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Pyrolysis oil upgrading to transportation fuels by catalytic hydrotreatment

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Chapter 5: Catalytic Hydrotreatment of Fast Pyrolysis oil: Model Studies on Reaction Pathways for the Carbohydrate Fraction.

Abstract

Fast pyrolysis oil can be upgraded by a catalytic hydrotreatment (250-400 °C, 100-200 bar) using heterogeneous catalysts like Ru/C to hydrocarbon like products that can serve as liquid transportation fuels. Insight in the complex reaction pathways of the various component fractions during hydrotreatment is desirable to reduce the formation of by-products such as char and gaseous components. This paper deals with the catalytic hydrotreatment of representative model components for the carbohydrate fraction (viz. D-glucose and D-cellobiose) present in concentrations of 20 to 40 % in fast pyrolysis oils. The hydrotreatment was conducted at a temperature of 250 °C and 100 bar hydrogen using Ru and Pd on carbon catalysts in water. Two parallel reaction pathways are then observed, a thermal, non-catalysed, pathway leading to insoluble humins (char) and a hydrogenation pathway leading to smaller polyols and gaseous hydrocarbons like methane and ethane. The implications of these findings for the catalytic hydrotreatment of fast pyrolysis oil will be discussed.

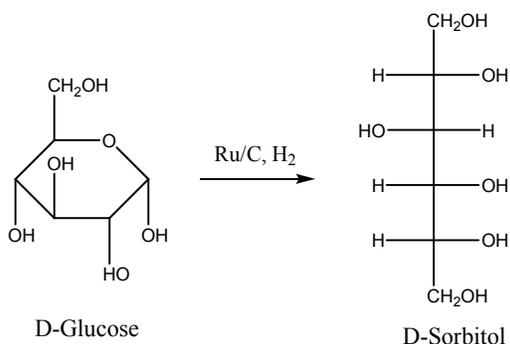
1. Introduction

Decline in easily accessible fossil resources, security of supply and global warming issues have boosted research on renewable resources for fuel and energy generation [1]. Biomass is considered a promising feedstock. A wide variety of technologies is available for biomass conversions [2]. Examples are gasification and liquefaction using thermochemical and biotechnological pathways. A very promising and versatile liquefaction technology is fast pyrolysis, leading to the formation of a liquid product in high yields [3]. Such pyrolysis oils are not suitable as a transportation fuel, because of their relatively low energy content, high acidity and relatively poor storage stability [4,5]. Various upgrading technologies have been proposed in the past, such as catalytic hydrotreatment, (reactive) blending with alcohols and catalytic cracking [6,7]. Catalytic hydrotreatment aims at reducing the oxygen content of the oil by hydrodeoxygenation, the removal of oxygen as water preferably by phase separation. Catalytic hydrotreatment of pyrolysis oil has been studied since 1980. Typical catalysts applied are (sulphided) NiMo and CoMo on alumina. Overviews covering the catalytic hydrotreatment of pyrolysis oil are given by Elliott *et al.* [8,9] and one of the major findings is that processing of the oil requires two steps. The first step at lower temperature (< 280 °C) is referred to as a stabilization step to avoid excessive solids formation, while the oil is further deoxygenated in a second hydrotreating step at higher temperatures (> 350 °C).

Earlier work in our laboratory focused on the catalytic hydrotreatment of fast pyrolysis oil using a variety of catalysts at relatively low (250 °C) and high temperatures (up to 350°C) [10,11]. Upgraded oils with a yield of approximately 55 %-wt. (dry basis) could be obtained with an oxygen content below 10 %-wt. for a Ru/C catalyst. Besides the preferred oil, solids and gas phase components (for example methane) were formed as well. At the milder conditions (lower temperature) the amount of solids formed ranged between 1 and 10 %-wt., whereas the yield of gas phase components ranged from 3 to 6 %-wt. At the higher temperatures, the amount of solids and gases increased up to 26 %-wt. and 15 %-wt., respectively. Obviously, the formation of solids and gas phase components are to be avoided as they have a negative effect on the mass- and energy balance of the process [11]. Moreover, excessive solids formation will lead to reactor blockage and other associated operational issues. Earlier studies in our group revealed

(for example formaldehyde). At these conditions, the reactions are very fast and decomposition to char takes place on the time scale of seconds to minutes.

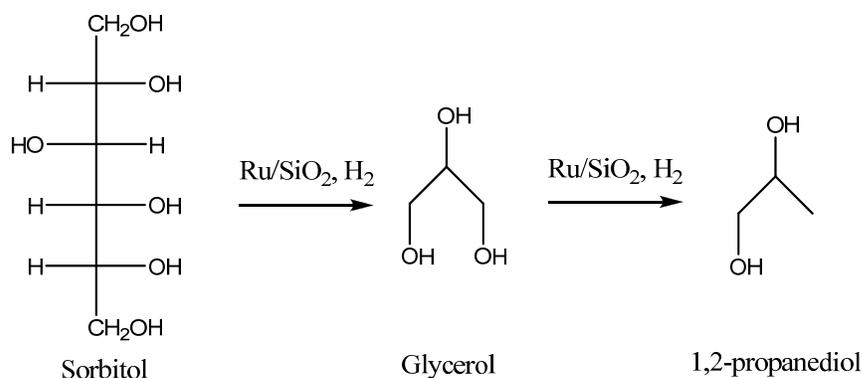
Catalytic hydrotreatment of carbohydrates using heterogeneous catalysts have been reported extensively in the literature. The main focus is on the hydrogenation of D-glucose to D-sorbitol, a well known chemical with use in the pharmaceutical and the food industry [20]. Catalytic hydrotreatment of D-glucose over Ni and Ru based catalysts at 80 °C, 80 bar yields D-sorbitol in high yields [20,21] (Scheme 2). Pd/C is also a well known catalyst for the hydrogenation of D-glucose to D-sorbitol and D-mannitol (60-80 °C and 20-75 bar) [22].



