ADSORPTION AND CHROMATOGRAPHY AT SUPERCRITICAL CONDITIONS

Arvind Rajendran [(a)], Marco Mazzotti [(a)] and Massimo Morbidelli [(b)]

[(a)] Institute of Process Engineering, ETH Zentrum, Sonneggstrasse 3, CH-8092 Zürich
[(b)] Institute of Chemical and Bioengineering, ETH Hönggerberg, Wolfgang-Pauli-Str. 10, CH-8093 Zürich

Adsorption at high pressures finds application among other processes in Supercritical Fluid Chromatography (SFC), high pressure gas storage systems and CO_2 sequestration. The key to design these processes is the measurement of the adsorption of supercritical fluids on adsorbents. Moreover, the study of adsorption of fluids at supercritical conditions, by itself, presents a fundamental scientific challenge. Excess adsorption isotherms of CO_2 on microporous and mesoporous adsorbents and N_2O on mesoporous adsorbent were measured. Interesting phenomena such as “critical adsorption” and “critical depletion” were observed at near-critical conditions. In the case of CO_2-13X zeolite system, spurious “bumps” were observed at near-critical conditions. Using theoretical models, it has been possible to explain these “bumps”. These models have also helped to understand behaviour of fluids confined to pores of different sizes.

An important application of supercritical fluids in the chemical process industry is as a solvent in preparative chromatography. Preparative SFC (prep-SFC) separations on packed columns are usually performed at high flow rates. These flow rates cause a pressure/density gradient across the column. The properties of the supercritical fluid: viscosity, solubility, diffusivity depend on the fluid density and hence they vary along the column too. In addition, the density gradient causes an increase of the velocity and the Henry's constant from the column inlet to the exit. Hence, the response of a chromatographic column to a pulse of injected solute under such conditions is a complex interplay of these variables. A method to predict column dynamics has been developed and the comparison of experimental and predicted results show good correlation.

The Simulated Moving Bed(SMB) process is a simulated counter-current process which offers the possibility to increase throughput while at the same time reducing solvent consumption. The Supercritical fluid Simulated Moving Bed (SF-SMB) uses a supercritical fluid with a modifier as a solvent, thereby helping to reduce organic solvents while simultaneously increasing the degrees of freedom for operation of the process. The enantioseparation of 1-phenyl-1-propanol has been performed on a pilot scale SF-SMB unit. Experiments were performed both under linear and non-linear conditions. Complete separation was achieved at linear conditions. Under non-linear conditions high purities were obtained with a productivity that was higher than the best reported productivity values in HPLC-SMB case.