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# Transfer Hydrogenation of Cellulose-based Oligomers over Carbon-supported Ruthenium Catalyst in a Fixed-bed Reactor

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Ru supported on activated carbon was found to be active for the transfer hydrogenation of cellulose oligomers, which were produced by the milling of acidulated microcrystalline cellulose. A C<sub>6</sub> sugar alcohol yield of 85% was obtained in less than 1 h reaction time in a batch reactor. Optimum reaction conditions for transfer hydrogenation were determined as 180 °C and a pH above 2.2 using glucose as a substrate. Use of deuterium as a marker established that direct transfer of hydride

species from 2-propanol to glucose occurs through the dihydride mechanism. Formation of molecular hydrogen from 2-propanol dehydrogenation was found to be a side reaction, with little influence on the glucose hydrogenation step. Conversion of cellulose oligomers to hexitols was also achieved in a continuous flow fixed-bed reactor with 36.4% yield at a liquid hourly space velocity of 4.7 h<sup>-1</sup>. The catalytic activity did not decrease even after 12 h of the onstream reaction.

## Introduction

Liquid hydrocarbon fossil fuels are soon expected to become economically unfavourable owing to high demand and short supply.<sup>[1]</sup> The global transport sector fuel demand, as of 2010, was 2200 million metric tons of oil equivalents,<sup>[2]</sup> and biofuels accounted for only 2.3% of this total demand.<sup>[3]</sup> To fulfil future demands, a sustainable technology needs to be developed that can facilitate the economic production of carbon-based fuels.<sup>[4]</sup> Carbohydrates derived from biomass are widely viewed as a sustainable raw material for the production of carbon-based liquid fuels in the future.<sup>[5]</sup> Cellulose is of particular interest because it is the most abundant carbohydrate on Earth and is not part of the human food supply.<sup>[6,7]</sup> Cellulose is a homopolymer composed only of glucose monomer units, a characteristic that allows a high yield of selective products. Cellulose can be depolymerised into glucose and then converted to various platform chemicals such as sugar alcohols.<sup>[8]</sup> The conversion of cellulose to C<sub>6</sub> sugar alcohols is achieved through successive hydrolysis and hydrogenation reactions in

an aqueous medium.<sup>[9]</sup> These sugar alcohols can then be used as a precursor for biofuels and various other chemicals.

The conversion of cellulose to C<sub>6</sub> sugar alcohols (hexitols) in a one-pot reaction with supported Pt and Ru catalysts under hydrogen pressure was reported in 2006.<sup>[10]</sup> Various other catalysts have since been reported to convert cellulose to hexitols.<sup>[11–14]</sup> The process involves a two-step reaction in which cellulose is first converted to glucose through hydrolysis.<sup>[15]</sup> The rate of hydrolysis is increased by the presence of a metal catalyst as well as hot compressed water.<sup>[16]</sup> Mineral and organic acid can also be added to promote the hydrolysis reaction.<sup>[17]</sup> In the second step, glucose undergoes hydrogenation over the metal surface to produce hexitols. Hydrolysis is the rate-limiting step in this process because the hydrogenation reaction is relatively fast.<sup>[11]</sup> Increasing the rate of hydrolysis holds the key to the industrial implementation of this process.

Liquid hydrocarbon fuels produced through hexitols can be a major contributor to total biofuel production. However, the technology is currently under development and there are many challenges yet to be addressed before the industrial-scale production of hexitols can be achieved. This reaction is currently studied only with laboratory-scale batch reactors, which are convenient for small-scale research and manufacturing of pharmaceutical drugs. A continuous flow reactor system is more suited for the large-scale production of hexitols from cellulosic biomass. Continuous processes not only are cost-effective and easily scalable but also offer improved energy efficiency, safety, and process control.<sup>[18]</sup> The use of a continuous flow reactor for hexitol production is hampered by unique challenges such as the insolubility of cellulose in water and the use of high-pressure hydrogen. These issues cannot be resolved by engineering solutions alone, and alternative reaction

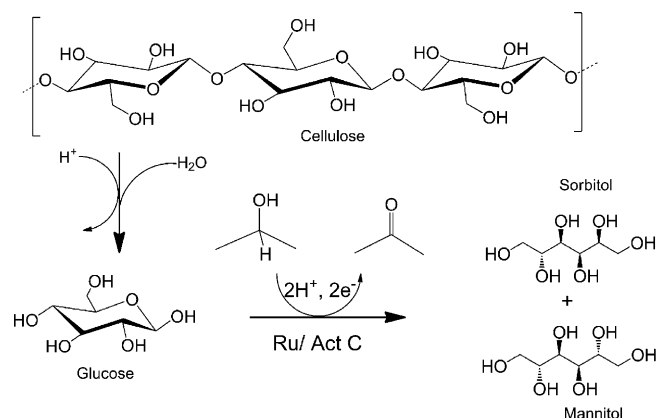
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pathways must be investigated to develop an easily scalable continuous process.

As mentioned previously, one of the issues associated with the scale-up of this process is the need for high-pressure hydrogen to achieve a fast hydrogenation rate. Excess hydrogen at high pressure is required to reduce degradation of glucose under the hydrothermal reaction conditions required for cellulose hydrolysis. Hydrogen pressure in excess of 40 bar (1 bar = 100 kPa) is needed to achieve maximum selectivity for the hydrogenation of glucose.<sup>[19]</sup> High-pressure hydrogen is not only a safety hazard but also increases the capital cost of reaction vessels. Furthermore, a headspace of pressurised hydrogen is needed to maintain equilibrium solubility because hydrogen is consumed during the reaction, which prohibits the use of a continuous flow fixed-bed reactor. A method to convert cellulose to hexitols through transfer hydrogenation with the carbon-supported Ru catalyst in the presence of 2-propanol was recently reported.<sup>[20]</sup> Hydrogen required for the reaction was produced in situ through the dehydrogenation of 2-propanol (Scheme 1). The carbon-supported Ru catalyst catalysed