Scheme 2. Catalytic hydrogenation of D-glucose to D-sorbitol

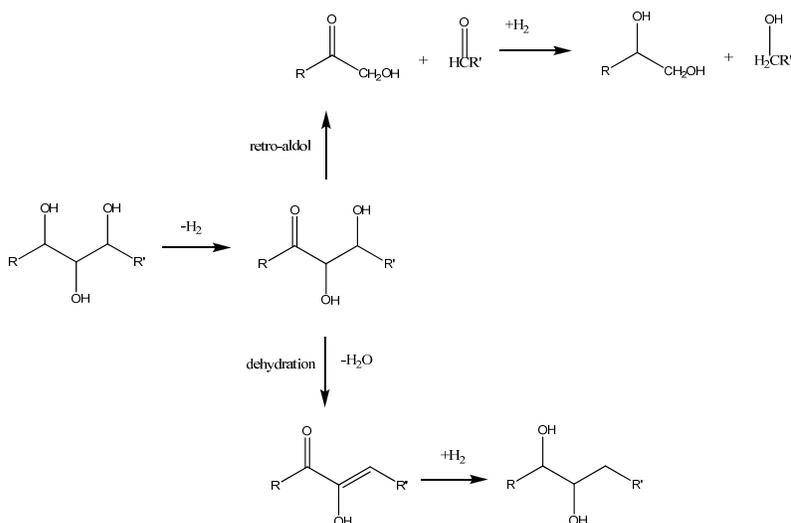
Kusserow [20] reported that besides the formation of D-sorbitol also other carbohydrates and their hydrogenated products (mannose, fructose, maltose, glycolaldehyde, dihydroxyacetone, formaldehyde, 5-hydroxymethylfurfural, mannitol, maltitol and iditol) may be formed in amounts up to 8 %-wt. (supported Ru and Ni as catalyst, 120 °C and 120 bar).

Further catalytic hydrogenation studies have shown that D-sorbitol is reactive at elevated temperatures (above 180 °C) and may be converted to a variety of products. For instance, Huber *et al.* [23] showed that D-sorbitol can be converted to n-hexane in high yield using Pd and Pt catalyst on SiO₂ or Al₂O₃ (225-265 °C and 26-58 bar). Over a Ru/SiO₂ catalyst hydrogenolysis of D-sorbitol at 180-240 °C and 80-125 bar hydrogen pressure yields mainly glycerol and 1,2-propanediol [24] (Scheme 3).



Scheme 3. Hydrogenolysis of D-sorbitol to glycerol and 1,2-propanediol.

Wang *et al* [25] provided more insights in the mechanism of such reactions by studying the hydrogenation of a variety of 1,3-diols (like 2,4-dimethyl-2,4-pentanediol, 2-methyl-2,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 2,2-dimethyl-1,3-propanediol, 2,4-pentanediol, 1,3-butanediol and 1,3-propanediol) at a temperature of 210 °C and 5 bar hydrogen using Raney Ni and Cu catalysts. A sequence consisting of dehydrogenation followed by either dehydration or a retro-aldol condensation and hydrogenation/dehydrogenation was proposed to explain the product composition (Scheme 4).



Scheme 4. Proposed mechanism for the formation of diols from D-sorbitol (adapted from Wang *et al.* [25]).

Larger carbohydrates can be hydrogenated to lower molecular weight products. Luo *et al.* [26,27] showed that cellulose is converted to D-glucose and D-fructose and subsequently in a mixture of D-sorbitol, D-mannitol and C₁-C₅ alcohols using a Ru/C catalyst at 200 °C and 20 bar hydrogen pressure. Yields up to 47 % of D-sorbitol were reported. Byproducts are mannitol, sorbitan, xylitol, erythritol, and methane.

Hydrogenation of D-cellobiose at lower temperatures (120 °C) and pressures (40 bar hydrogen) at acidic conditions (pH = 2) using Ru/C yields D-sorbitol in essentially quantitative yields, while at neutral conditions a mixture of D-sorbitol and 3-β-D-glucopyranosyl-D-glucitol (dideoxyhexitol) was formed (Yan *et al.*) [28].

Catalytic hydrogenations of mixtures of carbohydrates and ketones have also been reported. This is of relevance for the catalytic hydrotreatment of fast pyrolysis oil as ketones such as acetone are present in pyrolysis oil up to 3 %-wt. [12]. Huber *et al.* have shown that larger alkanes (up to C₁₅) can be obtained from D-glucose and acetone [29] using combined hydrogenation/ aldol condensation reactions. D-glucose first decomposes to HMF (Scheme 1), which subsequently reacts with acetone by an aldol condensation (basic conditions) to give (3-hydroxybutenyl)-hydroxymethylfuran. The latter is then hydrogenated at 250-265 °C using a Pt/SiO₂-Al₂O₃ catalyst to produce the larger alkanes.

1.1 This work

To gain insights in catalytic hydrogenation pathways of the carbohydrate fraction in fast pyrolysis oil, we here report model studies using D-glucose and D-cellobiose. The results will be of particular interest for pyrolysis oils rich in carbohydrates. Such oils are obtained by pyrolysing cellulose and hemi-cellulose rich biomass feedstocks (and consequently low lignin feedstocks) like soft and hard wood, bagasse, rice husk and straw [14,15,30].

The reactions were carried out at conditions representative for mild hydrotreatment: in aqueous media, temperatures ranging from 175 to 250 °C, pressures up to 100 bar and a reaction time of 4.3 h. Major components in the gas and liquid phase were identified and quantified and, in combination with the solids yield, allowed closure of the mass balances. The effect of the addition of acids, ketones and aldehydes to the reaction

mixture will also be explored. Implications of these findings for the catalytic hydrotreatment of fast pyrolysis oil will be addressed.

2. Materials and Methods

2.1 Chemicals

D-glucose, D-cellobiose, D-sorbitol, acetic acid, acetaldehyde and acetone were obtained in analytical grade from Sigma Aldrich. Ru/C and Pd/C (5 %-wt.) were obtained from Sigma Aldrich. Analytical grade hydrogen gas and technical grade nitrogen and helium were obtained from Hoekloos (Schiedam). Analytical grade tetrahydrofuran and n-decane were obtained from Acros.

