

Thesis title: Experimental and theoretical investigations into valorization of biomass-derived phenols by C-C coupling with light oxygenate

ABSTRACT

The global concern for fossil fuel depletion and emission of greenhouse gases has led to increased research on the production of transportation fuels, alternate fuels and value added chemicals from the renewable 2nd generation lignocellulosic biomass. Among the different routes, fast pyrolysis is an eco-friendly, efficient and cost-effective technology for biomass conversion, which produces liquid bio-oil (~80% yield), solid biochar, and pyrolytic gases. However, immediate commercial implementation of the condensed bio-oil formed by pyrolysis is impossible due to the presence of a high percentage of oxygen functionalities (~30-40%). The existing upgrading process includes the catalytic hydrodeoxygenation (HDO) of bio-oil (to remove oxygenates), however, it operates under harsh reaction conditions, which results in the loss of C₁–C₄ light oxygenate fractions (5-15%) in the form of non-condensable gases that could have otherwise contributed in increasing the heating value of the biofuel and chemicals. This loss can be suppressed by valorization of lignin-derived phenolic compounds via C–C coupling by alkylation reaction with such light oxygenates to produce C₁₀–C₁₃ fuel range alkylphenols, prior to HDO. The present work is focussed on alkylation of *m*-cresol, an abundant species in pyrolysis bio-oil, with *iso*-propanol (as light oxygenate) over metal loaded zeolites to form stable C₁₀ fuel precursor and important value-added chemical, thymol.

A thermodynamic analysis is performed to understand the thermodynamic limits of the *m*-cresol alkylation reaction with *iso*-propanol alongwith all the possible side-reactions to assess the thermodynamically controlled and kinetically controlled reactions. After identifying the thermodynamic boundaries of this reaction, the zeolites HZSM5, HMCM22, HBEA, and HY having different medium and large pore architecture and varied acidity are screened as catalysts for maximizing the desired mono-C-alkylated product, thymol, in a continuous flow

atmospheric packed bed reactor. The structure-activity relationship is found to be highly significant for this reaction. Therefore, the tuning of Bronsted and Lewis acidity and pore dimensions of the zeolite catalysts by ion exchanging with different metals are performed and amount of metal is optimized which enhances the conversion of *m*-cresol to near equilibrium conversion and with selective formation of thymol. The disruption in structure and stability of the zeolite framework and its degraded catalytic performance is also observed at very high amount of metal loading. After choosing the promising catalyst, statistical design of experiments is used to investigate the effect of important process parameters like reaction temperature, weight hourly space velocity, *iso*-propanol to *m*-cresol mole ratio and their individual and interactive effects on the conversion of *m*-cresol and thymol selectivity in alkylation reaction for optimization of process parameters over the most promising catalyst.

Mechanistic insights into this reaction mechanism over metal loaded zeolite is investigated using Density Functional Theory (DFT) calculations and the effect of acidity on the reaction mechanism is elucidated by comparing the results with the parent zeolite. The rate of reaction and thermodynamic stability of thymol is found to be higher in case of metal loaded large pore protonated zeolite, as a result of higher acidity of this catalyst. Finally, the kinetics of this reaction is investigated over the most promising catalyst in an external and intraparticle mass diffusion-free regime. The time-on-stream behaviour shows that the catalyst deactivates, especially at high temperatures (~300 °C) due to active site loss and pore plugging by coke. However, the rate of deactivation of this modified catalyst is significantly lower than the rate of deactivation of the parent zeolite. Based on the product distribution, a reaction network is elucidated and a kinetic model is developed. The kinetic parameters are estimated in the temperature range of 200 °C to 300 °C. The catalyst deactivation is also included in the model to check the temperature dependence of the catalyst deactivation parameters.

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