Experimental Measurements of Cryogenic Vapor-Liquid and Solid-Fluid Equilibria for the Hydrogen Liquefaction Process

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Hydrogen is expected to be one of the most important carbon-free energy vectors of the future. One challenge with this fuel is its low energy density at atmospheric conditions. Analogous to liquefied natural gas (LNG), the energy density of hydrogen can be increased by conversion to the liquid state at cryogenic temperatures (as low at 20 K at atmospheric pressure). However, relative to LNG production, hydrogen liquefaction is expensive. A significant portion of these costs relates to the inefficiency of the cryogenic refrigeration cycle and the need to over-design adsorption units which remove contaminants from the hydrogen feed stream.

Existing hydrogen liquefaction plants often utilise a nitrogen loop for pre-cooling, and a (hydrogen or helium) cryogenic refrigeration loop. The performance of the cryogenic loop can be improved by utilising a "mixed" refrigerant, which can consist of hydrogen, helium, and neon blends. Alongside providing better efficiency, the composition of the refrigerant can be tuned to afford greater flexibility. However, there is limited measured thermophysical property data available for these mixtures (especially for those with more than two components) at temperatures below 100 K. As a result, the accuracy of existing fluid property models at the conditions present during hydrogen liquefaction is uncertain, which impedes efforts to increase the efficiency of the process.

The removal of contaminants from the hydrogen feed stream is essential prior to the cryogenic cooling stage to avoid freeze-out. The identity of these impurities depends on the source of the hydrogen; for hydrogen produced from an electrolyser, N_2, O_2, Ar, and H_2O are relevant, while CO_2, CO and CH_4 are additional likely impurities resulting from steam methane reforming. Typically, adsorption units are used to reduce the concentration of these compounds to a level lower than their solubility in the hydrogen stream at liquefaction temperatures and pressures. Accurate measurements of impurity solubility are thus essential inputs into the design of adsorption units.

To address these challenges, here we present a new, unique cryogenic apparatus capable of measuring mixed refrigerant vapor-liquid (and solid-fluid) equilibrium, and the solubility of impurities at temperatures down to 6 K at pressures up to 10 MPa. This system combines a stereomicroscope for the visual detection of condensed phases, a high-pressure measurement cell, and a commercial cryocooler. This experimental capability will be essential to refining thermodynamic models for the accurate prediction of the thermophysical properties relevant to the hydrogen liquefaction process.