Thermodynamics and Fluid Characterization using Trajectory Optimization

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Accurate phase equilibrium modeling for complex mixtures such as hydrocarbon and organic compounds such as alcohols and ethers is necessary for the design and optimization of processes as well as for the development of new fuels and fuel blends. A straightforward methodology is proposed to tune a phase equilibrium model based on a relatively small amount of data. The data are collected using the Advanced Distillation Curve method developed by Bruno (2006) where boiling points are measured in the boiling liquid and are therefore thermodynamic state points. The data are modeled using the trajectory optimization method developed by Satyro and Yarranton (2009). The approach was first tested on methanol/water, iso-propanol/water and triethylene glycol/water mixtures. Each mixture was distilled at atmospheric pressure. The NRTL model was used to describe the phase behaviour, and the interaction parameters (interaction energies and randomness factor) were adjusted to fit the model to the distillation data. The tuned model was tested on literature vapour-liquid equilibrium data for each mixture and predicted the bubble and dew saturation temperatures with less than $\pm 2^{o}C$ deviation. The approach was then tested on more complex hydrocarbon mixtures such as gasoline, gasoline with methanol and gasoline with ethanol. The Peng Robinson equation of state was used to describe the phase behaviour. The methodology correctly described the phase behaviour including azeotropism of these complex mixtures by tuning the interaction parameters between the gasoline pseudo-components and the organic compounds. The combination of the Bruno distillation method with the trajectory optimization technique provides a useful tool for the characterization of ill defined fluids such as petroleum and for the prediction of basic phase behaviour, including saturation temperatures, azeotropes, and vapour-liquid equilibria.