Catalytic Hydrotreatment of Fast Pyrolysis Oil: Model Studies on Reaction Pathways for the Carbohydrate Fraction

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Fast pyrolysis oil can be upgraded by a catalytic hydrotreatment (250–400°C, 100–200 bar) using heterogeneous catalysts such as Ru/C to hydrocarbon-like products that can serve as liquid transportation fuels. Insight into 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 20–40% 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 noncatalyzed pathway leading to insoluble humins (char) and a hydrogenation pathway leading to smaller polyols and gaseous hydrocarbons such as methane and ethane. The implications of these findings for the catalytic hydrotreatment of fast pyrolysis oil are discussed. © 2009 American Institute of Chemical Engineers Environ Prog, 28: 450–460, 2009
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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, 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 (sulfided) NiMo and CoMo on alumina. Overviews covering the catalytic hydrotreatment of pyrolysis oil have been 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 fur-
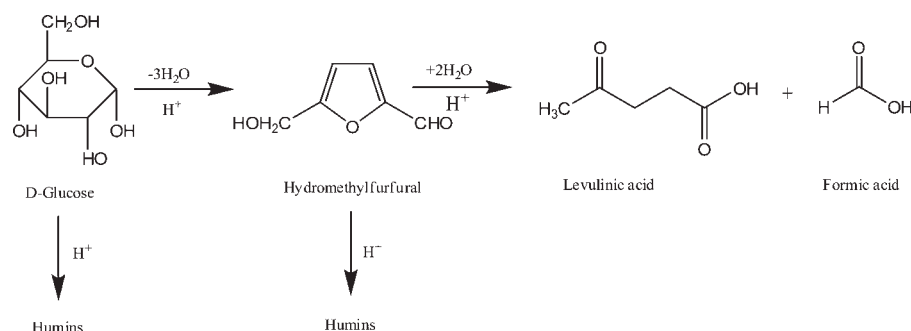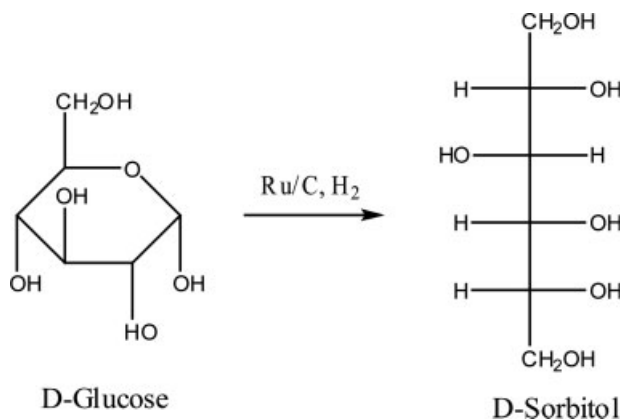
Scheme 1. Thermal decomposition of D-glucose.

ther 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 lower (250°C) and higher temperatures (up to 350°C) [10, 11]. Upgraded oils with a yield of approximately 53 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 that Pd/C, besides Ru/C, is also a promising catalyst for the catalytic hydrotreatment of pyrolysis oil [11].

A wide variety of organic components is likely involved in the solids (or "char"/coke) formation. One of the possible component groups is the cellulose-derived carbohydrate fraction. Carbohydrates can make up 30–40 wt % of pyrolysis oil, as shown by Oasmaa *et al.* [12, 13]. This fraction consists mainly of anhydrosugars and anhydrooligomers. Examples are levoglucosan and cellobiosan [12–14]. Diebold identified monomeric C5 and C6 sugars such as D-glucose, D-fructose, D-xylose, and D-arabinose in levels up to 3.2 wt % [12]. The presence of high amounts of oligomeric carbohydrates was demonstrated by Helle *et al.* [15].

Solids formation from such carbohydrates is known. Thermal decomposition, either catalytic or noncatalytic, leads to solid products referred to as humins [16–18]. The proposed reaction pathway consists of D-glucose conversion to 5-hydroxymethyl furfural (HMF) and subsequently levulinic acid (LA). Both reactions also accompanied by solids formation [17, 18] (Scheme 1).

Higher temperatures and the presence of acid catalysts (homogeneous and heterogeneous) increase the rate of D-glucose decomposition. Knesevic *et al.* [19]

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

studied the thermal decomposition of D-glucose in hot compressed water at elevated temperatures (240–374°C), where it was shown to decompose mainly to char and some gaseous components (primarily CO_2), while only a limited number of components remain in the water phase (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 has been reported extensively in the literature. The main focus is on the hydrogenation of D-glucose to D-sorbitol, a well-known chemical with uses in the pharmaceutical and food industries [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].

