Supercritical Fluid Applications in Manufacturing and Materials Production

TELEDYNE ISCO
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Syringe Pump Application Note
AN1

Introduction

Environmentally friendly supercritical CO_2 and its associated technologies are being used in many applications to replace hazardous solvents, lower costs, and improve efficiencies. Some of the applications requiring a supercritical fluid pump include:

- Supercritical Fluid Extraction (SFE)
- Supercritical Fluid Chromatography (SFC)
- Catalysis/Reaction Feed
- Injection molding and Extrusion
- Particle Formation
- Cleaning
- Electronic Chip Manufacturing
- Plastics Production

Teledyne ISCO Syringe Pumps, which are excellent CO_2 pumps or Supercritical Fluid pumps, are used in R&D and production in many of these applications. Syringe pumps are well-suited for use with Supercritical Fluids and can operate at high pressures with great accuracy and reliability.

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 in comparison to strong solvents, and its critical temperature point and operating pressures are relatively easy to work with.

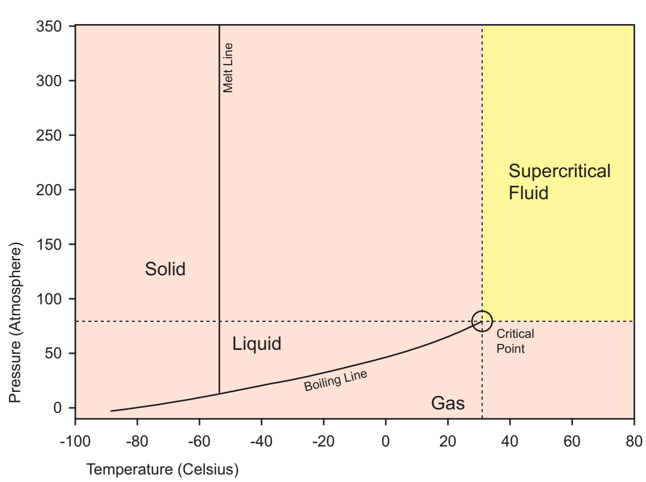

Figure 1: Phase Diagram of Carbon Dioxide

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, gas, or liquid. However, when above the critical temperature, T_c, CO_2 becomes supercritical, and can no longer be changed back into liquid by increasing 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, but with the penetrating or diffusion properties of a gas.

All molecules have both kinetic and potential energy. Kinetic energy is defined as energy of molecular motion, while potential energy is stored energy of an object relative to its position. The potential energy of attraction between molecules is known as the Van der Waal force.

The process of dissolving is directly affected by the Van der Waal force between solvent molecules and solute molecules. Surface tension and viscosity increase as this force makes solvent molecules draw closer together, leading to decreased diffusion and inhibiting the processes of solvating, extraction, and cleaning.

Kinetic energy will overcome the Van der Waal force if the solvent temperature is raised above the critical point, thereby reducing the attraction between the molecules. This lowers surface tension and viscosity, and increases diffusion capability, enabling the solvent to penetrate more deeply into and around small pores and features.

It should be noted that while supercritical CO2 is excellent for dissolving small, non-polar organic compounds, it is less effective in dissolving many polar or ionic compounds and large polymers (except for fluorinated oligomers).

Solvating properties can be improved with the addition of small amounts of other fluids or modifiers. This can include fluids, additives such as ethanol or water, or fluorinated detergents.

Applications

Due to lower toxicity as compared to common organic solvents, and being ubiquitous in nature, CO_2 has high promise in replacing Freon and organic solvents in many industrial manufacturing processes. Even though CO_2 does have some shortcomings, research is currently being done to overcome these problems

Supercritical Fluid Extraction (SFE) — Examples of extractions include removing fats from foods, or even pesticides from soils or foods. Traditionally, these extractions were performed with hazardous solvents, such as methylene chloride, using an apparatus called a Soxhlet extractor. Supercritical CO_2, with its ability to mimic solvents and penetrate matrices easily, can replace Soxhlet extractions while reducing a chemist's exposure to hazardous chemicals, improving the environment and reducing costs.

Other examples are the use of supercritical CO_2 combined with chelating agents for the extraction of uranium from aqueous solutions produced in the processing of the ore and removal of heavy metals from soils and sludges.