2.2 Hydrogenation set-up

The hydrogenation reactions were carried out in a 100 ml batch autoclave (Parr, maximum 350 bar and 350 °C) equipped with an electric heater and the possibility to cool with water. The reactor content was mixed efficiently with a magnetically driven impeller (Heidolph RZR 2050). The stirrer speed throughout an experiment was kept at 1300 rpm to avoid G-L mass transfer limitations. Temperature and pressure were monitored continuously using a PC.

A catalyst activation step was applied before the hydrotreatment reactions were initiated. For this purpose the reactor was charged with Ru/C (5 %-wt. based on reactant) and water (20 g). The reactor was pressurized with hydrogen (5 to 10 bar) at room temperature, and subsequently the temperature was increased to 250 °C and maintained for 2 h. After cooling down and venting of the gases, the model component (5 g) and catalyst (5 %-wt. on model component intake) were added. Subsequently, the reactor was flushed with nitrogen gas and then filled with hydrogen (about 10 bar) at room temperature. The reactor was heated to the pre-determined temperature with a heating rate of about 20 °C/min. When the desired reaction temperature was reached, the hydrogen pressure was set at the intended level. Liquid samples were taken every 10 minutes during the first hour. After 1 h reaction time, samples were taken on an hourly basis. Typically, a 4.3 h reaction time was applied. Subsequently, the reactor was cooled to ambient temperature. The final pressure at room temperature was recorded for mass

balance calculations. The remaining liquid product was recovered from the reactor using a syringe and weighed. Subsequently, the reactor was rinsed with acetone. The combined acetone fractions with suspended solids were filtered. After filtration, the filter was dried and weighed. The amount of solids minus the original catalyst intake was taken as the amount of solids formed during the HDO process.

2.3 Liquid analyses

Liquid samples were analysed with GC-MS, HPLC and Capillary Electrophoresis (CE). Solids were removed from the reaction mixture using filtration and washing with acetone. Samples were injected after dilution using water or tetrahydrofuran (THF).

GC-MS analysis were performed on a Quadrupole Hewlett Packard 5972 MSD attached to a Hewlett Packard 5890 GC equipped with a 30 m x 0.25 mm i.d. and 0.25 μm sol-gel capillary column. The injector temperature was set at 250 °C. The oven temperature was kept at 40 °C for 5 minutes then heated up to 250 °C at a rate of 3 °C min^{-1} and then held at 250 °C for 10 minutes.

The HPLC system consists of a Hewlett Packard 1050 pump, a Bio-Rad Organic Acid column Aminex HPX-87H, and a Waters 410 differential refractometer. The mobile phase consisted of aqueous sulphuric acid (5 mM) set at a flow rate of 0.55 cm^3/min . The column was operated at 60°C. The analysis for a sample was complete in 30 min. The concentrations of each compound in the product mixture were determined using calibration curves obtained by analyzing standard solutions of known concentrations.

The CE analyses were performed using a ^{3D}CE system (Agilent Technologies) equipped with a cassette containing standard fused-silica capillary (75 μm ID, 80.5 cm total length and 72 cm active length) and a diode array detector. An organic acid buffer (pH = 4.6) containing 5 mM cetyltrimethylammonium bromide (CTAB) was used as the running buffer. Samples were injected at a pressure of 50 mbar for 2 s, followed by post injection using the running buffer at 50 mbar for 4 s to avoid loss of sample. -25 kV voltage was applied and the capillary temperature was maintained at 20 °C. Electropherograms were recorded at 350 nm with a reference at 200 nm. The column was preconditioned prior to each measurement by flushing with the buffer solution for 4 minutes at 1 bar. Triplicate measurements were performed for each sample.

The elemental composition (C, H and N) of the products were determined in Euro Vector 3400 CHN-S analyzer (oxygen content by difference).

The water content in the samples was determined by a Karl Fischer titration using an Metrohm Titrino 758 titration device. A small amount of compound (0.03-0.05 g) was added to an isolated glass chamber containing Hydranal (Karl Fischer Solvent, Riedel de Haen). The titrations were carried out using the Karl Fischer titrant Composit 5K (Riedel de Haen). All measurements were performed in duplo.

NMR spectra were recorded on a 200 MHz NMR (Varian). The samples were dissolved in D₂O.

ICP was performed on a Perkin Elmer 4300 DV. Solids samples were converted to ash at 900 °C in an oven. The remaining ash was dissolved in a 2 % HNO₃ solution and analysed.

2.4 Gas phase analyses

The gas phase samples were collected and stored in a gasbag. GC-TCD analyses were performed on a Hewlett Packard 5890 Series II GC equipped with a Poraplot Q Al₂O₃/Na₂SO₄ column and a Molecular Sieve (5A) column. The amount of gas phase components formed during reaction could then be evaluated from the gas phase composition and the volume and pressure of the gas phase after reaction.

The GC injector temperature was set at 150 °C, the detector temperature at 90 °C. The oven temperature was kept at 40 °C for 2 minute then heated up to 90 °C at 20 °C/min and kept at this temperature for 2 minutes. The columns were flushed during 30 seconds with the gas sample before starting the actual measurement. A reference gas containing H₂, CH₄, CO, CO₂, ethylene, ethane, propylene and propane with known composition was used for peak identification and quantification.

3. Results and discussion

Catalytic hydrotreatment experiments using D-glucose, D-cellobiose and D-sorbitol were conducted at 250 °C, 100 bar of hydrogen and 4.3 h of reaction time. For D-glucose, two different catalysts were explored (Ru/C and Pd/C). The latter was selected as it was shown to be a promising catalyst for the hydrotreatment of fast pyrolysis oil [10]. Furthermore, the addition of several compounds (acetaldehyde, acetone and acetic acid) was explored to mimic the multi-component nature of pyrolysis oil.

3.1 Hydrotreatment of D-glucose

3.1.1 Experiments using a Ru/C catalyst

Catalytic hydrotreatment of D-glucose over Ru/C was studied at 250 °C and 100 bar. After the reaction, a colourless liquid phase and brown solids were formed. The overall mass balance closure was good (> 99%), with 71.4 %-wt. liquid phase product, 25.9 %-wt. gaseous and 1.5 %-wt. solids. With respect to the carbon balance, most is collected in the liquid phase (61%), with 37 % in the gas phase and 2 % in the solids. Thus, it may be concluded that the amount of gas phase components formed is considerable whereas solids formation is limited when performing the reactions at 250°C and 100 bar of hydrogen pressure.

