VALIDATING THE APPLICABILITY OF VAPOR-LIQUID PHASE EQUILIBRIA MODELS FOR FAST PYROLYSIS BIO-OILS THROUGH ADVANCED DISTILLATION CURVES

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Fractionation of fast-pyrolysis bio-oils (FPBOs) is very pertinent towards attaining a viable pyrolysis biorefinery. Fractional condensation is one key and efficient technology used for the fractionation of FPBOs into different fractions as it helps recover pyrolytic condensates based on boiling point differences. Theoretical thermodynamic phase equilibria modelling of fractional condensation processes helps predict the yield and composition of FPBOs. This saves a lot of time and effort required in investigating these systems in real setups. Pyrolysis vapors/FPBOs are highly non-ideal and complex in nature and the use of more advanced models (that account for association and other complex interactions between molecules) to model such mixtures is recommended. Additionally, most FPBO components lack model parameters in databases or in the literature and the use of group-contribution models in predicting their behavior is favorable. The modified UNIFAC Dortmund (UNIFAC-DMD) and the Group Contribution with Association Equation of State (GCA-EoS) are two typical and interesting examples of such models. In this study, the Advanced Distillation Curve (ADC) method was used as an experimental vapor-liquid equilibrium (VLE) validation tool for these thermodynamic models. This was conducted by distilling two different fractions of FPBOs; the organic-rich (ORC) and the Aqueous condensate (AC) recovered from the fast pyrolysis of wheat straw and miscanthus biomass feedstocks. Compared to other distillation methods, ADC enables experimental determination of thermodynamic state points.

ADC of ORCs and ACs obtained were conducted under vacuum pressure. Distillation under vacuum conditions allowed for lower temperatures and thus slowed down the rate of polymerization to enable a greater volume percentage of FPBOs to be distilled. The distillation process was subsequently modelled using UNIFAC-DMD and GCA-EoS models to evaluate how these theoretical models perform with experimental data, having chosen a suitable surrogate mixture. Distillate samples were collected and analyzed using GC-FID at every 5 and 10 vol.% distilled for ORC and AC, respectively. Root Mean Square Error (RMSE) was used to compare the extent of deviations of model predictions from experimental data.

Both the UNIFAC-DMD and GCA-EoS proved to be robust models for predicting the VLE behavior of water, acids (acetic acid), ketones (acetol), furans (furfural), phenols and dimethoxyphenols (syringol) equally present in the ORCs and ACs. Model predicted data for both models were in close alignment with experimental data and RMSEs calculated for both models in relation to experimental data were comparable. However, for the distillation curves of the ORC, RMSE data recorded for UNIFAC-DMD were significantly higher (14 times higher on average) than corresponding data obtained for GCA-EoS, which possibly suggests that the GCA-EoS has a better tendency to predicting the thermodynamic behavior of the ORC. This was corroborated to the comparatively wider distillation temperature ranges (45-250 ºC) of the ORC, which had a significant portion outside a range the UNIFAC-DMD model can accurately handle. Activity coefficient models that include UNIFAC-DMD are only valid to an upper limit temperature of 120 ºC. In effect, the GCA-EoS promises to deviate the least from experimental data as compared to UNIFAC-DMD and other simple models such as the ideal gas equation of state.

This study is relevant towards Product characterization, separation and upgrading with respect to the themes of the conference.