A-146

Modeling and Prediction of Phase Equilibria in Systems Containing Bio-Oil Compounds

A. Jalalinejad, Axel Funke, Nicolaus Dahmen
Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research & Technology (IKFT), Eggenstein-Leopoldshafen, Germany

Accurate prediction of phase equilibria is essential for the design, simulation, and optimization of separation and upgrading processes for pyrolysis-derived condensate fractions. Fast pyrolysis bio-oil is a complex renewable carbon carrier containing water and a wide range of polar oxygenated compounds, including acids, aldehydes, ketones, alcohols, phenols, furans, and carbohydrate-derived molecules. This chemical complexity leads to strong non-ideal behavior and makes the prediction of vapor-liquid and liquid-liquid equilibria challenging, especially for novel pyrolysis products with limited experimental data. The objective of this study is to evaluate and improve predictive thermodynamic models for bio-oil-derived mixtures, with emphasis on their application to fractionation, distillation, and extraction. COSMO-SAC, UNIFAC, UNIFAC-DMD, and NIST-modified UNIFAC are assessed using critically selected phase equilibrium data for representative bio-oil compounds and surrogate mixtures. The performance of each model is analyzed for binary and ternary systems containing water and oxygenated compounds commonly found in fast pyrolysis bio-oil. The evaluation indicates that general predictive models have important limitations for bio-oil-related systems. These limitations are mainly related to the insufficient representation of strong molecular interactions, the limited availability of reliable experimental phase equilibrium data, and inadequate group interaction parameters for complex oxygen-rich mixtures. In particular, group contribution models are highly sensitive to the quality of the data used during parameter estimation, while purely predictive approaches may not fully capture the separation behavior of highly polar bio-oil fractions. To overcome these limitations, selected interaction parameters are re-optimized using reliable vapor-liquid and liquid-liquid equilibrium data, and additional functional group descriptions are introduced for key bio-oil compounds, especially furan-based molecules. The refined thermodynamic framework is validated using phase equilibrium data and advanced distillation curve information. Its applicability is further demonstrated through the analysis of distillation and extraction processes relevant to bio-oil refining. This work shows that a bio-oil-oriented UNIFAC-type model can improve the prediction of phase behavior in fast pyrolysis bio-oil mixtures and provide a practical tool for process design. By improving thermodynamic predictions for pyrolysis-derived liquids, this study supports more efficient bio-oil upgrading and the sustainable utilization of renewable carbon resources for fuels and chemical production.