Kusserow [20] reported that besides the formation of D-sorbitol, other carbohydrates and 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 SiO_2 or Al_2O_3 (225–265°C and 26–58 bar). Over a Ru/SiO_2 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).

Wang *et al.* [25] provided more insights into the mechanism of such reactions by studying the hydrogenation of a variety of 1,3-diols (such as 2,4-dimethyl-2,4-pentanediol, 2-methyl-2,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 2,2-dimethyl-l,3-propanediol, 2,4-pentanediol, 1,3-butanediol, and 1,3-propandiol) 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).

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 C_1–C_5 alcohols using a Ru/C catalyst at 200°C and 20 bar hydrogen pressure. Yields up to 47% of sorbitol were reported. By-products 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 [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 because ketones such as acetone are present in pyrolysis oil up to 3 wt % [12]. Huber *et al.* have shown that larger alkanes (up to C_{15}) 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/SiO_2-Al_2O_3 catalyst to produce the larger alkanes.

To gain insight into catalytic hydrogenation pathways of the carbohydrate fraction in fast pyrolysis oil, we report here model studies using D-glucose and D-cellobiose. The results will be of particular interest for pyrolysis oils that are rich in carbohydrates. Such oils are obtained by pyrolyzing cellulose- and hemicellulose-rich (and thus low-lignin) biomass feedstocks such as soft and hard woods, bagasse, rice husks, 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 phases were identified and quantified and, in combination with the solids yield, allowed closure of the mass balances.
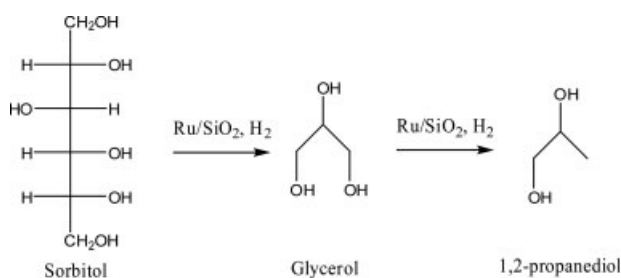
Scheme 3. Hydrogenolysis of D-sorbitol to glycerol and 1,2-propanediol.
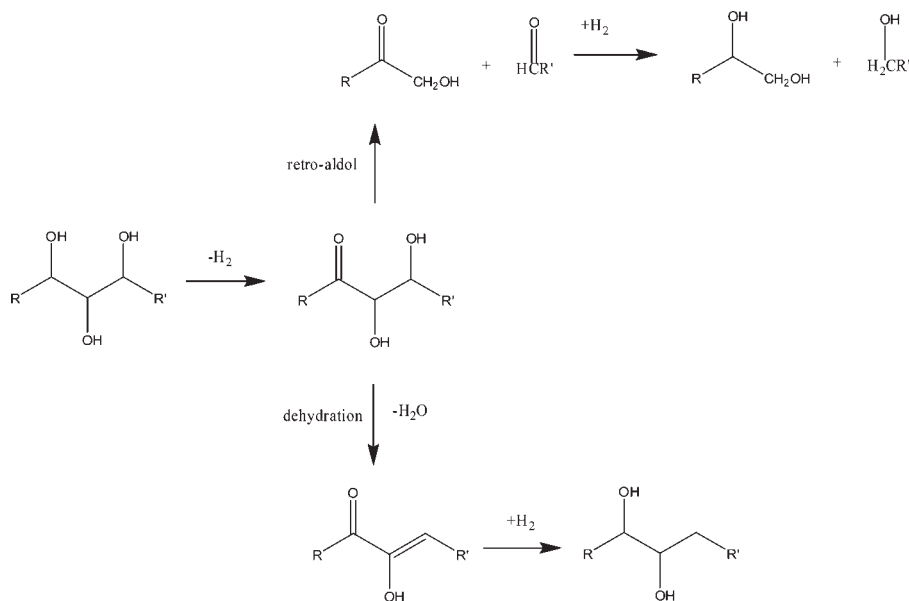
Scheme 4. Proposed mechanism for the formation of diols from D-sorbitol. (Adapted with permission from Wang *et al.* [25] Copyright 1995 American Chemical Society.)

The effect of the addition of acids, ketones, and aldehydes to the reaction mixture will also be explored. Implications of these finding for the catalytic hydrotreatment of fast pyrolysis oil will be addressed.

