The Separation of Detergent Range Alkanes and Alcohols: Supercritical Fluids as the Green Alternative Solvent

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Alcohol isomers with carbon numbers between 8 and 20 are commonly used in the detergent, surfactant and plasticizer industries. These alcohols are usually produced via oxidation of alkanes or the hydrogenation of alkenes. The product stream from both processes contains a mixture of alcohols and alkanes with a distribution of carbon numbers. These compounds often have overlapping boiling and melting points. Present separation processes usually involve azeotropic distillation using an entrainer. The best entrainers are unfortunately often toxic to humans.

Supercritical fluid fractionation was identified as a possible alternative process. Initially, 3 possible supercritical solvents were considered, namely CO_2, ethane and propane. Binary phase equilibria were measured for the relevant alcohols and alkanes. The initial test case was the separation of 1-dodecanol (BP 532K) and n-tetradecane (BP 526K). CO_2 and ethane were identified as the possible supercritical solvents, with CO_2 demonstrating the highest selectivity. A pilot plant with maximum operating pressure and temperature of 30 MPa and 420 K, respectively, and equipped with a 5m tall, 28 mm inner diameter column packed with Sulzer DX packing was used. The pilot plant experiments have shown that both CO_2 and ethane have the ability to separate mixtures of 1-dodecanol and n-tetradecane. Ethane is technically superior to CO_2, but the energy requirements are between 40 and 50% higher than for CO_2. Based on cost, safety considerations and environmental effects supercritical CO_2 is the preferred solvent.

The pilot plant study was expanded to a feed mixture consisting of 25 mass % each of 1-decanol, 3,7-dimethyl-1-octanol and 2,6-dimethyl-2-octanol using supercritical CO_2 as solvent. These pilot plant runs indicated that a lower operating temperature leads to better separation of the alkanes from the alcohol mixture. The possible operating pressure range at a specific temperature is determined by the phase behaviour of the components involved. Slightly higher operating pressures lead to an increase in the fraction of light components in the extract stream. A lower solvent-to-feed ratio leads to improved separation performance as well as other benefits (e.g. size and capacity of pumping, heating and cooling equipment).

The pilot plant studies demonstrated the feasibility of the supercritical extraction process, but some trends could not be explained with the available binary phase equilibria data. The high costs associated with the pilot plant work also necessitated the development of a reliable process model in order to optimize the process. These 2 factors made it necessary to investigate the solute-solute interactions and ternary (and higher) high pressure phase equilibria had to be measured for the typical components in the mixture.