.4H_2O$ at 80ºC and 30 bar N_2.

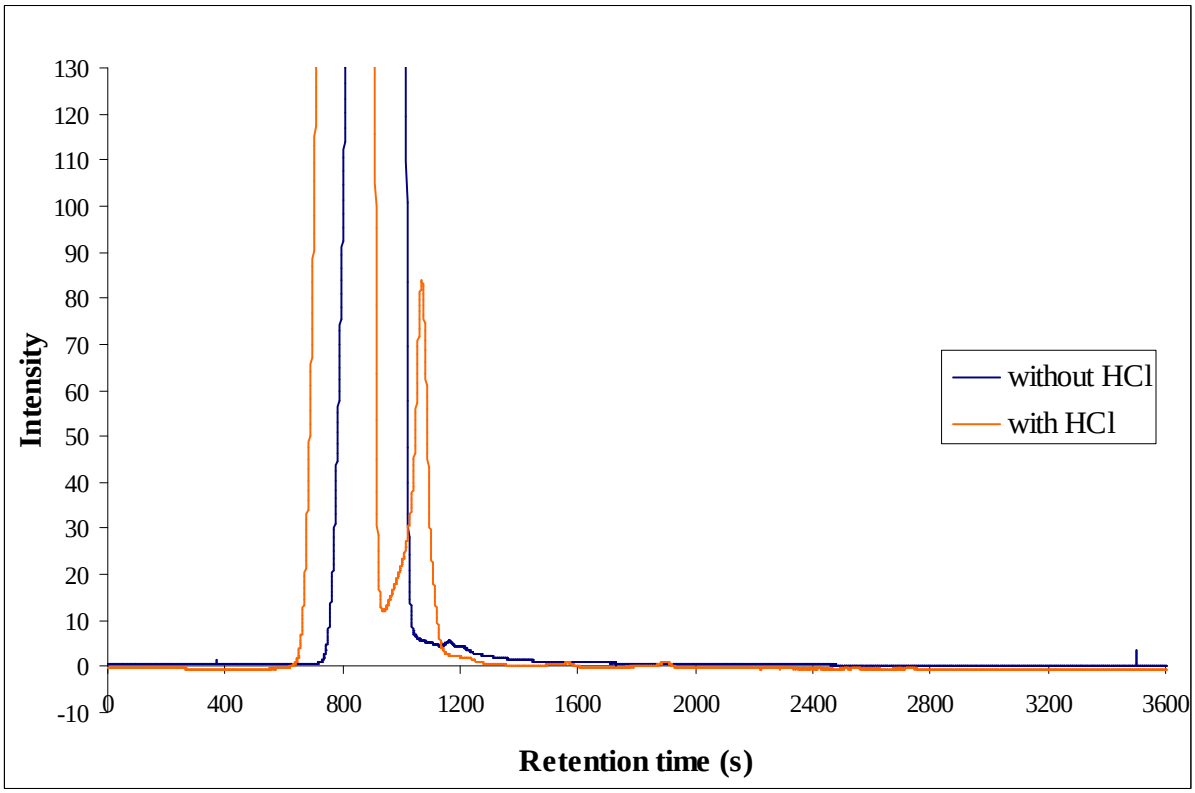

Figure 64 - Influence of acidic conditions in Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ at 80ºC and 30 bar N_2.

$LiCl.4H_2O$ is a light solvent. Cellobiose and Methylcellobiose did not react in these solvent. Different conditions were tested and never have reaction (figures 65 and 66).

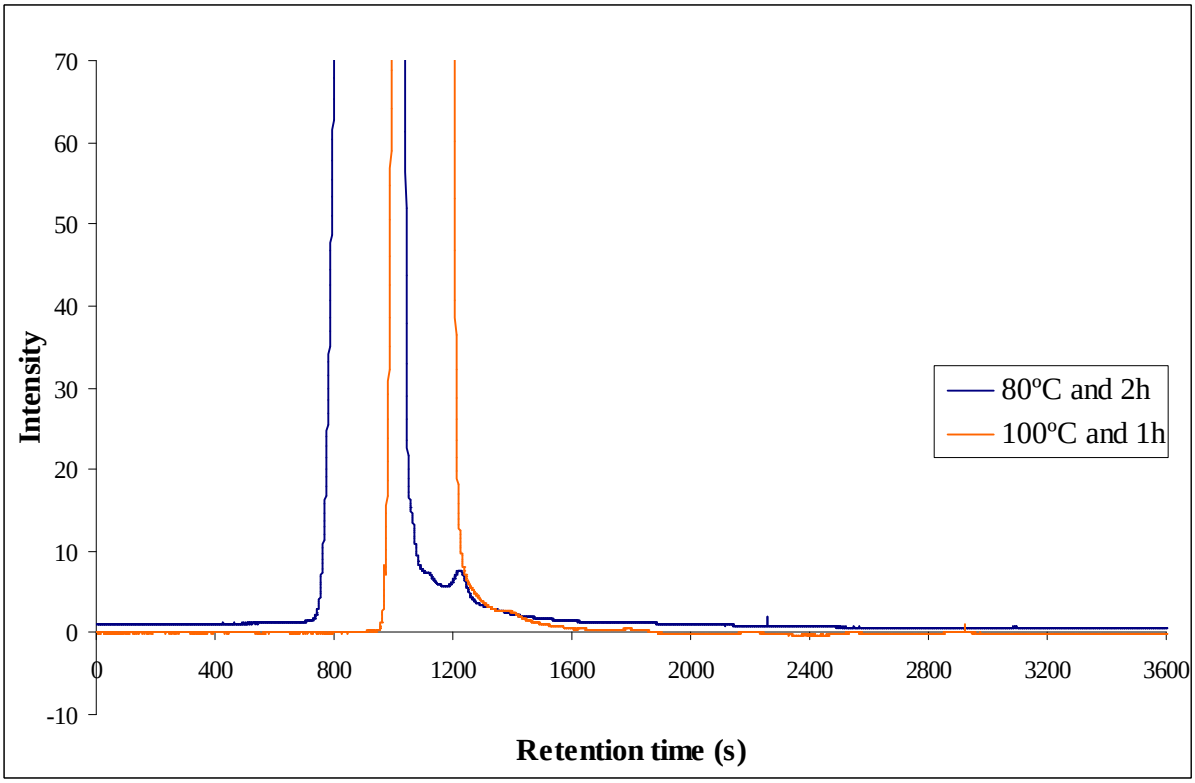

Figure 65 - Cellobiose hydrolysis in $LiCl.4H_2O$ with 30 bar N_2.

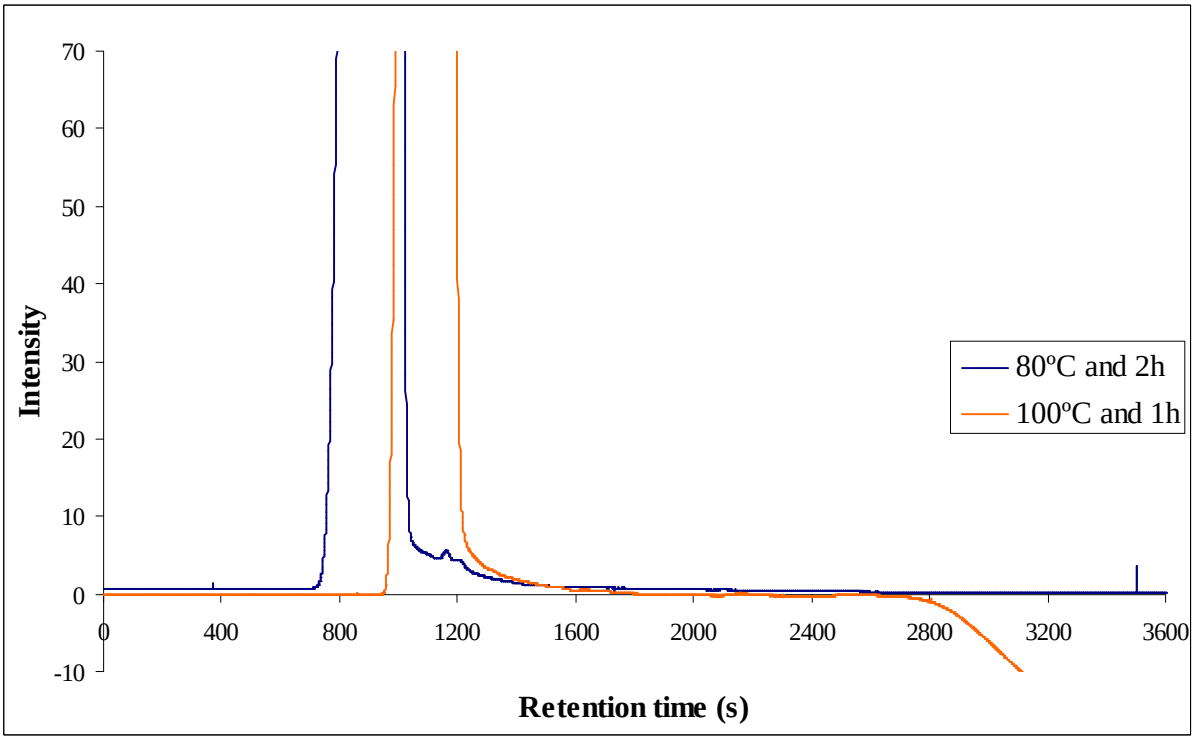

Figure 66 - Methylcellobiose hydrolysis in $LiCl.4H_2O$ with 30 bar N_2..

Figures 67-70 compares Cellobiose and Methylcellobiose hydrolysis in $ZnCl_2.4H_2O$ and in $LiCl.4H_2O$.

