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## Defunctionalisation of highly oxygenated lignin model compounds with NiMo/Al<sub>2</sub>O<sub>3</sub>

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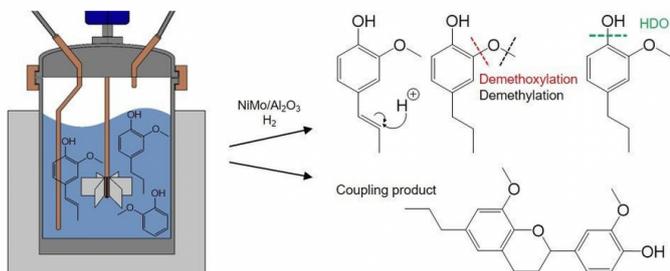
### PURPOSE OF THE ABSTRACT

Sustainable chemistry and greener production of chemicals, polymers (e.g. epoxy and formaldehyde resins) and fuels have encouraged scientists to develop procedures with alternative biobased and renewable material. Lignin, a constituent of lignocellulosic biomass, is highly functional and aromatic biopolymer being regarded as a suitable component of biomass for conversion to aromatic products.<sup>1</sup> However, the high oxygen content in lignin may cause several disadvantages including poor stability, high corrosion and low heat value which is detrimental for further applications in biofuels. Therefore, the catalytic upgrade of lignin black liquor is strongly recommended to attain the removal of the oxygen-containing groups.<sup>2</sup> On the other hand, the conversion of the lignin-derived components into products with higher content of hydroxyl (OH) groups (e.g. 1,2-dihydroxybenzene, 4-propylbenzene-1,2-diol) it is also of interest, as they can be used as precursors to fine chemicals or building blocks in organic synthesis.<sup>3</sup>

Hydrodeoxygenation (HDO) and demeth(ox)ylation of lignin-derived phenolics can be a primary step in understanding the reaction mechanisms and catalyst efficiency for defunctionalisation of lignin black liquor. Therefore, the lignin model components (guaiacol, propylguaiacol and eugenol) were used to examine the reactivity of unsaturated side-chain, OH and methoxyl groups. The experiments were performed in a batch reactor under the various temperatures and pressures with external hydrogen supply. The bimetallic sulfide NiMo catalyst on alumina support was used to explore HDO activity to deoxygenated products and dihydroxybenzenes.

Mechanistic study of guaiacol in the HDO process with NiMo/Al<sub>2</sub>O<sub>3</sub> favored demethylation yielding additional OH group and formation of 1,2-dihydroxybenzene while HDO of propylguaiacol and eugenol proceeded primarily via demethoxylation to phenolic component. Furthermore, it was observed that unsaturated side-chain in eugenol has a high tendency of coupling as we propose involving the phenolic OH group (Figure 1). The adsorbed coupling products on the catalyst surface accordingly reduce its catalytic activity to dihydroxybenzenes. Moreover, in case of eugenol and propylguaiacol higher amounts of deoxygenated products are produced than at the end of the guaiacol HDO. Therefore, NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst (before and after the reaction) was characterized by nano-computed tomography (nano-CT), Brunauer-Emmett-Teller (BET) method and pyridine diffuse reflectance infrared Fourier transform spectroscopy (py-DFTIR) to determine textural properties and quantification of acidic sites and to facilitate the engineering of more efficient bimetallic catalyst for the HDO of lignin-derived phenolics or lignin black liquor.

## FIGURES



**FIGURE 1**

Schematic illustration of defunctionalisation of guaiacol, propylguaiacol and eugenol. Proposed coupling reaction through the phenolic hydroxyl group.

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**FIGURE 2**

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## KEYWORDS

lignin model compound |  $\text{NiMo}/\text{Al}_2\text{O}_3$  | defunctionalisation | hydrodeoxygenation

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## BIBLIOGRAPHY