**Scheme 1.** Sequential hydrolysis and transfer hydrogenation of cellulose over the carbon-supported Ru catalyst using 2-propanol as a hydrogen donor to produce hexitols. Adapted from Ref. [20]. Act C = activated carbon.

the dehydrogenation of 2-propanol and the hydrogenation of glucose simultaneously. A hexitol yield of 46.9% was reported with Ru supported on activated carbon (Ru/AC) after 18 h of the reaction. Because no hydrogen pressure was required and a relatively cheap hydrogen precursor was used, we believe this could be a promising route for the economic production of hexitols. However, the limitation of this report was the long reaction time of 18 h. The authors used ball-milled amorphous cellulose instead of crystalline cellulose to increase the rate of hydrolysis, but despite that the reaction time was long. Furthermore, the mechanism of hydrogen transfer from 2-propanol to glucose is still unknown. The significance of molecular hydrogen generated through the dehydrogenation of 2-propanol, which creates overhead hydrogen gas pressure during the reaction, is also not clearly understood.

The reaction time required for the conversion of cellulose to hexitol can be decreased by increasing the reactivity of cellu-

lose. The ordered crystalline structure of cellulose makes it insoluble in water and other conventional solvents.<sup>[21]</sup> The crystalline structure and the insolubility of cellulose in water limits access to the  $\beta$  (1 $\rightarrow$ 4)-glycosidic bonds linking the individual monomer units.<sup>[22]</sup> Pretreatment methods such as ball milling is reported to be effective in decreasing the degree of crystallinity and increasing the yield of hydrolysis products.<sup>[23]</sup> Nevertheless, amorphous cellulose produced after pretreatment is also insoluble in water, which leads to long reaction times. Moreover, the application of solid cellulose on a commercial scale would require a slurry reactor, which is difficult to design and operate owing to clogging problems. The mechanocatalytic treatment for the depolymerisation of acidulated cellulose was recently reported as a successful method to produce water-soluble oligomers.<sup>[24,25]</sup> Those oligomers were highly reactive compared with solid cellulose, and a hexitol yield of more than 90% was achieved in only 1 h of the reaction time with a bimetallic Ni–Pt catalyst.<sup>[24]</sup> Therefore, the use of soluble cellulose oligomers can be an effective method to decrease the reaction time. It would also enable the use of a fixed-bed reactor for the continuous production of hexitols.

Herein, we investigate in detail the transfer hydrogenation of cellulose in a batch reactor with an objective to identify the optimum temperature and feed ratio for conducting the reaction in a fixed-bed reactor. We identify the optimum reaction conditions suitable for both hydrolysis and hydrogenation reactions. The pathway of hydrogen transfer from 2-propanol to glucose is also determined to ascertain the effect of overhead hydrogen pressure. Finally, we demonstrate the feasibility of producing hexitols from cellulose in a continuous flow fixed-bed reactor.

## Results and Discussion

### Catalyst characterisation

The catalyst support used for the transfer hydrogenation reaction was the NORIT SX ULTRA activated charcoal powder purchased from Sigma–Aldrich. This support was chosen for its superior performance in the transfer hydrogenation of cellulose.<sup>[20]</sup> The catalyst was prepared by loading the support with 2 wt% Ru using ruthenium(III) nitrosyl nitrate as a precursor. The catalyst was reduced under hydrogen flow before the reaction (hereafter referred to as Ru/AC(N)). The BET surface area of the support was 1210 m<sup>2</sup>g<sup>-1</sup>, which decreased to 1150 m<sup>2</sup>g<sup>-1</sup> after impregnation with Ru metal. The average metal particle size was 1.4 nm as observed in the TEM image (Figure 1). The dispersion of Ru on the catalyst was calculated to be 25.8% by using CO chemisorption. Therefore, Ru was found to be well dispersed on the carbon support with fairly uniform particle size. Ru is present in its trivalent and tetravalent forms because it quickly oxidises in the presence of air to RuO<sub>2</sub>·2H<sub>2</sub>O at room temperature before the reaction.<sup>[20]</sup> In the presence of 2-propanol, RuO<sub>2</sub>·2H<sub>2</sub>O reduces to the Ru metal during the reaction, and the metallic Ru particles formed act as the active catalyst species.<sup>[26]</sup>

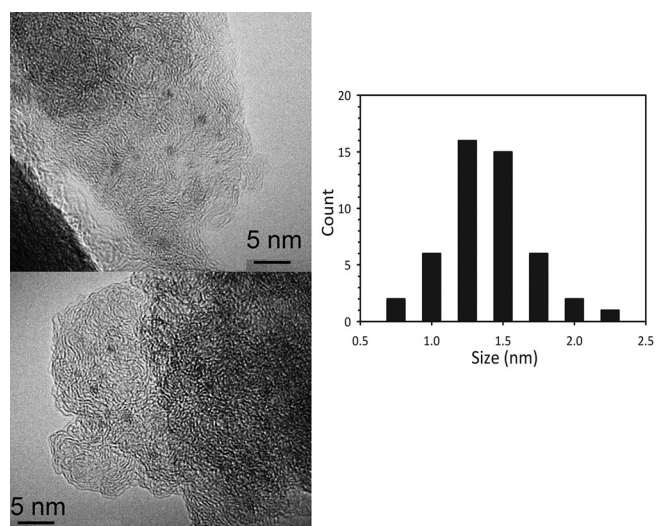


Figure 1. TEM image of 2 wt% Ru/AC(N) along with particle size distribution.

