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Hydrotreatment of technical lignins

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Lignin hydrotreatment, Hydrodeoxygenation (HDO), Depolymerization

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Oral Presentations #13

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The catalytic upgrading of lignin into fuels and value-added chemicals is a key challenge for the development of sustainable biorefineries due to lignin's structural complexity, high oxygen content, and resistance to depolymerization. In this work, silica-supported metal phosphide catalysts (Ni_2P, MoP, and CoP) were synthesized and evaluated for the hydrotreatment of two commercial lignins with different structures: organosolv lignin and enzymatic hydrolysis lignin. The influence of catalyst composition, reaction temperature, residence time, and solvent on lignin conversion, product selectivity, and molecular weight evolution was investigated. Reactions were carried out in a stirred batch reactor under 10 bar of hydrogen. Product distributions were analyzed by gas chromatography (GC), while molecular weight changes were monitored using gel permeation/size exclusion chromatography (GPC/SEC).

The results showed that lignin type strongly affects catalytic behavior. Organosolv lignin exhibited significantly higher reactivity than enzymatic hydrolysis lignin, owing to its greater content of cleavable β-O-4 linkages and lower degree of condensation. GPC/SEC analyses revealed substantial reductions in both number-average and weight-average molecular weights, confirming effective depolymerization. The decrease was more pronounced for organosolv lignin, indicating its higher susceptibility to catalytic upgrading under relatively mild conditions.

Among the catalysts studied, Ni_2P/SiO_2 displayed the highest activity for lignin depolymerization and hydrodeoxygenation, promoting extensive ether bond cleavage and hydrogenation of reactive intermediates, which resulted in higher yields of stabilized monomeric products. MoP/SiO_2 showed intermediate activity and favored partial hydrodeoxygenation while preserving aromaticity. CoP/SiO_2 exhibited lower overall activity but greater selectivity toward aromatic-ring hydrogenation. GC analysis identified phenolic monomers such as guaiacol, syringol derivatives, alkylphenols, and partially hydrogenated cyclohexanol-type compounds.

Reaction temperature and residence time had a significant impact on conversion and selectivity. Increasing temperature enhanced lignin solubilization and monomer formation; however, temperatures above 325 °C promoted secondary condensation reactions and the formation of heavier fractions. An optimum temperature near 300 °C provided the best balance between depolymerization and product stabilization. Overall, silica-supported metal phosphides, particularly Ni_2P/SiO_2, showed strong potential for lignin valorization, highlighting the importance of matching catalyst and operating conditions to the characteristics of the lignin feedstock.

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