Study on catalytic oxidative depolymerization of kraft lignin in water with copper-based catalysts

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Abstract: The oxidative catalytic conversion of a soluble kraft lignin in water is investigated. One of the objective is to evaluate some metallic heterogeneous catalysts in presence of air at 150 °C under basic condition in comparison with "blank" experiments to better understand and optimize the system. First results have shown that copper oxides led to improve significantly the yield in monomers like Vanilin.

Keywords: Lignin, oxidation, heterogeneous catalysis.

1. Introduction

Lignocellulosic feedstock has been identified as a renewable resource of energy and chemicals, without being competitive to the food chain. Currently different processes can fraction this biomass into cellulose, hemicelluloses and lignin with good yield and a relatively high purity.[1] Even though the use of cellulose and hemicelluloses in the paper industry is well established, upgrading lignin to high added value chemicals, next to combustion for energy purpose, appears to be a highly desirable route of valorization to improve the profitability of biorefineries. With this objective in mind we undergo researches aiming at depolymerizing lignin to aromatics for the chemical industry. In this work, we focused on the catalytic valorization of lignin in aqueous media under oxidative conditions with platinum and copper based homogeneous and heterogeneous catalysts. The ultimate goal of this project is to i) depolymerize lignin in small units that can be used directly after purification, ii) break the lignin matrix into smaller fractions easily convertible afterword, iii) maintain a low level of highly oxidized materials and/or char and condensed polyquinones formation.

2. Experimental

A softwood lignin extracted from paper industry black liquor by CO_2 precipitation was studied in this work. In a typical experiment, lignin (0.5 $\%_{wt}$) is solubilized in NaOH aqueous solution (1 $\%_{wt}$) and treated in stainless batch reactor (300 mL) equipped with a ballast under 40 bar air in the presence of metal based catalysts (2$\%_{wt}$ M / lignin) at temperatures varying from 50°C to 150°C for 1 hour. After fractionation of the reaction mixture following a "home developed" protocol allowing good mass balance[2], the products were analyzed using complementary analytical techniques (^{1}H, ^{13}C, HSQC and QQ-HSQC NMR, FT-IR, TGA, GC, GC-MS, HPLC-MS).

3. Results and discussion

The influence of various reaction parameters (time, air pressure, ratio catalyst/lignin…) was evaluated during the study; however, we focused here on the effect of adding a metal based catalyst to the reaction mixture while treating lignin in basic aqueous media under air (Figure 1). The results showed that while Pt/TiO_2 did not modify strongly the balance of the reaction mixture between the main components (i.e. aromatics [vanillin, acetovanilone…], oligomeric compounds and non-liquefied products [precipitate]), nor the mono-

aromatic distribution, the use of copper based catalysts helped to improve the yields in mono-aromatics, mainly, vanillin with a rise from *ca.* 2.8% without catalyst to 4.5% in the presence of CuO/TiO_2. At the same time, under copper catalysis, the level of non-liquefied compounds remains high (*ca.* 30% *versus* 15-20% in the presence of Pt/TiO_2 and without catalyst, resp.) and that of oligomerics was reduced to *ca.* 40-45%, allowing probably to enhance further the yields of mono-aromatics by optimizing the reaction conditions. With this aim, kinetic studies are currently under investigations and the results of these investigations, and those related to the optimization, will be discussed in more details.

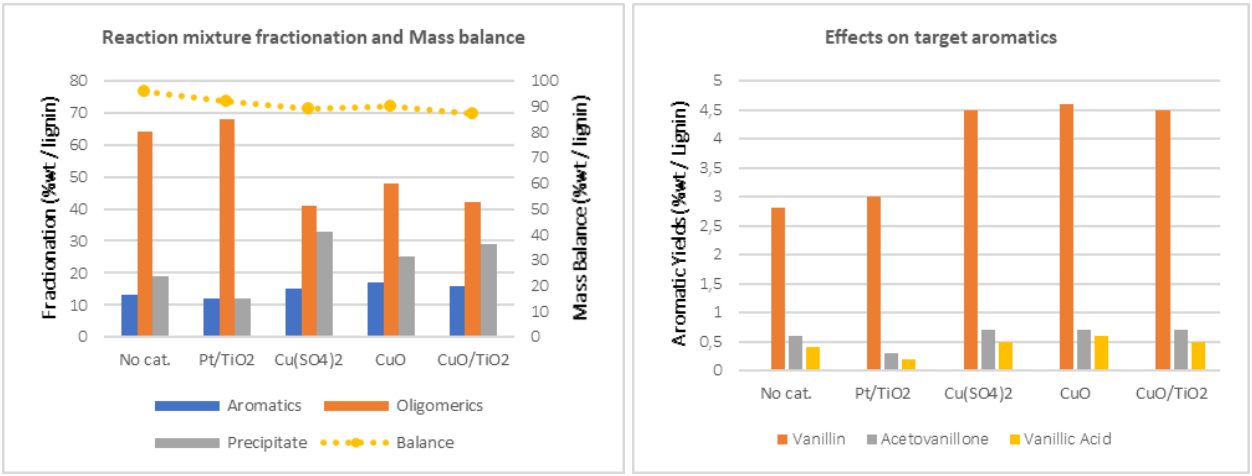

Figure 1. Evaluation of the effect of adding metal-based catalysts in lignin depolymerization in basic aqueous media. Conditions: 150°C, 1 h, P_{air}=40 bar, [NaOH] = 10g/L, [Lignin] = 5 g/L, Catalyst [M]/lignin = $2\%_{wt}$.

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4. Conclusions

In conclusion, the catalytic oxidation of lignin has been realized in an alkaline media under mild conditions in the presence of metal based catalysts. Among the catalysts evaluated, copper oxides, supported or not, allowed to improve the yield in mono-aromatic compounds like vanillin while maintaining the ratio of non-liquefied products relatively high offering thus very probably high level of improvements. For this, optimization and kinetic investigations are currently under progress. All these aspects will be discussed in more details.

Acknowledgements

The reported study was supported by French National Research Agency (ANR) through the projects CHEMLIVAL (ANR-12-CDII-0001-01) and PHENOLIQ (ANR-16-CE06-0007-03). The authors kindly acknowledge FCBA (D. Da Silva Perez) for providing sample of lignin.

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