Aqueous phase reforming in a microchannel reactor

Citation for published version (APA):

DOI:
10.1039/c3cy00577a

Document status and date:
Published: 01/10/2013

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 29. Oct. 2020
Aqueous phase reforming in a microchannel reactor: the effect of mass transfer on hydrogen selectivity

Maria Fernanda Neira D’Angelo, Vitaly Ordomsky, John van der Schaaf, Jaap C. Schouten and T. Alexander Nijhuis*

Aqueous phase reforming of sorbitol was carried out in a 1.7 m long, 320 μm ID microchannel reactor with a 5 μm Pt-based washcoated catalyst layer, combined with nitrogen stripping. The performance of this microchannel reactor is correlated to the mass transfer properties, reaction kinetics, hydrogen selectivity and product distribution. Mass transfer does not affect the rate of sorbitol consumption, which is limited by the kinetics of the reforming reaction. Mass transfer significantly affects the hydrogen selectivity and the product distribution. The rapid consumption of hydrogen in side reactions at the catalyst surface is prevented by a fast mass transfer of hydrogen from the catalyst site to the gas phase in the microchannel reactor. This results in a decrease of the concentration of hydrogen at the catalyst surface, which was found to enhance the desired reforming reaction rate at the expense of the undesired hydrogen consuming reactions. Compared to a fixed bed reactor, the selectivity to hydrogen in the microchannel reactor was increased by a factor of 2. The yield of side products (mainly C3 and heavier hydrodeoxygenated species) was suppressed while the yield of hydrogen was increased from 1.4 to 4 moles per mole of sorbitol fed.

1 Introduction

The decentralized conversion of biomass to hydrogen is an attractive alternative to feed highly efficient polymer electrolyte membrane (PEM) fuel cells for power generation.1 Hydrogen can be obtained from an aqueous solution of a (bio)carbohydrate over a Pt-based catalyst under mild conditions (ca. 200 °C, 30 bar) via aqueous phase reforming (APR):2–4

\[ C_{n}H_{2m}O_{n} + nH_{2}O \rightarrow nCO_{2} + (m + n)H_{2} \quad (1) \]

This route5–7 gives the possibility to upgrade liquid waste streams from bio-based industries into a nearly CO-free hydrogen gas mixture with minimized energy input.8,9 The production of hydrogen via APR is challenged by undesired side reactions like the acid catalyzed dehydration of the substrate, followed by hydrogenation over the metal surface. Rearrangement reactions may also occur given the high functionality of the intermediate products and the combined catalytic effect of the active metal, the support and the liquid medium. These reactions represent an overall consumption of hydrogen and result in the formation of a significant amount of liquid phase water-soluble oxygenated products, and eventually alkanes.10–12 The complexity of this chemistry and the extent of the undesired hydrogen-consuming reactions become more significant as the size of the substrate increases.2 For practical implementation, however, the conversion of larger carbohydrates is desired to minimize pre-treatment costs. Glucose is an attractive reactant for APR,13–16 but its conversion to hydrogen is additionally limited by homogeneous decomposition. Alternatively, glucose can be partially hydrogenated in a fast and nearly 100% selective step to sorbitol.17 This sugar-alcohol is not sensitive to homogeneous decomposition and can be consequently reformed to hydrogen with greater selectivities than glucose.18 In this case, the selectivity is only restricted by undesired hydrogen-consuming reactions on the catalyst surface.2

Various examples in the literature highlight the relevance of the interface mass transfer rate, and thus the reactor design, on the product selectivity.19,20 One example is a microreactor in which gas and liquid are forced to flow through channels with diameters of 10−4–10−3 m. At these scales, the hydrodynamics differ from those in conventional systems. Of possible flow regimes, the Taylor flow regime is one of the most stable.21–23 In the Taylor flow regime, gas bubbles and liquid slugs flow through the channel as a plug flow in an alternating sequence. The gas bubbles are longer than the channel diameter and a thin liquid film separates the gas bubbles from the channel walls, where the catalyst is deposited. This system benefits from high diffusion rates, short diffusion paths and large interfacial surface areas, resulting in excellent mass and heat transfer.
rates.\textsuperscript{24,25} Provided there is a good affinity between the liquid and the washcoated walls of the channel, this system offers an ideal wettability and a continuous renewal of reactants on the catalyst surface.\textsuperscript{26} Despite these advantages, the application of microreactor systems for heterogeneously catalyzed reactions is still under development because of issues like catalyst loading, catalyst stability, and scaling up need to be solved to make these processes industrially attractive.