MATERIALS AND METHODS

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.

HYDROGENATION SETUP

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 (5–10 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 predetermined 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 min 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 hydrogenation process.

Liquid Analyses

Liquid samples were analyzed with gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography (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 analyses were performed on a Quadruple Hewlett Packard 6890 MSD attached to a Hewlett Packard 5890 GC equipped with a 30 m- × 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 min, then heated up to 250°C at a rate of 3°C min^{-1} and then held at 250°C for 10 min.

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 sulfuric 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 i.d., 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 postinjection 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 min at 1 bar. Triplicate measurements were performed for each sample.

The elemental composition (C, H, and N) of the products was determined in a 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 Applicon 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 duplicate.

Nuclear magnetic resonance (NMR) spectra were recorded on a 200-MHz NMR (AMS100, Varian). The samples were dissolved in D_2O.

Inductively coupled plasma (ICP) analysis 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% HNO_3 solution and analyzed.

Gas-Phase Analyses

The gas-phase samples were collected and stored in a gasbag. GC-TCD analyses were performed on a
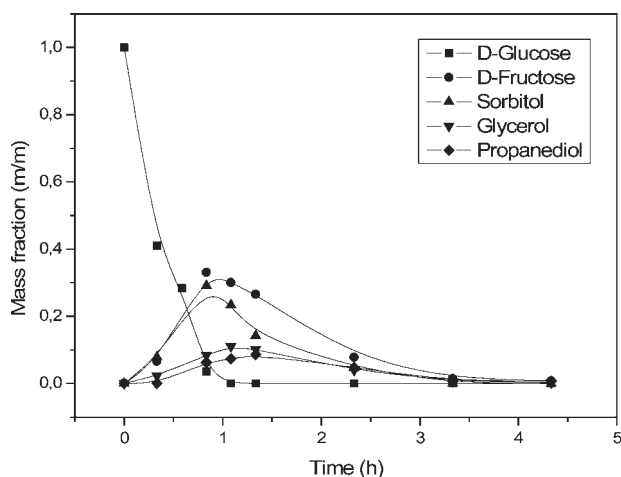
Figure 1. Product composition for the catalytic hydrotreatment of D-glucose in water versus time (250°C, 100 bar, and 5 wt % Ru/C). Lines are for illustrative purposes only.

Hewlett Packard 5890 Series II GC equipped with a Poraplot Q Al_2O_3/Na_2SO_4 column and a Molecular Sieve (5-Å) 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 min then heated up to 90°C at 20°C/min and kept at this temperature for 2 min. The columns were flushed during 30 s with the gas sample before starting the actual measurement. A reference gas containing H_2, CH_4, CO, CO_2, ethylene, ethane, propylene, and propane with known composition was used for peak identification and quantification.

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 hydrodeoxygenation of fast pyrolysis oil [10]. Furthermore, the addition of several compounds (acetaldehyde, acetone, and acetic acid) was explored to mimic the multicomponent nature of pyrolysis oil.

Hydrotreatment of D-Glucose

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 colorless liquid phase and brown solids were formed. 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 to be 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 isomerization product of D-glucose [20, 31]. The isomerization reaction is known to be catalyzed by bases and heterogeneous catalysts such as ZrO_2, TiO_2, and 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 to be not stable under such conditions, and after 4.3 h of reaction time their concentration levels are below the HPLC detection limit.

To gain further insight into the composition of the liquid phase after reaction, the solvent was removed in 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 such as propanediol, 1,2-butanediol, tetrahydrofuranmethanol, 1,2-pentanediol, and 1,2-hexanediol.