### Effect of temperature, pH, and feed ratio on the transfer hydrogenation of glucose

The yield of hexitol from the transfer hydrogenation of cellulose is limited by the slow rate of cellulose hydrolysis. Faster hydrolysis can be achieved by increasing the reaction temperature or decreasing the solution pH. However, under severe conditions, the rate of glucose degradation also increases and an optimum reaction condition must be established to maximise the hexitol yield. The reaction conditions for the efficient transfer hydrogenation of glucose with Ru/AC(N) were first investigated at different temperatures without the addition of any acid, which resulted in a pH of 5.3. The hexitol yield changed significantly within the temperature range of 170–200 °C (Figure 2a). After 20 min of the reaction, glucose conversion was 75 and 82% along with a hexitol yield of 73.6 and 79.7% at 170 and 180 °C, respectively. At higher temperatures, the yield and conversion were both lower. Possible factors for lower yield at higher temperature could be lower solubility of hydrogen produced by the dehydrogenation of 2-propanol, the deactivation of the catalyst, and the degradation of glucose.<sup>[27]</sup>

By using glucose as the feedstock, we found that the optimum temperature for transfer hydrogenation was 180 °C. However, the hydrolysis of cellulose is slow at this temperature in the absence of mineral acids. Therefore, we tested the effect of pH on the transfer hydrogenation of glucose because cellulose hydrolysis is accelerated at low pH. Furthermore, the oligomers mentioned in the “Transfer hydrogenation of cellulose oligomers” section contain a small amount of H<sub>2</sub>SO<sub>4</sub>, which leads to the formation of a mildly acidic reaction mixture of pH 2–3. As such, an equivalent amount of acid present in the oligomers (0.25 mmol of H<sub>2</sub>SO<sub>4</sub> per g of oligomers) was added to the glucose mixture, which resulted in a pH of 2.4 before the reaction. Lowering the pH from 5.3 (no acid) to 2.4 gave a higher conversion of glucose at 180 and 190 °C (Figure 2b). However, the yield of hexitol did not increase accordingly owing to an in-

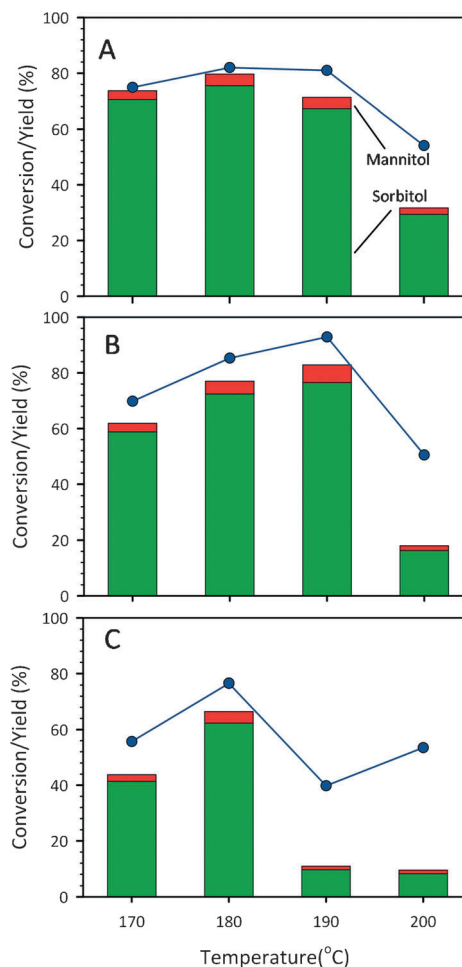


Figure 2. Transfer hydrogenation of glucose to hexitols in a batch reactor. Glucose conversion (●) and hexitol yield (bars) at a) pH 5.3, b) pH 2.4, and c) pH 2.2. Reaction conditions: 324 mg of glucose, 100 mg of the Ru/AC(N) catalyst (metal 2 wt%), 20 mL of water, 20 mL of 2-propanol,  $P = 15$  bar Ar at room temperature,  $t = 20$  min.

crease in the degradation of glucose. Lowering the pH to 2.2 by increasing the acid amount to 0.5 mmol significantly lowered the yield of hexitol at all temperatures (Figure 2c). These results suggest that as the severity of reaction increases with the increase in acid concentration or temperature, the catalyst is deactivated, which decreases the yield of hexitol, probably owing to the adsorption of glucose degradation products on the catalyst surface.

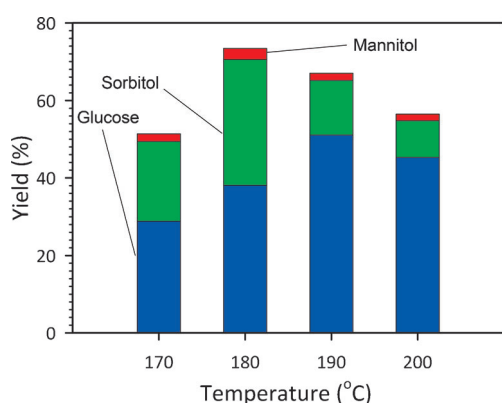
Another important factor affecting the rate of transfer hydrogenation was found to be the ratio of water to 2-propanol in the feed. Changes in this ratio affect the transfer hydrogenation reaction by changing the solubility of hydrogen, the thermodynamic interaction of the solvent with the reactants and products, and the competitive adsorption of 2-propanol versus glucose on the catalyst surface.<sup>[28]</sup> Increasing 2-propanol decreases the rate of hydrogenation by using conventional hydrogenation methods.<sup>[29]</sup> During the transfer hydrogenation of glucose in the presence of Ru/AC(N) at 180 °C, we observed a hexitol yield of 68.5% with 25 vol% 2-propanol, which increased to 79.7% with 50 vol% 2-propanol. Increasing the

amount of 2-propanol to 75 vol% decreased the hexitol yield to 29.8%.