We have recently reported that APR of ethylene glycol can be successfully conducted in a catalytically washed microchannel reactor that operates under the Taylor flow regime with continuous phase-transfer hydrogen separation.\textsuperscript{27} The focus of that study, as initial proof of concept, was the preparation of the catalyst as well as the evaluation of its activity and stability during APR. In that study, a visible increase of the hydrogen selectivity compared to a conventional fixed bed reactor was detected. This was attributed to the high mass transfer rates and to the hydrodynamic characteristics of the microchannel reactor. The use of a microchannel reactor is expected to be even more beneficial during APR of larger carbohydrates like sorbitol with stronger proclivity for undesired hydrogen-consuming reactions than ethylene glycol.

In this study, we investigate the benefits of using a microchannel reactor for the production of hydrogen via APR of sorbitol.

\begin{equation}
C_6H_{14}O_6 + 6H_2O \rightleftharpoons 6CO_2 + 13H_2
\end{equation}

The implications of the mass transfer effects of the microchannel reactor for the hydrogen selectivity and the reaction kinetics are investigated. As a model system, APR of sorbitol is conducted in a 1.7 m long, 320 \( \mu \)m ID microchannel reactor with a 5 \( \mu \)m Pt-based washcoated catalyst layer as well as in a conventional fixed bed reactor. The performance of the reactors is evaluated in terms of sorbitol conversion, hydrogen selectivity and the observed product distribution, which is analyzed according to the reaction pathways earlier suggested in the literature.\textsuperscript{10,28} In this way, we are able to correlate mass transfer characteristics of the microchannel reactor with the hydrogen selectivity and the reaction kinetics.

2 Experimental

2.1 Catalyst preparation

A 5 \( \mu \)m boehmite layer was deposited on the walls of a 1 m long, 320 \( \mu \)m ID fused silica microchannel (Varian) by following a static washcoating methodology, fully described in a previous work.\textsuperscript{27} Pt was loaded on the support by impregnation using a solution of Pt(C\textsubscript{6}H\textsubscript{4}O\textsubscript{6})\textsubscript{2} in Cl\textsubscript{2}CH\textsubscript{2} with the desired concentration to obtain 0.7 mg Pt per 1.7 m or 2 wt% Pt/AlO(OH). Activation of this layer was done by calcination at 350 °C for 6 h and reduction at 220 °C with hydrogen for 2 h prior to the reaction.

The catalytic activity of the washcoated microchannel was compared to that of a reference bulk catalyst in a fixed bed reactor. For the preparation of this catalyst, the AlO(OH) precursor was calcined, impregnated and activated in the same fashion as the washcoated layer. The resulting powder was pressed and sieved to obtain particle size between 422 and 600 \( \mu \)m.

2.2 Experimental setup

The experimental setup in Fig. 1 was used to conduct the conversion of sorbitol to hydrogen by APR. The washcoated microchannel is located in an oven with circulating hot air that provides constant heating to the reactor to maintain isothermal operation at 220 °C. The adiabatic temperature decrease at 100% conversion is less than 8 K (calculated as \( \Delta T = 6 \times 10^5 \) J mol\(^{-1}\) sorbitol \times 10\(^{-3}\) mol sorbitol/mol water/76 J mol\(^{-1}\) water K), which can be easily overcome due to the excellent heat transfer characteristics of the microchannel reactor. Prior to operation, the washcoated microchannel reactor was pressurized, pre-heated and pre-wetted. A syringe pump (Teledyne ISCO 500D) was used to feed the liquid solution of 1 wt% sorbitol (Sigma) in water. During the reaction, the microchannel reactor was operated under the Taylor flow regime by co-feeding the liquid reactant and nitrogen. Both phases were pre-mixed before the reactor inlet in a Y-mixer (VICI Valco). The reaction products were quenched downstream and collected in a pressurized stainless steel vessel where the gas phase was separated from the liquid phase. The pressure of the system (i.e. 35 bar) was controlled by a back pressure regulator connected to the gas line that exited the steel vessel. To ensure proper control of the pressure, an argon flow was fed to this vessel, also serving as an external standard to quantify the gas composition.

