Supercritical Fluids in Reaction Engineering

Introduction

The benefits of Supercritical Fluids in Reaction Engineering applications can greatly exceed the initial equipment outlay. Research in reactions involving supercritical fluids, e.g., $SFCO_2$, has shown it possible to obtain the following advantages:

- better product uniformity
- faster reaction rates
- improved selectivity
- greater energy savings compared to evaporation of traditional bulk solvents
- more environmentally benign
- non-flammable
- non-toxic

Teledyne Isco syringe pumps provide accurate pulseless flow and are excellent CO_2 pumps or Supercritical Fluid pumps. They are commonly used in SF reaction engineering research at lab and pilot scales.

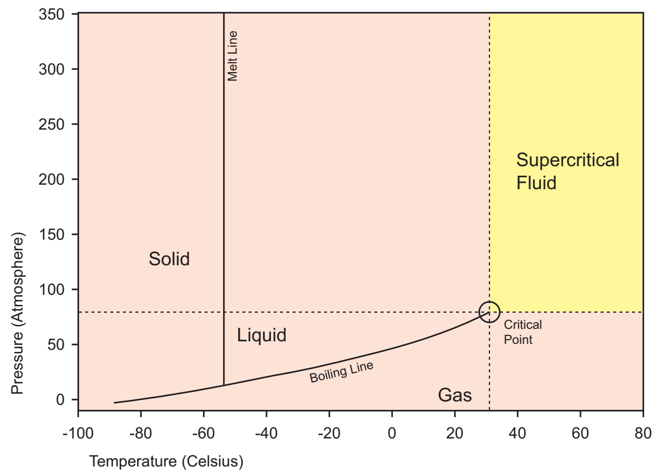

Figure 1: Phase Diagram of Carbon Dioxide

Theory

Supercritical fluids are very dense gases with many properties superior to liquids or solvents. While there are many fluids that can be used in their supercritical state, CO_2 is the one most often used because it is considered environmentally friendly, and its critical temperature and operating pressures are relatively easy to work with. In the supercritical state, molecular forces that give liquids their particular properties of surface tension, viscosity or slower diffusion are altered. Molecules do not “stick together” as well, so viscosities are lower with higher diffusion rates. Such enhanced properties can be beneficial to the reaction process since mixing is improved thereby improving distribution and enhancing product quality.

A phase diagram for CO_2, shown in Figure 1, displays the relationship between pressure and temperature. When the conditions of pressure and temperature are altered, the phases of CO_2 can be changed to a solid, liquid, or gas. However, when above the critical temperature, TC, CO_2 becomes supercritical, and can no longer be changed back into liquid by increasing the pressure. In this state, CO_2 will remain a gas-like fluid even though it may be approaching the density of a liquid at very high pressures. Its supercritical properties include solvating power similar to liquids, the penetrating or diffusion properties of a gas, and a “zero” surface tension.

CO_2 is a naturally occurring component of our atmosphere. CO_2 is non-toxic in small amounts (consider your own breath), and not a volatile organic compound (VOC), hence not contributing to smog formation. CO_2 is also non-flammable—a great advantage over many conventional liquid solvents.

Supercritical CO_2 has a low viscosity and high diffusivity compared to the usual liquid solvents used as a medium for reactions. Low viscosity and high diffusivity cause the reagents (or soluble catalysts) to rapidly travel to all locations inside a reactor. With uniform conditions throughout the reactor, the reaction process can obtain desirable results: better product uniformity, faster reaction rates, and improved selectivity. It should be noted that, despite all the advantages, $SFCO_2$ is best at dissolving small, non-polar organic compounds, but has difficulty dissolving many polar or ionic compounds, or most large polymers (fluorinated oligomers are an exception). Solvating properties can be improved with the addition of small amounts of other fluids or modifiers. These can include additives such as surfactants, or modifiers such as ethanol or methanol.

After completing supercritical fluid reaction, $SFCO_2$ is depressurized to a gaseous state, and solutes generally precipitate and fall out of solution. That is, the reaction product(s) is no longer soluble in gaseous CO_2. In the manufacture of chemical solids, often the product must be dried after the reaction process to remove solvents. A large amount of energy is used for drying in these conventional processes. With a reaction process involving $SFCO_2$, the product is left dry after the reaction, and following depressurization; hence no further drying is required. This has also been shown in polymer manufacturing, where by using $SFCO_2$, dry product can be obtained with a resultant significant energy savings compared to the traditional drying procedures required to evaporate liquid solvents or water. Therefore, there can be very large savings in energy costs for a process utilizing CO_2.