The liquid product was analyzed by ^{1}H 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 ^{1}H-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 around δ 3–4 ppm. These findings are confirmed by ^{13}C-NMR, showing methyl groups at around δ 14–18.9 ppm, aliphatic —CH_2— 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, 0.78, 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 analyzed by GC and consisted of 73 mol % residual H_2, 24 mol % CH_4, and 0.1 mol % CO_2. 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 % 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
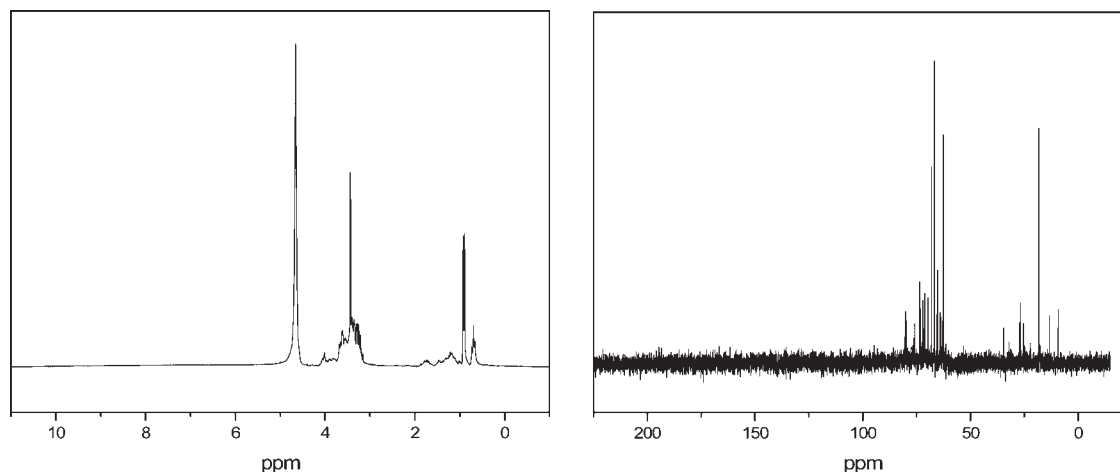
Figure 2. ^{1}H- and ^{13}C-NMR (D$_2$O) of the isolated liquid phase of catalytic hydrotreatment of glucose at 250°C and 100 bar after 4.3 h of reaction time.

humins formed by thermal decomposition of D-glucose.

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 that Pd/C can be a factor of more than 6 times less active than Ru/C in terms of intial reaction rate.

The initial reaction products are D-fructose (due to D-glucose isomerization) 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). In addition, a multitude of smaller polyols are produced, the major ones being pentitol, glycerol, and propanediol isomers.

Analyses of the reaction mixture after reaction by CE revealed the presence of organic acids such as formic acid (2.4 wt %), acetic acid (0.1 wt %), and levulinic acid (2–3 wt %). HMF and benzenetriol were also observed (2–3 wt %, HPLC). The presence of levulinic acid, formic acid, and HMF are indicative of 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% 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 because of 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
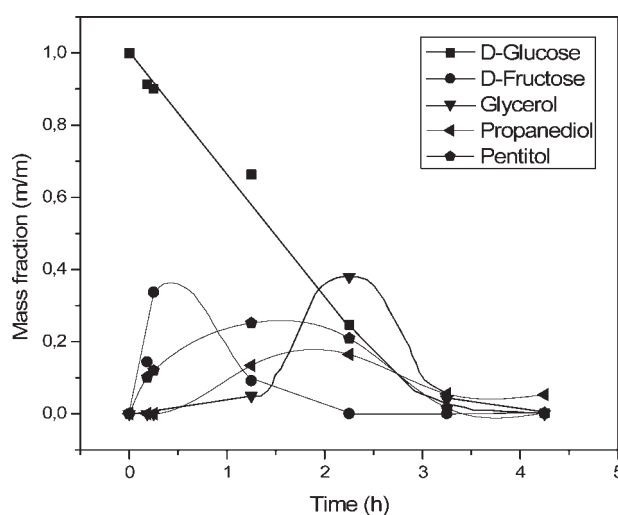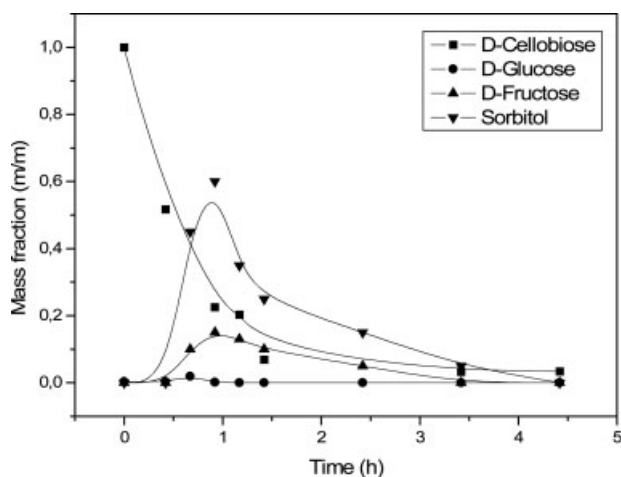

Figure 3. Product composition for the catalytic hydrotreatment of D-glucose in water versus time (250°C, 100 bar H$_2$, 5 wt % Pd/C). Lines are for illustrative purposes only.

higher amounts of levulinic acid, formic acid, and solids.