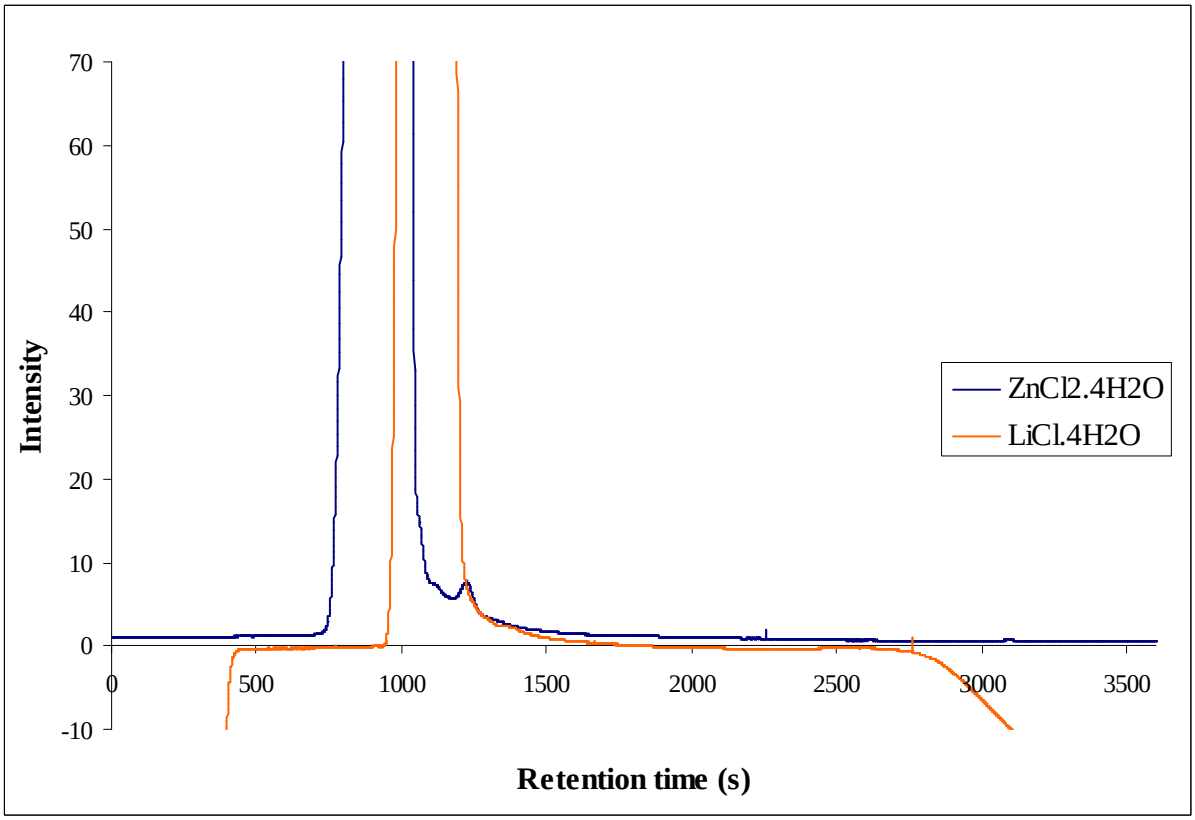

Figure 67 - Cellobiose hydrolysis at 80ºC during 120 minutes and 30 bar N_2.

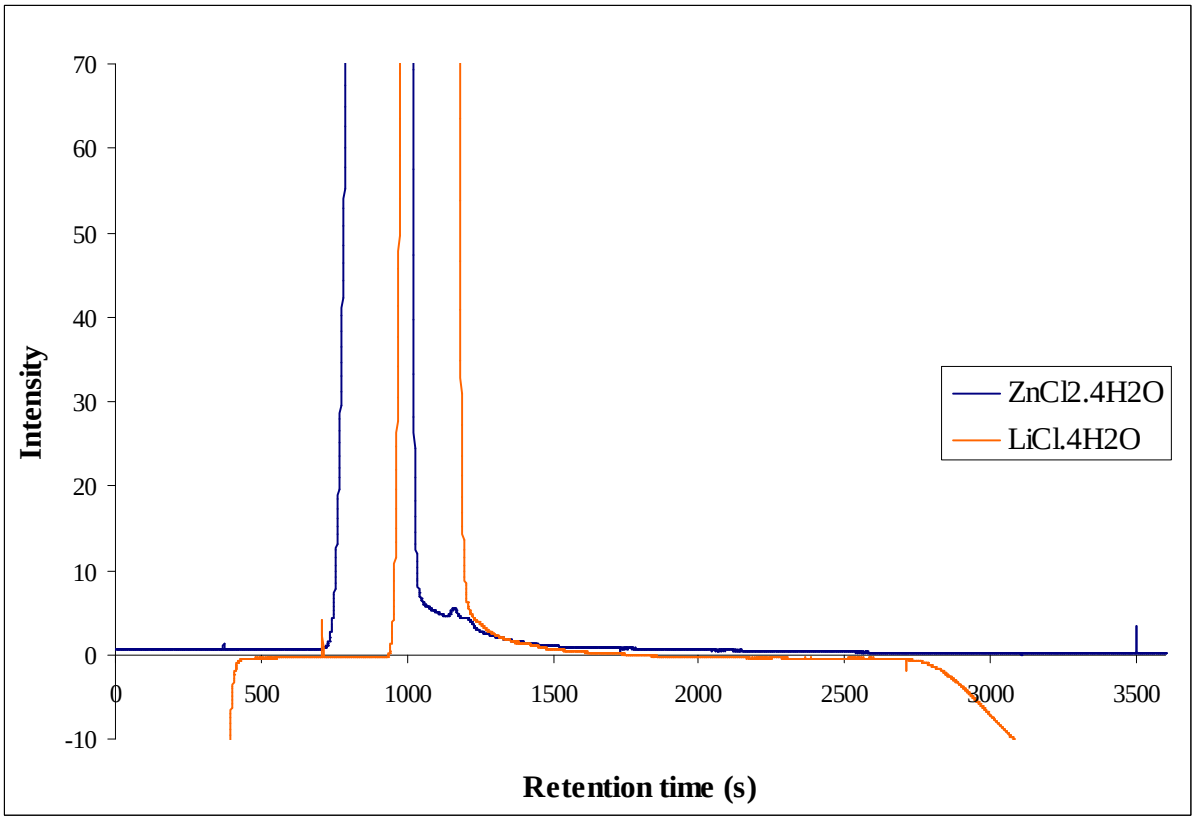

Figure 68 - Methylcellobiose hydrolysis at 80ºC and 30 bar N_2.

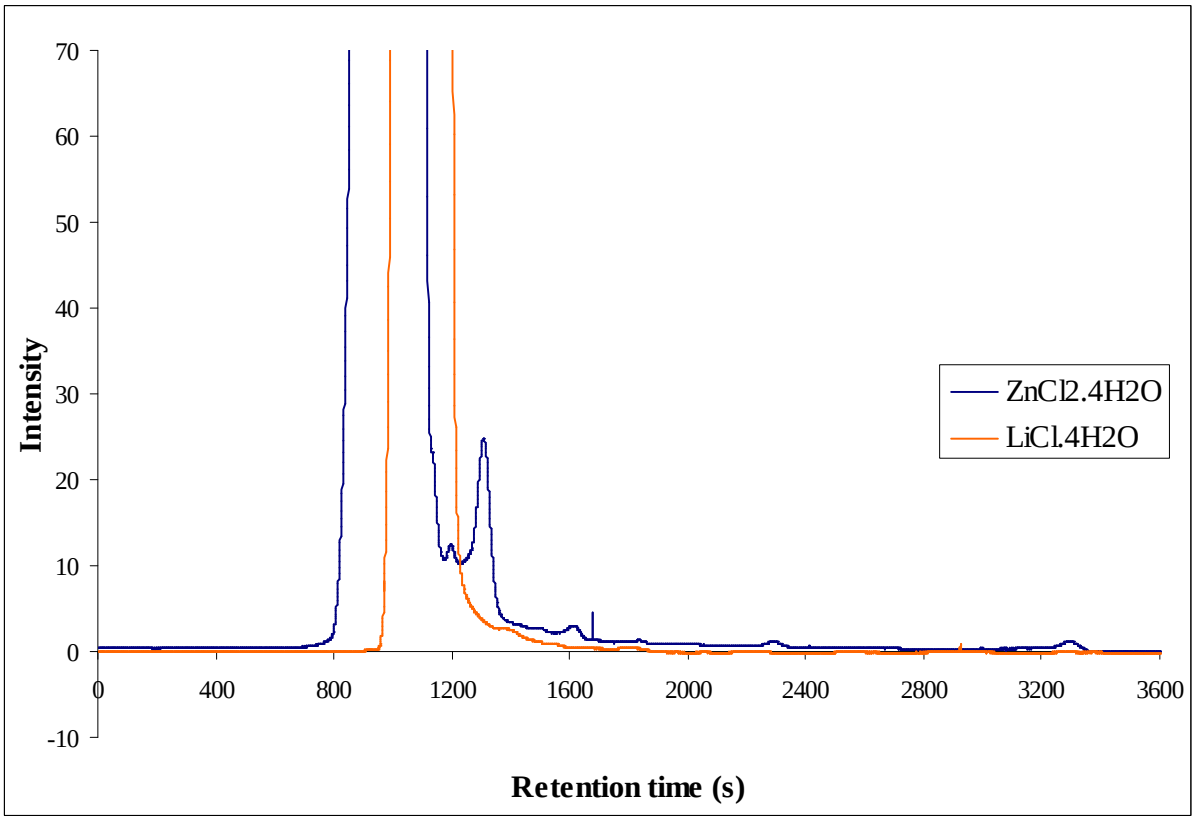

Figure 69 - Cellobiose hydrolysis at 100ºC and 30 bar N_2.