The CO_2 gas can then be recycled, another major cost reduction. When using CO_2 in a continuous manufacturing process, large amounts of CO_2, which could function as greenhouse gas, are recycled instead of being released into the environment. Small CO_2 leaks do not harm the environment.

Applications Using Supercritical CO_2

Catalysis — Homogeneous catalysts are highly active and selective, while heterogeneous catalysts are less active but easier to separate and re-use. In 2006, Liotta, Eckert, Hallett, and Pollet reported techniques for recycling homogeneous catalysts using $SFCO_2$ by changing pressure of the CO_2 in the reaction. This allowed the homogeneity to be turned on and off. Another example comes from Toghiani et al, where $SFCO_2$ was used to oxidize unsaturated fatty acids to make diacids and epoxides. The reaction medium was $SFCO_2$, which was completely oxidized.

Nanotechnology — $SFCO_2$ is becoming an enabling solvent for producing nanomaterials such as aerogels of Al_2O_3, SiO_2, TiO_2, and ZrO_2. These nanomaterials, which often have new and exciting properties such as tunable pore sizes and high surface areas, have applications as biomaterials, and catalysts for fuel cells and solar cells. Also, $SFCO_2$ drying has been widely used to produce aerogels that exhibit a very high specific surface area and maintain the nanoarchitecture due to the zero surface tension.

Pharmaceuticals and Biomedical Devices — Supercritical fluids have emerged as the green solvents in the pharmaceutical industry for micronization of inhalable medicines, and separation of chiral enantiomers. $SFCO_2$ is also playing a role as a valuable tool in tissue engineering and preparing biomedical devices, as CO_2 is largely anti-bacterial and can be used in producing tissue scaffolds.

Polymerization — Previously, DeSimone and coworkers have shown that $SFCO_2$ is a promising alternative medium for free-radical, cationic, and step-growth polymerizations, and continuous processes. The free radical initiator AIBN was shown to have a higher efficiency in $SFCO_2$ than in benzene, due to low viscosity of $SFCO_2$.

Polymer Functionalization and Processing — In 1994 and 1995, Watkins and McCarthy showed how $SFCO_2$ could be used to carry small molecules for functionalization of a polymer.

Applications - CO_2 as reactant

In some reactions, CO_2 may be consumed, i.e. mitigated. For example, Noyori et al described the use of $SFCO_2$ reacting with hydrogen to make formic acid. It is possible to obtain higher reaction rates and longer catalyst lifetimes using this method.

Implementation

Case 1: Pressure Control

In this example, the pump is used in constant pressure mode. In constant pressure mode, the pump automatically displaces its volume to achieve the pressure requested by the operator. For $SFCO_2$, pressure is directly related to solubility.

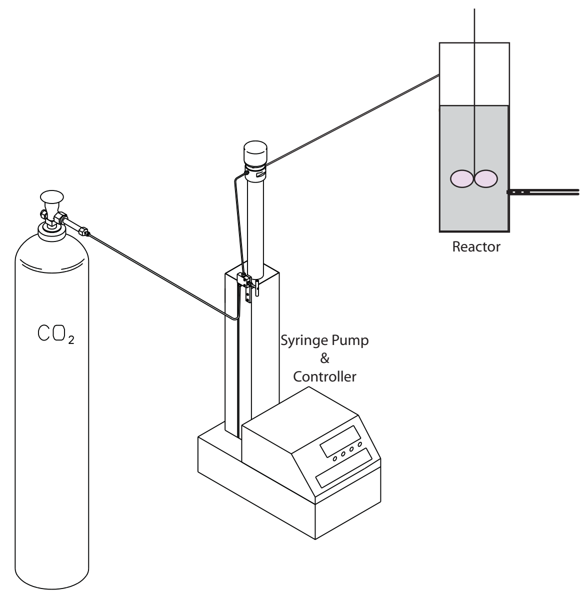

Figure 2: Configuration for pressure control of $SFCO_2$ density and solubility during reaction

Case 2: Stable Mass Delivery

In this example, the pump is maintained at a constant temperature and is operated in constant flow mode. Steady back pressure is provided by the back pressure device. With known pressure, temperature, and volumetric displacement rate (“flow rate”), the mass of CO_2 delivered to the reactor is predictive.