The composition of the gas phase was determined and shown to consist of 96 mol % unreacted H$_2$, 1.0 mol % CH$_4$, 0.4 mol % CO, 2.5 mol % CO$_2$, 0.06 mol % ethane, and 0.08 mol % propane. The methane yield was considerably lower than that observed with Ru/C (24 mol %). This implies that Pd/C is a not a very active methanization 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.

Catalytic Hydrotreatment of D-Cellobiose

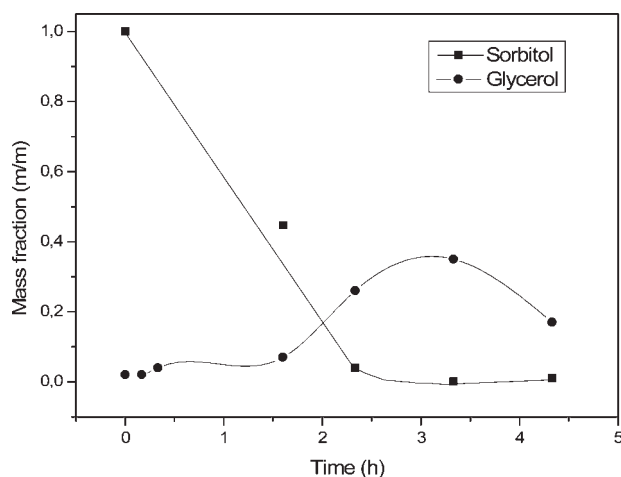The carbohydrates fraction of fast pyrolysis oil consists not only of monosaccharides and derivatives

Figure 4. Product composition for the catalytic hydro-treatment of D-cellobiose in water versus time (250°C, 100 bar H_2, 5 wt % Ru/C). Lines are for illustrative purposes only.

Figure 5. Product composition for the catalytic hydro-treatment of D-sorbitol in water versus time (250°C, 100 bar H_2, 5 wt % Ru/C). Lines are for illustrative purposes only.

(e.g., levoglucosan), but mainly of larger polysaccharides. D-Cellobiose was selected as a model compound to investigate the behavior 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.

D-Cellobiose conversion exceeded 90% within 2 h of reaction time. The major intermediates were D-fructose and the hydrogenated product D-sorbitol. D-Glucose was present only in minor amounts. The anticipated smaller polyols from the subsequent hydrogenation of D-sorbitol, such as glycerol and propane glycol, 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 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 isomerization 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 isomerization 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 H_2 (72.7 mol %), 15.3 mol % CH_4, 0.33 mol % CO_2, 0.82 mol % ethane, and 0.53 mol % propane. The amount of solids formed during reac-

tion 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 to only a minor extent.

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 those 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 mainly to glycerol and other C_1–C_5 polyols such as propanediol and ethanol (quantities of max 1.75 wt %). These observations are in line with research by Sohonloue *et al.* on the hydrotreatment of D-sorbitol using Ru/SiO_2 (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 (see 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 H_2, 7.8 mol % CH_4, 0.06 mol % CO_2, 0.57 mol % ethane, and 0.33 mol % propane. Thus, as with D-glucose, methane is the major gas-phase component. Analysis of the solid phase produced indicated that it consisted solely of the catalyst, indicating that char/humins are not formed during the reaction. This is in contrast to the reactions starting with D-glucose and D-cellobiose and implies that solids forma-

Table 1. Maximum D-sorbitol, solid, and gas yields for catalytic hydrotreatment reactions of D-glucose (5 wt % Ru/C, 100 bar H_2, 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.

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

Reagent	Co-reagent	Gas phase	Catalyts	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

tion is indeed related to the presence of D-glucose (and D-fructose) in the reaction mixture.

Catalytic Hydrotreatment of Glucose Using Ru/C in the Presence of Acetic Acid, Acetaldehyde, and Acetone

To better mimic fast pyrolysis oil (a multicomponent 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 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 of 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 was considerably lower. This is a clear indication that the reaction pathways at lower temperatures are affected by the presence of such co-reagents.

Of particular interest is the amount of solids formed during the reaction at 250°C. Compared to the base 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.