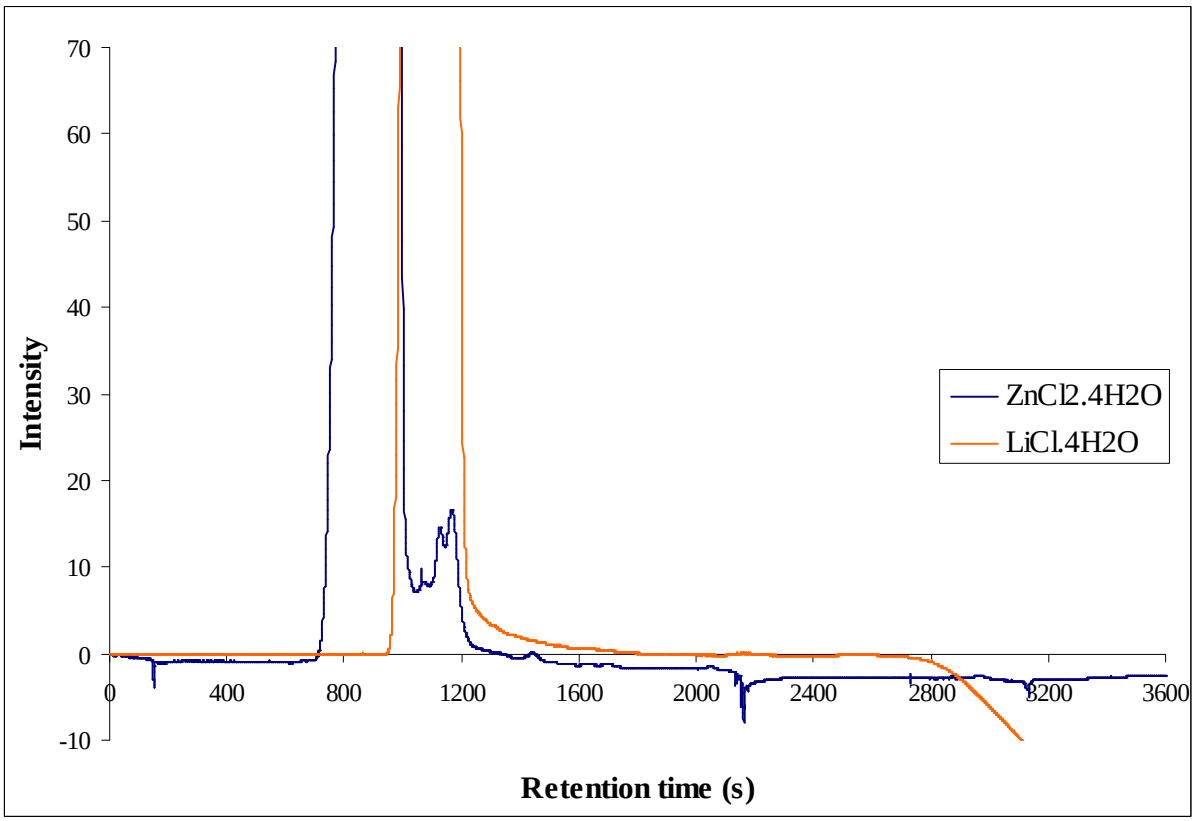

Figure 70 - Methylcellobiose hydrolysis at 100ºC.

$ZnCl_2.4H_2O$ is the solvent with bigger conversion so, it is expected that the final solutions should be darker than for $LiCl.4H_2O$ (figures 71-74).

Figure 71 - Final solutions from Cellobiose hydrolysis at 80ºC in $LiCl.4H_2O$ and in $ZnCl_2.4H_2O$.

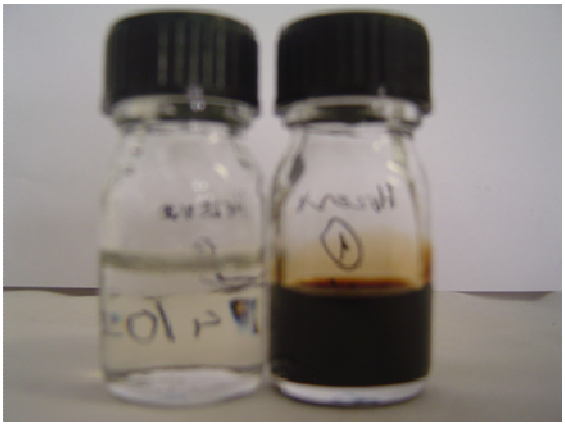

Figure 72 - Final solutions from Methylcellobiose hydrolysis at 80ºC in $LiCl.4H_2O$ and in $ZnCl_2.4H_2O$.

Figure 73 – Final solutions from Cellobiose hydrolysis at 100ºC in $LiCl.4H_2O$ and in $ZnCl_2.4H_2O$.

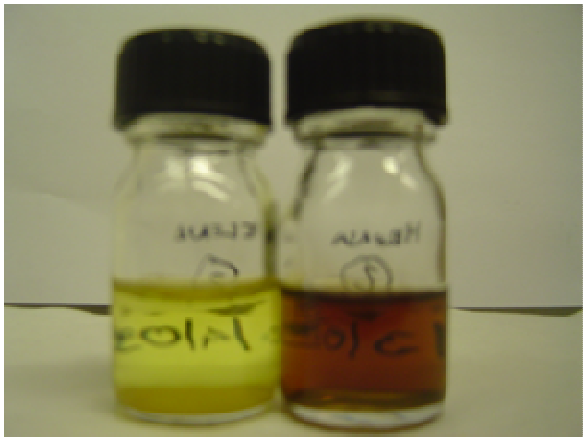

Figure 74 - End solutions from Methylcellobiose hydrolysis at 100ºC in $LiCl.4H_2O$ and in $ZnCl_2.4H_2O$.

C Hydrogenation reactions

This is the last section of this report. In this chapter are presented some chromatograms from hydrogenation reactions and, also, some secondary experiments to understand some results.

During Cellobiose and Methylcellobiose hydrogenation different conditions was studied. First is the influence of the amount of catalyst in Cellobiose and Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$ and in H_2O (figures 75-78).

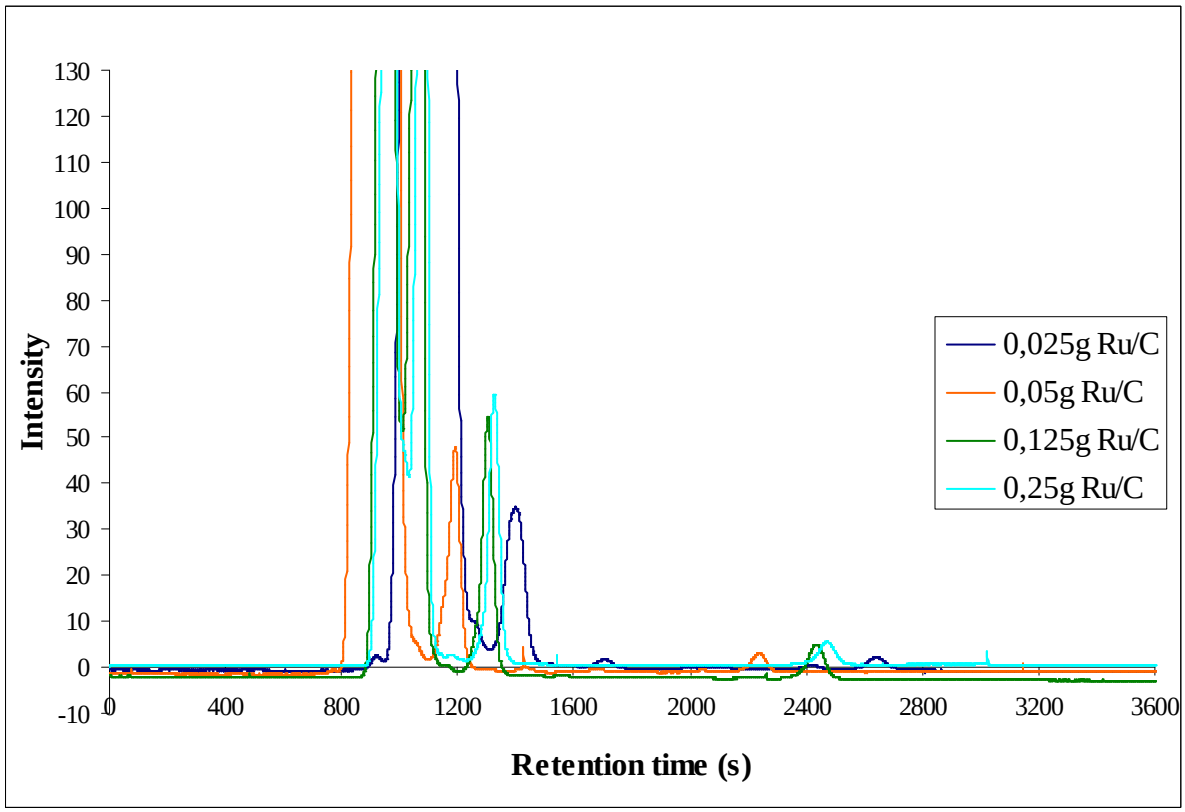

Figure 75 – HPLC chromatograms of Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC and 40 bar H_2 during 1 hour.