The composition of the liquid phase of the reaction mixture versus time is given in Figure 1. D-glucose appears fully converted within 1 h, producing (intermediate) D-sorbitol, D-fructose, glycerol and propanediol isomers (1,3-propanediol and/or 1,2-propanediol). D-fructose is a known isomerisation product of D-glucose [20,31]. The isomerisation reaction is known to be catalysed by bases and heterogeneous catalysts like ZrO₂, TiO₂, hydrothalcites, as shown by Watanabe *et al.* and Moreu *et al.* [17,32]. The formation of D-sorbitol is in line with literature data [20]. D-sorbitol is a clear intermediate and is converted under the prevailing reaction conditions to mainly glycerol and propanediol (*vide infra*) [20,21,24].

The polyols appear not stable under such conditions and after 4.3 h of reaction time their concentration levels are below the HPLC detection limit.

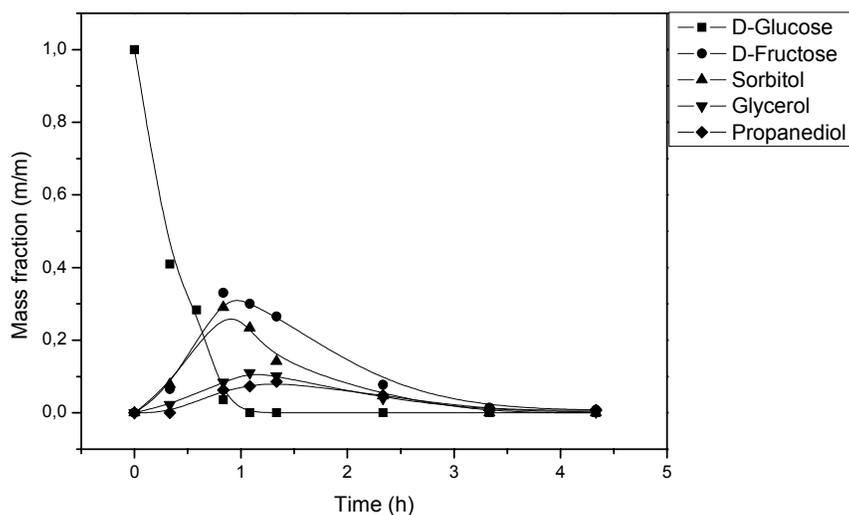


Figure 1. Product composition for the catalytic hydrotreatment of D-glucose in water versus the time (250 °C, 100 bar and 5 %-wt. Ru/C). Lines are for illustrative purposes only.

To gain further insights in the composition of the liquid phase after reaction, the solvent was removed under vacuum (35 °C and 30 mbar) and the viscous yellow product was weighed and analyzed. Analyses by GC-MS (diluted in dichloromethane) showed a large number of components. The major components, although present in minor amounts, were (poly-)alcohols like propanediol, 1,2-butanediol, tetrahydrofuranmethanol, 1,2-pentanediol and 1,2-hexanediol.

The liquid product was analyzed by ^1H and ^{13}C -NMR (D_2O) and the results are depicted in Figure 2. The spectra confirm the presence of a complex mixture of polyols. The ^1H -NMR spectrum shows typical shifts of aliphatic CH_2 and CH_3 groups in the region δ 0.5-2 ppm and CH_n groups adjacent to an OH group between δ 3-4 ppm.

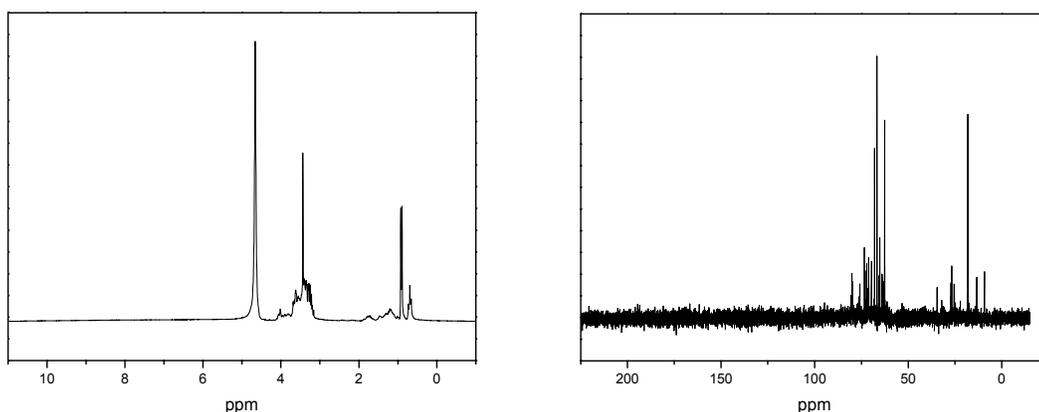


Figure 2. ¹H- and ¹³C-NMR (D₂O) of the isolated liquid phase of catalytic hydrotreatment of D-glucose at 250 °C and 100 bar after 4.3 h of reaction time.

These findings are confirmed by ¹³C-NMR, showing methyl groups at around δ 14-18.9 ppm, aliphatic -CH₂- groups at δ 22.8- 32.9 ppm and carbons adjacent to an OH group at δ 57.8- 73 ppm. Analysis of the liquid product with CE also shows the presence of various organic acids namely acetic acid, formic acid and glycolic acid in quantities of 2.7 %-wt., 0.78 %-wt. and 0.7 %-wt. respectively. This is also in line with the measured pH of 3.0 of the liquid phase after reaction. Formic acid results from the thermal pathway (Scheme 1), acetic acid and glycolic acid may originate from D-glucose or D-fructose decomposition as shown by Srokol *et al.* and Watanabe *et al.* [17,18,33]

The gas phase was analysed by GC and consisted of 73 %-mol of residual H₂, 24 %-mol CH₄, and 0.1 %-mol CO₂. Remaining gases are ethane (1.7 %-mol) and propane (1.2 %-mol). Ru/C is an excellent methanation catalyst and this explains the presence of high amounts of methane in the gas phase [34].

