Catalytic oxidation of Kraft Softwood Lignin: a comparison between CuO/TiO_2 and Fe_2O_3/TiO_2

GALLINELLA Margherita[a,b,c], JASIUKAITYTE GROJZDEK Edita[d,c], VILCOCQ Léa[a] , LORENTZ Chantal[a], CORNIER Thibaut[a], ETERNOT Marion[a], DJAKOVITCH Laurent[a]

[a] Institute de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 UCBL-CNRS, 2 Av. Albert Einstein, 69616 Villeurbanne, France

[b] Kemijski Inštitut, Hajdrihova ulica 19, 1000 Ljubljana, Slovenia

[c] Univerza v Novi Gorici, Vipavska cesta 13, 5000 Nova Gorica, Slovenia

Abstract

The shortage of non-renewable petroleum-based chemical resources has led to seek new sustainable resources; there is increased interest in the conversion and valorisation of biomass[1], particularly lignocellulose. In this case of study, the aim is to oxidise with heterogeneous catalysts (CuO/TiO_2 and Fe_2O_3/TiO_2) Kraft Softwood lignin extracted from black liquor (KBL). KBL is a second-generation biomass readily available from pulp and paper industries[2], making its conversion to highly valuable products like aromatics (vanillin, for example) and oligomers a highly interesting research area. Both products can be used as building blocks for organic synthesis and materials[3]. Hence, identifying a pathway for green lignin oxidation could help the transition process to a more sustainable chemical industry.

Lignin is an aromatic biopolymer with a very complex structure and composition. Still, the concentration of its structural units, guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) along with its molecular weight and the number of inter-units can effectively describe it. In this project, Kraft pine softwood lignin, which is mainly composed of G units (88%) and a small part of H units (12%), is used[4]. SEC analyses gave an average molecular weight of 3694 g/mol, with a dispersion index of 2.5. This work investigates the catalytic oxidation of KBL using two heterogeneous catalysts, CuO/TiO_2 (5 wt% of Cu) **1** and Fe_2O_3/TiO_2 (5 wt% of Fe) **2**, which has not yet been explored for this transformation. The synthesis of **1** and **2** was done according to previously reported protocols[5]. Their catalytic activity was evaluated in a batch reactor with a maximum capacity of 150 ml using a fixed catalytic load at 0.75 g. The investigated parameters were the temperature (100-150°C), the concentration of oxygen by changing the air pressure (P=20-30 bar), the lignin concentration (5-10 g/L) and the reaction time (1-2 hours). The pH was kept constant at 13 close to that of the kraft process, envisioning potential industrial implementation of this process.

The tests have shown that **2** has a higher catalytic activity (conversion up to 99 %), but **1** has a higher yield for vanillin. The highest vanillin yield (4%) was obtained with **1** at T=150°C, t=1 h, P= 20 bar of air (4.2 bar of O_2) and 5 g/L of lignin. Moreover for **2**, due to its high catalytic activity, several tests were done by creating gas mixture of air/N2 in order to study how the selectivity of this catalyst can be modulated by changing the oxygen concentration. From table 1, it's possible to see how the vanillin yield decreases with the decreases of the oxygen concentration.

*Table 1: Catalytic tests done by varying the oxygen concentration in a 20 bar mixture of air and N2. (T=150°C, t=1h, V=150ml, 5 g/L of lignin and 0.75 g of **2**)*

Partial pressure of O_2 (bar)	Vanillin yield (%)
0	0.36
2.1	1.19
2.5	1.25
4.2	1.90

However, the analysis on the remaining lignin by HSQC, SEC and FT-IR (ATR) revealed that **2** led selectively to oxidised lignin oligomers. In particular for **2** several catalytic tests were done by varying the concentration oxygen by creating. HSQC analyses reveal that 64% of the aromatic units correspond to oxidised biopolymer that imply that the HO-benzylic position on the C3 chain are converted to carbonyl moieties. 96% of these oligomers had an average weight of 1929 g/mol to compare to that of the original lignin material.

In conclusion, 1 and 2 were synthetized successfully, **1** has shown a higher selectivity towards the production of vanillin but **2** has some potential for synthetizing oxidized lignin oligomers and it needs a more in dept study.

Acknowledgments

This project has received funding from the European Union's Horizon Europe program under the grant agreement N°101130523.

References

(1) Kobayashi, T.; Nakajima, L. *Curr. Opin. Green Sustain. Chem.* **2021**, *28*, 100439.
(2) Bajwa, D. S. et al. *Ind. Crops Prod.* **2019**, *139*, 111526.
(3) Han, Y. et al. *Ind. Chem. Mater.* **2023**, *1* (2), 207.
(4) Cabral Almada, et al. *Biomass Convers. Biorefinery* **2022**, *12* (9), 3795.
(5) Hernandez Mañas, et al. *ChemPlusChem* **2025**, *90* (3).