### Transfer hydrogenation of cellulose oligomers

The optimised conditions for the transfer hydrogenation of glucose (pH 2.4, water to 2-propanol volume ratio 1:1) were tested for the transfer hydrogenation of cellulose oligomers at different temperatures. These oligomers were produced by milling cellulose impregnated with  $\text{H}_2\text{SO}_4$ , which resulted in the rapid depolymerisation of the polymer chain. A completely soluble substrate was obtained on milling cellulose impregnated with 0.25 mmol of  $\text{H}_2\text{SO}_4$  per g of oligomers for 10 h. An earlier study of these soluble oligomers had revealed that the soluble oligomers have an average degree of polymerisation of five to six monomer units. A fraction of these monomers are linked via  $\alpha$  (1 $\rightarrow$ 6) linkages, which, along with other factors, resulted in an instant solubility of the oligomers in water despite their high degree of polymerisation.<sup>[24]</sup> However, the solubility of oligomers in the reaction mixture was affected by the presence of 2-propanol. The oligomers were not completely soluble in the 50 vol% 2-propanol solution at room temperature, and a cloudy solution was obtained.

The conversion of cellulose oligomers to hexitols through transfer hydrogenation at various temperatures is shown in Figure 3. After 20 min of the reaction, the highest yield of hexitols (35.3%) was obtained at 180 °C. Upon decreasing the tem-



**Figure 3.** Yield of products from the transfer hydrogenation of cellulose oligomers in a batch reactor. Reaction conditions: 324 mg of cellulose oligomers, 100 mg of the Ru/AC(N) catalyst (metal 2 wt%), 20 mL of water, 20 mL of 2-propanol, pH 2.4,  $P = 15$  bar Ar at room temperature,  $t = 20$  min.

perature to 170 °C, a lower yield of 22.2% was obtained, which was likely due to the slower hydrolysis of oligomers as well as slow hydrogenation. As observed above, glucose hydrogenation is not favoured at higher temperature, which resulted in a high amount of glucose in the product at 190 and 200 °C because the hydrolysis of oligomers accelerated but the hydrogenation of glucose was slow. Upon increasing the reaction time to 40 min, the hexitol yield increased to 77.5% at 180 °C and a maximum yield of 83.4% was obtained after 1 h of the reaction.

### Mechanism of hydrogen transfer

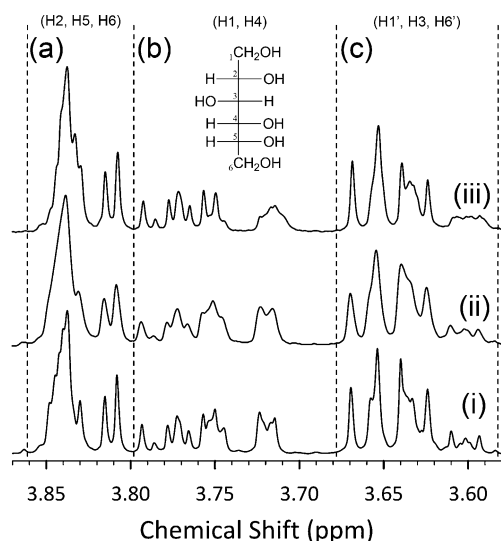
During transfer hydrogenation experiments, it was observed that after the reaction temperature was reached, the pressure of the reactor gradually increased by 3–5 bar. Even after the reactor was cooled to room temperature, an increased pressure of 3–5 bar was maintained, which indicated that a gaseous product was generated. By using GC, this gaseous product was identified as hydrogen gas, which was likely produced through the dehydrogenation of 2-propanol. In an earlier article, Ru/AC(N) was found to be active for hydrogenation under 8 bar hydrogen pressure as well as under transfer hydrogenation conditions in which hydrogen gas was produced through the dehydrogenation of 2-propanol.<sup>[20]</sup> In a fixed-bed reactor, this overhead space is not available and hydrogen gas formed would quickly leave the system. Hence, it is imperative to determine the role of overhead hydrogen pressure in this reaction.

It is unlikely that such a low partial pressure of hydrogen may produce the high rates of hydrogenation observed in our results. The low partial pressure of hydrogen would result in low solubility of hydrogen, which would limit the adsorption of hydrogen over the catalyst surface. Thus, the effect of molecular hydrogen in our reaction was investigated by repeating the reaction in the presence of hydrogen gas. To simulate the solvent effect of 2-propanol during transfer hydrogenation, an equivalent amount of *n*-propanol was used, which does not undergo dehydrogenation to produce hydrogen. In comparison to 79.5% yield of hexitols during transfer hydrogenation at 180 °C, only 2.9% of hexitols was obtained with 5 bar hydrogen partial pressure in the presence of *n*-propanol. Increasing the pressure of hydrogen to 15 bar increased the yield to 11.9%, which was still substantially lower compared with the yield obtained during transfer hydrogenation. On the basis of these observations, we conclude that it is unlikely for the reaction to proceed through the formation of hydrogen gas and the effect of hydrogen gas pressure on the rate of hydrogenation is minimal.