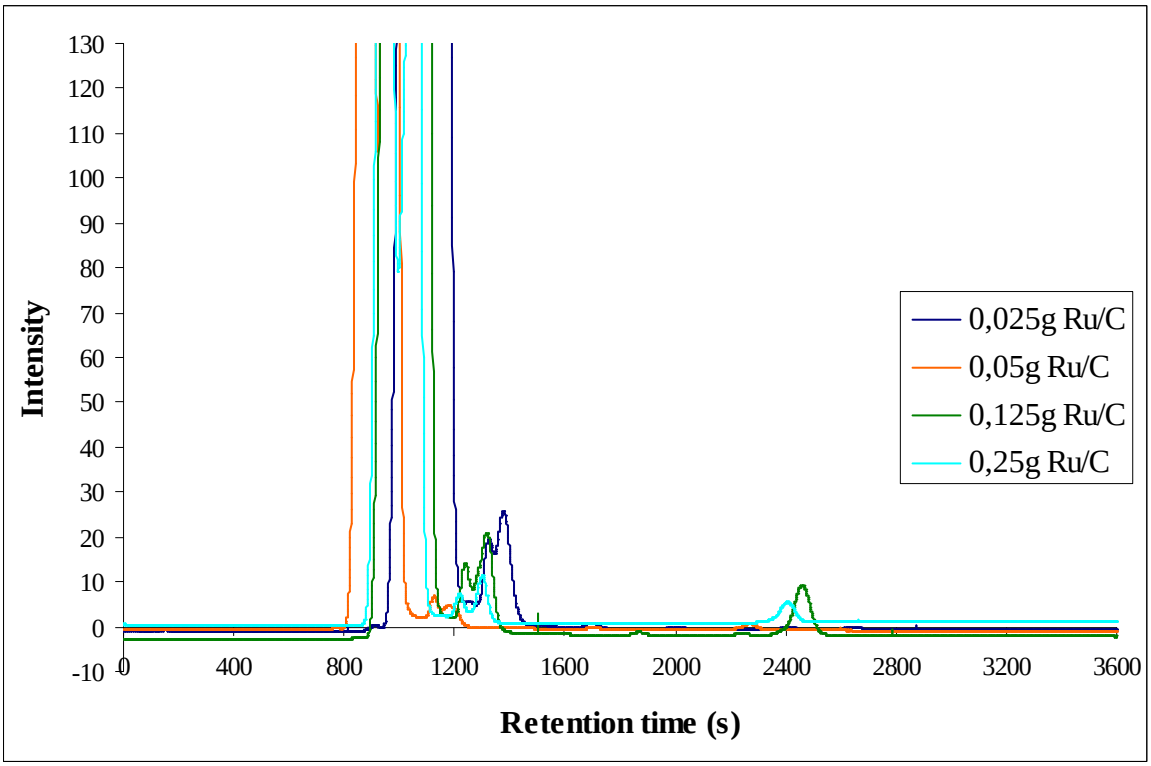

Figure 76 – HPLC chromatograms of Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC and 40 bar H_2 during 1 hour.

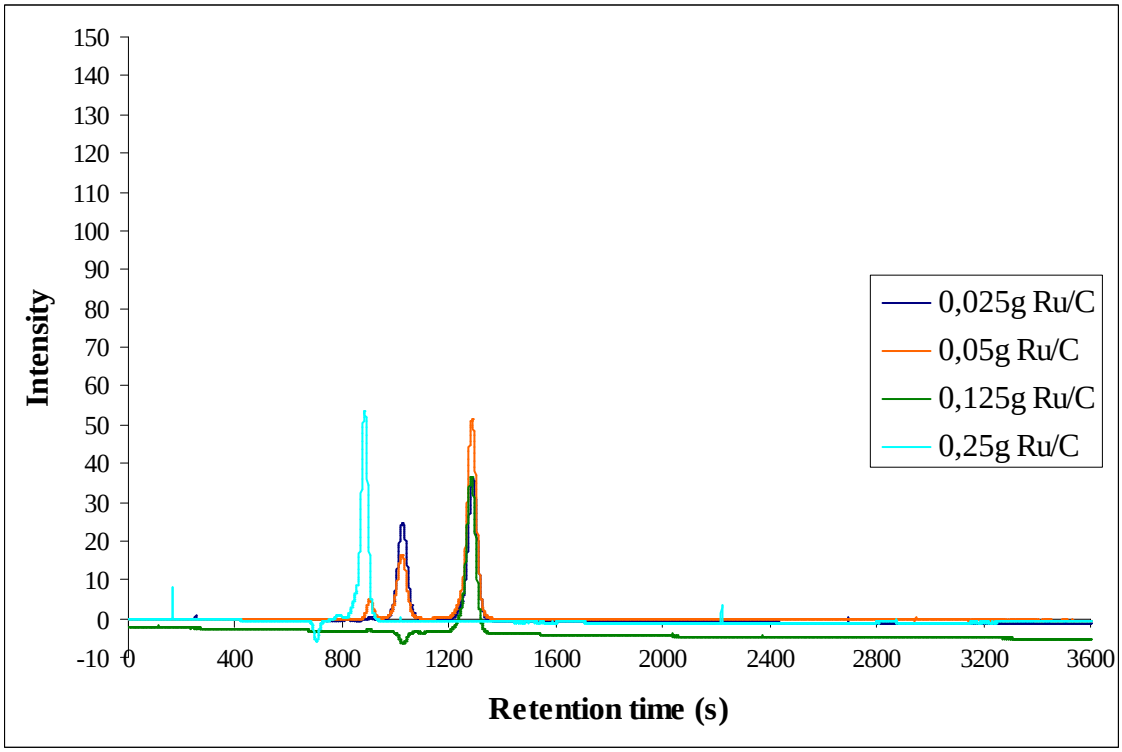

Figure 77 – HPLC chromatograms of Cellobiose hydrogenation in H_2O at 100ºC and 40 bar H_2 during 1 hour.

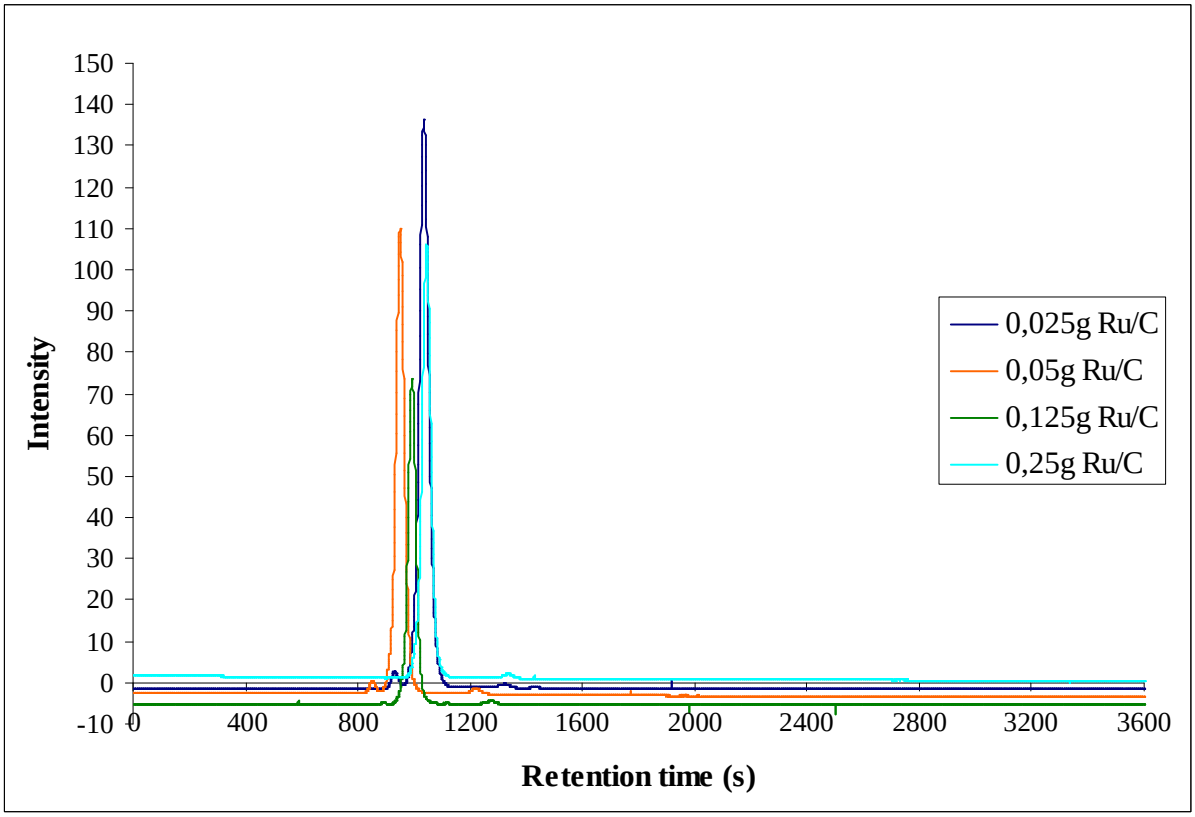

Figure 78 – HPLC chromatogram of Methylcellobiose hydrogenation in H_2O at 100ºC during 1 hour.

