Kinetic study of the reactivity of lignin model compounds towards H-transfer hydrogenolysis under hydrothermal conditions

Nolven Guilhaume*, Xavier Besse, Yves Schuurman
Univ Lyon, CNRS, UMR 5256, IRCELYON, 2 avenue Albert Einstein, 69626 Villeurbanne Cedex, France
**Corresponding author: Nolven.Guilhaume@ircelyon.univ-lyon1.fr; Fax: (33) 472 445 399*

Abstract: This work presents kinetic studies on the hydrogenolysis of eight lignin model compounds emulating various C-O and C-C linkages under hydrothermal conditions. Reaction rate constants and apparent activation energies of bond cleavage were determined, allowing ranking the bonds reactivity.

Keywords: lignin model compounds; hydrogenolysis; kinetic study.

1. Introduction

The conversion of lignin into useful bio-based chemicals and fuels requires a fundamental understanding of the reaction mechanisms involved in the cleavage of the specific chemical bonds that constitute its polymeric structure. The reactivity of eight model compounds emulating prevalent C-O and C-C linkages present in lignin, was investigated under hydrothermal conditions in an ethanol/water mixture, ethanol serving as both H-donor an co-solvent. Apparent activation energies were determined from catalytic runs at different temperatures, allowing a comparison of the model compounds reactivity.

2. Experimental

The reaction setup and analytical methods are similar to those described elsewhere [1]. The reactions were run in a batch Hastelloy reactor, under autogenous pressure of an ethanol / water mixture, in the presence of a 2 wt.% Pt/C catalyst. The reactor was loaded with the catalyst suspended in water, purged under N_2 then heated to the intended temperature. After temperature stabilization, the solution of model compound dissolved in ethanol was rapidly injected in the hot autoclave using a high pressure pump. This procedure provided an accurate onset of the reaction, prevented the reactions from starting during heat-up and allowed running kinetic studies that provided reaction rate constants and apparent activation energies for the cleavage of the considered model bonds.

3. Results and discussion

The compounds selected to emulate β-O-4, α-O-4, 4-O-5 (C-O bonds), β-1 and α-1 (C-C bonds) of lignin were 1-(2,4-dihydroxyphenyl)-2-(4-methoxyphenoxy)-ethanone (DHPMPE), guaiacylglycerol-β-guaiacylether (GGGE), benzylphenylether (BPE), 4-phenoxyphenol (4PP), bibenzyle (BBZ), α-phenylcinnamic acid (PCA), bisphenol A (BPA) and bisphenol F (BPF) (Fig. 1).

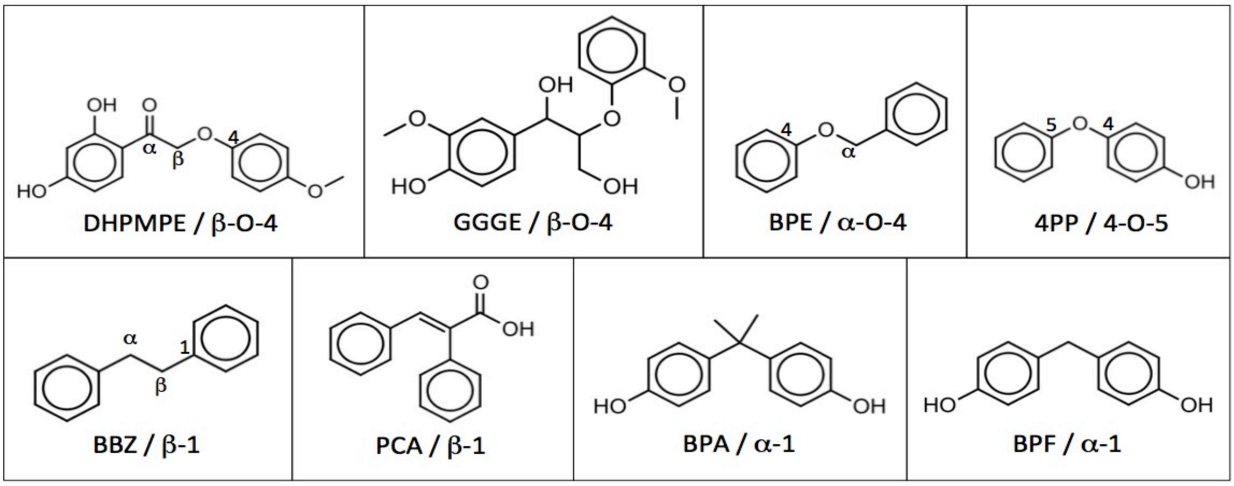
DHPMPE / β-O-4
GGGE / β-O-4
BPE / α-O-4
4PP / 4-O-5
BBZ / β-1
PCA / β-1
BPA / α-1
BPF / α-1

Figure 1. Model compounds selected to emulate typical C-O and C-C lignin bonds.

