# Effect of Methane Co-Feeding on Product Selectivity of Lignin Pyrolysis

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Lignocellulosic biomass composed mainly of cellulose, hemicellulose and lignin is an attractive sustainable source for production of fuels and chemicals. Lignin which constitutes 15-30% of biomass weight and 40% of biomass energy has a complex phenolic structure [1]. Therefore, phenolic compounds such as alkylphenols and methoxyphenols (particularly methoxyphenols) are produced from thermal decomposition (pyrolysis) of lignin. Deoxygenation of methoxyphenols to alkylphenols and hydrocarbons (BTEX (benzene, toluene, ethylbenzene, xylenes) and naphthalenes) is a great point of interest due to the vast industrial applications of alkylphenols and hydrocarbons. A variety of alkylphenols and their derivatives can be used in the manufacture of pharmaceuticals, detergents, stabilizers and etc. Employing catalyst (in-situ and ex-situ) in lignin pyrolysis could efficiently shift the product selectivity from methoxyphenols to alkylphenols and hydrocarbons. So far, ZSM-5 catalyst has been immensely applied in catalytic pyrolysis of lignin [2]. In addition to catalyst, co-pyrolysis of lignin with hydrogen-rich compounds such as plastics, alcohols and methane could change the selectivity of products.

In this work, methane was co-fed as both carrier gas and reactant with lignin in order to study the product selectivity of in-situ and ex-situ catalytic pyrolysis of lignin. HY with $SiO_2/Al_2O_3$ of 5.1 was used as in-situ catalyst. HZSM-5 ($SiO_2/Al_2O_3$: 30), $WO_3/ZrO_2$, 3wt% Cu/HZSM-5 (30), 3wt% Ni/HZSM-5 (30), 3wt% Fe/HZSM-5 (30) and 3wt% Zn/HZSM-5 (30) were used as ex-situ catalysts. Use of methane considerably shifted the product selectivity towards alkylphenols (Figs. 1 and 2). Methane and phenolic compounds produced from in-situ pyrolysis of lignin are competitively activated over catalytic sites. Selectivities of alkylphenols in the catalytic system of HY-HZSM-5 using $N_2$ and $CH_4$/He gases were 2.69 and 63.57%, respectively. Incorporation of Ni and Zn metal catalysts over HZSM-5 support increased the selectivity of alkylphenols, while Fe and Cu supported on HZSM-5 shifted the reaction selectivity towards hydrocarbon formation.

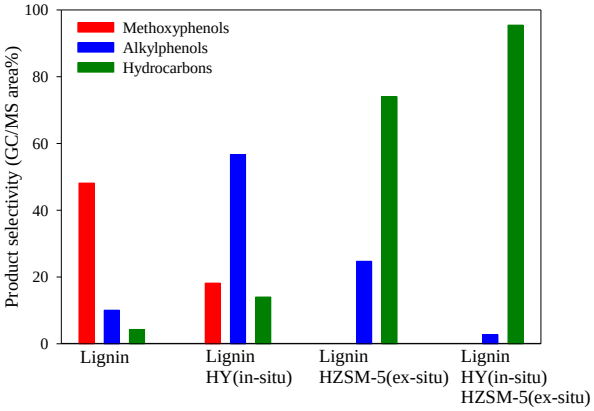


Fig.1 Product selectivity of catalytic pyrolysis of lignin at 600 ℃ using $N_2$ carrier gas (100 ml/min).

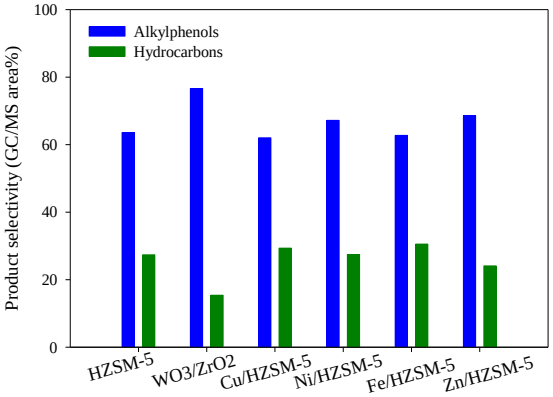


Fig. 2 Product selectivity of catalytic pyrolysis of lignin at 600 ℃ using different ex-situ catalysts, HY as in-situ catalyst and $CH_4$/He (100 ml/min) as carrier gas.

## REFERENCES

[1] V.B.F. Custodis, P. Hemberger, Z. Ma, and J.A. van Bokhoven, J. Phys. Chem. B, 118 (2014) 8524.
[2] K. Wang, P.A. Johnston, and R.C. Brown, Bioresour. Technol., 173 (2014) 124.