All of the hydrogenation work until now was at 100ºC and 0,025g Ru/C. However, some different temperatures were studied (80ºC and 130ºC) – figures 79-86

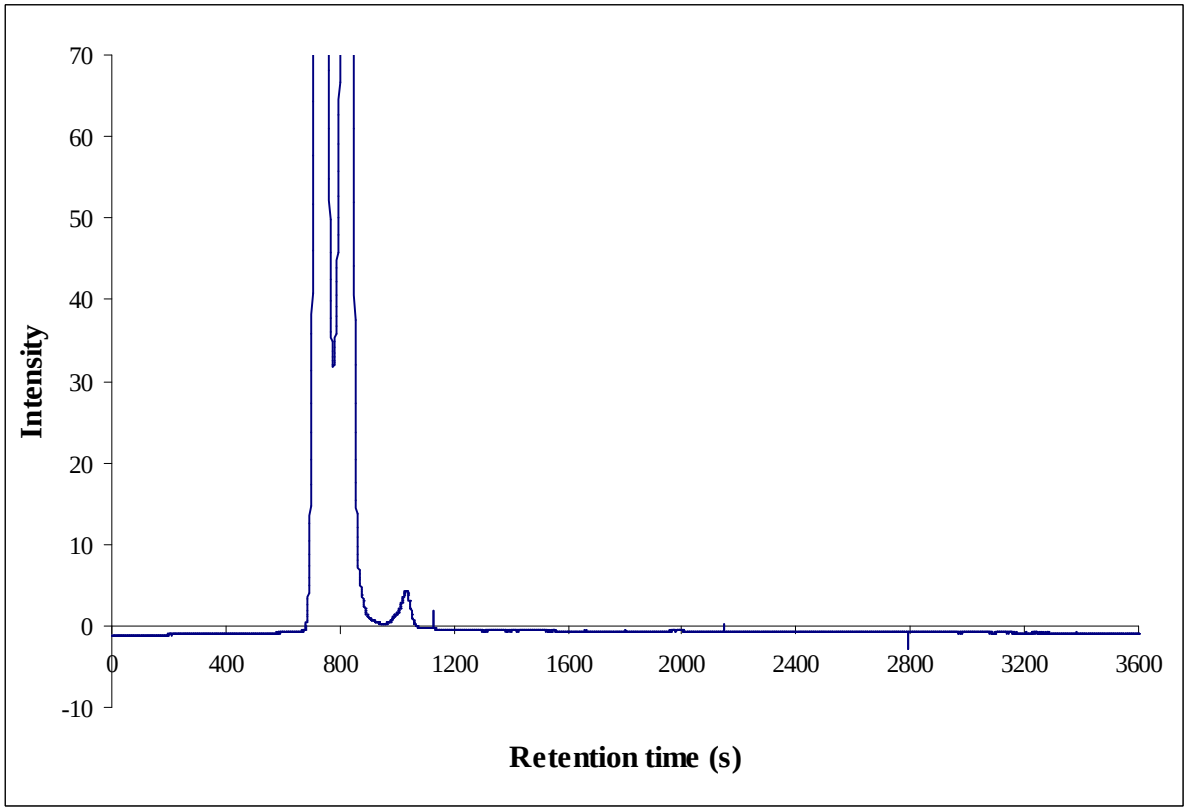

Figure 79 – HPLC Chromatogram for Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 80ºC and 40 bar H_2.

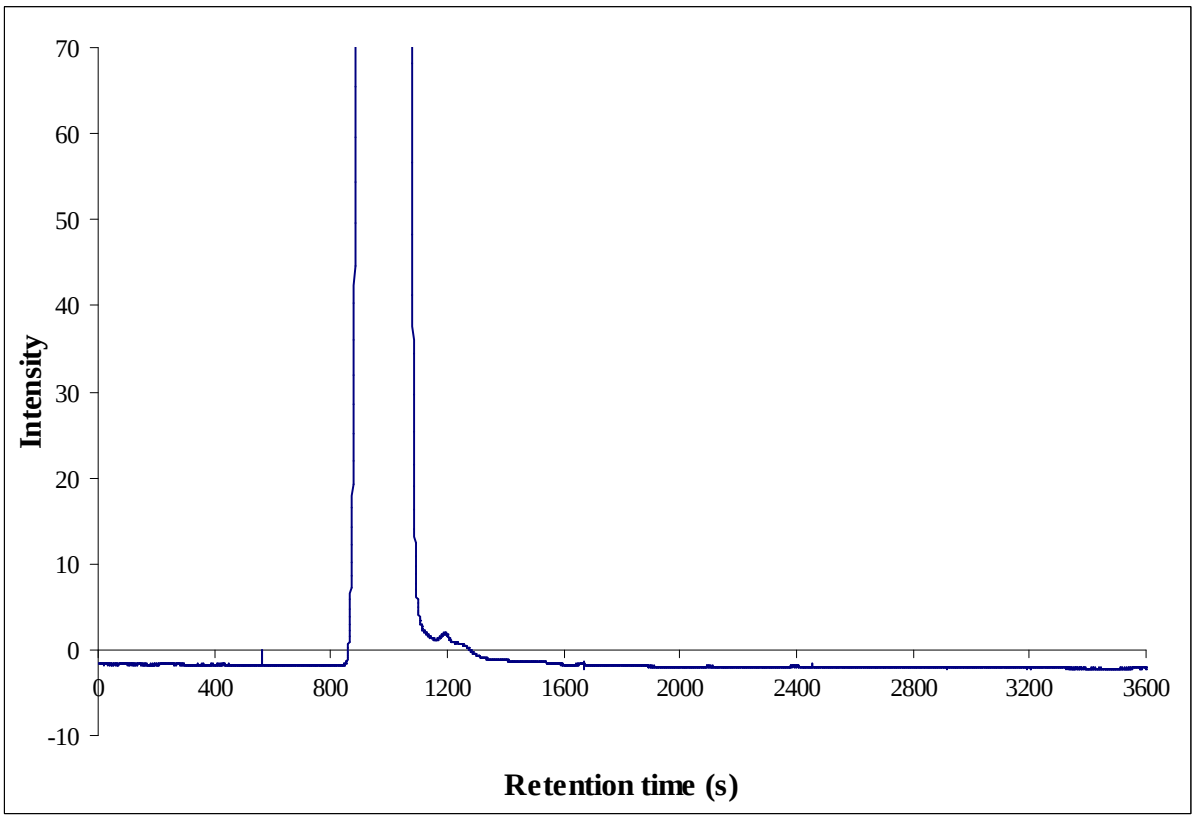

Figure 80 - HPLC chromatogram for Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$ at 80ºC and 40 bar H_2.

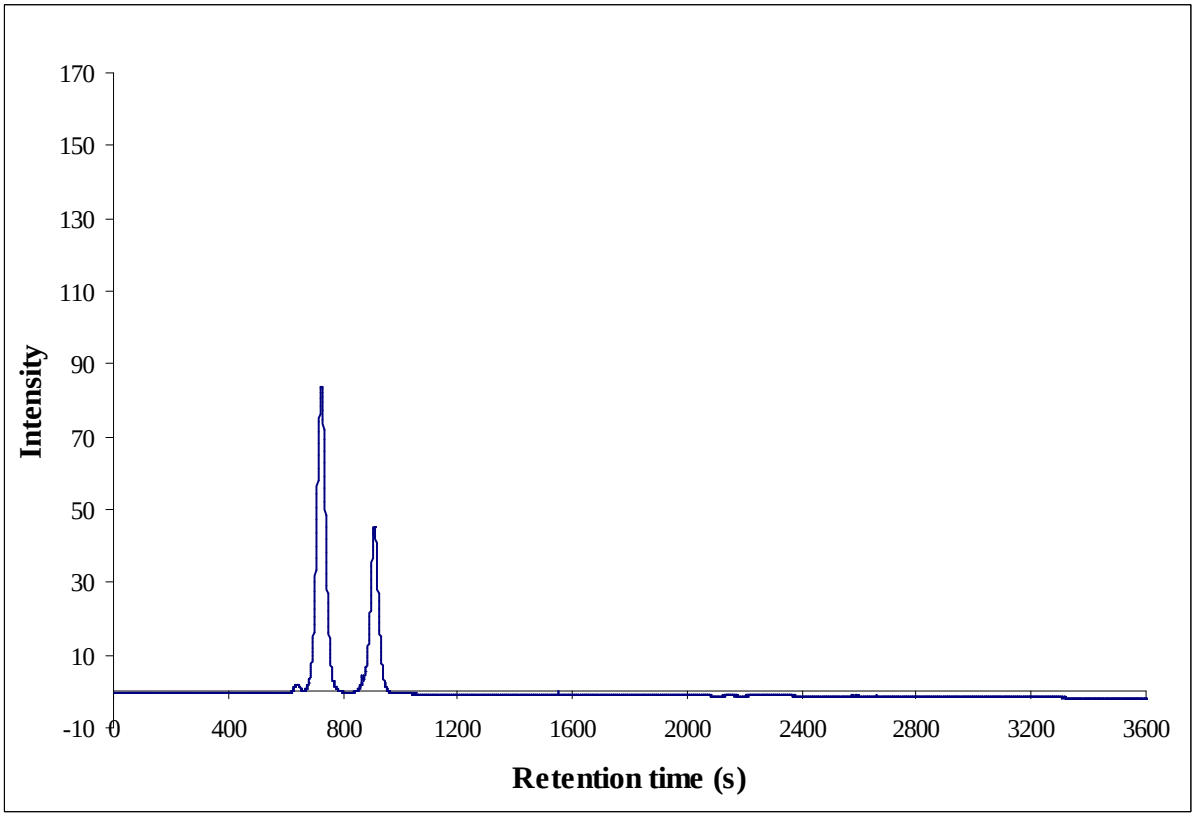

Figure 81 – HPLC chromatogram for Cellobiose hydrogenation in H_2O at 80ºC and 40 bar H_2.

