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Published in: Bioresource Technology

DOI: 10.1016/j.biortech.2022.126809

Published: 01/03/2022

Document Version Final published version

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Link to publication

Please cite the original version:

Aho, A., Alvear, M., Ahola, J., Kangas, J., Tanskanen, J., Simakova, I., Santos, J. L., Eränen, K., Salmi, T., Murzin, D. Y., & Grénman, H. (2022). Aqueous phase reforming of birch and pine hemicellulose hydrolysates. *Bioresource Technology*, *348*, Article 126809. https://doi.org/10.1016/j.biortech.2022.126809

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Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech



Aqueous phase reforming of birch and pine hemicellulose hydrolysates

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HIGHLIGHTS

• Aqueous phase reforming of real hemicellulose hydrolysates was performed.

• The best results were obtain with a tailored bimetallic Pd-Pt/sibunit catalyst.

• Complete conversion was achieved for C5 and C6 sugars and formic acid.

ARTICLE INFO

Keywords: Aqueous phase reforming Hemicellulose hydrolysate Bi-metallic catalysts Renewable hydrogen Renewable alkanes

ABSTRACT

The current work focuses on studying the aqueous phase reforming (APR) of pine and birch hydrolysate obtained from waste wood by using organic acids available from biorefineries. Processing of representative synthetic mixtures was utilized in the work in order to support data interpretation related to the influence of different chemical compound and processing parameters on the APR of the actual hydrolysates. It was shown, that hydrogenation of the hydrolysates prior to APR was not feasible in the presence of formic acid, which ruled out one potential processing route. However, it was successfully demonstrated that birch and pine hydrolysates could be directly processed obtaining close to full conversion. The best results were obtained with tailored bimetallic Pd-Pt/sibunit catalyst in a trickle bed reactor system in the temperature range 175 °C–225 °C.

1. Introduction

One of the key processing operations in the production of advanced biofuels and biochemicals is hydrotreatment (hydrodeoxygenation, hydroisomerization) and currently, the hydrogen required for these and many other applications is predominantly obtained through steam reforming of natural gas. This fact undermines the renewability and sustainability of many bio-products.

Increasing amounts of aqueous side/waste-streams containing rather low concentrations of bio-based compounds, such as carbohydrates, are available with various existing and emerging bio-refinery concepts. Moreover, water containing solid side-streams are plenty in industry e.g. in the form of sawdust and they can be efficiently processed with reactive extraction to obtain carbohydrate containing aqueous solutions. Instead of having these side-streams burden the waste treatment at the plants, they can be utilized for value added further processing. These types of hemicellulose hydrolysates and industrial side-streams containing mono- and oligosaccharides can be used as a feedstock in aqueous phase reforming (APR), with the aim of producing hydrogen, more specifically renewable hydrogen, as well as alkanes (Arandia et al., 2019). The renewable hydrogen can be used instead of the fossil-based hydrogen for chemical valorization or for bioenergy production and the alkanes can be utilized for energy production (Murzin et al., 2017).

Aqueous phase reforming was reported for the first time back in 2002 by Dumesic and co-workers (Cortright et al., 2002). An advantage of the APR process compared to steam reforming of natural gas, in addition to the use of renewable feedstock, is the fact that there is no need for reactant evaporation and thereby significant energy saving can be achieved. Since the first report (Cortright et al., 2002), the majority of studies has been carried out with reactants not containing carbonyl groups such as methanol (Cortright et al., 2002; Stekrova et al., 2018), ethanol (Zhao et al., 2019), ethylene glycol (Cortright et al., 2002;

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https://doi.org/10.1016/j.biortech.2022.126809

Received 24 November 2021; Received in revised form 28 January 2022; Accepted 30 January 2022 Available online 4 February 2022