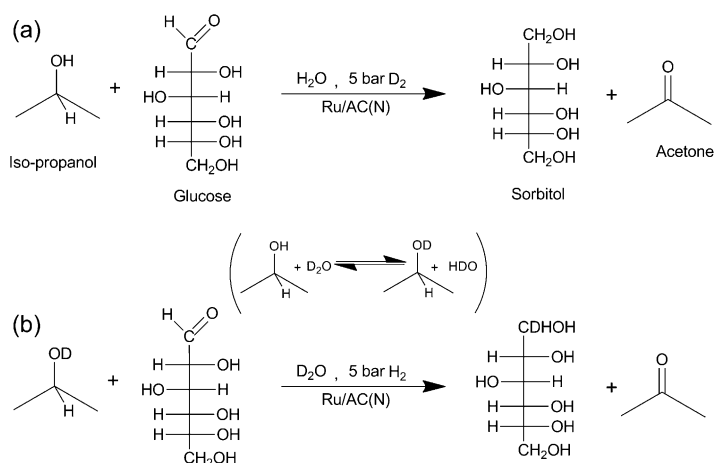
Adsorbed hydrogen species on the surface of the catalyst, which is produced through the dehydrogenation of 2-propanol, could be directly transferred onto the adsorbed glucose molecule. The mechanism of such direct transfer of hydrogen using homogeneous Ru complex catalysts has been extensively investigated.<sup>[30]</sup> However, the heterogeneous transfer hydrogenation mechanism is not well understood. To establish the source of hydrogen that is taking part in the hydrogenation reaction, we performed two experiments with deuterium instead of hydrogen in the form of  $\text{D}_2$  and  $\text{D}_2\text{O}$ . The sorbitol product obtained from these reactions can be isolated and analysed by using proton NMR spectroscopy. Deuterium is inactive towards magnetisation during NMR spectroscopy and can serve as a marker to determine the source of hydrogen taking part in the reaction. Therefore, the presence of deuterium attached to the carbon atom of sorbitol will lead to the absence of the corresponding proton peak in the NMR spectrum. The hydrogenation of glucose adds one H atom to the carbonyl oxygen and one to the anomeric carbon.<sup>[31]</sup> The latter H atom is observed

in the proton NMR spectrum at positions H1 and H1' (Figure 4). Doublets centred at a chemical shift of 3.63 and 3.72 ppm represent the positions H1 and H1' in the NMR spectrum.<sup>[32]</sup> Owing to the overlap of multiple peaks, it is not possible to evaluate the area for individual protons. However, a relative reduction in the peak can be calculated by dividing the spectrum into three sections (a, b, and c) such that there is no overlap of peaks between adjacent sections. Upon integrating individual sections, the ratio of areas was found to be 3.00:2.05:3.02 for sections a, b, and c, respectively, for a standard sorbitol sample. This observed ratio is in accordance with the expected theoretical ratio of 3:2:3.

In experiment 1, the hydrogenation of glucose was performed in the presence of 2-propanol, water, and 5 bar D<sub>2</sub> (Scheme 2a). In the proton NMR spectrum of the sorbitol product, all proton peaks were observed despite a lower resolution owing to a limited amount of the sample obtained through HPLC (Figure 4, spectrum ii). The area ratio was 3.00:1.99:3.05 for sections a, b, and c, respectively. The area ratio is same as that for the standard spectrum, which indicates that D was not present on positions H1 and H1'. In experiment 2, the reaction was performed in the presence of 2-propanol, D<sub>2</sub>O, and 5 bar hydrogen (Scheme 2b). Under these conditions, the proton attached to the hydroxyl group in 2-propanol would quickly exchange with deuterium. This deuterium would then participate in the hydrogenation of glucose. In the proton NMR spectra for sorbitol obtained from this reaction, a clear reduction in peak intensities for H1 and H1' is observed at a chemical shift of 3.63 and 3.72 ppm (Figure 4, spectrum iii). The ratio of areas in this case was 3.00:1.62:2.72 for sections a, b, and c, respectively. The decrease in area corre-



**Figure 4.** Proton NMR spectrum of sorbitol dissolved in D<sub>2</sub>O at 298 K. i) Standard sorbitol, ii) sorbitol obtained after the reaction in the presence of water, 2-propanol, and D<sub>2</sub>, and iii) sorbitol obtained after the reaction in the presence of D<sub>2</sub>O, 2-propanol, and hydrogen.



**Scheme 2.** Experiments showing use of deuterium as a marker to identify the source of hydrogen taking part in glucose hydrogenation. a) Use of D<sub>2</sub> gas did not show any presence of deuterated sorbitol. b) In the presence of D<sub>2</sub>O, deuterated 2-propanol was formed, which led to the formation of deuterated sorbitol.

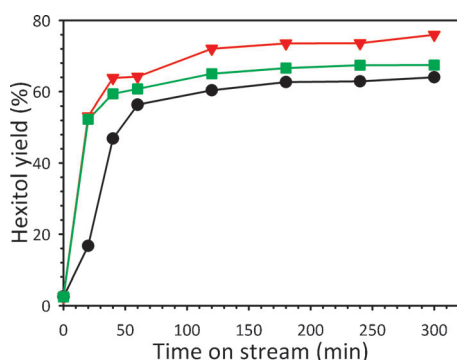
sponds to 66% of sorbitol molecules, with D attached to its carbon atom. These results support the dihydride mechanism, in which both the hydrogen atoms are transferred to the metal surface, which causes them to lose their identity.<sup>[33]</sup> The decrease in area was higher than the predicted 50% if hydroxyl hydrogen in all 2-propanol molecules is replaced by deuterium. An increased presence of deuterium can be attributed to the dissociative adsorption of deuterated water over the Ru surface, forming surface hydroxyl intermediates and protons, which can take part in the reaction.<sup>[34]</sup> These findings confirm that the primary source of hydrogen for hydrogenation is through direct transfer of adsorbed hydrogen species from 2-propanol to glucose over the Ru surface. The NMR results further confirm that gaseous hydrogen formed as a byproduct of the dehydrogenation reaction did not take part in the hydrogenation of glucose.