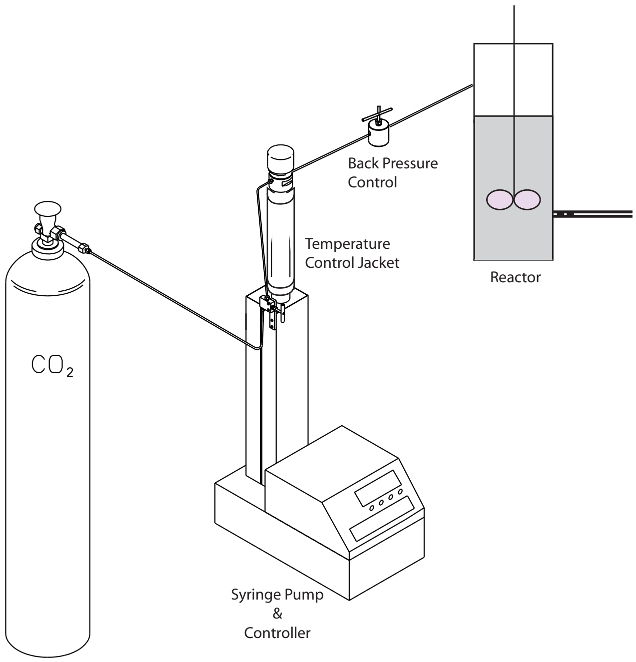

Figure 3: Configuration for stable mass delivery rate of CO_2 to reactor

Supercritical Fluid Pumps

For the applications described above, there are generally two types of pumps used: reciprocating and syringe. Reciprocating pumps have pistons with short strokes, so they need to refill frequently. Since fluid flow stops during refill, pressure fluctuations and density changes will result. This can cause unwanted precipitation of components, or other problems. Syringe pumps, considered pulseless, are better suited for these applications as the pressure and flow rates can be more accurately controlled. For most supercritical fluid applications, pressure must be maintained, so a constant pressure mode is needed. When pumps compress CO_2, even in the liquid state, heat generated will accumulate in the pump head. If this heat is not removed, incoming CO_2 could be inadvertently heated above the critical point, thereby impacting fill efficiencies. For proper operation, CO_2 pumps must incorporate some means to remove this heat.

Not all materials are suitable for use with CO_2, so wetted materials must be checked for compatibility.

Why Use Teledyne Isco Pumps?

Teledyne Isco syringe pumps are well suited for use with CO_2 and provide the best in accuracy and reliability. Flow rate accuracy is +/- 0.5% or better, and flows are pulseless. Pulseless flow means fluid pressure and density are constant, without changes in solvating properties. Pumps can be operated in either constant flow or constant pressure. For continuous operation, dual pump systems deliver fluid in unattended operation. Pumps can be operated as stand-alone or via external control. Teledyne Isco syringe pumps have a “poor fill alarm” which can alert the user if changing to a full supply bottle is needed.

Cooling jackets are available to maintain proper fluid temperature in the pump. Special valve packages for dual pump systems are CO_2 compatible.

Recommendations for Teledyne Isco Pumps

Typically, chemical engineers who work with supercritical fluids choose to work with the Model 500D or 500HL pump. Sometimes, Model 260D or 100DM pumps are used in order to achieve higher pressure and/or more accurate flows at very slow flow rates. Single pumps are most often used in batch applications, while dual pumps are used in continuous flow.

Table 1: Commonly Recommended Supercritical Fluid Pumps

	Model	Wetted Materials for CO_2	Cooling/Heating Jacket	External Control Option
Single Pump	260D	Standard	Available	Labview Driver
	500D	Standard	Available	Labview Driver
Continuous Flow Pump	A260	Standard	Available	Labview Driver

Table 2: Other Pump Models Available

	1000D	500D	260D	100DX	100DM	65D
Flow Range (ml/min)	0.100 - 408	0.001 - 204	0.001 - 107	0.00001 - 60	0.00001 - 30	0.00001 - 25
Pressure Rnage (psi)	0 - 2,000	0 - 3,750	0 - 7,500	0 - 10,000	0 - 10,000	0 - 20,000

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