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Davda et al., 2003; Park et al., 2012; D'Angelo et al., 2013), 1-propanol, 1,2-propanediol and glycerol (Cortright et al., 2002; Rahman et al., 2013; Godina et al., 2018a), as well as sugar alcohols namely, sorbitol, galactitol and xylitol (Cortright et al., 2002; Park et al. 2012; Kirilin et al., 2010; D'Angelo et al., 2014; Godina et al., 2015, 2018b). One of the reasons that the use of sugars has not been widely employed, even though it would be a natural choice for feedstock, is that sugars tend to form solid deposits, such as humins, in the elevated temperatures required for the APR process. The solid deposits easily block reactors, prevent sampling and analysis in laboratory experiments, and present significant challenges for larger scale operations. The carbonyl group in sugars can be hydrogenated to form sugar alcohols for the APR (Cortright et al., 2002), however, the possibility of direct utilization of sugars from various dilute biomass processing side streams would be a significant step towards industrial use of the versatile process.

From a practical large-scale APR point of view, it is not enough to study the use of model compounds, such as pure monosaccharide solutions, but rather actual hydrolysate mixtures should be employed. These hydrolysates typically include acid catalysts, which enable efficient hydrolysis of the polysaccharides to mono- and oligoaccharides. Moreover, the acids assist in extracting the hemicelluloses from the biomass. Typical acids widely available and utilized in biorefineries are formic acid and acetic acid, as they can be obtained directly from the biomass processing and they are also the acids typically formed during hydrothermal treatment of biomass.

The current work investigates the aqueous phase reforming of birch (*betula pendula*) and pine (*pinus sylverstries*) hydrolysates in a continuous reactor setup in the presence of formic and acetic acids. A more traditional two-step route via first hydrogenation to sugar alcohols and subsequent APR was followed by a direct utilization of the acid containing hydrolysates in a single-step process.

The selectivities to carbon dioxide and hydrogen are calculated with equations (1) and (2), the selectivity to alkanes is calculated with Eq. (3).

$$S_{CO2} = \frac{\dot{n}_{CO2}}{\dot{n}_{carbon}} \tag{1}$$

$$S_{H2} = \frac{\dot{n}_{H2}}{\dot{n}_{carbon}} \cdot \frac{1}{RR}$$
(2)

$$S_A = \frac{\dot{n}_{CA}}{\dot{n}_{carbon}} \tag{3}$$

Where \dot{n}_{co2} is the molar flow of carbon dioxide, \dot{n}_{carbon} is the molar flow of atomic carbon in the carbon containing gases, \dot{n}_{H2} is the molar flow of hydrogen and \dot{n}_{CA} is the molar flow of atomic carbon in the alkanes. The reforming ratio, *RR*, describes how many moles of hydrogen in relation to carbon dioxide can be maximaly formed from one mole of reactant. The RR for xylose and formic acid is 2 and 1, respectively.

2. Materials and methods

Formic acid, acetic acid and glucose were supplied by VWR International. Mannose, xylose, galactose and arabinose were purchased from Acros Organics and HMF and furfural were from Sigma Aldrich. All chemicals were analytical grade and used without further purification. All solutions were prepared in ultrapure water (resistivity 18.2 M Ω -cm). Birch (*Betula pendula*) as a raw material was used as small shavings (0.1 × 3 × 6–12 mm³) and chips (5 × 22 × 40 mm³). Pine (*Pinus Sylvestris*) was applied as sawdust with the average diameter of 1.4 mm.

2.1. Extraction experiments

Reactive extraction of birch and pine hemicellulose was carried out in a pressurized extraction equipment ASE350 (Dionex) with zirconium alloy extraction cells. The volume of the extraction cells was 66 mL and the pressure was 100 bar. The reactive extraction experiments were performed by weighing a specified weight of the biomass (birch or pine) and loaded to the cells, which were inserted into an oven, preheated and filled with a known volume of the extraction solution. The solid to liquid ratio in the extractions were 4.8. After the extraction, the liquid was purged from the cell to a collection bottle and the cell was flushed with nitrogen, after which the cell was removed from the oven. The product liquid was weighed and samples were taken from the cooled extraction mixtures. The samples were filtered through a 0.45 μm syringe filter before HPLC analysis.