After isolation, the elemental composition of the solid phase was determined and it was shown to consist of almost 60 %-wt. of carbon. This number is close to the value for the humins produced by thermal D-glucose decomposition (61.2 %-wt.) [35], indicating that the solid reaction products are most likely humins formed by thermal decomposition of D-glucose.

3.1.2 Hydrotreatment of D-glucose using a Pd/C catalyst

Experiments have been performed with Pd/C at reaction conditions similar to that for Ru/C (250 °C, 100 bar hydrogen, 4.3 h). The profiles of various reaction products are given in Figure 3. Apparently, Pd/C is less active than Ru/C. Full conversion of D-glucose was observed after about 3.5 h, compared to 1 h for Ru/C. The lower reactivity of Pd/C for the hydrogenation of D-glucose was also reported by Makkee *et al.* [22], showing Pd/C can be a factor of more than 6 times less active than Ru/C in terms of initial reaction rate

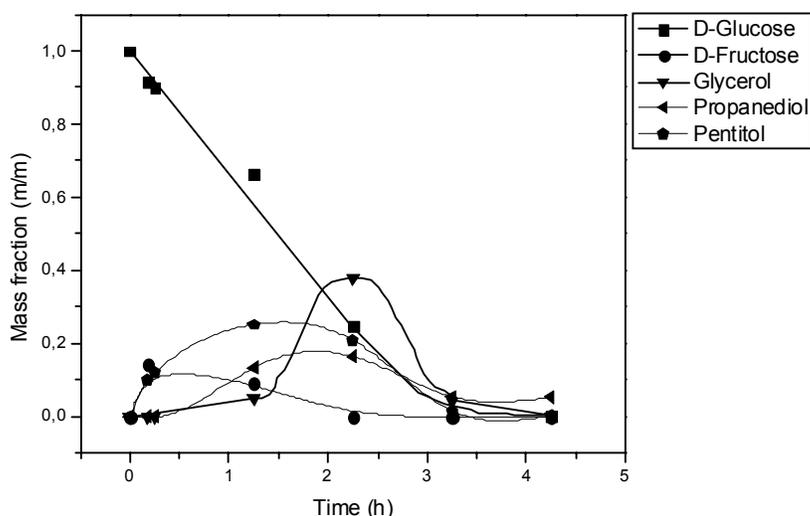


Figure 3. Product composition for the catalytic hydrotreatment of D-glucose in water versus time (250 °C, 100 bar H₂, 5 %-wt. Pd/C). Lines are for illustrative purposes only.

The initial reaction products are D-fructose (due to D-glucose isomerisation) and D-sorbitol by hydrogenation of either D-glucose or D-fructose. The maximum amount of D-sorbitol is 8.7 %-wt. (not shown in Figure 3 for brevity). Besides, a multitude of smaller polyols are produced, the major being pentitol, glycerol and propanediol isomers.

Analyses of the reaction mixture after reaction by CE reveals the presence of organic acids like formic acid (2.4 %-wt.), acetic acid (0.1 %-wt.) and levulinic acid (2-3 %-wt.). In addition, HMF and benzenetriol were observed as well (2-3 %-wt., HPLC). The presence of levulinic acid, formic acid and HMF are indicative for the occurrence of the

thermal degradation pathway of D-glucose (Scheme 1). Benzenetriol is a known product of the thermal route. For instance van Luijkx *et al.* [36] obtained 46 % of benzenetriol when reacting HMF in water at elevated conditions (290-400 °C and 275 bar pressure). The occurrence of the thermal route is expected to be accompanied by the formation of solid humin reaction products [36]. This was indeed the case in our experiments and the solid yield was 2.6 %-wt. It may be proposed that due to the relatively lower hydrogenation activity of Pd/C for D-glucose, the thermal route is more dominant for this catalyst than for Ru/C leading to higher amounts of levulinic acid, formic acid and solids. The composition of the gas phase was determined and shown to consist of 96 %-mol of unreacted H₂, 1.0 %-mol of CH₄, 0.4 %-mol of CO, 2.5 %-mol CO₂, 0.06 %-mol of ethane and 0.08 %-mol of propane. The methane yield is considerably lower than observed for Ru/C (24 %-mol). This implies that Pd/C is not a very active methanisation catalyst under such conditions. This observation is in line with data reported by Mckee *et al.* [37] showing that Pd is a less active methanation catalyst than Ru.

3.2 Catalytic hydrotreatment of D-cellobiose

The carbohydrates fraction of fast pyrolysis oil not only consists of mono-saccharides and derivatives (e.g. levoglucosan) but mainly of larger polysaccharides. D-cellobiose was selected as a model compound to investigate the behaviour of such polymeric components. D-cellobiose contains two glucose units linked in a 1,4-fashion. The reactions were performed at 250 °C and 100 bar during 4.3 h using Ru/C. The various components detected in the liquid phase as a function of time are given in Figure 4.

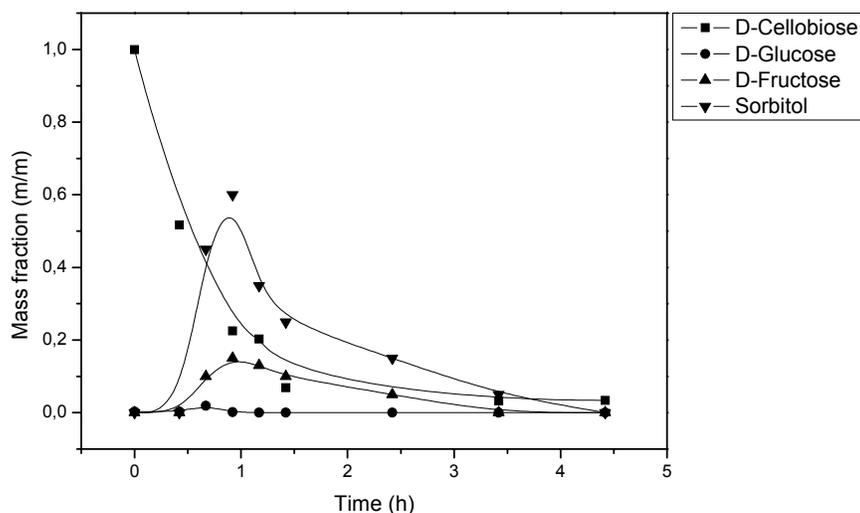


Figure 4. Product composition for the catalytic hydrotreatment of D-cellobiose in water versus time (250 °C, 100 bar hydrogen, 5 %-wt. Ru/C). Lines are for illustrative purposes only.