The identification and quantification of the liquid phase reaction products were done by a combination of HPLC (column: Metacarb 67H, detector: RI), GC (column: Cp-sil5, detector: FID) and GC-MS (column: DB-200, detector: MS) analysis. The composition of the gas phase was monitored on-line with GC (columns: Poraplot/Molsieve 5A, detectors: TCD/FID).

The composition of gas and liquid was used to determine the conversion of sorbitol and the selectivity towards the main products when varying the liquid flow rate (0.75–9 ml h\(^{-1}\)) and the gas to liquid ratio at the microchannel inlet (\( R_{\text{GL}} = 0–2 \) \( m_{\text{gas}}/m_{\text{liquid}} \)). These results were compared to those obtained in analogous experiments conducted in a stainless steel tubular reactor (10 cm long, 2.5 mm ID) with a porous bed.
of 110 mg of bulk catalyst (2 wt% Pt/AlO(OH)). The porosity of the bed was ca. 0.3. This reactor was exchanged by the washcoated microchannel in the same experimental setup depicted in Fig. 1. In these experiments, the fixed bed reactor was placed vertically and operated downflow. After pre-wetting of the catalyst with the liquid reactant, a nitrogen flow was fed co-currently in the same fashion as previously done with the washcoated microchannel reactor. The liquid and gas flow rates were adjusted according to the amount of Pt in the reactor to maintain a comparable WHSV and equal \( R_{\text{GL}} \) as those in the microchannel. If not indicated otherwise, the gas stream fed is pure nitrogen. An extended series of experiments were conducted in the fixed bed reactor to investigate the effect of the hydrogen partial pressure on the reaction rate and the hydrogen selectivity. In these experiments, various mixtures of nitrogen and hydrogen were pre-mixed with the liquid stream with a constant gas to liquid ratio of \( R_{\text{GL}} = 2m_{\text{gas}}/m_{\text{liquid}} \).

### 2.3 Conversion, selectivity and yield

The following expressions were used to calculate the conversion of sorbitol (\( X_{\text{SB}} \)), the selectivity to hydrogen on the basis of the sorbitol converted (\( S_{\text{H}} \)), the selectivity to hydrogen on the basis of the gas phase products (\( S_{\text{H, gas}} \)), and the yield of carbon products (\( Y_{C_i} \)):

\[
X_{\text{SB}} = \left( F_{\text{SB, in}} - F_{\text{SB, out}} \right) / F_{\text{SB, in}} \times 100%
\]

\[
S_{\text{H}} = F_{\text{H}} / \left( 13 \times F_{\text{SB, in}} \times X_{\text{SB}} / 100 \right) \times 100%
\]

\[
S_{\text{H, gas}} = F_{\text{H}} / \left( 13 / 6 \times F_{C_{\text{gas}}} \right) \times 100%
\]

\[
Y_{C_i} = F_{C_i} / \left( F_{C_{\text{prod}}s} \right) \times 100%
\]

where \( F_{\text{SB, in}} \) and \( F_{\text{SB, out}} \) are the molar flows of sorbitol in the liquid phase at the inlet and outlet respectively, \( F_{\text{H}} \) is the molar flow of hydrogen produced, \( F_{C_{\text{gas}}} \) is the molar flow of carbon atoms in the gas phase products (i.e. alkanes and CO\(_2\)), \( F_{C_i} \) is the molar flow of carbon atoms in the component \( i \) and \( F_{C_{\text{prod}}s} \) is the total molar flow of carbon atoms in the products. Notice that two definitions for the selectivity to hydrogen are given (i.e. \( S_{\text{H}} \) and \( S_{\text{H, gas}} \)). The first definition is preferred in this work since we observed a significant amount of products in the liquid phase at all space velocities studied. The second definition is widely used in the literature\(^{10,29}\) and has been calculated in this study for the sake of comparison.