Supercritical Fluid Chromatography (SFC) — Chromatography is an analytical technique used in separating chemical mixtures into separate components. SFC uses supercritical CO_2 to replace solvents as the mobile phase in HPLC. Because of supercritical CO_2, advantages in diffusion and performance of the separation columns are improved, with higher resolutions and faster separations.

Catalysis/Reactant Feed — Reactions with supercritical CO_2 may have important applications in fields such as catalysis and polymerization. The use of supercritical CO_2 to replace solvents has the benefit of increasing and controlling reaction kinetics by altering the pressure. Also, there is the possibility of producing unique materials, which would be difficult to do with conventional techniques.

Injection Molding and Extrusion — The presence of CO_2 in plastic melts lowers viscosities thereby decreasing the injection molding pressures required, and/or decreasing the injection times. These advantages will increase the life of molding equipment and increase production rates. Also by lowering the melt temperatures, you can mold thermally labile compounds.

CO_2 is also used as an expanding or foaming agent for injection molding or extrusions. Adding air pockets in plastic reduces the amount of material used, decreases shrinkage, warpage and improved tolerances. The use of CO_2 in forming micro cells produces denser foams, making thin wall applications possible.

Particle Formation — Supercritical fluids can be used in the production of powders or microparticles with possible uses in the pharmaceutical industry. With conventional techniques, there is little control over powder properties, such as particle size. By rapidly depressurizing materials dissolved in CO_2, microparticles are produced with drugs or other components of interest embedded in a substrate. This is accomplished by pumping the mixture through a capillary where the CO_2 is vaporized at the outlet, leaving powders behind. This powder has uses such as time released drugs.

Cleaning — Supercritical fluids can be an effective solvent for cleaning many kinds of parts, electronics, plastics, or clothing. With the enhanced wetting and diffusion properties, supercritical CO_2 can improve the cleaning of components with small openings, delicate equipment, or porous materials. It can remove oils, fats, waxes, and other contaminates without damaging the matrix.

Electronic Chip Manufacturing — One possible important industrial application may be in the electronic chip fabrication process. Chip manufacturing creates a large environmental burden. It is estimated that the production of a 2.0g chip consumes at a minimum 72g of chemicals and 1.6Kg of fossil fuels. This gives a 630:1 weight ratio of chemical–fossil fuels and product. In comparison, the manufacturing of a typical automobile has a corresponding ratio of 2:1. Also, in the manufacturing of a 2.0g chip, 32L of water are used during the washing and rinsing steps during photolithography. Even though water can be recycled, this process requires extra energy. Supercritical CO_2 along with appropriate detergents may eliminate the need for water and reduce energy consumption in the manufacturing process. Due to the low surface-tension of supercritical fluids compared to water, finer surface features and structures can be better cleaned without risk of causing damage.

Plastics Production — Currently, PTFE and other fluoropolymers are being synthesized in refrigerant, and since perfluoro monomers and oligomers are soluble in CO_2, it can replace refrigerant in this application. After the 1986 Montreal Protocol, CO_2 has successfully replaced Freon as a polymer foaming agent. Finally, due to its inertness, CO_2 can be an excellent solvent for reaction involving a strong oxidizing or reducing agent.

Supercritical Fluid Pumps

For the applications above, there are generally two types of pumps used: reciprocating and syringe. Reciprocating pumps have pistons with short strokes, so they need to frequently refill. 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 pressure and flow rates can be more accurately controlled.

For most supercritical fluids 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 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, our dual pump systems deliver fluid in unattended operation. Pumps can be operated as stand-alone or via external control. Accessories, such as cooling/heating jackets, are available to maintain proper fluid temperature.

Recommendations for Teledyne ISCO Pumps

Typically, chemists and chemical engineers who work with supercritical fluids choose to work with the Model 260x pump in order to achieve high pressure and accurate flows. 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	260x	Standard	Available	Labview Driver
Continuous Flow Pump	A260	Standard	Available	Labview Driver

Table 2: Other Pump Models Available

	1000x	500x	260x	65x
Flow Range (mL/min)	0.100 - 408	0.001 - 204	0.001 - 107	0.00001 - 25
Pressure Range (psi)	0 - 2,000	0 - 5,000	0 - 9,500	0 - 20,000

References:

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

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