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Biohydrogen from waste wood hemicellulose hydrolysate

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PURPOSE OF THE ABSTRACT

Introduction

Currently, one of the key processing operations in the versatile utilization of biomolecules to value added products is hydrotreatment e.g. the stabilization and refining of bio-oils originating from biomass pyrolysis and liquefaction lead typically to different hydrotreatments and the valorization of ?waste? lignin requires hydrotreatment in many pathways [1-2]. One potential source for the hydrogen used in the hydrotreatments is biohydrogen produced from waste wood and wood hydrolysates. In this study we investigate biohydrogen production applying first selective reactive extraction of hemicellulose from waste wood to monosaccharides. After the reactive extraction we evaluate if the monosaccharides can be used directly, or first after hydrogenation to sugar alcohols, as a raw material to produce hydrogen using aqueous phase reforming (APR) over a solid catalyst. Aqueous phase reforming of sugar alcohols, and more generally polyols, to hydrogen and light alkanes can be performed over various supported metal catalysts at relatively mild operating conditions (ca. 225 °C, 30-50 bar) [3,4].

Experimental

The reactive extraction experiments were performed using ground softwood (Pinus sylvestris) particles. Extraction solvent was a mixture of water and formic acid, which acted as the catalyst. The effects of operation conditions (reaction time, temperature and acid concentration) and particle size to the quality of the hydrolysate were investigated in an Accelerated Solvent Extraction equipment.

To enable initial evaluation of the characteristics and feasibility of the selected biohydrogen production route from wood hemicellulose, APR experiments were performed using a water solution of xylitol, mixtures of xylitol and xylose, and finally with a mixture of xylose and formic acid. Commercially available and tailor made catalysts were employed in the experiments. The effects of temperature, residence time and gas flow through the reactor on the conversion and selectivity to hydrogen and CO2 were investigated. A schematic of the set-up is displayed below

in Fig. 1. The reactor was operated in co-current trickle flow.

Results and discussion

Based on the reactive extraction experiment results, formic acid catalyzed hemicellulose extraction results in the recovery of hemicellulose as monosaccharides with the efficiency ranging from 60% to 75% at the optimal extraction time. Maximum recovery is relatively independent on the reaction temperature or formic acid concentration, when temperature is over 140 °C and formic acid concentration is over 4 wt-%.

In the APR experiments, it was observed that in order to achieve high conversion of xylitol the temperature should be preferably above 225°C. Additionally a three phase system with a flow of inert gas is very beneficial for increasing the conversion. No significant changes in selectivity to hydrogen was observed at different xylitol conversions obtained at varying experimental condition, as displayed in Fig. 2.

Mixtures with different ratios of xylose and xylitol were tested in the same experimental conditions with the idea that the hydrogen produced from the xylitol could in situ hydrogenate the xylose and initiate the further APR reaction. All of the experiments resulted in the same conclusion; the mixture caramelized rapidly and blocked the reactor due to humane formation. Experiments were also performed with the xylose and formic acid mixture. Promising results were obtained at relatively mild, but even at higher temperatures utilizing a tailor made catalyst and the caramelization due to humine formation was avoided. These results strongly indicate that APR can be performed on sugar solutions directly, which would be a breaktrough in the field.

FIGURES

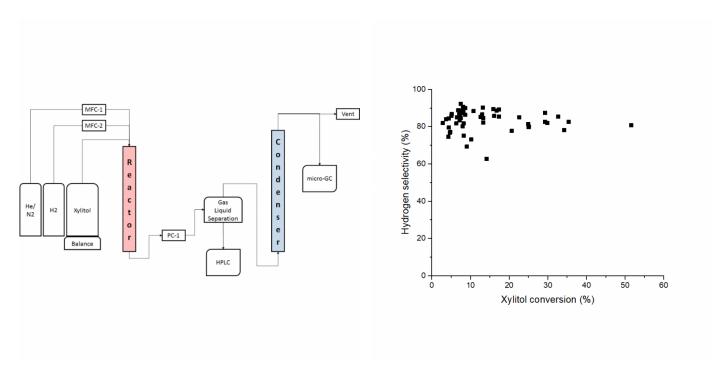


FIGURE 1

Fig. 1 Figure 1. APR reactor set-up.

FIGURE 2

Fig 2 Figure 4. Selectivity of xylitol to hydrogen at different xylitol conversion levels in the APR experiments.

KEYWORDS

Waste wood | biohydrogen | Conversion of waste biomass fractions | Aqueous phase reforming

BIBLIOGRAPHY

J. Wildschut, F.H. Mahfud, R.H. Venderbosch, H.J. Heeres, 2009.
Ind. Eng. Chem. Res. 48(23), 10324–10334.
H. Wang, J. Male, Y. Wang, 2013. ACS Catalysis, 3(5), 1047–1070.
I. Coronado, M. Stekrova, M. Reinikainen, P. Simell, L. Lefferts, J. Lehtonen,
2016. Int. J. Hydrog. Energy 41(26), 11003–11032.
D.Y. Murzin, S. Garcia, V. Russo, T. Kilpiö, L.I. Godina, A. Tokarev, A. Kirilin, I. Simakova, S. Poulston,
D.A.Sladkovskiy, J. Wärnå, 2017, Ind. Eng. Chem. Res. 56, 13240–13253.