### 3 Results and discussion

#### 3.1 Conversion of sorbitol

Fig. 2 shows the conversion of sorbitol in the washcoated microchannel and the fixed bed reactor as a function of the residence time (calculated on the basis of the total Pt loading). Both reactor types present a similar rate of consumption of sorbitol. The two reactors were operated in the same fashion. They were equally pre-heated, pre-wetted and they were maintained under analogous reactor conditions. Notice that in both cases, nitrogen was pre-mixed with the liquid reactant in a gas to liquid ratio of \( R_{\text{GL}} = 2m_{\text{gas}}/m_{\text{liquid}} \). The differences in terms of hydrodynamics of the two reactor types seem not to influence the conversion of sorbitol. Intra-particle mass transfer does not play a role in the overall rate of sorbitol consumption and liquid-solid external mass transfer is orders of magnitude faster than the reforming reaction rate (Table 1). Therefore, the bulk catalyst used in the fixed bed reactor and the catalyst washcoat deposited on the microchannel walls are comparable in terms of activity. The characterization of these catalysts by TEM analysis confirms the same result: both presented a similar Pt particle size (i.e. 1.5 nm), which is generally a good indicator of a comparable catalytic activity.

#### 3.2 Selectivity to hydrogen

The selectivity towards hydrogen as a function of conversion and the reactor type is shown in Fig. 3. In the case of the fixed...
The hydrogen selectivity based on the carbon in the gas phase
(exceeds that of the fixed bed reactor (hydrogen per sorbitol feed in the microchannel significantly
hydrogen selectivity. As a result, the maximum production of
it is possible to reach a larger sorbitol conversion with a greater
nearly double in the whole conversion range. In the microchannel,
fixed bed reactor in terms of hydrogen selectivity. The selectivity is
explained by the formation of hydrogen from intermediates
sorbitol and hydrogen (i.e. from the catalyst site to the gas phase,
the liquid by capillary forces during the pre-wetting procedure.
the large interfacial mass transfer rate in the microchannel
reactor is the result of an increased mass transfer coefficient
and a large interfacial surface area.

In principle, the increase in hydrogen selectivity in the
microchannel reactor may be ascribed to additional factors derived
from the distinct hydrodynamics of this reactor compared to the
conventional fixed bed reactor. For example, fixed bed reactors
typically present problems of catalyst wettability, probably not
present in the microchannel reactor. However, an insufficient
wettability of the catalyst is not expected in any of the two reactors.
Given the hydrophilic nature of the catalyst support and the liquid
medium, it is expected that the catalyst pores are rapidly filled with
liquid by capillary forces during the pre-wetting procedure. Besides,
any difference in catalyst wettability would have been
reflected in the trend of sorbitol conversion of the two reactor types
(Fig. 2). Therefore, the enhanced mass transfer of hydrogen will be
the most important difference between the two reactors and we
will discuss the results accordingly. As not only the mass transfer
of hydrogen is enhanced but also that of the liquid components,
the rapid surface renewal of the liquid film in the washcoated
microchannel reactor in the Taylor flow regime will also influence
the hydrogen selectivity. The concentration of water-soluble
oxygenates on the catalyst surface determines the rate of hydrogen-consuming side reactions, previously referred as $F_{kh}$.

### 3.3 Mass transfer limitations

Table 1 shows the reaction rate constants and the mass transfer
coefficients that quantify the speed of each step during the

<table>
<thead>
<tr>
<th>Chemical Step</th>
<th>Rate Constant</th>
<th>Mass Transfer Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reforming</td>
<td>$R$</td>
<td>$MT1$</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>$F_{hk}$</td>
<td>$MT2$</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>$F_{hk}$</td>
<td>$MT2$</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>$F_{hk}$</td>
<td>$MT2$</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>$F_{hk}$</td>
<td>$MT2$</td>
</tr>
</tbody>
</table>

Fig. 3 Selection to hydrogen versus sorbitol conversion for the fixed bed reactor (open circles), with 2 mg Pt loading; and the microchannel reactor (full circles), with 0.7 mg Pt loading. Reaction conditions: 220 °C, 35 bar, 1 wt% of sorbitol in water. $R_{O2} = 2m_{O2}/m_{Reac}^{3}$ at the reactor inlet, liquid flows were adjusted in each case to achieve analogous WHSV.