2.2. HPLC

Two different HPLCs were used in the work. The reactive extraction hydrolysates were analyzed for the amounts of monosaccharides, di- and trisaccharides, furfural and HMF with an HPLC system (Agilent Technologies) equipped with Rezex ROA Organic acid H + column (Phenomenex) and a refractive index detector. 5 mM sulphuric acid was used as the mobile phase with the flow rate of 0.8 mL/min and the column was operated at 60 °C. Compounds were detected with a refractive index detector. The quantitation of the compounds was based on a multiple point external calibration. The eluent from the APR experiments was analyzed with HPLC (Hewlett Packard, Series 1100) equipped with a Biorad column (Aminex HPX-87H) and using 5 mM sulfuric acid as the eluent (0.6 mL/min, 45 °C). The hydrogenation reaction was followed with the same HPLC as for the APR.

2.3. Hydrogenation reactor set-up

Hydrogenation of xylose, both in the presence and absence of formic acid, was carried out in a 300 mL Parr autoclave using the commercial Ru/C catalyst. The set-up was equipped with an electrical heating jacket, an impeller, a sampling line, as well as temperature and stirring rate controllers. Prior to hydrogenation, the sugar solution was preheated to 80 °C in a separate pre-heater connected to the hydrogenation set-up. The hydrogenation reaction temperature and pressure was 120 °C and 20 bar (total pressure).

2.4. Aqueous phase reforming reactor set-up

The reactor set-up used in the aqueous phase reforming of the hemicellulose hydrolysates consisted of a 50 cm long 4.2 mm inner diameter stainless steel tube reactor. The reactor was filled with acid washed glass beads (Sigma-Aldrich) and the catalyst (0.5 g) in 6:1 wt ratio. The flow of the inert He/N2 gas was controlled with a Brooks (5850S) mass flow controller. The hemicellulose hydrolysates were pumped to the reactor with an Eldex HPLC pump, the feed solution bottle was placed on a scale to monitor the flow. The reactor was operated in the trickle-flow mode, i.e. both gas and liquid entered the reactor from the top. The reactor was heated with an electrical oven (ATS, 3210). The pressure of the set-up was controlled with an Equilibar gas/liquid back pressure regulator. The gas/liquid flow out from the pressure controller was separated in a 25 mL 3-neck flask. The 3-neck bottle was utilized in such a way that one neck acted as the inlet, another one was needed for the gas flow out and the third one was used for periodical liquid sampling. The gas flow from the gas/liquid separator was passed through a condenser operated at -5 °C (LAUDA, RE106) to dry the gases prior to gas analysis with an Agilent 3000A Micro GC. The products quantified with the micro GC were H₂, CO₂, CO, He and short-chain alkanes CH₄, C₂H₆, C₃H₈, i-C₄H₁₀, n-C₄H₁₀, neo- $C_5H_{12}, i\text{-}C_5H_{12}, n\text{-}C_5H_{12}, i\text{-}C_6H_{14}, n\text{-}C_6H_{14}, c\text{-}C_6H_{14} \text{ and } n\text{-}C_7H_{16}. \text{ Helium}$ in the inert gas mixture was used as an internal standard to calculate the molar flows of different gases formed during APR. The reproducibility of the reactor system and analytics was recently investigated and concluded to be good, with deviations being typically within a few percent (Winkler et al., 2021). A schematic representation of the reactor

set-up is shown in the supplementary material along with the experimental scheme.

2.5. Catalyst preparation and characterization

A commercial (4.6 wt%) Ru/C catalyst was applied in the attempt of xylose hydrogenation both in the presence and in the absence of formic acid. The catalyst has been successfully applied in similar reactions (Aho et al., 2015) and extensively characterized before. The surface area of Ru/C was measured to be 700 m²/g (Micromeritics 3Flex) (Lassfolk et al., 2020) and the ruthenium particle size was 2.5 nm (Aho et al., 2015).

