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A REVIEW: SUPERCRITICAL FLUID AND APPLICATIONS

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ABSTRACT

Using high pressure as a processing tool can overcome the legal limitations for solvent residues and restrictions on the use of conventional solvents in chemical processes. Additionally, particulate products can also be achieved by means of supercritical fluid (SCF) processing. This contribution will give a limited overview of applications of subcritical fluid and SCF and will present the energy savings compared with conventional production methods. Supercritical fluids are finding increasing application in the pharma industry for the solution of difficult processing problems. Supercritical fluids exhibit a pressure-tunable dissolving power, they possess a liquid like density (and thus a high solvent strength), and their gas like transport properties allow facile extraction from dense botanical materials to be achieved. This unique combination of properties is ideally suited for developing processes for extracting, purifying, and recrystallizing fine chemicals and pharmaceuticals and producing new product forms that cannot be obtained by industry's more traditional processing technologies.

KEYWORDS: Supercritical fluid, Phase diagram, Applications.

INTRODUCTION

Supercritical fluids are finding increasing application in the pharma industry for the solution of difficult processing problems. Supercritical fluids exhibit a pressure-tunable dissolving power, they possess a liquid like density (and thus a high solvent strength), and their gas like transport properties allow facile extraction from dense botanical materials to be achieved. This unique combination of properties is ideally suited for developing processes for extracting, purifying, and recrystallizing fine chemicals and pharmaceuticals and producing new product forms that cannot be obtained by industry's more traditional processing technologies.

SUPERCRITICAL FLUID

A supercritical fluid is a substance that is at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. It can diffuse through solids like a gas, and dissolve materials like a liquid. Above Tc and Pc the material is in a single homogeneous state with properties of those between that of liquid and gas. As the temperature of the liquid rises it becomes less dense and as the pressure of gas rises it becomes denser, at the critical point it becomes equal. In general SCF’s have densities nearer to liquid and diffusivities nearer to gases leading to high diffusion rates. The properties of SCF’s can be altered by changing the temperature and pressure as long as long as they remain above critical point.[1]

A fluid is said to be supercritical, when its pressure and temperature exceed their respective critical value (Tc- critical temperature and Pc- critical pressure). In the phase diagram (Fig. **1**), the critical point located at the right upper end and the phase area beyond of this point is the SCF region.[2] Fluids such as supercritical xenon, ethane and carbon- dioxide have a range of unusual chemical possibilities. The Main interest of supercritical fluids is related to their “tuneable” properties that can be changed easily by monitoring pressure and temperature good solvent power at high densities (temperature near critical temperature and pressure much over critical pressure) to very low solvent power at low densities (temperature near or higher critical temperature and pressure lower than critical pressure).[3]

Supercritical fluids (SCFs) are replacing the organic solvents that are used in industrial purification and recrystallization operations because of regulatory and environmental pressures on hydrocarbon and ozone-depleting emissions. With increasing scrutiny of solvent residues in pharmaceuticals and medical products use of SCFs is rapidly being used in all industrial sectors.

Phase Diagram

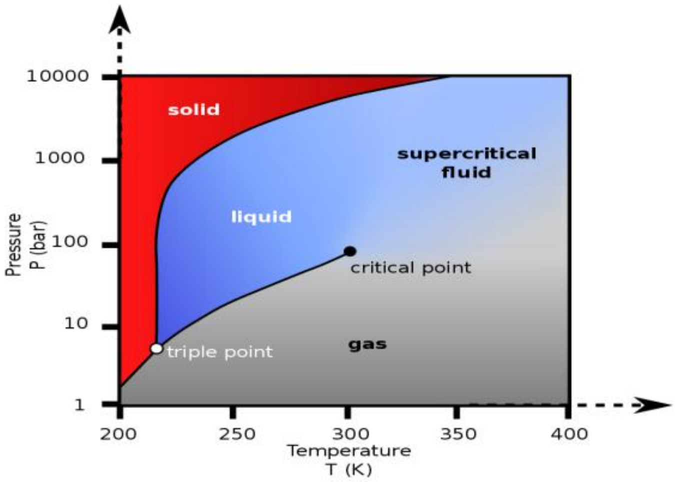

Figure 1.1: Carbon dioxide pressure-temperature.[1]

It is important to understand the phase behaviour of supercritical fluids. To understand the phenomenon of solubility in supercritical fluids, it is first necessary to understand the unique characteristics of supercritical fluids. The typical PT phase diagram of a pure substance is shown in the above figure 1.1. The diagram shows which state of matter (solid, liquid, vapour) exists for the pure substance at all possible combinations of temperature and pressure. There is only a single combination of temperature and pressure at which all three phases can coexist; that point is the triple point The vaporisation curve begins at the triple point and ends at critical point.

