High Pressure Separations of Supercritical Nitrogen and Carbon Dioxide

Using a Teledyne ISCO Syringe Pump

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Syringe Pump Application Note
AN37

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Abstract & Introduction

Supercritical fluids exist at high pressures and offer potential for effective and efficient separations. This investigation involves exploring the equilibrium behavior of supercritical fluid mixtures with two or more species, one being carbon dioxide (CO_2). Teledyne ISCO 260D syringe pumps [see note] are essential parts of the experimental apparatus used in the investigation, which is located in the Carbon Recycling Center in the Department of Biological Engineering at the University of Missouri. The pumps precisely meter pure fluids into the high pressure separation chamber. The results describe a nonhomogeneous supercritical fluid mixture with density driven concentration gradients at pressures greater than 20 MPa and temperatures at ambient or below. Most supercritical fluids and supercritical fluid mixtures are thought to be homogeneous; however, for a binary or tertiary mixture, the term supercritical is more arbitrary than for a pure substance. This kind of separation has “carbon capture” applications in continuous processing of pressurized gasification products, other biomass refinery operations, and in the natural gas industry.

Experimental Procedures

Experimental Setup:

Experiments were done in an isolated high pressure equilibrium phase separator (HEPS) made of stainless steel. The cylindrical separator had a volume of about 1 L. The separator was plumbed to a Teledyne ISCO syringe pump (260D), which was plumbed to high pressure reservoir tanks with 99.9% purity so that individual species could be pumped from the syringe pump through a one way valve (mass flow controller) into the HEPS.

By monitoring conditions in the ISCO syringe pump (i.e. temperature, pressure), the amount of each species pumped into the separator can be known.Constant flow mode was used to pump each species into the separator. During loading of the HEPS, conditions in the syringe pump were carefully monitored. The amount of each pure species pumped into the separator was known from observed volume changes and density estimation by an equation of state for pure species. Reference equations of state for CO_2 and N_2 are given by Span (1994) and Span (1998). Similar equations of state specifically designed for high pressure conditions were used for all other species.

After filling the separator with species of interest for each respective experiment, the separator was allowed to sit undisturbed for several hours to ensure equilibrium was reached. In experiments done at reduced temperature, the HEPS was allowed to equilibrate in a freezer. A schematic of the experimental setup is shown in Figure 1. From Figure 1 it is seen that the HEPS has four equally spaced sampling ports designated as follows: (1) top, (2) high ($^1/_3$ of the height below top); (3) low ($^1/_3$ of the height above bottom); (4) bottom. The four sampling ports gave composition samples at four locations in the HEPS which was important since a concentration gradient is observed.

For any separation to occur in the HEPS, the pressure needed to be greater than the saturation pressure of CO_2 at the given temperature. The saturation pressure of CO_2 as a function of temperature is well known. These observations were consistent with formation of a dense CO_2 phase at high pressures. The overall mole fraction of each species was known by carefully monitoring the amount of each species loaded into the HEPS. The composition of fluid at each port was sampled with gas chromatography (GC).

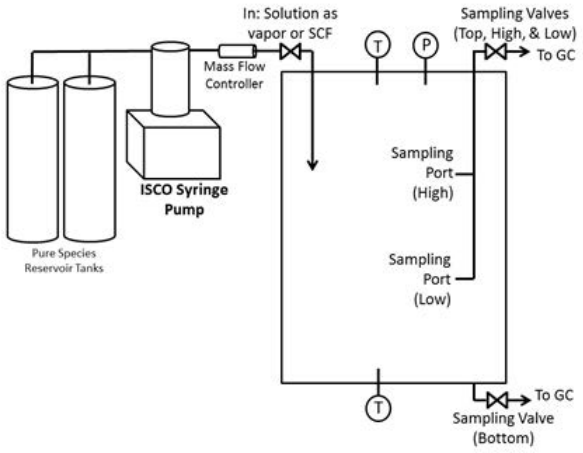

Figure 1: Experimental setup for loading high pressure equilibrium separator with supercritical fluid
Precise amounts of pure species can be loaded with the ISCO syringe pump

Results Summary

A density driven concentration gradient was observed at sufficiently high pressures. This gradient forms the basis of an effective separation. The effectiveness of this separation was found to increase with increasing temperature and decreasing temperature. Figure 2 shows the effect of increasing pressure using the supercritical mixture of CO_2 and N_2 as an example. The temperature was maintained at ambient and the overall mole fraction of CO_2 and N_2 was kept at 0.5.