D-cellobiose conversion exceeded 90 % within 2 h of reaction time. The major intermediates are D-fructose and the hydrogenated product D-sorbitol. D-glucose is present only in minor amounts. The anticipated smaller polyols from the subsequent hydrogenation of D-sorbitol such as glycerol and propanediol were present in low amounts at the end of the reaction (max 0.80 %-wt.). Small amounts of formic acid and acetic acid were also detected (0.2 %-wt. and 0.4 %-wt. respectively). The results are in line with literature data on catalytic hydrogenations of cellulose [26].

The reaction mechanism likely involves hydrolysis of D-cellobiose to D-glucose, partial isomerisation of D-glucose to D-fructose, followed by hydrogenation to D-sorbitol and subsequent hydrogenolysis to lower polyols [28]. The near absence of D-glucose in the course of the reaction here is remarkable. It implies that either the isomerisation reaction to D-fructose is very fast or that the hydrogenation reaction of D-glucose to D-sorbitol is (much) faster than the hydrogenation reaction of D-fructose to D-sorbitol. The latter argument is more likely as it is well known that D-glucose hydrogenation using Ru/C is much faster than D-fructose hydrogenation [20].

Mass balance calculations indicate that about 30 %-wt. of the original intake is converted to gas phase components, similar to the D-glucose experiments. Gas phase analysis shows that the gas consists mainly of unconverted H₂ (72.7 %-mol), 15.3 %-mol of CH₄, 0.33 %-mol of CO₂, 0.82 %-mol of ethane and 0.53 %-mol of propane. The amount of solids formed during reaction was slightly lower (1.1 %-wt.) than for D-glucose (1.5 %-wt.). This low amount of solids (combined with the absence of LA and HMF) implies that the thermal pathway (Scheme 1) occurs only to a minor extent.

3.3 Catalytic hydrotreatment of D-sorbitol

The catalytic hydrotreatment experiments with D-glucose and D-cellobiose indicate that D-sorbitol indeed is an important intermediate. Separate hydrotreatment experiments were conducted with D-sorbitol at conditions similar to that for D-glucose and D-cellobiose using Ru/C as the catalyst. The concentration of D-sorbitol and the main product (glycerol) as a function of time are given in Figure 5. D-sorbitol is, as expected based on the D-glucose experiments, converted to mainly glycerol and other C₁-C₅ polyols like propanediol and ethanol (quantities of max 1.75 %-wt.). These observations are in line with research of Sohonloue *et al.* on the hydrotreatment of D-sorbitol using Ru/SiO₂ (250 °C, 100 bar) [24]. It takes about 2.5 h to achieve full D-sorbitol conversion. The product polyols, however, are not stable and are converted to other components. A clear example is glycerol (Figure 5), which reaches a maximum concentration at 3.5 h reaction time, after which the concentration drops again. Some of the polyols are likely converted to gas phase components. GC analyses indicate that the gas phase consists of 91.2 %-mol unreacted H₂, 7.8 %-mol CH₄, 0.06 %-mol CO₂, 0.57 %-mol ethane and 0.33 %-mol of propane. Thus, like with D-glucose, methane is the major gas phase component. Analysis of the solid phase produced indicates that it solely consists of the catalyst, indicating that char/humins are not formed during the reaction. This is in contrast with the reactions starting with D-glucose and D-cellobiose and implies that solids formation is indeed related to the presence of D-glucose (and D-fructose) in the reaction mixture.

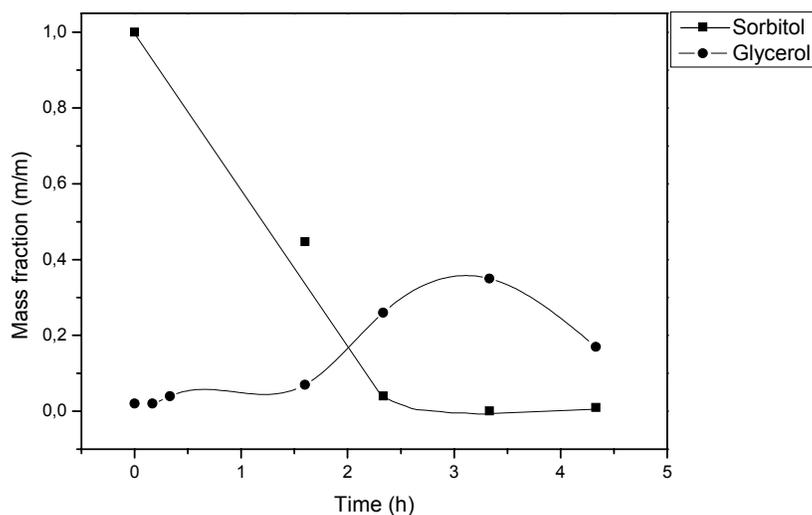


Figure 5. Product composition for the catalytic hydrotreatment of D-sorbitol in water versus time (250 °C, 100 bar H₂, 5 %-wt. Ru/C). Lines are for illustrative purposes only.

3.4 Catalytic hydrotreatment of glucose using Ru/C in the presence of acetic acid, acetaldehyde and acetone.

To better mimic fast-pyrolysis oil (a multi-component mixture containing a variety of oxygen functionalities), a number of catalytic experiments for D-glucose were carried out in the presence of co-reagents (acetic acid, acetaldehyde and acetone). For each experiment, D-glucose was mixed with either acetic acid, acetaldehyde or acetone in a 5 %-wt. basis (relative to the D-glucose intake). The reactions were carried out at 100 bar pressure and three different temperatures (175, 200 and 250 °C) using Ru/C. A multitude of liquid components was formed during these reactions (HPLC), of which the most could not yet be identified. Therefore, only the maximum yield of the most relevant and positively identified components (particularly D-sorbitol) will be provided. The results of the experiments are given in Table 1. The maximum D-sorbitol yield is a clear function of the reaction temperature, but also the type of co-reagent. In the absence of a co-reagent, the D-sorbitol yield is 97 %-wt. at both 175 and 200 °C. The maximum yield drops at higher temperatures and was found to be only 29 % at 250 °C. A similar trend was observed for experiments in the presence of acetic acid. To exclude possible effects

of catalyst deactivation by leaching of active metal from the support due to the presence of acids, the Ru-content in the water phase after reaction was determined (ICP). Ruthenium was not detected implying that Ru leaching from the support does not occur to a significant extent, in line with literature data on the stability of Ru/C in compressed water and acidic conditions [20].