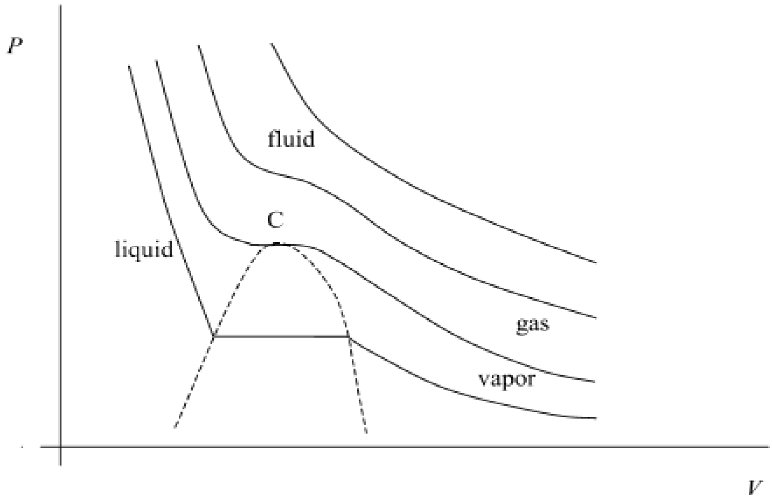

Fig: P-V curve.[4]

At critical point the properties of both the phases become equal and it exists as a single continuous phase. This is demonstrated by a P-V curve in the figure. The curves in Figure represent isotherms. Isotherms at temperatures above the critical temperature are continuous.[4] The point C is the inflection point where the derivative and double derivative becomes equal.

In the density pressure curve for carbon dioxide it can be observed that below the critical temperature, e.g., 280K, as the pressure increases, the gas compresses and eventually (at just over 40 bar) condenses into a much denser liquid. Hence the density of gas is less and that of liquid is more. As the critical temperature is approached (300K), the density of the gas at equilibrium becomes higher, and that of the liquid lower.

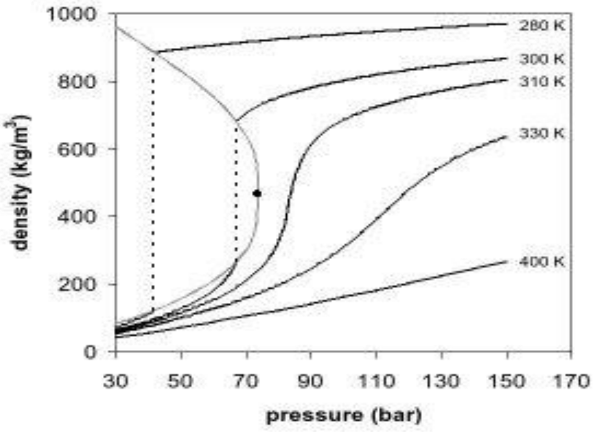

Fig: Density vs. Pressure Curve.[1]

At the critical point, (304.1 K and 7.38 MPa (73.8 bar)), there is no difference in density, and the 2 phases become a single fluid phase. Thus, above the critical temperature a gas cannot be liquefied by pressure. At slightly above the critical temperature (310K), near the critical pressure, the line is almost vertical. A small increase in pressure causes a large increase in the density of the supercritical phase. Hence above critical temperature and pressure a slight increase in pressure causes a large increase in specific volume.

APPLICATIONS

Supercritical fluid extraction

The advantages of supercritical fluid extraction (compared with liquid extraction) are that it is relatively rapid because of the low viscosities and high diffusivities associated with supercritical fluids. The extraction can be selective to some extent by controlling the density of the medium, and the extracted material is easily recovered by simply depressurizing, allowing the supercritical fluid to return to gas phase and evaporate leaving little or no solvent residues. Carbon dioxide is the most common supercritical solvent. It is used on a large scale for the decaffeination of green coffee beans, the extraction of hops for beer production, and the production of essential oils and pharmaceutical products from plants. A few laboratory test methods include the use of supercritical fluid extraction as an extraction method instead of using traditional solvents.

Supercritical fluid decomposition

Supercritical water can be used to decompose biomass via supercritical water gasification of biomass. This type of biomass gasification can be used to produce hydrocarbon fuels for use in an efficient combustion device or to produce hydrogen for use in a fuel cell. In the latter case, hydrogen yield can be much higher than the hydrogen content of the biomass due to steam reforming where water is a hydrogen-providing participant in the overall reaction.

