ABSTRACT

Lignocellulosic biomass has been recognized as a promising crude oil alternative especially in terms of the bio-based chemicals production within a bio-refinery. In pursuit of a competitive and sustainable bio-refinery, lignin valorisation represents a crucial factor. Lignin is a particularly interesting feedstock for chemicals production considering its aromatic structure, abundancy, carbon-neutral and non-edible nature. Enormous work has been done in the field of its characterisation, isolation from other lignocellulosic components (cellulose and hemicellulose), depolymerisation and upgrading of obtained platform chemicals. However, much less work has been done in the kinetics investigation. In this regard, the present thesis is devoted to the micro-kinetic model development which would be able to describe the catalytic hydrodeoxygenation (HDO) of lignin-derived compounds at more fundamental level relaying directly on the experimental data and some catalyst characteristics.

The thesis is composed of the two main parts: 1) catalytic HDO of lignin monomer model compound and 2) catalytic HDO of lignin dimer model compounds. HDO of eugenol has been investigated within three steps (subsections): 1) HDO of eugenol over Ru/C at various operating conditions (temperature, initial hydrogen pressure, catalyst loading, agitation speed), micro-kinetic model development and kinetic parameters determination, 2) HDO of eugenol over carbon supported noble (Pt, Pd, Rh) and non-noble (Ni and Cu) catalysts and kinetic parameters determination 3) eugenol HDO over noble and non-noble metals supported on several acidic supports (Al_2O_3, SiO_2, SiO_2-Al_2O_3, HZSM-5 and TiO_2), model upgrading by involving acid active sites besides previously accounted metal active sites and kinetic parameters determination. The second part of the thesis, HDO of dimer model compounds, is aimed at kinetic investigation of typical lignin bonds cleavage using several best performing catalysts from the previous part. The HDO of biphenyl, 2,2'-bihenol, 3-methoxy-biphenyl and 2-phenoxy-1-phenylethanol was investigated which mimic two lignin bridges, ether β–O–4 and direct C–C, between two monomeric units.

The model is aimed to describe a three phase system taking into account thermodynamics of hydrogen dissolution in the solvent, transport phenomena, bulk (homogeneous) reactions, components adsorption and desorption and surface reactions. In contrast to usually reported models, this one does not presume any reaction step as rate determining and does not neglect reactions steps that are not very pronounced under tested operating conditions. Kinetic parameters determined in this thesis are: components adsorption and desorption constants, reaction rate constants and activation energies for mentioned metals and supports.

Key words: micro-kinetic model, lignin valorization, hydrodeoxygenation, bio-based chemicals, heterogeneous catalysis.