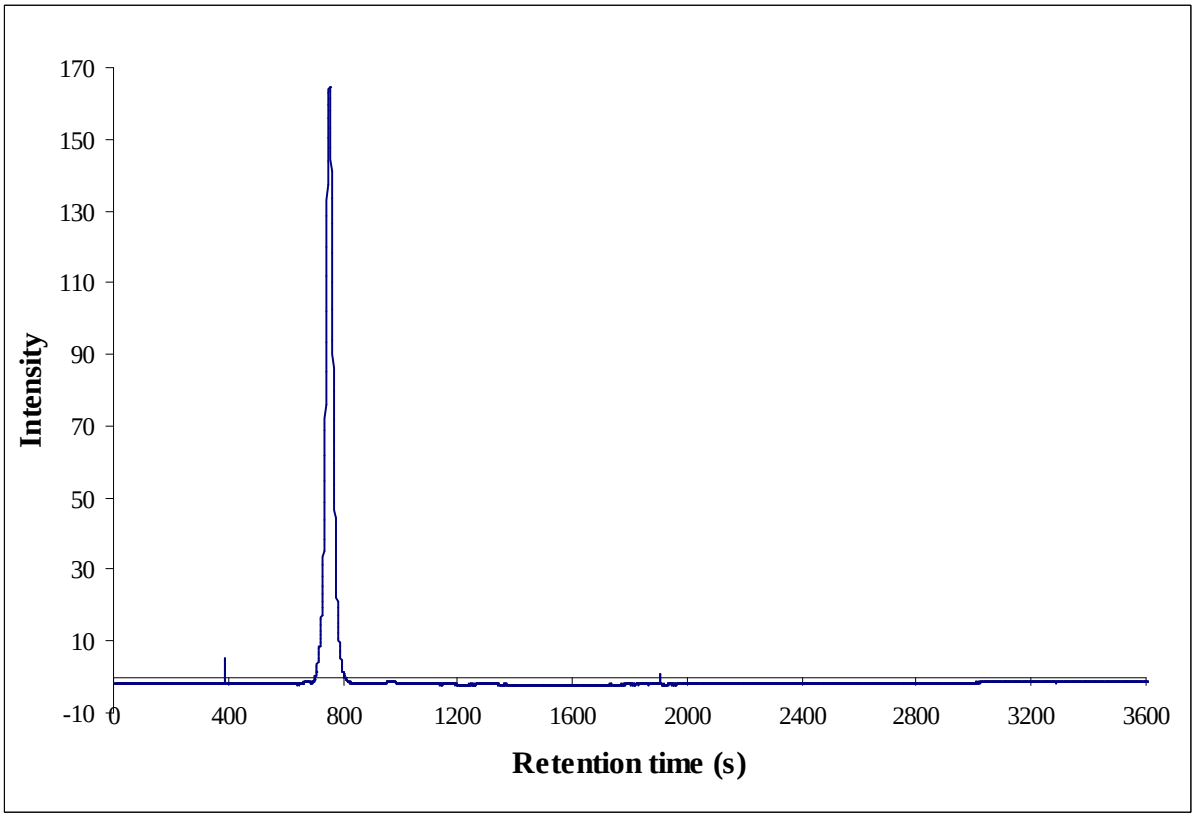

Figure 82 – HPLC chromatogram for Methylcellobiose hydrogenation in H_2O at 80ºC and 40 bar H_2.

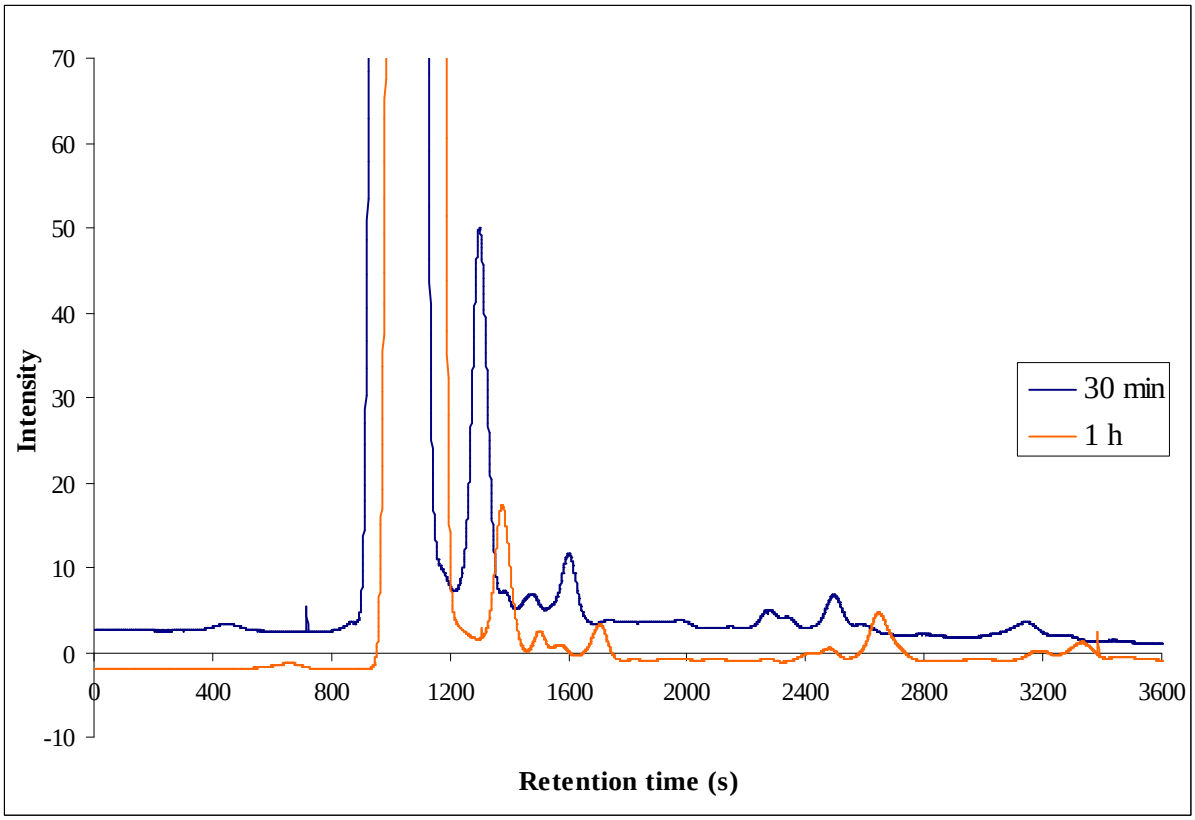

Figure 83 – HPLC chromatogram for Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 130ºC and 40 bar H_2.

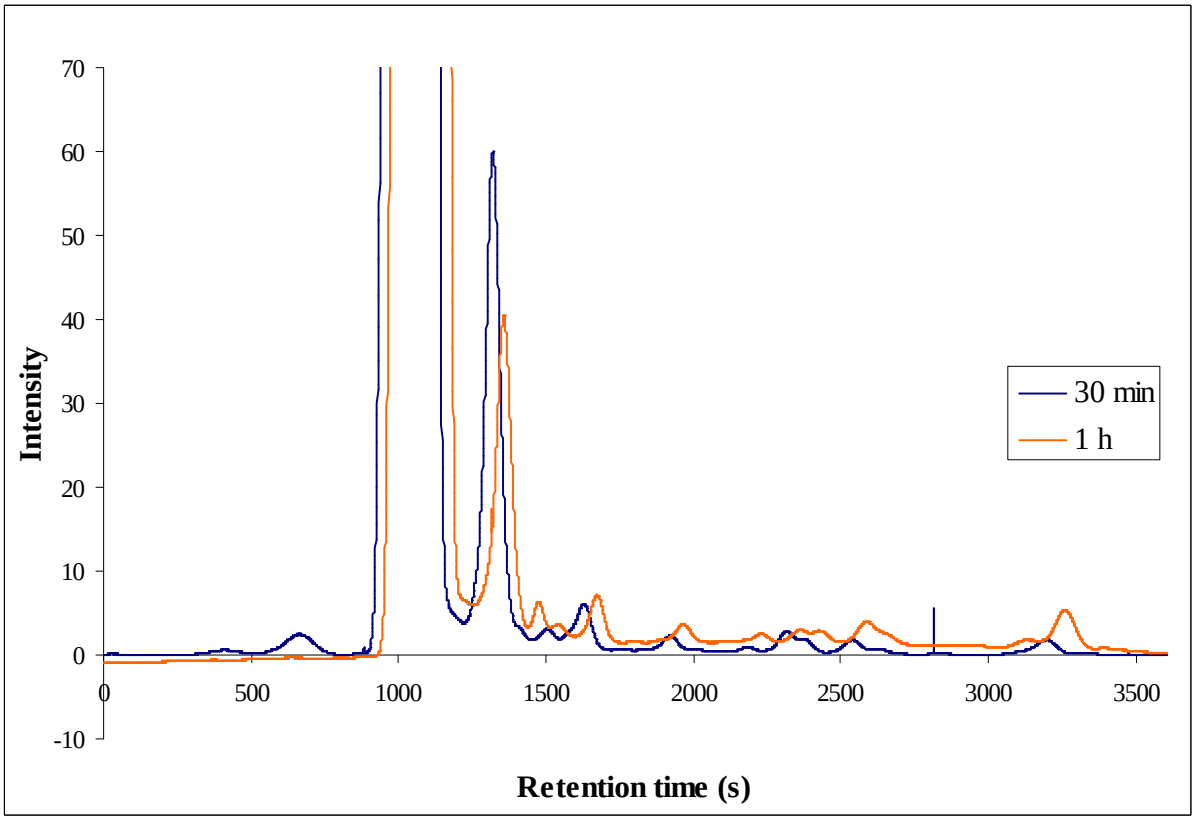

Figure 84 – HPLC chromatogram for Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$ at 130ºC and 40 bar H_2.