In the presence of acetone or acetaldehyde, the maximum sorbitol yield at 175-200 °C is considerably lower. This is a clear indication that the reaction pathways at lower temperatures are affected by the presence of such co-reagents.

Table 1. Maximum D-sorbitol, solid and gas yield for catalytic hydrotreatment reactions of D-glucose (5 %-wt. Ru/C, 100 bar hydrogen, 4.3 h) in the presence of co-reagent.

co-reagent*	Maximum D-sorbitol yield at 175 °C (%-wt.)	Maximum D-sorbitol yield at 200 °C (%-wt.)	Maximum D-sorbitol yield at 250 °C (%-wt.)	Gas yield** (%-wt.)	Solids yield** (%-wt.)
none	97	97	29	25.9	1.5
Acetic acid	95	99	29	32.4	6.8
Acetaldehyde	84	43	43	28.2	0.3
Acetone	91	77	45	27.6	1.3

* 5 %-wt. on D-glucose intake.

** Based on D-glucose intake and for 250 °C experiments

Of particular interest is the amount of solids formed during the reaction at 250 °C. Compared to the blank experiment (1.5 %-wt.), the amount of solids formed in the presence of acetic acid (6.8 %-wt.) is considerably higher. Apparently, solids formation is more severe at acidic conditions. These findings may be rationalized by considering the reaction pathway for humin formation (Scheme 1), showing that the rate of humin formation is enhanced in the presence of acids [16,38]. The rate of the hydrogenation pathways is expected to be relatively independent of the acidity, leading to higher amounts of humins/char when hydrotreating D-glucose in the presence of acids.

3.5 Solids formation as a function of process conditions, catalyst and co-reagent

Table 2 shows an overview of the amount of solids formed in the various experiments reported in this paper. For comparison, the solids yield for an experiment using D-glucose at 250 °C, 4.3 h reaction time, Ru/C and 100 bar of nitrogen instead of hydrogen is also included. This value (43.2 %-wt.) is the upper limit of solids formation by the thermal pathway to humins under these conditions (Scheme 1).

Table 2. Overview of solids formation at 250 °C.

Reagent	Co-reagent	Gas phase	Catalyst	Solids yield (%-wt.)
D-cellobiose	-	Hydrogen	Ru/C	1.1
D-glucose	-	Hydrogen	Ru/C	1.5
D-glucose	acetic acid	Hydrogen	Ru/C	6.8
D-glucose	acetaldehyde	Hydrogen	Ru/C	0.3
D-glucose	acetone	Hydrogen	Ru/C	1.3
D-glucose	-	nitrogen	Ru/C	43.2
D-glucose	-	Hydrogen	Pd/C	2.6

It is clear that solids formation for all experiments is much lower than the limit at thermal conditions (43.2 %-wt.). Thus, the rate of the catalytic hydrogenation of D-glucose to D-sorbitol is considerably higher than the rate of thermal decomposition to LA/HMF and humins (Scheme 1). Solids formation in the subsequent hydrogenation/hydrogenolysis reactions of D-sorbitol to polyols does not occur as was shown by separate experiments with D-sorbitol. In the presence of acetic acid, larger amounts of humins are formed. This may be rationalized by considering that the thermal route to humins is catalysed by acids [16,38].

The existence of two important pathways for D-glucose (hydrogenation to D-sorbitol and thermal reactions to LA/HMF/humins) is also supported by comparing the experiments with Pd/C and Ru/C. The reaction rate for D-glucose is much higher when using Ru/C (compare Figure 1 and 3) and effectively the average D-glucose concentration is lower

throughout an experiment. Less solids formation by the thermal pathway is thus expected for Ru/C and this is indeed the case.

It is of particular interest to have insights in the reactivity of the humins under catalytic hydrotreatment conditions. For this purpose, a batch of humins was produced by treatment of D-glucose in water (1 M) in the absence of catalyst and hydrogen at 180 °C for 2 h. The solids yield was 41 %. Elemental analysis gave the following composition: 64.83 %-wt. of carbon, 4.06 %-wt. of hydrogen and 30.11 %-wt. of oxygen. The humin product was hydrotreated in a batch autoclave at 350 °C and 200 bar hydrogen using 5 %-wt. Ru/C in water. After reaction, the liquid phase was analysed, the solid conversion was determined and the gas phase was analysed and quantified.