A Pd/C catalyst was applied in the decomposition of formic acid. The preparation method is described in detail in ref. (Santos et al., 2018). Briefly, 2 wt% of Pd/C was prepared through wetness impregnation using both acetone and water as the solvents. The Pd metal precursor was palladium (II) acetate (Johnson Matthey) while the carbon support DARCO was used (Sigma-Aldrich).

A bimetallic Pt-Pd/C catalyst was prepared for the use in the APR experiments. It is well known that Pt is a highly active and selective metal for APR of polyols aiming at hydrogen production (Godina et al., 2018c). Good performance of Pd catalysts in the gas phase decomposition of formic acid has been reported (Winkler et al., 2021). Therefore, bimetallic Pt-Pd/C catalyst was synthesized through incipient wetness co-impregnation of the mesoporous carbon Sibunit. The Sibunit was synthetized through pyrolytic deposition of carbon according to (Surovikin et al., 1990), in-house prepared at the Boreskov Institute of Catalysis in Russia. The metal precursors were H₂PtCl₆ (Kraszvetmet, Krasnoyarsk, Russia) and PdCl₂ (Kraszvetmet, Krasnoyarsk, Russia), the nominal loadings of Pt and Pd were 2.5 wt% and 1.25 wt%, respectively. The Pt-Pd/C catalyst was thermally treated after the metal impregnation, first by drying at 110 °C overnight and thereafter in hydrogen atmosphere (40 mL/min) at 400 °C for 3 h (2 °C/min) in order to reduce the metals.

The metal dispersion was analyzed with a Micromeritics Autochem 2910 device by CO chemisorption. Prior to CO chemisorption the catalyst sample was reduced *in-situ* at 300 °C and the dispersion was calculated by assuming 1:1 ratio of CO:metal. The dispersion was calculated to be 51.6%, corresponding to 2.2 nm (Oliveira et al., 2021). A similar catalyst sample was also investigated by transmission electron microscopy (TEM) showing the mean metal particle size of 1.4 nm (Alvear et al., 2020), the difference between the sample in this work and in ref. (Alvear et al., 2020) is the palladium loading being 0.6 wt% in the latter.

3. Results and discussion

3.1. Hydrolysate production

Simultaneous extraction and hydrolysis of wood saccharides was applied to produce hydrolysate for APR process. Formic and acetic acids were used as homogeneous catalysts in the acid catalyzed extraction of hemicelluloses. Operation conditions were selected in such a way that the monosaccharide content of hydrolysate was maximized. Hydrolysate was produced at 160 °C with 60 min reaction time using an extraction solvent which contained 20 g/L formic acid or 150 g/L acetic acid as a catalyst in water. The wood to solvent ratio was 1:4.8. Hydrolysates contained monosaccharides, sugar oligomers, furfural, 5-HMF as well as acetic and formic acids. We estimated proviously the lignin content in the liquid phase from hydrolydsates obtained utilizing the same raw materials and extraction methododlogy, as in the current work. (Goldmann et al., 2017) The results showed, that in both birch and pine hydrolysates, the lignin content was clearly under the detection limit of the combined HPLC/UV analysis methods, which corresponded to a dissolved amount of about 23 mg/g dry wood. This is most probably due to back condensation of the dissolved lignin on the solid phase, mainly the cellulose fibers. It can be concluded, that even though some lignin based compound remains in the liquid phase, the concentrations are rather low.

Hydrolysate compositions in formic acid catalyzed extractions are shown in Table 1. Hydrolysis of pine with 150 g/L acetic acid as catalyst produced slightly smaller combined concentration (g/L) of mannose and galactose (13.9 vs. 19.7), the concentrations of glucose (2.7), arabinose (1.2), 5-HMF (1.8), furfural (2.1), disaccharides (5.3) and trisaccharides (2.6) can be considered comparable with the concentrations obtained using formic acid as catalyst.

