Valorization of hemicellulose-biomass side streams via catalytic hydrogenation into value added chemicals and fuels

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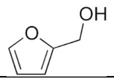
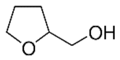
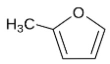
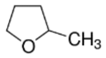
Lignocellulosic biomass composed of cellulose, hemicellulose and lignin can be an alternative source of chemicals and fuels towards the substitution of crude oil derived products. Cellulose is a linear polymer consisting of glucose molecules linked via β-1,4-glycosidic bonds while hemicellulose is a branched polysaccharide composed of C5 and C6 sugars. Lignin is an amorphous polymer with p-coumaryl, coniferyl, and sinapyl alcohols being its primary building units, linked with β-O-4 ether and C-C bonds. Lignocellulosic agricultural and forestry residues (e.g. prunings) as well as food industries wastes (e.g. kernels, shells) can be converted into a wide variety of platform chemicals. The first step in biomass valorization is a pretreatment process for the selective fractionation into the three main components. The hemicellulose stream may contain different types of carbohydrates and sugars such as xylose and arabinose, depending on the nature of biomass source (hardwood, softwood, grass, etc.). A pretreatment method proposed for the efficient recovery of hemicellulose is the hydrothermal process in neat water under relatively mild reaction (temperature and time) conditions, often refer to as Liquid Hot Water (LHW) (Nitsos, 2013). The severity of the process controls the composition of the aqueous solution product, ranging from xylan oligomers at milder conditions to monomeric xylose, furfural and formic acid at more intense conditions. Furfural itseld is a very useful platform chemical and one route of valorization is via its catalytic hydrogenation/hydrogenolysis to furfuryl alcohol (FA), 2-methylfuran (MF), 2-methyltetrahydrofuran (MTHF), tetrahydrofurfuryl alcohol (THFA), furan, tetrahydrofuran (THF) and pentanediols. These chemicals can be used as fuel additives and for producing polymers and resins (Wang, 2018a and Wang, 2018b). The present work focuses on the development of efficient catalysts and related hydrogenation processes for the conversion of furfural, as well as of real hemicellulose-derived streams, towards the above chemicals, mainly furfuryl alcohol (FA), 2-methylfuran (MF) and 2-methyltetrahydrofuran (MTHF).

The catalytic experiments were conducted in a high-pressure stirred batch autoclave reactor, with a series of monometallic (Pd, Pt, Cu, Ni) and bimetallic (Ni-W) catalysts supported on micro/mesoporous activated carbon, under H_2 pressure (30 bar, initial pressure) with ethyl acetate as solvent/medium. The effect of hydrogen donor solvents (isopropanol, ethanol) was also investigated. The effects of reaction medium, temperature (180-220 °C) and time (1-9 h) was also investigated in order to optimize the catalytic system. The analysis of the products was carried out by GC and GC-MS.

In the presence of monometallic catalysts, the highest conversion of furfural, i.e. 72.9 %, was achieved by the 3% Pt/AC at 180 °C for 3 h, with 74.3% selectivity to 2-MF, as can be observed in Table 1. Palladium catalyst (3% Pd/AC) exhibited lower conversion (19.6 %) and selectivity to 2-MF (58.4 %). In the case of 10% Ni/AC the conversion was slightly lower (19.3%) compared to the Pd catalyst, but with high selectivity to 2-MF (75.9 %) and simultaneous production of FAL (selectivity of 21.7 %). The effect of support's acidity was also investigated by doping the Ni/AC catalyst with WOx, increasing the conversion to 53.7 % but leading to a reduced selectivity to 2-MF of 42.1 %. With regard to the effect of hydrogen donor solvents (i.e. EtOH and isopropanol) substituting an inert solvent such as ethyl acetate, it was observed that furfural conversion was increased but selectivity to the above mentioned products was decreased as high molecular weight condensation products between furfural and the alcohols, i.e. acetals, were formed. The possible mechanism of furfural hydrogenation is presented in Figure 1. In the first step, furfural is converted to furfural alcohol followed by different routes depending on the catalyst and reaction conditions.

Table 1. Representative results for furfural hydrogenation (conditions: 180 °C, 3 h, 30 bar H_2, solvent: EtOAc).

Catalyst	***X* (%)**	**FAL**  	**THFAL**  	**2-MF**  	**2-MTHF** 
3%Pd/AC	19.6	6.0	0.0	58.4	0.0
3%Pt/AC	72.9	3.5	1.5	74.3	0.0
10% Ni/AC	19.3	21.7	1.3	75.9	0.0
10%Ni/15%W-AC	53.7	18.0	5.4	42.1	0.0

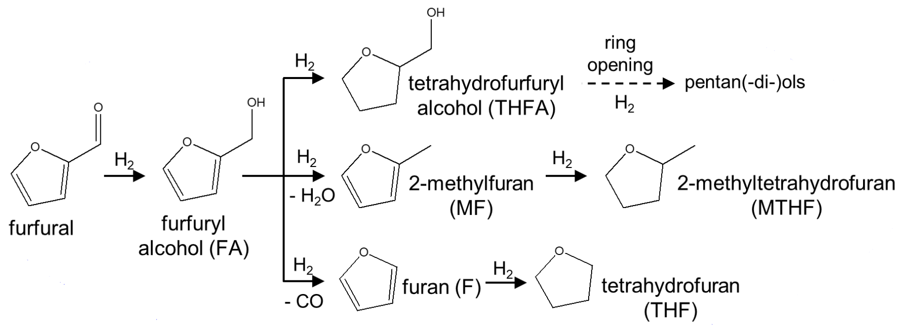


Figure 1. Possible reaction pathways in furfural hydrogenation

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