

Catalytic fast pyrolysis of lignin – Tuning selectivity

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Introduction

Catalytic fast pyrolysis is an efficient way to depolymerize the complex lignin structure and stabilize reactive intermediates.¹ Lignin is the third most common biopolymer and the only renewable source for aromatic compounds. Non-catalyzed pyrolysis yields up to 40 wt.% of pyrolysis oil, which consists of more than 300 different compounds, mainly oxygenated products, water, and phenols. The relatively low selectivity for one specific product and the reactivity of the phenolic compounds causes problems with usage and separation of the pyrolysis oil.

Increasing selectivity to either one single product or a group of products is therefore crucial to enable lignin to emerge as a biomass-based resource for chemicals and fuels. Zeolites not only increase the yield of the liquid fraction but also produce more deoxygenated products, which have a higher energy density as well as lower reactivity during separation.^{2,4,4} Due to the complexity of the lignin structure and the high degree of molecular interaction of the polymeric matrix it is of greatest importance to test the depolymerization and deoxygenation efficiency with the lignin polymer and not single model compounds.

Materials and Methods

Alkaline Lignin (TCI Europe) was reacted with a catalyst to lignin ratio of 4:1 in a pyroprobe micro-reactor (5150, CDS Analytical) at 650°C for 60 seconds at a heating rate of 20°C/ms in a helium carrier gas stream. Pyrolysis products were directly injected into the GC/MS (Agilent 7890A GC with Agilent 5975C MS) equipped with a TCD detector to quantify non-condensable products. The liquid fraction was characterized by peak identification according to NIST08 MS library. Metal-supported zeolites were prepared by wetness impregnation (5wt.% metal basis) and calcination and the metal oxides by calcination at 550°C for 5h from the corresponding nitrates.

Results and Discussion

When aiming for aromatic hydrocarbons, such as benzene, toluene or xylene (BTX), different zeolitic characteristics are most influential: Acidity, pore shape and size, and the available surface area. The selectivity to aromatic hydrocarbons increases with the Si/Al-ratio (Figure 1a). H-USY(7) yields the highest liquid fraction with a comparable selectivity to hydrocarbon compared to H-ZSM5(15).²

The influence of the metals on the selectivity can best be compared with a ZSM-5 zeolite, which shows a medium selectivity towards BTX and naphthalene (Fig.1b). While cobalt enhances production of aromatics, molybdenum decreases it and phenols are the most abundant compounds. Nickel shows the highest selectivity for BTX, which increases the selectivity by 20% on H-ZSM5(50). Other tested metals do not show this enhancing effect (not shown).

The surface area of H-USY is decreasing when doped with cobalt and is even smaller in the Na-Form (Fig.1c). Accordingly the yield decreases while the selectivity stays similar.⁵ H-USY is the most promising catalyst in terms of yield and selectivity to aromatic hydrocarbons.

Metal oxides do not catalyze deoxygenation (Fig.1d), but molybdenum oxide or copper oxide can direct the selectivity to a single product, in this case vanillin (S>30%). Guaiacol (S~28%) is especially produced in the presence of nickel and cobalt oxide, while cobalt oxide produces also non-phenolic aromatic alkoxy.

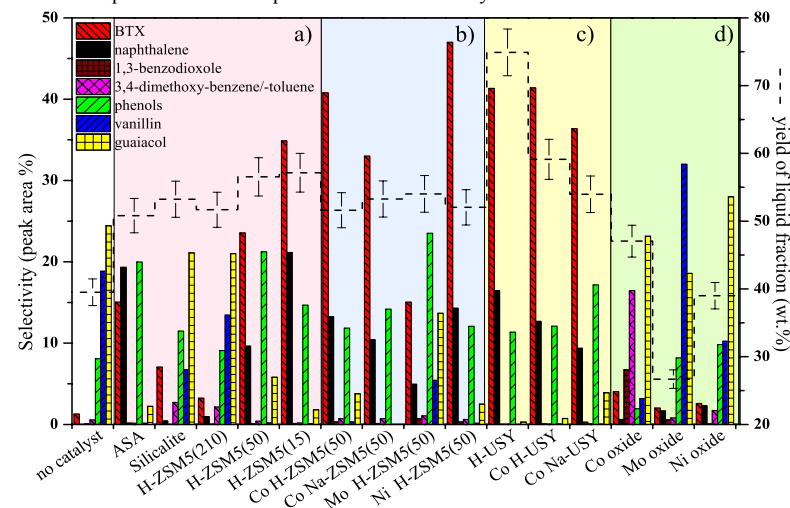


Figure 1. Selectivity (bars) based on peak area percentage of selected products and liquid fraction yield (---) of the pyrolysis with the stated catalysts grouped by the variable (a-d) and a blank experiment for comparison.^{2,5}

Significance

The selectivity of fast pyrolysis towards a single compound or a class of compounds can be tuned by the right choice of catalytic system. Intrinsic zeolitic deoxygenation behavior is enhanced by metal doping and thus reduces the need of an extra deoxygenation step in lignin conversion. This high degree of deoxygenation and the vast increase in liquid yield simplify the lignin conversion process and facilitate a separation of the products so that these aromatic compounds can be used more effectively.

References

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