Fig. 4 Schematic representation of the mass transfer and reaction steps towards the formation of hydrogen from sorbitol. $F_{MT1}$ is the mass transfer rate of sorbitol from the liquid to the catalyst site, $F_{R}$ is the reforming reaction rate, $F_{hk}$ is the hydrogenation reaction rate, and $F_{MT2}$ is the mass transfer rate of hydrogen from the catalyst site to the gas phase. $(CHO)_n$, $(CHO)_o$ and $(CHO)_w$ are intermediate polyhydroxy species.
transformation of sorbitol to hydrogen (Fig. 4). These are the mass transfer of sorbitol from the liquid to the catalyst active site ($F_{MT,1}$), the surface reforming reaction that produces hydrogen ($F_H$), the reactions that consume hydrogen ($F_{R,H}$), and the mass transfer of hydrogen from the catalyst active site to the gas phase ($F_{MT,2}$). While the slow kinetics of the reforming reaction are the limiting factor for the sorbitol conversion rate ($F_{MT,1} \gg F_{R,H}$), the high rate of hydrogen consumption is highly competitive with the rate of mass transfer of hydrogen from the catalyst active site to the gas phase ($F_{MT,2} \approx F_{R,H}$). Therefore, the excellent mass transfer properties of the microchannel do not have a significant effect on the conversion rate (Fig. 2) but strongly influence the selectivity of the reaction (Fig. 3). By improving the mass transfer rate, the hydrogen-consuming reactions are depressed and the selectivity towards hydrogen is increased.

According to the values in Table 1, the mass transfer rate of hydrogen is improved in the microchannel reactor compared to the fixed bed reactor due to an increase of both intra-particle mass transfer rate (diffusion of hydrogen through the catalyst particle) and external mass transfer rate (from the catalyst surface to the gas phase). The intra-particle mass transfer limitations of hydrogen were quantified in this study by estimating the Thiele modulus ($\phi_H$), although this term is typically used when the diffusion of the reactant and the chemical reaction occur as two steps in series. In this case, the intra-particle diffusion and the hydrogenation reaction are two parallel steps, but still the Thiele modulus can be used as an indicator of the ratio between the rate of hydrogenation and the rate of hydrogen diffusion through the pores. A value of $\phi_H > 0.3$ indicates that the intra-particle mass transfer of hydrogen is slower than the hydrogenation reaction, thus predicting a more severe effect of hydrogenation (i.e. lower hydrogen selectivity and higher yield of hydrogenated products). The intra-particle hydrogen diffusion limitation is prevented by the thin catalytic layer in the microchannel reactor, whereas the larger catalyst particle size in the fixed bed reactor results in a Thiele modulus $\phi_H \approx 0.3$. Smaller particle sizes in the fixed bed reactor would increase the internal diffusion rate but would represent an increase in pressure drop, which might become significant in larger units where longer tubes and larger liquid flow rates are used. The external mass transfer rate of hydrogen from solid to gas is also intensified in the microchannel reactor under the Taylor flow regime. This is due to the large and uniformly distributed contact area between the catalytic layer on the microchannel walls and the gas bubbles (Fig. 5), and due to the large mass transfer coefficient of hydrogen from the catalyst surface to the gas bubbles through the thin liquid film formed between these two phases.21,24

The high external mass transfer rate of hydrogen has however a milder effect on the hydrogen selectivity, since it is higher than the hydrogenation rate for both reactors.

3.4 Effect of hydrogen partial pressure

The effect of the hydrogen partial pressure on the reforming rate and on the selectivity of APR was examined by co-feeding mixtures of hydrogen and nitrogen at the inlet of the fixed bed reactor. The mass transfer coefficients were constant and only the hydrogen partial pressure was varied. Fig. 6 shows that the hydrogen partial pressure has an inhibiting effect on the kinetics of the reforming reaction. The negative reaction order of hydrogen concentration on the reforming kinetics, which can be attributed to a decrease in the availability of the catalyst active sites, might also explain the saturating tendency observed in Fig. 2 as the conversion increases. As the hydrogen partial pressure increases with increasing residence time, the reforming rate decreases.