### Transfer hydrogenation of glucose and cellulose oligomers in the fixed-bed reactor system

A major advantage of using soluble cellulose oligomers for the transfer hydrogenation reaction is the ability to perform the reaction in a continuous flow fixed-bed reactor. The process is further simplified, as overhead hydrogen pressure is not required for transfer hydrogenation as concluded from the NMR results. A simple U-shaped fixed-bed reactor was designed by using 1/4 in. OD SS316 Swagelok tubing and tube fittings. Liquid feed was pumped into the reactor at a steady flow with an HPLC pump. The system was pressurised to 60 bar by restricting the liquid flow with a back pressure regulator, which prevented vaporisation of liquids at reaction temperatures. Once the required pressure was reached and the flow was steady, the reactor was dipped in a stirred oil bath maintained at the reaction temperature. Notably, effects owing to mass and heat transfer cannot be ignored in such a simple system, and therefore an attempt to evaluate kinetics of the reaction

was not made. Furthermore, owing to back mixing of liquid in the pressure regulator, which has a substantially high volume than the reactor, an induction phase in the first 50 min was observed. Efficiency of the reaction was calculated in terms of liquid hourly space velocity (LHSV), defined here as the ratio of the volumetric flow rate of the feed solution (in  $\text{mL h}^{-1}$ ) and the heated volume of the reactor (in mL). The LHSV was calculated in terms of reactor volume instead of catalyst mass, because the rate-limiting hydrolysis reaction is not catalysed by the Ru catalyst.

The glucose solution was initially used as a feed to test the feasibility of transfer hydrogenation in a fixed-bed reactor. A small reactor with a heated volume of 0.95 mL was loaded with 250 mg of the reduced Ru/AC(N), which resulted in a catalyst to reactor volume ratio of  $263 \text{ mg mL}^{-1}$ . As shown in Figure 5, a high yield of hexitols was obtained at liquid flow

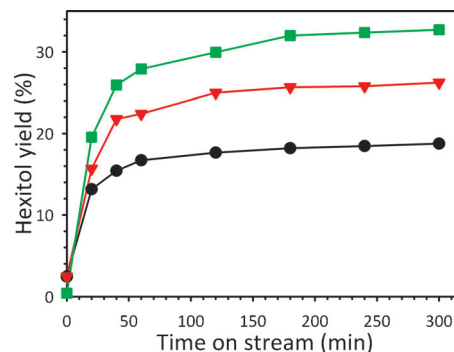


**Figure 5.** Yield of hexitols obtained at different flow rates in a fixed-bed reactor of a heated volume of 0.95 mL: LHSV 12.6 (●), LHSV 18.9 (▼), and LHSV 25.2 (■). Reaction conditions: feed concentration of  $8.1 \text{ mg mL}^{-1}$  glucose in 50 vol% 2-propanol in water, 2 wt% Ru/AC(N) ( $263 \text{ mg}_{\text{catalyst}} \text{ mL}^{-1}$  of the heated volume),  $T = 180^\circ\text{C}$ ,  $P = 60 \text{ bar}$ .

rates between  $0.2$  and  $0.4 \text{ mL min}^{-1}$ , which corresponds to an LHSV of  $12.6$ – $25.2 \text{ h}^{-1}$ . Significantly high hexitol yields were obtained despite a short residence time in the reactor. The highest hexitol yield of 75.9% was obtained at an LHSV of  $18.9 \text{ h}^{-1}$ . The selectivity towards hexitols was 66.0, 77.5, and 85.1% at an LHSV of 12.6, 18.9, and  $25.2 \text{ h}^{-1}$ , respectively. A lower selectivity than that in the batch reactor was presumably owing to the presence of a non-catalytic heated zone inside the reactor, in which glucose would degrade. This is also the cause of increase in selectivity at a higher LHSV if the residence time is lowered. The molar ratio of acetone produced to hexitol yield was 20.1, 12.8, and 10.6, respectively, which indicates an increased efficiency of hydrogen transfer at a higher LHSV. Hydrogen gas was produced during the reaction, which travelled through the system under biphasic flow conditions before exiting through the pressure regulator.

The glucose solution was later replaced with the cellulose oligomer solution as the feed for sequential hydrolysis and hydrogenation in the fixed-bed reactor. As mentioned above, the oligomers were not completely soluble in 50 vol% 2-propanol solution at room temperature. Therefore, to operate the continuous flow reactor, the feed was prepared with 25 vol%

2-propanol in water with a pH of 2.7. By using the 0.95 mL heated volume reactor with 250 mg of the catalyst and an LHSV of  $18.9 \text{ h}^{-1}$ , a hexitol yield of 18.7% was obtained (Figure 6). The low hexitol yield was attributed to the incomplete conversion of oligomers to glucose owing to small resi-



**Figure 6.** Yield of hexitols from the transfer hydrogenation of cellulose oligomers in a fixed-bed reactor of different volumes at a flow rate of  $0.3 \text{ mL min}^{-1}$ : LHSV 18.9 (●), LHSV 9.5 (▼), and LHSV 4.7 (■). Reaction conditions: feed concentration of  $8.1 \text{ mg mL}^{-1}$  cellulose oligomers in 25 vol% 2-propanol in water, 2 wt% Ru/AC(N) ( $263 \text{ mg mL}^{-1}$  of the heated volume), flow rate =  $0.3 \text{ mL min}^{-1}$ ,  $T = 180^\circ\text{C}$ ,  $P = 60 \text{ bar}$ , pH 2.7.

dence time. Increasing the catalyst loading to  $370 \text{ mg mL}^{-1}$  did not have any significant effect, which resulted in a hexitol yield of only 19.7% (result not shown in the graph). This finding further confirms that the hydrolysis of oligomers is the limiting reaction under fixed-bed reaction conditions. To promote the hydrolysis of oligomers, the residence time was increased by increasing the reactor volume, keeping the flow rate constant at  $0.3 \text{ mL min}^{-1}$  and thereby decreasing the LHSV. The catalyst loading was also kept constant at  $263 \text{ mg mL}^{-1}$ . The hexitol yield increased to 26.2% at an LHSV of  $9.5 \text{ h}^{-1}$ . Decreasing the LHSV to  $4.7 \text{ h}^{-1}$  increased the hexitol yield to 32.7%. This result suggests that the only limiting factor in this process is the incomplete hydrolysis, which can be eliminated by increasing the residence time of the reactant. Finally, to increase the efficiency of the process, feed concentration was increased to  $16.2 \text{ mg mL}^{-1}$  of cellulose oligomers. The pH of the solution also decreased to 2.35 with a higher concentration of  $\text{H}_2\text{SO}_4$ . The hexitol yield of 36.4% was obtained at an LHSV of  $4.7 \text{ h}^{-1}$ . The higher hexitol yield was due to the increased rate of hydrolysis at lower pH. This reaction was performed for over 12 h on stream and the catalytic activity did not decrease during this period, which suggested that the catalyst was highly stable for continuous process.

