KP2

Supercritical Fluid Extraction and Fractionation: Two South African Feasibility Studies

J.H. Knoetze[a,*], C.E. Schwarz[a], T.F.N. Madzimbamuto[a,b]
[a] Department of Process Engineering, Stellenbosch University, Banhoekweg, Stellenbosch, 7600, South Africa
[b] Department of Chemical Engineering, Cape Peninsula University of Technology, Bellville , Cape Town, South Africa
[*] jhk@sun.ac.za

Alcohol isomers with carbon numbers from 8 to 20 are used in the detergent, surfactant and plasticizer industries. These alcohols are produced via oxidation of alkanes or the hydrogenation of alkenes, resulting in a mixture of alcohols and alkanes with a distribution of carbon numbers. Present separation processes usually involve azeotropic distillation using an entrainer, with the best entrainers toxic to humans. Supercritical fluid fractionation was identified as a possible alternative process. Binary phase equilibria were measured. The initial test case was the separation of 1-dodecanol (BP 532K) and n-tetradecane (BP 526K), with CO_2 and ethane as the possible supercritical solvents, and CO_2 demonstrating the highest selectivity. The pilot plant has maximum operating pressure and temperature of 30 MPa and 420 K, respectively, and is equipped with a 5m tall, 28 mm ID column packed with Sulzer DX packing. The pilot plant work showed that both supercritical CO_2 and ethane have the ability to separate mixtures of 1-dodecanol and n-tetradecane. 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 n-decane, 1-decanol, 3,7-dimethyl-1-octanol and 2,6-dimethyl-2-octanol using supercritical CO_2 as solvent. 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 of the pilot plant work necessitated the development of a reliable process model. These 2 factors made it necessary to investigate the solute-solute interactions and ternary (and higher) high pressure phase equilibria had to be measured and modelled for the components in the mixture.

Buchu (*Agathosma crenulata*) is a shrub that is indigenous to the south-western parts of South Africa. It is valued for its fruity-minty-herbal smell and its proven therapeutic properties. The essential oil (EO) is made up mainly of monoterpene hydrocarbon compounds (MT) and their oxygenated derivatives (OT), and, in much smaller quantities, some highly valued sulphur derivatives of monoterpene hydrocarbons (ST), used in the flavour and fragrance industries. Separation of the high value compounds from the terpenes and their derivatives is essential, as monoterpenes are prone to oxidation. Pulegone present in high concentration in Buchu essential oil, is a hepatotoxin, and undesirable in the product. The feasibility of separation of ST from MT and OT using supercritical CO_2 (sCO_2) was investigated. Phase behaviour data for the binary systems of the main components of the EO were measured and modelled. The calculated distribution coefficients and separation factors for a simulated feed indicated a high selectivity for the separation ST/MT, and modest selectivity for the MT/OT separation. The separation ST/OT was predicted to be more difficult. A process model was developed using the commercial process simulator Aspen Plus®, and validated using pilot plant data. The pilot plant data and model demonstrated that it is feasible to separate ST from MT and OT using sCO_2.