3.2. Hydrogenation of xylose prior to APR

Aqueous phase reforming of polyols has been previously studied over Pt catalysts showing high selectivity to hydrogen (Alvear et al., 2020; Aho et al., 2020). The aim of this work was to utilize hydrolysates from reactive extraction of hemicellulose from both birch and pine wood. It has been reported that APR of sugars is problematic due to caramellization of the sugar and low selectivity to hydrogen (Davda et al., 2005), as was observed in the current study. Therefore, it was decided that the hydrolysate should be hydrogenated prior to APR.

A synthetic hydrolysate was prepared containing 25 g/L of xylose and 10 g/L formic acid (FA). The result from the hydrogenation using the commercial Ru/C catalyst is displayed in Fig. 1.As observed from the Figure, the hydrogenation of xylose to xylitol is slow in the presence of formic acid (FA). Similar hydrogenation with a reactant solution containing only xylose is also displayed in Fig. 1 and it can be seen, that the hydrogenation proceeds rapidly in the absence of formic acid. The comparison clearly shows the retarding effect of formic acid on the hydrogenation of xylose to xylitol.

A possible reason for the very slow hydrogenation of xylose in the presence of formic acid is attributed to the stronger competitive adsorption of formic acid compared to xylose on the surface of the active metal.

3.3. Degrading formic acid prior to hydrogenation

Due to the challenges related to hydrogenating xylose to xylitol in the presence of formic acid, it was attempted to degrade the formic acid to hydrogen and carbon dioxide prior to hydrogenation of the sugar. Literature reports Cu and Pd being effective catalysts for decomposition of formic acid (Winkler et al., 2021; Shiozawa et al., 2015). Decomposition of formic acid over a copper catalyst resulted in severe leaching of copper to the liquid phase, therefore Cu was excluded from the subsequent experiments. Decomposition of formic acid was continued over Pd/C catalyst in the APR set-up with an aqueous formic acid solution. The formic acid conversion and hydrogen selectivity is shown in Fig. 2 a.

From Fig. 2 a, it can be seen that full conversion of formic acid can be achieved at a relatively low temperature (150 $^{\circ}$ C) by adjusting the concentration and the flow rate. Selectivity to hydrogen is close to

Table 1	
Hydrolysate content in formic acid hydrolysis.	

	Pine sawdust	Pine 2* sawdust	Birch shavings	Birch chips
	g/dm ³	g/dm ³	g/dm ³	g/dm ³
Glucose	4.0	4.4	1.5	1.2
Mannose, Galactose, Xylose	18.4	20.9	24.9	22.4
Arabinose	1.6	1.9	-	-
Formic acid	19.4	19.5	19.3	19.8
Acetic acid	2.4	2.6	7.7	6.9
HMF	1.7	1.5	0.3	0.5
Furfural	1.7	1.5	4.0	2.1
Disaccharides	4.0	5.0	2.3	2.7
Trisaccharides	1.4	1.5	1.3	1.1

*Second campaign.



Fig. 1. Hydrogenation of xylose to xylitol in the presence or absence of formic acid. Reaction conditions: 120 °C, 20 bar hydrogen (total pressure at operational temperature), 1400 rpm, 0.2 g Ru/C.



Fig. 2. a) Decomposition of formic acid to hydrogen and CO_2 over Pd/C catalyst. Reaction conditions: 150 °C, 16 bar, 7 wt% and 2 wt% formic acid, 0.2 and 0.1 mL/min liquid flow, 0.5 g Pd/C. b) Conversion of formic acid and xylose and molar flows of carbon dioxide and hydrogen during decomposition of synthetic hydrolysate containing 20 g/L formic acid and 30 g/L xylose as a function of temperature. Reaction conditions: 150–175 °C, 0.5 g Pd/C, 0.1 mL/min.