## Conclusions

Ru supported on activated carbon was prepared for transfer hydrogenation. A high dispersion of Ru was obtained, which led to high hexitol yields. The rate of glucose hydrogenation was found to be dependent on temperature, and the maximum hexitol yield was obtained at  $180^\circ\text{C}$ . Other influencing factors were the presence of acids and the amount of 2-propa-

mol present. The hydrogen gas produced through the dehydrogenation of 2-propanol played a negligible role in the hydrogenation reaction owing to low hydrogen partial pressure. The direct transfer of hydrogen from 2-propanol to glucose was proven through the dihydride mechanism without the participation of molecular hydrogen. The transfer hydrogenation process was effective for the direct conversion of cellulose oligomers to hexitols. A maximum yield of 83.4% hexitols was obtained in a batch reactor, which is the highest reported yield of hexitols from cellulose without using molecular hydrogen. This process was efficiently performed in a fixed-bed reactor. A maximum hexitol yield of 36.4% was obtained at a liquid hourly space velocity of  $4.7 \text{ h}^{-1}$ , and no apparent deactivation of the catalyst was observed over 12 h run. The yield of hexitols was limited by the extent of oligomer hydrolysis, which can be increased by increasing the retention time. These results increase the economic viability of producing hexitols from cellulose at large scale. Further work to improve this process is now focused towards reducing the formation of hydrogen gas, increasing the efficiency of hydrogen transfer, and identifying the reaction kinetics in the fixed-bed reactor.

## Experimental Section

### Catalyst preparation and characterisation

NORIT SX ULTRA activated charcoal and ruthenium(III) nitrosyl nitrate solution (1.5 wt% Ru) were purchased from Sigma-Aldrich. The Ru catalyst (2 wt%) was prepared by using the conventional impregnation method. The required amount of ruthenium(III) nitrosyl nitrate solution was added dropwise to the carbon support (1 g) dispersed in water (10 mL). The mixture was diluted to a total volume of 25 mL and then stirred for 16 h at RT. After stirring, water was removed with the rotary evaporator and the catalyst was dried under vacuum for 18 h. The dried catalyst was then reduced under  $\text{H}_2$  flow ( $30 \text{ mL min}^{-1}$ ) for 2 h at  $400^\circ\text{C}$ . The surface area and the pore size of the catalyst were measured by using  $\text{N}_2$  physisorption with a BELSORB-Mini II instrument at 77 K. The metal surface area was measured by using dynamic CO chemisorption performed on a BELCAT-A instrument equipped with a thermal conductivity detector. Before CO pulse adsorption, the catalyst was reduced at  $400^\circ\text{C}$  for 2 h, followed by purging with He at  $400^\circ\text{C}$  for 1 h before cooling to  $30^\circ\text{C}$  under He flow. TEM images were recorded on a JEOL JEM-2100 microscope operating at 200 kV.

### Cellulose depolymerisation

Water-soluble, cellulose-based oligomers were produced by using methods described elsewhere.<sup>[24]</sup> In a typical method,  $\text{H}_2\text{SO}_4$  (2.5 mmol) was diluted to a total volume of 25 mL. Sigmacell microcrystalline cellulose (10 g, Aldrich) was then added to this solution, and the solution was stirred for a few minutes. The resulting slurry was dried with a rotary evaporator, followed by overnight air drying at  $50^\circ\text{C}$ . The acidulated cellulose powder thus obtained was then milled in a planetary ball mill using 5 mm stainless steel balls, with a cellulose to ball weight ratio of 1:10. The mill was operated at 300 rpm, with a 20 min pause after every 15 min of continuous milling. The pause allowed dissipation of heat generated during milling, which prevented overheating of reactants. The milling time reported refers only to the active milling time.

### Catalytic reactions

Catalytic batch reactions were performed with a Hastelloy C22 batch reactor supplied by OM LAB-TECH CO., LTD., Japan. The reactor was charged with a substrate (324 mg) along with the catalyst (100 mg) and a water–2-propanol mixture (40 mL). The reactor was purged to remove air and then pressurised with Ar at 15 bar before heating. After the reaction was complete, the catalyst was separated through centrifugation and the solution was analysed by using HPLC.

Continuous flow fixed-bed reactions were performed on a custom-built reaction system. An Alltech HPLC pump was used for feeding the liquid into the fixed-bed reactor. A U-shaped fixed-bed reactor was designed by using 1/4 in. OD SS316 Swagelok tubing and tube fittings. The powdered Ru/AC(N) catalyst was used as is without any pelletisation. The reduced catalyst was loaded into the reactor, and a small amount of quartz wool was inserted from both sides of the reactor to hold the catalyst in place. A  $7 \mu\text{m}$  Swagelok inline filter was connected to the reactor exit, which was followed by a Swagelok back pressure regulator. A steady flow was established through the system until the desired pressure was achieved. The reactor was then dipped slowly into a stirred oil bath set at the reaction temperature; at that moment, the reaction time was noted as 0 min.

Liquid products were analysed with a Shimadzu HPLC system equipped with Rezex RPM/RCM monosaccharide columns, with a mobile phase flow rate of  $0.6 \text{ mL min}^{-1}$ . The products were detected with a refractive index detector and a Shimadzu ELSD-LTII detector operating at  $30^\circ\text{C}$ .