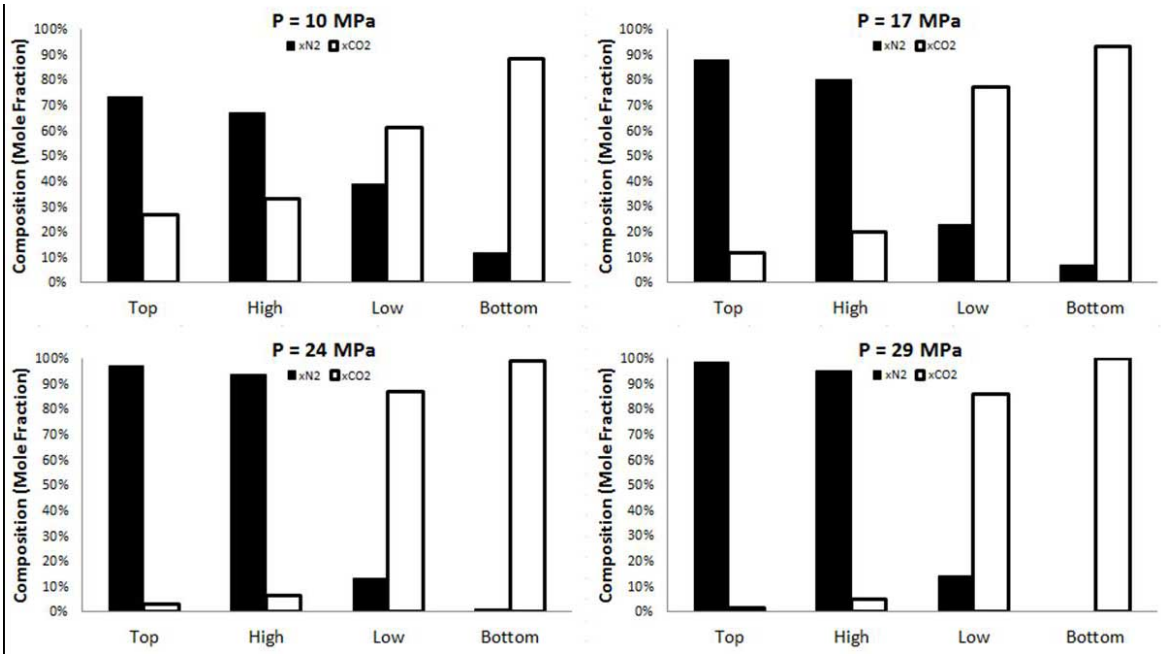

Figure 2: Effect of pressure on the separation of CO_2, and N_2 in the HEPS T=23 C; $^z CO_2=N_2=0.5$

Conclusion

The equilibrium of high pressure mixtures with CO_2 were explored using a high pressure equilibrium phase separator. The specific mixtures studied included CO_2/N_2, CO_2/Air, CO_2/CH_4, and CO_2/H_2. Teledyne ISCO syringe pumps were used to load the mixtures, one species at a time, into the separator. A nonhomogeneous supercritical fluid mixture with density driven concentration gradients was observed at sufficiently high pressures (20 MPa) and sufficiently low temperatures (25°C). This concentration gradient is the basis of an effective equilibrium separation and has "carbon capture" applications in continuous processing of pressurized gasification products, other biomass refinery operations, and in the natural gas industry.

A reference in the literature from our lab has more figures describing the effect of temperature on the concentration gradient and separation (Hendry 2012). The reference also describes that the system approaches equilibrium relatively quickly. At 31 MPa and ambient temperature, the CO_2/N_2 system reached equilibrium, and thus maximum separation, in 60 s. The time to reach equilibrium decreases with increasing pressure. Other supercritical fluid mixtures with CO_2 including CO_2/Air, CO_2/CH_4, and CO_2/H_2 behave similarly to the CO_2/N_2 system.

References

1. D. Hendry, A. Miller, N. Wilkinson, W. Jacoby, Exploration of High Pressure Separations of Supercritical Nitrogen and Carbon Dioxide. In press at *Ind & Engr Chem Res.* 2012.
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3. R. Span, E. W. Lemmon, R. T. Jacobsen, W. Wagner, and A. Yokozeki, 1998. A Reference Quality Thermodynamic Property Formulation for Nitrogen, *Int. J. Thermophys*. 14(4):1121-1132.

Note

The 260D model pump, which was used during the original experiment, is discontinued. Current model 260x is the recommended replacement for the older 260D model.

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Product model names have been updated in this document to reflect current pump offerings.