100%.

After successful decomposition of formic acid in aqueous solutions, the following aim was to decompose formic acid from a synthetic hydrolysate solution containing both formic acid and xylose over the same Pd/C catalyst used to decompose only formic acid shown in Fig. 2 b. The hypothesis was that xylose would not react due to a relatively low temperature.

As can be seen in Fig. 2 a displaying the catalytic results, full conversion of formic acid was achieved already at 150 °C. However, xylose present in the solution reacted as well. Already at the lowest temperature tested (150 °C) 85% conversion of xylose was observed increasing with temperature elevation. The molar flows of hydrogen and carbon dioxide presented in Fig. 2 b, indicated that the simultaneous decomposition and APR of the synthetic hydrolysate was not selective to hydrogen as the molecular ratio of hydrogen to carbon dioxide was about 0.4, when it theoretically should be about 1.3 at full conversion.

3.4. Direct APR of synthetic hydrolysate

Based on the results presented in Fig. 1, a bi-metallic catalyst was prepared and tested for the hydrolysates. The aim was to combine decomposition of formic acid over Pd and APR of polyols over Pt, which was reported to be selective for hydrogen formation.

The above-described bi-metallic Pt-Pd/C catalyst was evaluated in APR of synthetic hydrolysate containing, 30 g/L xylose and 20 g/L formic acid at 3 different temperatures, 175, 200 and 225 °C. Conversion of xylose and formic acid is shown in Fig. S3a in the Supplementary material, while selectivity to different gases is presented in Fig. S3b and c. It can be concluded, that the conversion of both formic acid and xylose were close to 100% at 200 °C. Comparing the results shown in Fig. S3c with the results obtained in our previous work with xylitol (Aho et al., 2020) it can be concluded that selectivity to hydrogen is significantly lower in the case of the synthetic hydrolysate, as with pure xylitol selectivity was typically ca. 70–80%. Furthermore, selectivity to alkanes is shifted to pentane and interestingly to hexane via condensation and dehydration reactions with synthetic xylose/formic acid hydrolysate while xylitol APR exhibited the highest selectivity for ethane and propane among different alkanes.

3.5. Direct APR of birch and pine hydrolysates

Two different hydrolysates, namely birch and pine, were utilized as a feedstock in APR over the bi-metallic Pt-Pd/C catalyst at varying reaction temperatures.

The birch hydrolysate contained mainly xylose and formic acid, but also a significant amount of acetic acid as reported in Table 1. The concentrations of the most abundant compounds at different temperatures are illustrated in Fig. 3a and the concentrations of other compounds observed in the solution are displayed in Fig. 3b.

As can be seen from Fig. 3a and b, the concentrations of all compounds except furfural and acetic acid decreased with increasing temperature until complete disappearance reflecting the total conversion when APR of the birch hydrolysate is carried out at 225 °C. The temperature dependent conversion of the compounds that underwent APR reactions is shown in Fig. 3c. It can be clearly noticed that the conversion increased strongly with temperature displaying a relatively high activation energy.

It can be speculated based on the results presented in Fig. 3 c, that hydrolysis of tri-saccharides and di-saccharides might take place in the presence of formic acid prior to APR of the monosaccharides xylose and glucose. This would explain faster oligosaccharide conversion compared to the monosaccharides. Selectivity to different gaseous products is displayed in Fig. 4a.

Selectivity to different gases during APR of birch hydrolysate Fig. 4a is quite similar to the one obtained during APR of the synthetic hydrolysate (Fig. S3b). A selectivity of about 30% to hydrogen was achieved



Fig. 3. a) Concentration of the major compounds xylose, formic and acetic acids after APR of birch hydrolysate at different temperatures. Reaction conditions: 175–225 °C, 0.1 mL/min, 0.5 g Pt-Pd/C catalyst. b) Concentration of glucose, di- and tri-saccharides, furfural and hydroxmethylfurfural (HMF) after APR of birch hydrolysate at different temperatures. Reaction conditions: 175–225 °C, 0.1 mL/min, 0.5 g Pt-Pd/C catalyst. c) Conversion as a function of temperature for xylose, glucose, di- and trisaccharides as well as for formic acid in the birch hydrolysate APR.



