

N°167 / OC

TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Which role for hydrogen transfer in organosolv pulping?

AUTHORS

Francesco DI RENZO / INSTITUT CHARLES GERHARDT MONTPELLIER, 240 AVENUE JEANBRAU - ENSCM, MONTPELLIER

Iqra Zubair AWAN / DPT INDUSTRIAL CHEMISTRY UNIVERSITY OF BOLOGNA, VIALE RISORGIMENTO, 4, BOLOGNA

Olinda GIMELLO / INSTITUT CHARLES GERHARDT MONTPELLIER, 240 AVENUE JEANBRAU - ENSCM, MONTPELLIER

Thomas CACCIAGUERRA / INSTITUT CHARLES GERHARDT MONTPELLIER, 240 AVENUE JEANBRAU - ENSCM, MONTPELLIER

Nathalie TANCHOUX / INSTITUT CHARLES GERHARDT MONTPELLIER, 240 AVENUE JEANBRAU - ENSCM, MONTPELLIER

Stefania ALBONETTI / DPT INDUSTRIAL CHEMISTRY UNIVERSITY OF BOLOGNA, VIALE RISORGIMENTO 4, BOLOGNA

Fabrizio CAVANI / DPT INDUSTRIAL CHEMISTRY UNIVERSITY OF BOLOGNA, VIALE RISORGIMENTO 4, BOLOGNA

PURPOSE OF THE ABSTRACT

Organosolv pulping is finding a new revival in second generation ethanol refineries. Most interest in the conditions of pulping has been addressed to acid hydrolysis and solvation effects. The role of hydrogen-donor effects in pulping is just starting to receive proper attention. The increase of the H/C and decrease of O/C ratios can open new markets for lignin products. However, many questions have to be answered to assess the economics of implementing proper conditions, catalysts and processes to boost oxydehydrogenation in lignocellulose pulping. Does the increased added-value of lignin products compensate the lower energy recovery? How the oxidation of solvent fractions affects inventory and recycling of the pulping solution? Which recovery or in-plant utilisation of the solvent oxidation products have to be planned? Can heterogeneous catalysts allow to overcome the rentability threshold of organosolv pulping?

More data about H-transfer on substituted phenolic moieties in realistic conditions are needed to evaluate possible options. In this communication, we propose experimental data on the action of several solvents on model lignin systems in the presence of non-noble metals heterogeneous catalysts. Mixed oxides in the Ni-Cu-Fe and Ni-Cu-Al systems, designed for magnetic separation of catalysts, have been prepared from layered double oxide precursors. Relative rates of MPV reaction, O-H and C-C bonds hydrogenation and ether bonds hydrogenolysis have been determined and allowed to define which catalysts are more effective in deep dehydrogenation or in control of the polymerisation degree of lignin-derived products.

Oxides obtained by thermal decomposition of LDH precursors are effective catalysts for H-transfer reactions to lignin model molecules, also in absence of the basic properties induced by Mg²⁺ cations in the most usual catalysts ex hydrotalcites. In the case of the mixed Cu-Ni-Fe oxide catalysts, the conversion was always higher than for the single-component oxides but the reactivity was enormously influenced by the Cu/Ni ratio in the catalyst. If benzyloxymethoxybenzaldehyde model dimer was converted at nearly 30% on the Ni-Fe catalyst in methanol at 200°C, the conversion rapidly rose to nearly 100% for Cu/divalents ratio of 0.4 or higher. With the increase of the conversion, formation of volatile products became relevant. Deeper hydrogenation was reached at the increase of the copper content. For catalysts with low copper content, the main product was

benzyloxymethoxybenzyl alcohol, viz. the first MPV hydrogenation product of the substrate. At increasing copper content, the main product became benzyloxymethoxybenzene, the product of successive C-O hydrogenolysis of the alcohol group of benzyloxymethoxybenzyl alcohol and C-C hydrogenolysis of the intermediate product. When the Cu/divalent ratio approaches 0.5, the presence of nickel oxide accelerated the β -O-4 hydrogenolysis, as observed also on the single-component oxides, and the main products became methoxycresol and toluene, respectively the C-O and C-C reduction products of the vanillic and benzylic moieties of the parent substrate. The relevance of benzyloxymethoxybenzene among the products clearly indicates that also aliphatic C-C bonds are hydrogenated. No products of hydrogenation of the aromatic ring were observed. The doping of CuO and NiO by iron undoubtedly affects the activity of the catalysts. Interestingly, the relative effectiveness of MPV hydrogenation and hydrogenolysis of phenylether bonds can orient the choice of the catalyst in a lignin organosolv environment towards the obtention of products with different molecular weight and level of functionalisation.

FIGURES

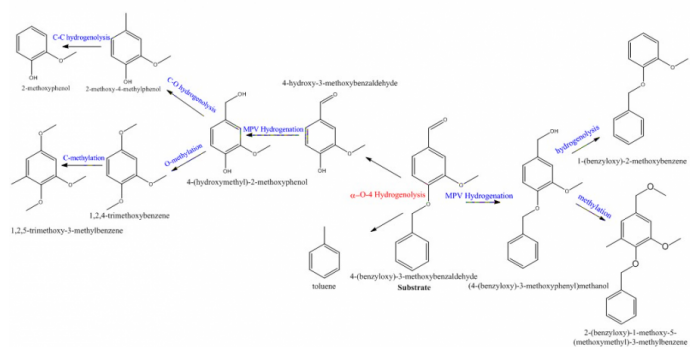


FIGURE 1

Main hydrodeoxygenation pathways

Lignin model dimer in methanol at 200°C on Ni-Cu-Fe oxide catalyst calcined at 600°C

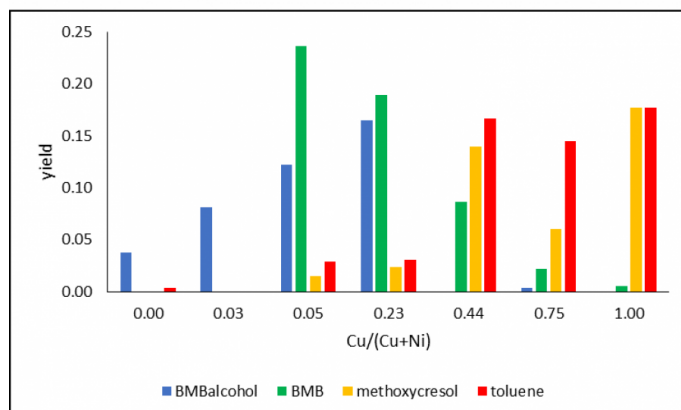


FIGURE 2

Effect of the catalyst composition

Yields of benzyloxymethoxybenzyl alcohol, benzyloxymethoxybenzene, methoxycresol and toluene with the copper fraction of the Ni-Cu-Fe catalysts

KEYWORDS

hydrodeoxygenation | non-noble metal catalysts | lignin | layered double oxides

BIBLIOGRAPHY