The importance of catalysis for future biorefineries.

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Highlights

- Catalysis will play a major role for the production of renewable fuels and chemicals
- Co-processing Kraft lignin with pyrolysis oil could suppress the solid char formation
- 5-HMF could effectively be upgraded using Ni catalyst, but it can be deactivated by residual DMSO
- Tests in a refinery unit for advanced biofuel production showed the contaminants Fe, P, K and Na

1. Introduction

Biorefineries will be critical for the future in order to produce chemicals and materials from biomass. Biomass is composed mainly of lignocellulose, which largely consist of cellulose (~40-50%), hemicellulose (~20-30%) and lignin (~20-30%) [1]. In order to produce chemicals and fuels from biomass it needs first to be depolymerized, which could be done for example by catalytic fast pyrolysis or reductive catalytic fractionation (RCF) to produce bio-oils. Another possibility is to first take out the cellulose and hemi-cellulose and make valuable products out of these, and thereafter depolymerize the lignin. Lignin is a highly branched complex 3D amorphous network of aromatic compounds and after depolymerization it results in very complex bio-oils, with hundreds and hundreds of components. In addition, during lignin depolymerization it forms unwanted char. The cellulose can be used to produce sugars, from which different platform chemicals can be produced by catalytic processes, such as e.g. 5-hydroxymethylfurfural (5-HMF) [2], 2,5-Furandicarboxylic acid (FDCA) and levulinic acid (LA). From these platform chemicals various chemicals can be produced.

2. Methods

Catalysts were prepared, both supported catalysts [2] as well as unsupported catalysts [3]. The catalysts were characterized using multiple methods such as BET, ICP, SEM, TEM, XRD, CO chemisorption and NH_3 TPD. The feedstock, e.g. sawdust, lignin, pyrolysis oil was upgraded in three-phase batch reactors at high hydrogen pressure. The produced bio-oils are examined using GCxGC/MS, NMR, Karl Fischer, TGA, FTIR and elemental analysis.

3. Results and discussion

Different catalytic reactions for producing renewable fuels and chemicals from biomass and waste feed stock will be shown. In this section a few examples are given. Reductive catalytic liquefication was examined for Kraft lignin depolymerization [3]. A major issue with lignin depolymerization is the formation of solid char formation, which reduces the bio-oil yield and also results in catalyst deactivation. When using a NiMoS catalyst at 400 ºC and 75 bar H_2 about 14 % char was observed (see Figure 1). We thereafter added small amount of pyrolysis oil and found an increase of char. Interestingly, when adding about 50% pyrolysis oil together with the Kraft lignin the char formation was suppressed and when using the same amount of pyrolysis oil and lignin no char was detected [3]. Based on several experiments with model compounds, we suggest that the reason for the char suppressing effect of pyrolysis oil is that the small molecules in the pyrolysis oil act as capping agents thereby blocking the lignin radicals and hindering the repolymerization. We also found that upgrading of hydrolysis lignin decreased the char formation compared to Kraft lignin and we suggest that this is due to that hydrolysis lignin contain less ash, has a more reactive structure and that the remaining cellulose compounds could act as capping agents [4].

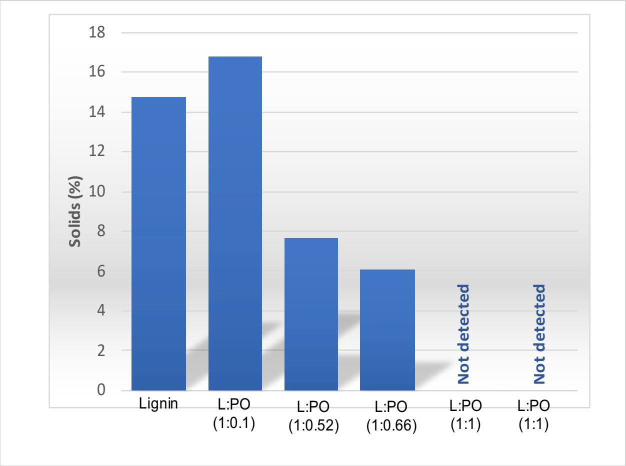

Figure 1. The solid residue formation from slurry-hydrocracking experiments using a NiMoS catalyst at 400 ºC and 75 bar H_2 using Kraft lignin (L), and co-processing Kraft lignin with different fractions of pyrolysis oil (PO).

The sugar platform from cellulose, opens up for very large possibilities to produce various renewable chemicals. We have studied the upgrading of 5-HMF to valuable products, such as 2.5-Bis (hydroxymethyl)furan (BHMF) [4]. We found that Ni/SiO_2 catalysts exhibited superior performance with a total yield of BHMF of up to 99 wt.% at 180 ºC, 75 bar H_2 for 2 h. This excellent performance might be attributed to the high Ni dispersion and low acidity of the support. Moreover, in some routes to prepare 5-HMF, DMSO is used, and we found that residues of DMSO was detrimental for the process.

We have prepared $NiMo/Al_2O_3$ catalysts at Chalmers and added these to a real refinery unit for advanced biofuel production for several months and the spent catalysts were thereafter recovered. We found contaminants such as Fe, P and alkalis (like Na and K) in the spent catalysts. Further model deactivation studies were conducted.

4. Conclusions

To summarize, catalysis will play a key role in a future bio-refinery. Catalysts can aid the depolymerization in for example RCF and catalytic fast pyrolysis. It is also crucial for the upgrading of the different components, for example for producing chemicals from the cellulose platform and upgrading the depolymerized bio-oils to produce different chemical compounds and renewable fuels. We have shown a catalytic process for HMF upgrading using a nickel-based catalyst and that it can be deactivated by residuals of DMSO from the 5-HMF production. Renewable fuel production can be enhanced by the usage of hydrolysis lignin compared to Kraft lignin. The char formation during Kraft lignin depolymerization could be completely suppressed by a co-process with pyrolysis oil. Moreover, results showed that contaminants such as Fe, P and alkalis (like Na and K) were present after experiments in a real refinery unit for advanced biofuel production.

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Keywords
Bio-refinery, heterogeneous catalysis, biofuel, renewable chemicals