The higher selectivity to hydrogen observed in the microchannel reactor compared to the fixed bed reactor resulted in higher concentrations of hydrogen in the gas phase (Fig. 7). A stronger inhibiting effect of the hydrogen concentration on the reaction kinetics would be expected in the case of the microchannel reactor. Nevertheless, no significant difference was observed in the sorbitol conversion achieved by the two reactors (Fig. 2). This suggests that the higher mass transfer coefficient in the microchannel reactor leads to a reduction of the hydrogen concentration over the catalyst surface, thus minimizing the inhibiting effect of hydrogen on the reforming rate.

According to Fig. 6, the hydrogen partial pressure also presents a negative effect on the selectivity towards hydrogen. The negative values of $S_{H_2}$ observed at hydrogen pressures above 4 bar are explained by a net mass transfer of hydrogen from the gas phase to the catalyst surface where it is consumed in side reactions. The total amount of hydrogen consumed is greater than the amount of hydrogen produced.

![Fig. 5](image-url) Formation of the Taylor flow regime in a glass micro-mixer prior to the washcoated microchannel reactor.

![Fig. 6](image-url) Effect of hydrogen partial pressure on the sorbitol conversion (open circles) and on the selectivity to hydrogen (full circles) in the fixed bed reactor. Reaction conditions: 220 °C, 35 bar, 1 wt% of sorbitol in water, liquid flow rate of 7 ml h⁻¹, $R_{GL} = \frac{2m_{gas}}{m_{liquid}}$ at the reactor inlet, with increasing hydrogen concentration in the inlet gas feed from 0 to 100%.
3.5 Effect of nitrogen addition

According to our analysis, the selectivity towards hydrogen depends on the mass transfer rate of hydrogen from the catalyst surface to the gas phase. This was enhanced by a combination of two factors: increase of the mass transfer coefficient (microchannel operating under the Taylor flow regime vs. fixed bed reactor); and increase of the driving force for the mass transfer by a decrease of the hydrogen concentration in the gas phase (addition of nitrogen). The combined effect of these factors is observed in Fig. 8, where the conversion and the selectivity to hydrogen have been compared for two different gas to liquid ratios at the inlet. If only liquid is fed to the microchannel reactor and the conversion to gaseous products is limited, the development of the desired Taylor flow regime in the microchannel is not successful. The gas produced is highly concentrated in hydrogen, thus limiting the possibility of hydrogen removal from the catalyst surface via mass transfer to the gas phase. In this case, the performance of the microchannel reactor is analogous to that of the fixed bed reactor. The effect of adding nitrogen as a stripping agent is beneficial for both reactors. The conversion is increased due to a kinetic effect of reducing hydrogen partial pressure. The selectivity also rises due to an increase of the driving force for the mass transfer. The increase in selectivity is larger in the case of the microchannel reactor due to an increase in the mass transfer coefficient.