### NMR analysis

The sorbitol product for NMR analysis was obtained by isolating it from the reaction mixture by using HPLC. After approximately 15 repetitions, the collected sorbitol solution was dried to remove water and then dissolved in  $\text{D}_2\text{O}$  for NMR analysis. The proton NMR spectra of the sorbitol solution were obtained on a JEOL JNM-ECP400 spectrometer operating at 400 MHz using a pulse repetition time of 1 s with 64 scans. The obtained spectrum was referenced externally to 4,4-dimethyl-4-silapentane-1-sulphonic acid.

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- [1] British Petroleum, *BP Statistical Review of World Energy*, 2013.
- [2] World Energy Council, *Global transport scenarios 2050*, 2011.
- [3] International Energy Agency, *Tracking clean energy progress*, 2013.
- [4] International Energy Agency, *Technology Roadmap—Biofuels for Transport*, Paris, 2011.
- [5] J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem. Int. Ed.* **2007**, *46*, 7164–7183; *Angew. Chem.* **2007**, *119*, 7298–7318.
- [6] S. N. Naik, V. V. Goud, P. K. Rout, A. K. Dalai, *Renewable Sustainable Energy Rev.* **2010**, *14*, 578–597.
- [7] D. Klemm, B. Heublein, H.-P. Fink, A. Bohn, *Angew. Chem. Int. Ed.* **2005**, *44*, 3358–3393; *Angew. Chem.* **2005**, *117*, 3422–3458.
- [8] H. Kobayashi, A. Fukuoka, *Green Chem.* **2013**, *15*, 1740–1763.

- [9] H. Kobayashi, T. Komanoya, S. K. Guha, K. Hara, A. Fukuoka, *Appl. Catal. A* **2011**, *409–410*, 13–20.
- [10] A. Fukuoka, P. L. Dhepe, *Angew. Chem. Int. Ed.* **2006**, *45*, 5161–5163; *Angew. Chem.* **2006**, *118*, 5285–5287.
- [11] H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P. L. Dhepe, K. Hara, A. Fukuoka, *Green Chem.* **2011**, *13*, 326–333.
- [12] S. Van de Vyver, J. Geboers, P. A. Jacobs, B. F. Sels, *ChemCatChem* **2011**, *3*, 82–94.
- [13] A. Shrotri, A. Tanksale, J. N. Beltramini, H. Gurav, S. V. Chilukuri, *Catal. Sci. Technol.* **2012**, *2*, 1852–1858.
- [14] C. Luo, S. Wang, H. Liu, *Angew. Chem. Int. Ed.* **2007**, *46*, 7636–7639; *Angew. Chem.* **2007**, *119*, 7780–7783.
- [15] M. Yabushita, H. Kobayashi, A. Fukuoka, *Appl. Catal. B* **2014**, *145*, 1–9.
- [16] P. L. Dhepe, A. Fukuoka, *ChemSusChem* **2008**, *1*, 969–975.
- [17] R. Rinaldi, F. Schüth, *ChemSusChem* **2009**, *2*, 1096–1107.
- [18] N. G. Anderson, *Org. Process Res. Dev.* **2001**, *5*, 613–621.
- [19] J. Wisnlak, R. Simon, *Ind. Eng. Chem. Prod. Res. Dev.* **1979**, *18*, 50–57.
- [20] H. Kobayashi, H. Matsuhashi, T. Komanoya, K. Hara, A. Fukuoka, *Chem. Commun.* **2011**, *47*, 2366–2368.
- [21] A. Pinkert, K. N. Marsh, S. Pang, *Ind. Eng. Chem. Res.* **2010**, *49*, 11121–11130.
- [22] H. Zhao, J. H. Kwak, Y. Wang, J. A. Franz, J. M. White, J. E. Holladay, *Energy Fuels* **2006**, *20*, 807–811.
- [23] A. Onda, T. Ochi, K. Yanagisawa, *Green Chem.* **2008**, *10*, 1033–1037.
- [24] A. Shrotri, L. K. Lambert, A. Tanksale, J. Beltramini, *Green Chem.* **2013**, *15*, 2761–2768.
- [25] N. Meine, R. Rinaldi, F. Schüth, *ChemSusChem* **2012**, *5*, 1449–1454.
- [26] T. Komanoya, H. Kobayashi, K. Hara, W.-J. Chun, A. Fukuoka, *ChemCatChem* **2014**, 230–236.
- [27] N. S. Mosier, C. M. Ladisch, M. R. Ladisch, *Biotechnol. Bioeng.* **2002**, *79*, 610–618.
- [28] R. A. Rajadhyaksha, S. L. Karwa, *Chem. Eng. Sci.* **1986**, *41*, 1765–1770.
- [29] B. S. Akpa, C. D'Agostino, L. F. Gladden, K. Hindle, H. Manyar, J. McGregor, R. Li, M. Neurock, N. Sinha, E. H. Stitt, D. Weber, J. A. Zeitler, D. W. Rooney, *J. Catal.* **2012**, *289*, 30–41.
- [30] J. S. M. Samec, J.-E. Backvall, P. G. Andersson, P. Brandt, *Chem. Soc. Rev.* **2006**, *35*, 237–248.
- [31] L. A. Maranhao, F. Sales, J. F. R. Pereira, C. M. Abreu, *React. Kinet. Catal. Lett.* **2004**, *81*, 169–175.
- [32] D. S. Wishart, et al., *Nucleic Acids Res.* **2007**, *35*, D521–D526.
- [33] F. Alonso, P. Riente, M. Yus, *Acc. Chem. Res.* **2011**, *44*, 379–391.
- [34] J. Weissenrieder, A. Mikkelsen, J. N. Andersen, P. J. Feibelman, G. Held, *Phys. Rev. Lett.* **2004**, *93*, 196102.

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