Linking Surrogate Fuel Properties to Liquid Structure *via* Molecular Dynamics

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Predicting thermophysical properties and combustion behavior of petroleum-based fuels, which contain hundreds of components, is difficult. As a result, fuel surrogates, less-complex hydrocarbon mixtures of a few components that match important thermophysical properties of the conventional fuel, are often studied. Even for these simplified mixtures, determining the composition that will yield a desired set of properties can be a time-consuming and expensive task. Molecular dynamics (MD) simulations can be used to predict thermophysical properties of fuel surrogates as a function of molecule type and composition, thus narrowing the phase space that must be examined experimentally. Additionally, MD simulations can provide atomic-level insights into the behavior of fuels that are difficult or impossible to obtain experimentally. In this study, we used MD simulations to predict thermophysical properties of surrogate fuels for Catalytic Hydrothermal Conversion (CHC) diesel and jet fuels. These surrogates are ternary mixtures consisting of *n*-alkylbenzenes (toluene to *n*-hexylbenzene), *n*-butylcyclohexane, and *n*-alkanes. Densities, bulk modulus, and excess molar volumes were calculated at ambient temperature and pressure using the OPLS-AA force field and MD. We found densities in quantitative agreement with experimental values, whereas there was qualitative agreement with experimental isoentropic bulk modulus and excess molar volume. Although pure *n*-hexylbenzene has lower density than both toluene and *n*-butylbenzene, the surrogate mixtures with *n*-hexylbenzene have higher densities, because these mixtures have a lower excess molar volume than those containing toluene or *n*-butylbenzene. In addition to calculating thermophysical properties, we examined the liquid structure of the mixtures as a function of composition and molecule structure. For example, angular radial distribution functions showed that the relative orientation of toluene molecules differs between the pure fluid and in the surrogates, while changing composition has little effect on the packing of the longer-chain *n*-alkylbenzenes.