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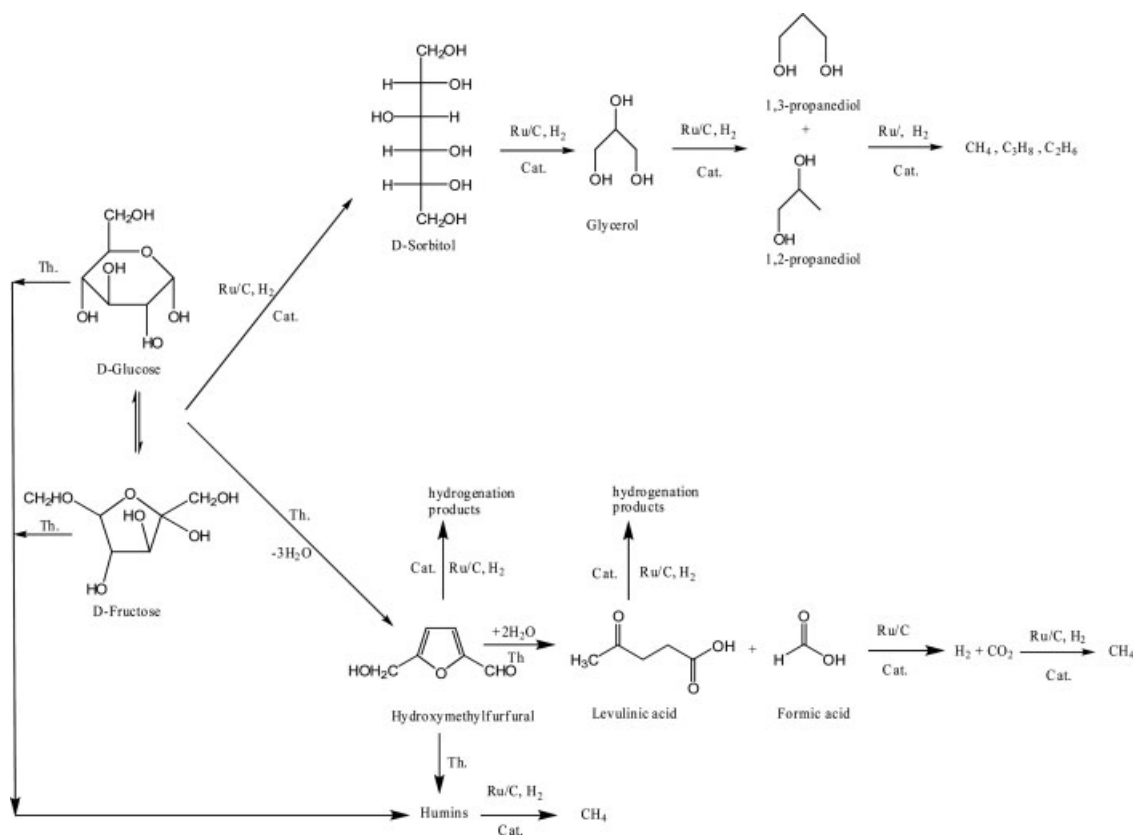
Scheme 5. Proposed pathway for the catalytic hydrotreatment of D-glucose. (Th. represents mainly the thermal route and Cat. represents a catalytic route.)

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).

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 catalyzed 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 Figures 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 with Ru/C, and this is indeed the case.

It is of particular interest to have insight into 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 % carbon, 4.06 wt % 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 analyzed, the solid conversion was determined, and the gas phase was analyzed and quantified.

Mass balance calculations showed that 65% of the humins reacted to mainly liquid-phase components and some gas-phase components. The gas phase consisted of mainly unreacted hydrogen (96.8 mol %), 2.5 mol % CH_4, 0.49 mol % CO_2, and 0.16 mol % ethane and propane. Analysis of the liquid phase using HPLC showed the presence of a large amount of as-yet-unknown components. 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 depolymerized/hydrotreated to both gas-phase components and water-soluble products.

Reaction Pathways and Implications for Catalytic Fast-Pyrolysis Hydotreatment

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). 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) catalyzes 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 depolymerized/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 one being methane if Ru/C is used. A variety of possible reaction pathways may be envisaged for the formation of methane. Examples are methanization of smaller polyols, the catalytic methanization reaction of CO and hydrogen in the gas phase, as well as conversion of the solids formed by the thermal pathways to gas-phase components.

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 monosaccharides (D-glucose, D-fructose) should thus be much lower than the hydrogenation reactions (Scheme 1). In practice, this may be achieved by performing a pretreatment 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.

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 one 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 hydro-

treated to a give large numbers 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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