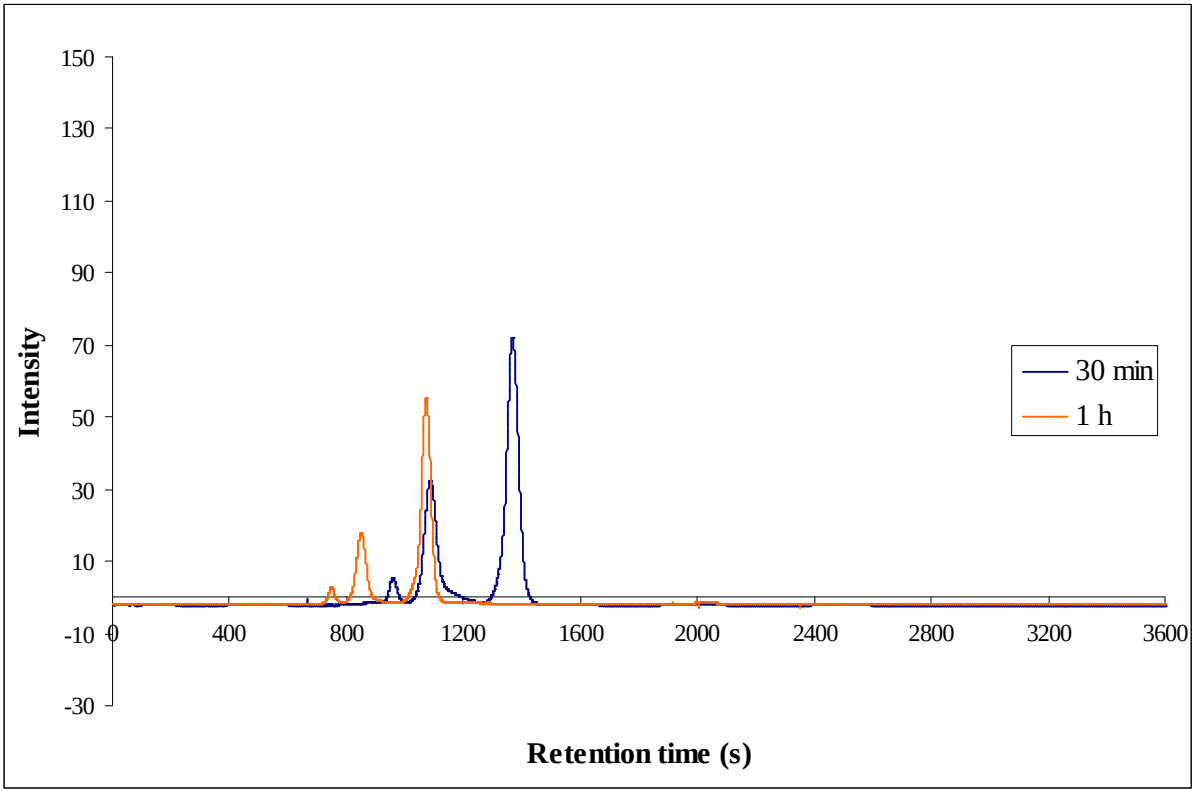

Figure 85 - Results for Cellobiose hydrogenation in H_2O at 130ºC and 40 bar H_2.

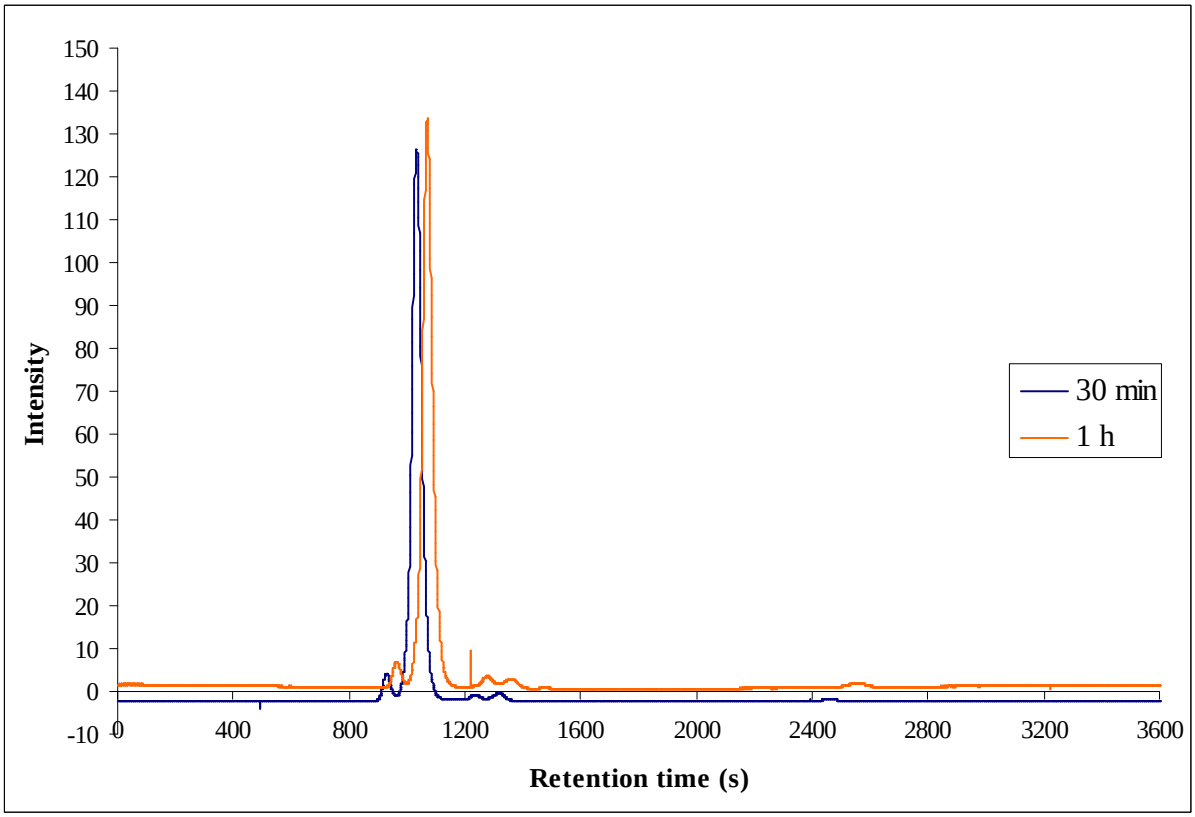

Figure 86 – HPLC chromatogram for Methylcellobiose hydrogenation in H_2O at 130ºC and 40 bar H_2.

To finish, the influence of the reaction time in Cellobiose and Methylcellobiose hydrogenation were studied (figures 87-90).

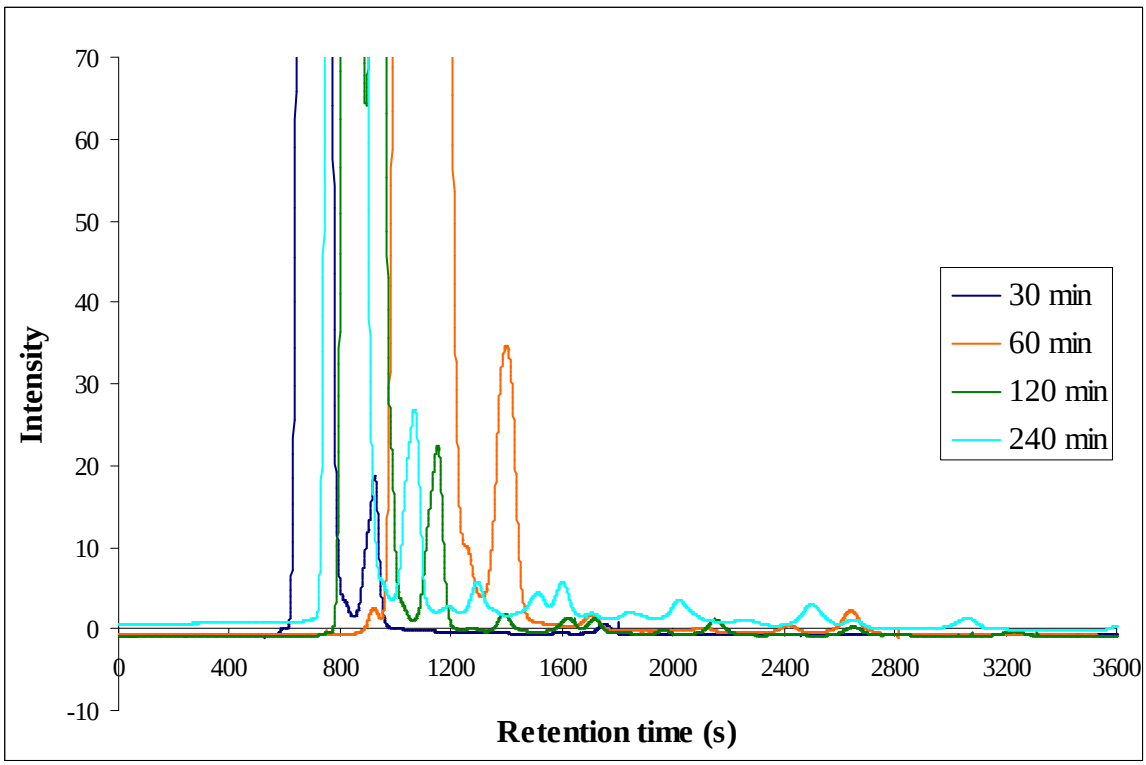

Figure 87 - Cellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC and 40 bar H_2 with 0,025g Ru/C.