Dry-cleaning

Supercritical carbon dioxide (SCD) can be used instead of PERC (perchloroethylene) or other undesirable solvents for dry-cleaning. Supercritical carbon dioxide sometimes intercalates into buttons, and, when the SCD is depressurized, the buttons pop, or break apart. Detergents that are soluble in carbon dioxide improve the solvating power of the solvent.

Supercritical fluid chromatography

Supercritical fluid chromatography (SFC) can be used on an analytical scale, where it combines many of the advantages of high performance liquid chromatography (HPLC) and gas chromatography (GC). It can be used with non-volatile and thermally labile analytes (unlike GC) and can be used with the universal flame ionization detector (unlike HPLC), as well as producing narrower peaks due to rapid diffusion. In practice, the advantages offered by SFC have not been sufficient to displace the widely used HPLC and GC, except in a few cases such as chiral separations and analysis of high-molecular-weight hydrocarbons.[5] For manufacturing, efficient preparative simulated moving bed units are available.[6] The purity of the final products is very high, but the cost makes it suitable only for very high-value materials such as pharmaceuticals.

Chemical reactions

Changing the conditions of the reaction solvent can allow separation of phases for product removal, or single phase for reaction. Rapid diffusion accelerates diffusion controlled reactions. Temperature and pressure can tune the reaction down preferred pathways, e.g., to improve yield of a particular chiral isomer. There are also significant environmental benefits over conventional organic solvents. An electrochemical carboxylation of a para-isobutylbenzyl chloride to Ibuprofen is promoted under supercritical carbon dioxide.

Impregnation and dyeing

Impregnation is, in essence, the converse of extraction. A substance is dissolved in the supercritical fluid, the solution flowed past a solid substrate, and is deposited on or dissolves in the substrate. Dyeing, which is readily carried out on polymer fibres such as polyester using disperse (non-ionic) dyes, is a special case of this. Carbon dioxide also dissolves in many polymers, considerably swelling and plasticising them and further accelerating the diffusion process.

Nano and micro particle formation

The formation of small particles of a substance with a narrow size distribution is an important process in the pharmaceutical and other industries. Supercritical fluids provide a number of ways of achieving this by rapidly exceeding the saturation point of a solute by dilution, depressurization or a combination of these. These processes occur faster in supercritical fluids than in liquids, promoting nucleation or spinodal decomposition over crystal growth and yielding very small and regularly sized particles. Recent supercritical fluids have shown the capability to reduce particles up to a range of 5-2000 nm.

Generation of pharmaceutical cocrystals

Supercritical fluids act as a new media for the generation of novel crystalline forms of APIs (Active Pharmaceutical Ingredients) named as pharmaceutical cocrystals. Supercritical fluid technology offers a new platform that allows a single-step generation of particles that are difficult or even impossible to obtain by traditional techniques. The generation of pure and dried new cocrystals (crystalline molecular complexes comprising the API and one or more conformers in the crystal lattice) can be achieved due to unique properties of SCFs by using different supercritical fluid properties: supercritical CO_2 solvent power, anti-solvent effect and its atomization enhancement.

Supercritical drying

Supercritical drying is a method of removing solvent without surface tension effects. As a liquid dries, the surface tension drags on small structures within a solid, causing distortion and shrinkage. Under supercritical conditions there is no surface tension, and the supercritical fluid can be removed without distortion. Supercritical drying is used for manufacture of aerogels and drying of delicate materials such as archeological samples and biological samples for electron microscopy. Carbon dioxide is used as a supercritical solvent in some dry cleaning processes.

Supercritical water oxidation

Supercritical water oxidation uses supercritical water as a medium in which to oxidize hazardous waste, eliminating production of toxic combustion products that burning can produce. The waste product to be oxidised is dissolved in the supercritical water along with molecular oxygen (or an oxidising agent that gives up oxygen upon decomposition, e.g. hydrogen peroxide) at which point the oxidation reaction occurs.

Supercritical water hydrolysis

Supercritical hydrolysis is a method of converting all biomass polysaccharides as well the associated lignin into low molecular compounds by contacting with water alone under supercritical conditions. The supercritical water, acts as a solvent, a supplier of bond-breaking thermal energy, a heat transfer agent and as a source of hydrogen atoms. All polysaccharides are converted into simple sugars in near-quantitative yield in a second or less. The aliphatic inter-ring linkages of lignin are also readily cleaved into free radicals that are stabilized by hydrogen originating from the water. The aromatic rings of the lignin are unaffected under short reaction times so that the lignin-derived products are low molecular weight mixed phenols. To take advantage of the very short reaction times needed for cleavage a continuous reaction system must be devised. The amount of water heated to a supercritical state is thereby minimized.