Fig. 4. a) Selectivity to different gaseous products during APR of birch hydrolysate. Reaction conditions: 175–225 °C, 0.1 mL/min, 0.5 g Pt-Pd/C catalyst. b) Conversion as a function of temperature for mannose/galactose, glucose, arabinose, di- and trisaccharides as well as for formic acid in the pine hydrolysate APR.

with both feeds and the major alkane was pentane with approximately 20% selectivity. Moreover, selectivity to all products can be considered independent on the reaction temperature. Similar observations were also reported previously by our research group (Aho et al., 2020) although the feed was different, namely a pure aqueous solution of xylitol.

The composition of the pine hydrolysate differs to some extent from the birch hydrolysate, as presented in Section 3.1. The conversion profiles of the APR eluent is shown in Fig. 4b.

As observed from Fig. 4b full conversion was achieved at 225 $^{\circ}$ C for all compounds except formic acid. Selectivity to different gases is shown in Fig. 5a. A comparison between the alkane selectivity with birch and pine hydrolysates is depicted in Fig. 5b.

Selectivity to different gases varied to some extent between the APR of birch and pine hydrolysates. Higher selectivity to hydrogen could be achieved with pine hydrolysate compared to birch. The C5/C6 sugar ratio in pine is about 0.38 (Andérez Fernández et al., 2018), while it is about 8.2 in birch (Lu et al., 2021), which is rather well reflected in the results presented in Fig. 5b, From Fig. 5a and b it is also evident that chain cleavage occurred. The distribution of alkanes was fairly similar for both hydrolysates, however, the total selectivity to alkanes was



Fig. 5. a) Selectivity to different gases during APR of pine hydrolysate and b) comparison of the alkane selectivity during APR of birch and pine hydrolysate. Reaction conditions: 175–225 °C, 0.1 mL/min, 0.5 g Pt-Pd/C catalyst.

lower in the case of pine hydrolysate.

4. Conclusions

Aqueous phase reforming of actual hydrolysates from reactive extraction of pine and birch waste wood was attempted. Prehydrogenation of the hydrolysates was not successful due to the presence of formic acid, which hindered the possibility of a two-step process. Full conversion of the C5 and C6 sugars as well as formic acid was achieved in direct APR over bi-metallic Pt-Pd/C (Sibunit) catalysts in a trickle bed reactor. Selectivity to hydrogen during APR of the hydrolysates was, however, lower (roughly 30%) compared to APR of polyols. The APR of real biomass hydrolysate containing sugars and formic acid was demonstrated.

CRediT authorship contribution statement

Atte Aho: Data curation, Writing – original draft. Matias Alvear: Data curation. Juha Ahola: Data curation. Jani Kangas: Project administration. Juha Tanskanen: Conceptualization. Irina Simakova: Investigation. José Luis Santos: Investigation. Kari Eränen: Methodology. Tapio Salmi: Conceptualization, Methodology. Dmitry Yu. Murzin: Conceptualization, Methodology, Writing – review & editing. Henrik Grénman: Writing – review & editing, Supervision, Methodology, Conceptualization, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was a part of the activities at the Johan Gadolin Process Chemistry Centre at Åbo Akademi and at the Chemical Process Engineering at the University of Oulu. Financial support was obtained from Business Finland through the HemiH2-project. I. Simakova is grateful for the support from the Ministry of Science and Higher Education of the Russian Federation, under the governmental order for Boreskov Institute of Catalysis (Project No. AAAA-A21- 121011390055-8). Support from Academy of Finland (310652) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2022.126809.

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