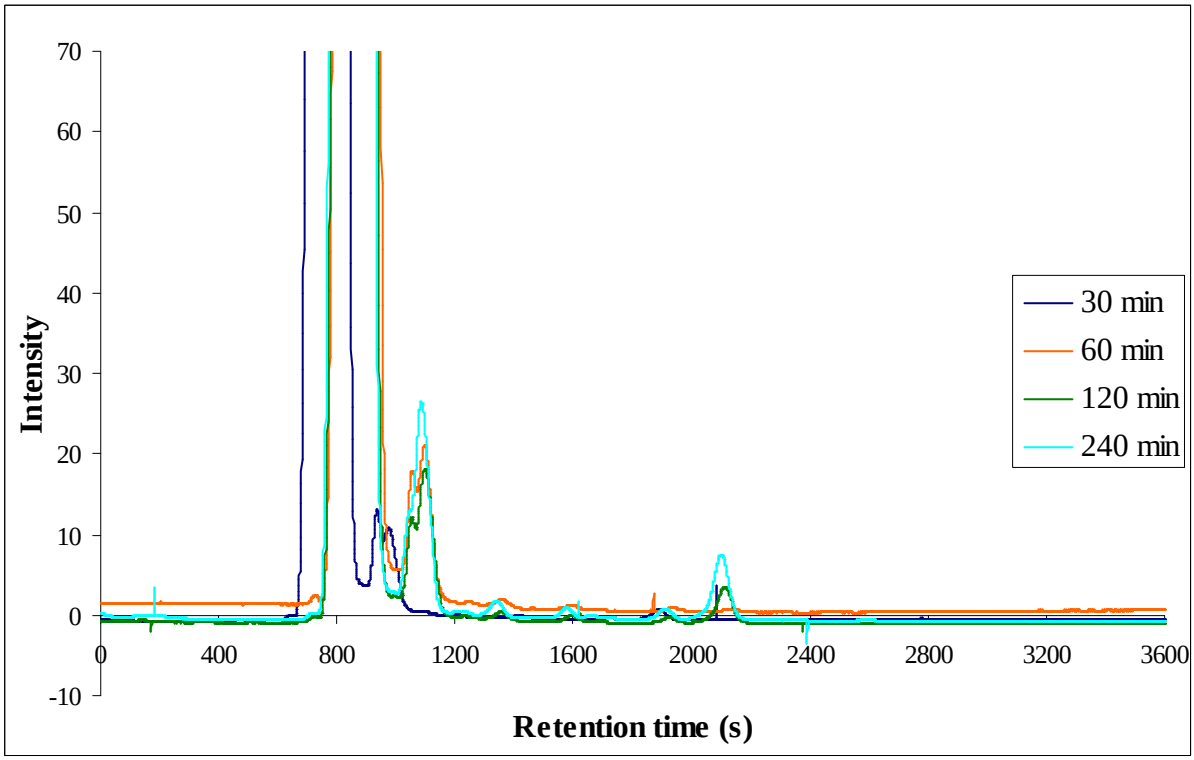

Figure 88 - Methylcellobiose hydrogenation in $ZnCl_2.4H_2O$ at 100ºC and 40 bar H_2 with 0,025g Ru/C.

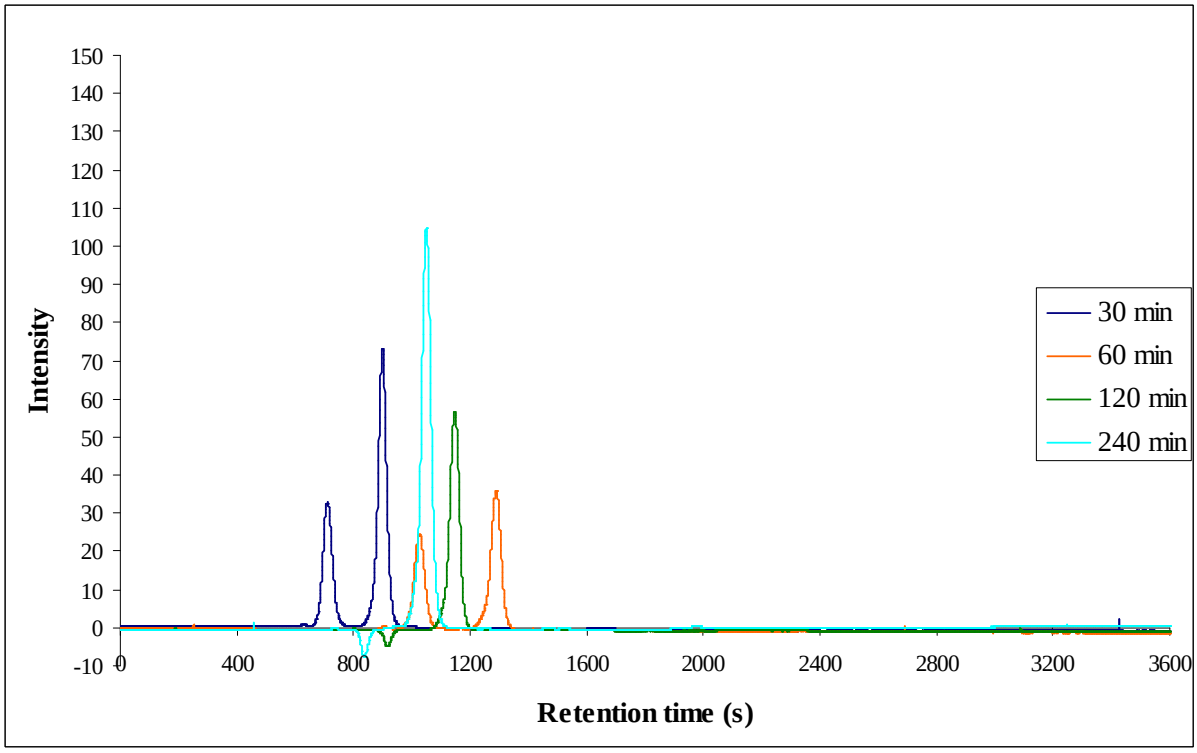

Figure 89 - Cellobiose hydrogenation in H_2O at 100°C and 40 bar H_2 with 0,025g Ru/C.

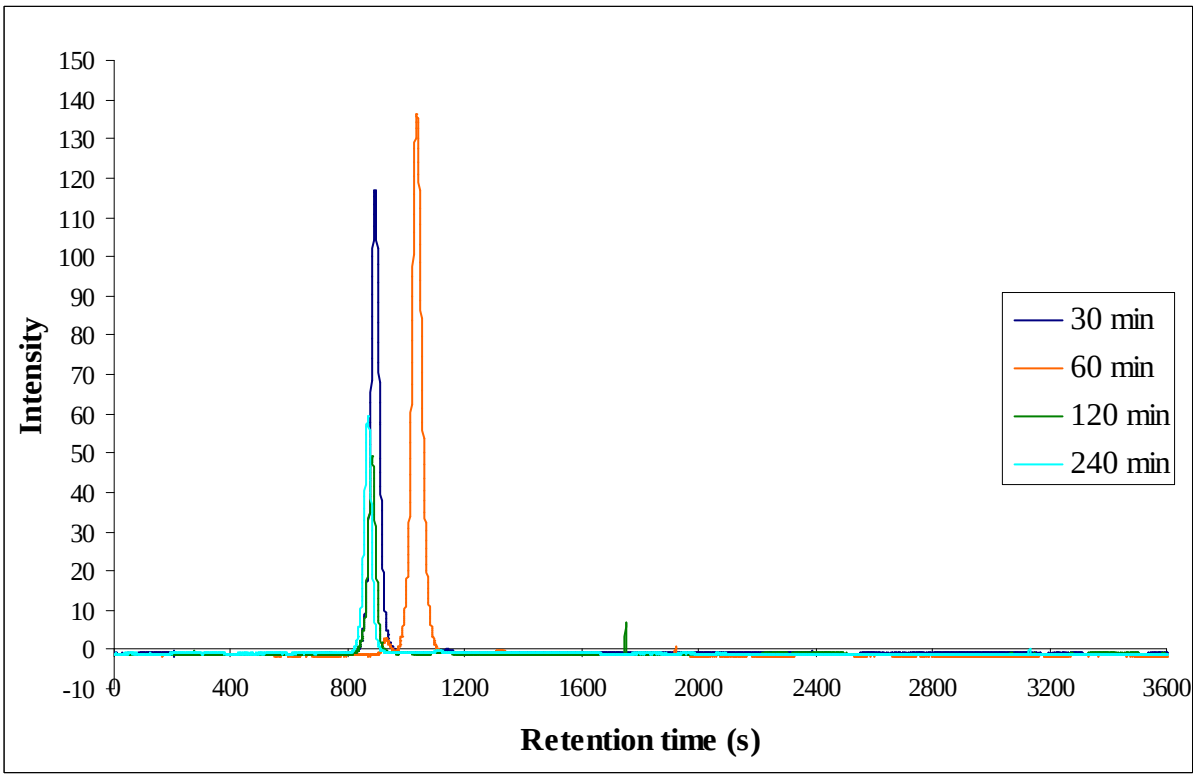

Figure 90 - Methylcellobiose hydrogenation in H_2O at 100°C and 40 bar H_2 with 0,025g Ru/C.