3.6 Reaction mechanism

So far we have simplified the surface chemistry to two types of reactions: one that produces hydrogen (i.e. the reforming reactions) and another that consumes hydrogen. Earlier investigations on APR\textsuperscript{10,28} reveal a more complicated chemistry comprising many chemical reactions and intermediates (Fig. 9). The general belief is that hydrogen is produced by initial dehydrogenation of the substrate, followed by decarboxylation or decarbonylation and water gas shift on the metal sites (i.e. the reforming pathway).\textsuperscript{11} This pathway leads to the production of hydrogen, CO\textsubscript{2} and a series of smaller carbohydrates that are sensitive to further reforming reactions. In a hydrogen rich medium, direct hydrogenolysis of the internal C–C bonds of sorbitol may also occur\textsuperscript{34} on the metal sites. Due to the large yields of glycerol, we believe that direct hydrogenolysis of the intermediate C–C bond is one of the preferential routes. In addition to C–C cleavage reactions, sorbitol and the smaller carbohydrates undergo dehydration of the C–O bonds that may also occur\textsuperscript{34} on the metal sites. Due to the low reaction temperature and the high concentration of water that shift the water-gas-shift reaction towards the formation of CO\textsubscript{2}. It may also indicate that CO\textsubscript{2} is mainly produced by decarbonylation, rather than decarboxylation and water-gas-shift. According to the results of the present study, it is not possible to elucidate the preferential route for CO\textsubscript{2} production. Further research should be conducted to
Minor amounts of C1–C3 alkanes were found, while only traces of C4–C6 alkanes were detected (i.e. yields lower than 0.05%). In the liquid phase, the C3 fraction is noticeably larger than the rest, followed by C6, C5 and C4 species. In these fractions, a significant amount of hydrodeoxygenated species (e.g. 1,2-propanediol, butanediols, furan derivatives, isosorbide) are found. These results suggest a significant rate of hydrogenolysis of the intermediate C–C bond of sorbitol towards C3 products, as well as a significant rate of the dehydration–hydrogenation reactions due to a highly acidic (catalyst support/liquid phase) and hydrogen rich environment. The conversion of these species to alkanes is expected to occur at larger residence times.

Fig. 10 also highlights a different chemistry in each reactor type. The yield of CO₂ is distinctively higher in the case of the microchannel reactor than in the fixed bed reactor, suggesting that the reforming pathway is facilitated in the former compared to the latter. This difference is attributed to the increased mass transfer rate of the hydrogen from the catalyst active site to the inert gas phase in the microchannel reactor, which aids the rapid turnover of the catalyst sites and therefore favors the rate of C–C cleavage reactions. On the other hand, the yield of heavier liquid products, in particular C3 species, is remarkably higher in the case of the fixed bed reactor. A breakdown of the yield of the main components of the C3 fraction is given in Fig. 11. Formation of glycerol, the major side product in this fraction, is clearly more pronounced in the fixed bed reactor. This can be explained by a more rapid hydrogenolysis of the sorbitol due to a higher concentration of hydrogen at the surface of the bulk catalyst in the fixed bed reactor.

Further conversion of glycerol can explain the production of the remaining components of the C3 fraction. Earlier studies on glycerol conversion propose the formation of glyceraldehyde...
addition of hydrogen enhances the conversion to glycerol and 
reactions (acetone are nearly the same in both reactor types, suggesting an 
analogous balance between dehydrogenation and dehydrogenation reactions (i.e. comparable balance metal/acid sites) in both 
cases. This is in line with the initial statement of the two 
catalytic systems being comparable in terms of their reactivity. These two intermediates may undergo a sequence of hydro-
genation reactions towards 1,2-propanediol. Compared to the 
microchannel reactor, in the fixed bed reactor the yield of 1,2-propanediol relative to the total yield of C3 products is 
significantly higher, whereas that of the intermediates (i.e. 
glyceraldehyde and hydroxyacetone) is lower. This indicates 
that the selectivity for hydrogenation reactions is remarkably 
higher in the fixed bed reactor. An important amount of 
propionic acid is also detected in both reactors. This suggests 
a significant contribution of the rearrangement reactions to the 
overall reaction network. This acid may be produced by the 
reaction between glyceraldehyde and water, with a subsequent 
sequence of dehydration and hydrogenation reactions. The 
yield of this product with respect to the total yield of C3 
products is slightly larger in the case of the fixed bed reactor.

We have previously presented that the addition of hydrogen at 
the inlet of the reactor represented a decrease in the reaction 
rate and the hydrogen selectivity. This was attributed to the 
preferential dehydrogenation of the substrate and its intermediates 
rather than the desired reforming pathway with increasing 
hydrogen partial pressures. The yield of the most significant 
carbon containing products obtained at different hydrogen 
partial pressures is given in Fig. 12. A higher hydrogen concen-
tration is detrimental for the conversion to CO2. Instead, the 
addition of hydrogen enhances the conversion to glycerol and 
1,2-propanediol via hydrogenolysis of C-C and C-O bonds. There 
is a consistency between the products that are enhanced when 
increasing the hydrogen partial pressure and those that were 
favored in the fixed bed reactor compared to the microchannel 
reactor. This suggests that the main difference between these 
reactors is the concentration of hydrogen at the catalyst surface, 
and therefore its availability to participate in hydrogenolysis 
reactions. This is in line with the previous argument of the 
microchannel reactor offering a more rapid removal of hydrogen 
from the catalyst surface and thus favoring the hydrogen producing 
reactions while preventing hydrogen consuming reactions.