Supercritical water gasification

Supercritical water gasification is a process of exploiting the beneficial effect of supercritical water to convert aqueous biomass streams into clean water and gases like H_2, CH_4, CO_2, CO etc.[1]

Supercritical fluid in power generation

The efficiency of a heat engine is ultimately dependent on the temperature difference between heat source and sink (Carnot cycle). To improve efficiency of power stations the operating temperature must be raised. Using water as the working fluid, this takes it into supercritical conditions. Efficiencies can be raised from about 39% for subcritical operation to about 45% using current technology. Supercritical water reactors (SCWRs) are promising advanced nuclear systems that offer similar thermal efficiency gains. Carbon dioxide can also be used in supercritical cycle nuclear power plants, with similar efficiency gains.[7] Many coal-fired supercritical steam generators are operational all over the world, and have enhanced the efficiency of traditional steam-power plants.

Biodiesel production

Conversion of vegetable oil to biodiesel is via a trans esterification reaction, where the triglyceride is converted to the methyl ester plus glycerol. This is usually done using methanol and caustic or acid catalysts, but can be achieved using supercritical methanol without a catalyst. The method of using supercritical methanol for biodiesel production was first studied by Saka and his coworkers. This has the advantage of allowing a greater range and water content of feedstocks (in particular, used cooking oil), the product does not need to be washed to remove catalyst, and is easier to design as a continuous process.

Enhanced oil recovery and carbon capture and storage

Supercritical carbon dioxide is used to enhance oil recovery in mature oil fields. At the same time, there is the possibility of using "clean coal technology" to combine enhanced recovery methods with carbon sequestration. The CO_2 is separated from other flue gases, compressed to the supercritical state, and injected into geological storage, possibly into existing oil fields to improve yields.

At present, only schemes isolating fossil CO_2 from natural gas actually use carbon storage, (e.g., Sleipner gas field),[8] but there are many plans for future CCS schemes involving pre- or post- combustion CO_2.[9] [1] There is also the possibility to reduce the amount of CO_2 in the atmosphere by using biomass to generate power and sequestering the CO_2 produced. The use of supercritical carbon dioxide, instead of water, has been examined as a geothermal working fluid.

Refrigeration

Supercritical carbon dioxide is also an important emerging refrigerant, being used in new, low-carbon solutions for domestic heat pumps.[10] These systems are undergoing continuous development with supercritical carbon dioxide heat pumps already being successfully marketed in Asia. The EcoCute systems from Japan, developed by consortium of companies including Mitsubishi, develop high-temperature domestic water with small inputs of electric power by moving heat into the system from their surroundings. Their success makes a future use in other world regions possible.[11]

Supercritical fluid deposition

Supercritical fluids can be used to deposit functional nanostructured films and nanometer-size particles of metals onto surfaces. The high diffusivities and concentrations of precursor in the fluid as compared to the vacuum systems used in chemical vapour deposition allow deposition to occur in a surface reaction rate limited regime, providing stable and uniform interfacial growth.[12] This is crucial in developing more powerful electronic components, and metal particles deposited in this way are also powerful catalysts for chemical synthesis and electrochemical reactions. Additionally, due to the high rates of precursor transport in solution, it is possible to coat high surface area particles which under chemical vapour deposition would exhibit depletion near the outlet of the system and also be likely to result in unstable interfacial growth features such as dendrites. The result is very thin and uniform films deposited at rates much faster than atomic layer deposition, the best other tool for particle coating at this size scale.[13]

CONCLUSION

Supercritical fluids are the stepping stone to a more modern technology which is environmentally benign as well as gives better results than what is being traditionally used in the chemical industries. Though a lot of research is still being carried out there are few promising avenues opened up due to the use of supercritical fluids for example in the extraction Supercritical fluids are being used with great success. In the decaffeination sector supercritical fluids have replaced the traditional solvents that are more toxic and can cause a great degree of environmental pollution. Its most important property is its recyclability unlike the other chemicals which are used tends to increase pollution. It is also being developed in other applications such as drying, impregnation, transestrification, refrigerant and chromatography. Its main limitation is that it requires a lot of energy in reaching its supercritical state and then maintaining it for the time of operation and in some cases it may not be viable.

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