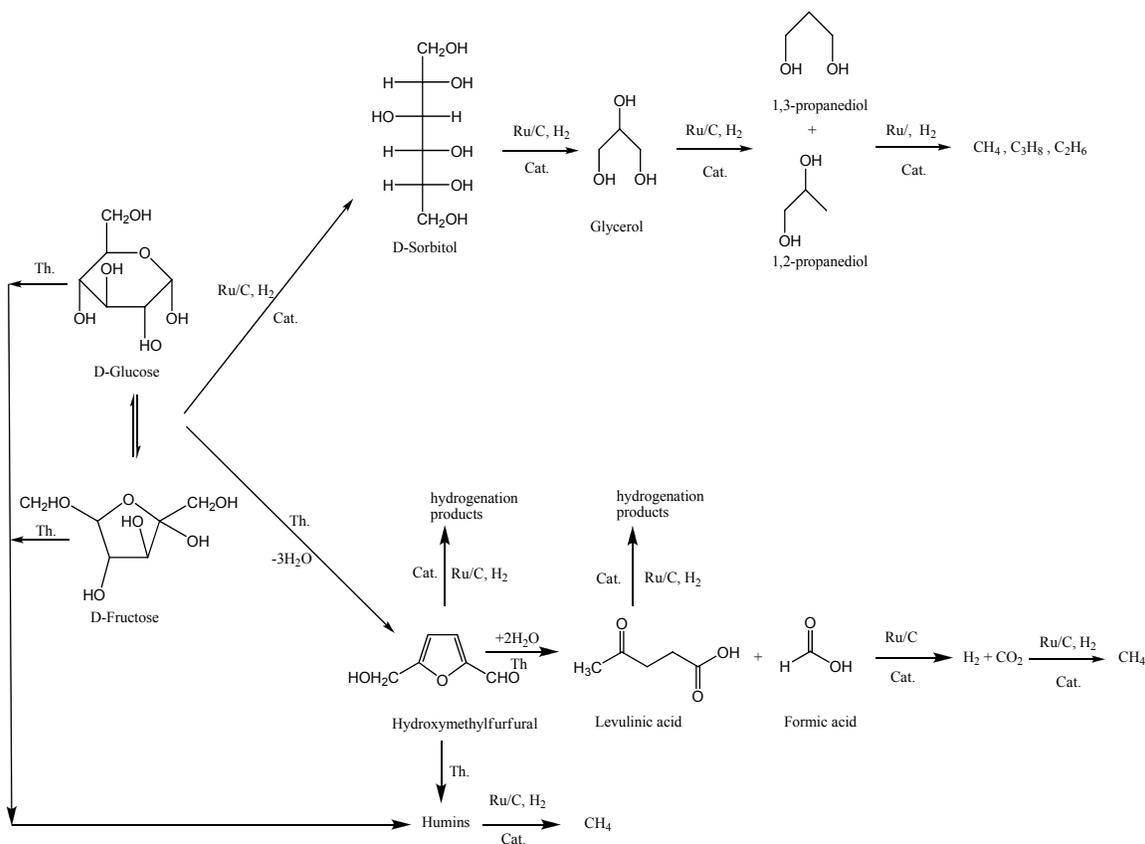
Mass balance calculations showed that 65 % of the humins have reacted to mainly liquid phase components and some gas phase components. The gas phase consists of mainly unreacted hydrogen (96.8 %-mol), 2.5 %-mol CH₄, 0.49 %-mol of CO₂, 0.16 %-mol of ethane and propane. Analysis of the liquid phase using HPLC showed the presence of a large amount of as yet unknown components. The identification and quantification of the liquid reaction products are in progress and will be reported in due course. Thus, the catalytic hydrogenation experiment indicates that the solids formed during the reaction by the thermal route are not inert under reaction conditions and may be depolymerised/hydrotreated to both gas phase components and water soluble products.

3.6 Reaction pathways and implications for catalytic fast-pyrolysis hydrotreatment

The catalytic hydrogenation experiments using D-glucose, D-cellobiose and D-sorbitol reveal that the main reaction pathway is a hydrogenation pathway to D-sorbitol followed by subsequent hydrogenolysis to smaller polyols (for instance glycerol, propanediol). In addition, a thermal pathway leading to the formation of LA/HMF takes place as well, but to a minor extent. This pathway also produces solid products (humins). Both pathways are depicted in Scheme 5. The presence of acids (e.g. acetic acid) catalyses the thermal route and leads to higher amounts of solids. Thus, the solids formed by the hydrotreatment of fast-pyrolysis oil may indeed be formed (partly) by thermal decomposition of monomeric sugars (D-glucose/D-fructose). The solids are apparently

not inert and may be depolymerised/converted to both gas and liquid phase components, adding to the complexity of the process.

All reactions were accompanied by the formation of gas phase components, the major being methane if Ru/C is used. A variety of possible reaction pathways may be envisaged for the formation of methane. Examples are methanisation of smaller polyols, the catalytic methanisation reaction of CO and hydrogen in the gasphase as well as conversion of the solids formed by the thermal pathways to gas phase components.



Scheme 5. Proposed pathway for the catalytic hydrotreatment of D-glucose. (Th. represents mainly the thermal route and Cat. represents a catalytic route.)

The results of this study imply that at least part of the gas phase components and solids formed upon hydrotreatment of fast-pyrolysis oils arise from the carbohydrate fraction in the oil. To reduce the solids formation, the rate of the thermal decomposition route of mono-saccharides (D-glucose, D-fructose) should thus be much lower than the hydrogenation reactions (Scheme 1). In practice, this may be achieved by performing a

pre-treatment step at low temperatures (< 150 °C). The rate of thermal decomposition to humins is low at these conditions, even in the presence of acid catalysts [39] whereas the rate of hydrogenation to D-sorbitol, the first intermediate in the sequence, is expected to be much faster. This is also clearly expressed by the difference in activation energy for key steps in both pathways, viz 55-75 kJ/mol for the hydrogenation of D-glucose to D-sorbitol [21] and 152 kJ/mol for humin formation from D-glucose [40]. In addition, humin formation may likely also be suppressed by performing the reaction at neutral conditions as the rate of the thermal decomposition pathway is known to be catalyzed by (organic) acids. Thus, a neutralization step and perhaps an acid removal step (distillation, reactive extraction) prior to fast pyrolysis oil hydrotreatment may also lead to reduced solids formation. Both hypotheses will be studied in future fast pyrolysis hydrotreatment experiments.

4. Conclusions

Catalytic hydrotreatment of D-glucose, D-cellobiose and D-sorbitol using a Ru/C catalyst has been conducted at 250 °C, 100 bar for 4.3 h. Main products of the catalytic hydrotreatment of D-glucose are a complex mixture of polyols and gas phase components, the major being methane. The results show that the catalytic hydrotreatment route at the prevailing reaction conditions is preferred over the thermal route leading to solids. Addition of acetic acid increases solids formation by catalyzing the thermal route. It has also been shown that the solids formed by the thermal route are not inert and may be hydrotreated to give a large number of yet unidentified water soluble products and methane. The results of this study imply that at least part of the gas phase components and solids formed upon hydrotreatment of fast-pyrolysis oils arise from the carbohydrate fraction in the oil. On the basis of these findings, a number of measures are proposed to reduce solids formation during hydrotreatment of fast-pyrolysis oil.

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