3.8 Practical considerations

Whereas the technology of fixed bed reactors is well estab-
lished, for a practical implementation of the microreactor 
concept, several considerations should be taken into account. Since 
the catalyst is immobilized on the microchannel walls, 
the recovery and regeneration of the catalyst is difficult. There-
fore, the catalyst stability is an important requirement. In this 
study, a washcoated microchannel was tested for 3 weeks of 
time on stream. This test included numerous runs under 
various reaction conditions, as well as several intermediate 
checks under the same reaction conditions to identify any loss 
of activity. During this time, the catalytic activity remained 
constant. Further discussion on the stability of this catalytic 
system under APR conditions is given in our previous work.27 
The use of nitrogen as a stripping agent introduces some 
calls regarding the production costs, which can be miti-
gated by recirculation of this gas after the hydrogen content is 
consumed, for example, in a PEM fuel cell. Combustion of the 
alkane fraction of the gaseous products can be conducted on 
the outer side of the microchannels to supply the heat of the 
reaction. Due to the large surface to volume ratio, microchan-
nel reactors are also very efficient heat exchangers.35 In a final 
hydrogen generation unit, the desired production scale can be 
achieved by parallelization of identical microchannels in a 
stack configuration with intermediate heating. Nevertheless, 
numbering up of multiphase microchannel reactors is a field 
still under development. Promising results have been recently 
published by our group with gas–liquid applications that can 
meet a small/medium production scale.38 Scaling up of cataly-
tic washcoated microchannel reactors for this application is a 
work in progress.

4 Conclusions

The Pt-based washcoated microchannel reactor for aqueous 
phase reforming of sorbitol, combined with nitrogen stripping, 
has excellent mass transfer from the catalyst active site to the 
inert gas phase, which aided the rapid removal of hydrogen 
from the catalyst surface and limited its availability to partici-
pate in undesired hydrogenation reactions. Compared to a 
fixed bed reactor, the selectivity to hydrogen obtained in the 
microchannel reactor was increased by a factor of 2 regardless 
of the sorbitol conversion. The yield of hydrogen was increased 
from 1.4 to 4 moles per mole of sorbitol fed. The mass transfer
properties of the microchannel reactor did not affect the rate of sorbitol consumption, which is limited by the kinetics of the reforming reaction. Hydrogen inhibits the reforming reaction and favors side – hydrogen consuming – reactions. A decrease of the hydrogen partial pressure is beneficial in both the microchannel reactor and the fixed bed reactor. These benefits are more significant for the microchannel reactor, since it combines the effect of a reduced hydrogen partial pressure in the gas phase with a high mass transfer coefficient, resulting in a greater reduction of the hydrogen concentration at the catalyst. This has significant implications for the product distribution. The analysis of the products reveals an important contribution of the hydrogenolysis of the C–C and C–O bonds of sorbitol and its intermediates as an important source of hydrogen selectivity loss. The most significant products of the hydrogen consuming reactions are water-soluble C3 species like glycerol and 1,2-propanediol, followed by heavier hydrodeoxygenated compounds in the C6, C5 and C4 fractions. The formation of these species rises when the hydrogen partial pressure increases. Since the hydrogen concentration at the catalyst surface is lower in the microchannel reactor, the yield of the hydrogenated products is severely depressed while the products of the reforming route \( \text{i.e. CO}_2 \) are remarkably increased.

**Acknowledgements**

This research has been performed within the framework of the CatchBio program. The authors gratefully acknowledge the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs and the Netherlands Ministry of Education, Culture and Science. Yagmur Karakus is acknowledged for her contribution to this work.

**References**