The reaction profile of DHPMPE (model compound for β-O-4 linkage) at 275°C is displayed in Fig. 2A. The apparent activation energy for the cleavage of model β-O-4 linkage was calculated from similar runs at 250 and 300°C (data not shown).

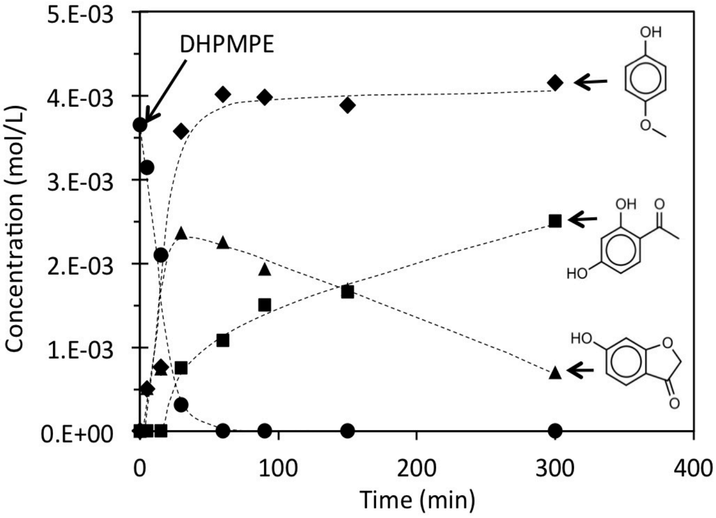

Fig. 2A: Reaction profile of DHPMPE in ethanol-water mixture. Conditions: 1 g/L DHPMPE in 50 vol.% ethanol + 50 vol.% water, 18.69 mg Pt/C, 275°C, 80 bar.

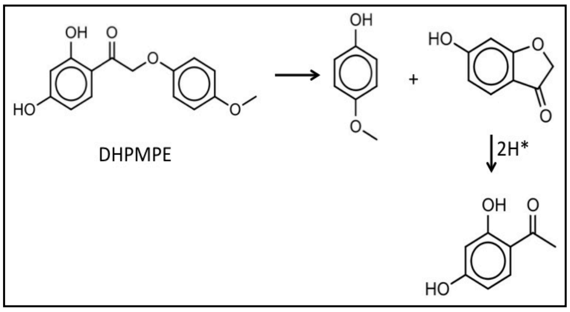

Fig. 2B: Reaction pathway of DHPMPE in ethanol-water mixture.

Table 1 summarizes the results obtained with the lignin model compounds considered in this study.

Table 1: Summary of studied model compounds and their reactions (k' is the pseudo 1st order rate constant at 300°C).

Compound	Model bond	cleavage / deoxygenation	Ea (kJ/mol)	k' (min^{-1}) at 300°C	Effect of Pt/C catalyst on reaction rate	Effect of Pt/C catalyst on reaction selectivity
BPE	α-O-4	yes / no	99	0.014	yes	no
4PP	4-O-5	yes / no	130	0.0002	no	no
DHPMPE	β-O-4	yes / no	58	0.155	no	no
GGGE	β-O-4	yes / yes	55	0.215	no	yes
BPA	α−1	yes / no	77	0.011	yes	yes
BPF	α−1	yes / no	-	-	yes	no
BBZ	β−1	no / -	-	-	no	no
PCA	β−1	no / yes	-	-	yes	yes

4. Conclusions

The reactions of eight model compounds of lignin emulating various C-O and C-C lignin linkages have been investigated under catalytic hydrothermal conditions (275-350°C, Pt/C catalyst) in ethanol/water mixtures, ethanol being used as H-donor. C-O model bonds of lignin were very selectively cleaved by hydrogenolysis. The order of reactivity of C-O model bonds was found: β-O-4 > α-O-4 >> 4-O-5, the 4-O-5 bond exhibiting a very low reactivity. This order was in agreement with the rate constants and apparent activation energies calculated for the cleavage of the corresponding bonds. Phenolic hydroxyl and methoxyl groups were totally unreactive, whereas aliphatic hydroxyl groups could be eliminated by dehydration, leading to an overall partial deoxygenation. α-1 model C-C bonds were also cleaved by hydrogenolysis, but β-1 bonds were not, although carboxyl groups on Cα could be eliminated by decarboxylation.

References

1. X. Besse, Y. Schuurman, N. Guilhaume, Appl. Catal. A-Gen., 524 (2016) 139-148.