**Biohydrogen from waste wood hemicellulose hydrolysate**

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**Highlights**

* APR performed directly on sugar solutions has been a challenge hindering the development
* Experiments were performed with model solutions followed by actual hydrolysates
* 100% conversion was obtained with tailor made catalysts
* The selectivity of the process could be steered by choice of catalyst

**1. 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/catalytic 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].

**2. Methods**

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. The actual extracts were tested after the evaluation with the model mixtures. 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. The fixed bed continuous reactor was operated in co-current trickle flow and the gas analysis was performed online with micro-GC while the liquid phase was analyzed with HPLC.

**3. Results and discussion**

Based on the reactive extraction experiments, formic acid catalyzed hemicellulose extraction results in the recovery of hemicellulose as monosaccharides with the efficiency ranging from 60%-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. 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 humine formation. Attempts to hydrogenate the sugar mixture were unsuccessful as the formic acid prevented the hydrogenation. Experiments were then performed with the xylose and formic acid mixtures. Promising results were obtained at relatively mild conditions, but even at higher temperatures the caramelization due to humine formation was avoided utilizing a tailor made catalyst and 100% conversion was obtained.

**4. Conclusions**

These results show that Aqueous phase reforming can be performed on actual hydrolysate sugar solutions directly, which is a significant advancement in the field. It enables the flexible supply of biohydrogen in locations that process biomass with side streams of sugars and .

**References**

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