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A Review of Supercritical Fluid Extraction Technology and Application

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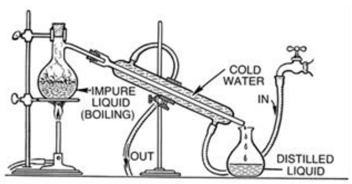
Graphical abstract



Abstract

The supercritical fluid extraction (SFE) technology was firstly documented on 1822. In this review paper, the authors contemplated the inhibiting factors that resulted in limited industrial application and analysis using SFE. The driving trend nowadays is to apply what have been discovered almost 200 years ago is in an escalating fashion. The major application of the supercritical state of a common gas (carbon dioxide) is an extremely important technology, since at the critical pressure and temperature carbon dioxide is not a solid, not a liquid neither a gas and it has a no surface tension, which qualifies to be an extremely good 'non polar solvent' and therefore applicable for extraction of essential oils, caffeine and several other applications. The major advantages on the SFE are over the lower operating energy cost and the extracted compound remains intact as there is not thermal decomposition and the final concentrate is free of any residual processing solvent due to carbon dioxide's natural tendency being a gas which however, is volatile in ambient temperature and pressure. The process of purification does not require any distillation to purify the extracted compound, just the pressure is released and the carbon dioxide as a solvent will leave the concentrate liquid at the bottom of the vessel, as a gas, and will not have any binding or forming azeotrope mixture that are difficult to separate to high purity. The supercritical condition of a gas or liquid is not fully being exploited and there is a great opportunity for more industrial application as to be elaborated in this paper.

Keywords: Supercritical fluid extraction; distillation; fractional distillation

1.0 INTRODUCTION

Supercritical fluid extraction (SFE) is not a new technology as back in 1822 Baron Charles Cagniard de la Tour discovered the critical point of a substance in his famous cannon barrel experiments. Listening to discontinuities in the sound of a rolling flint ball in his sealed cannon filled with fluids at various temperatures, he observed the critical temperature. Above a particular temperature, the densities of the liquid and gas phases become equal and the distinction between them disappears, resulting in a single supercritical fluid phase [1]. Nowadays the uses of SFE is largely apparent in the decaffeination of green coffee, food, nutraceuticals, perfumes and cosmetics, pharmaceuticals, textile, electronics, aerogels, ceramic and innovative materials, oil industry, laundry dry cleaning, analytical processes supercritical fluid chromatography, nano and micro particle formation, generation of co-crystals in pharmaceutical processes, biodiesel production and several other new and upcoming applications.

2.0 OPERATIONAL DEFINITION

The following are related operational definitions used in this paper:

- SFE: Supercritical Fluid Extraction is a methodology to extract a substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist.
- Non-polar solvent: solvents are compounds of two or more elements whose negativities are almost the same. The compounds are as a result of normal sharing of electrons and not polar attractions. A good example of a non-polar compound is Benzene, Hexane and Toluene.
- Azeotrope: is a mixture of two or more liquids in such a way that its components cannot be altered and separated by simple distillation.
- Dew point: The dew point is the temperature at which the water vapor in air at constant barometric pressure condenses into liquid water at the same rate at which it evaporates. At temperatures below the dew point, water will leave the air. The condensed water is called dew when it forms on a solid surface.
- Distillation: Distillation is a method of separating mixtures based on differences in volatility of components in a boiling liquid mixture. Distillation is a unit operation, or a physical separation process, and not a chemical reaction.
- Fractional Distillation: Fractional distillation is the separation of a mixture into its component parts, or fractions,

such as in separating chemical compounds by their boiling point by heating them to a temperature at which one or more fractions of the compound will vaporize.

3.0 SFE CURRENT APPLICATIONS

3.1 Textile and Leather or Other Fiber Dyeing:

In this application, a lot of water is usually used. By using a supercritical condition (Co2) instead, the dyes are made to penetrate the fiber (leather or textile) with virtually no waste water at all. This technology is still in the infancy stage but the industry is under pressure to save water, particularly in developed country.

3.2 Dietary Supplement Food:

Several products or by-product wastes considered without any commercial value now days are turned into highly valuable dietary products like extraction of protein from rape seeds, anti-oxidant from olive leaves, and caffeine from green coffee, high purity organic oils from seeds and many more.

3.3 Cosmetics Essential Oils, Antioxidants, Colorants:

Highly in demand are the essential oils for the perfume or fragrance industry, which are mostly aromatic compounds that are easily soluble in non-polar solvent usually extracted by distillation from fruits, flowers, vegetables and algae with a poor yield. These essential oils are now extracted by SFE technologies by using CO2 as a solvent with a much higher yield due two main factors; low temperature process and low contact with oxygen, which make the final essential oil much more valuable and of higher quality then the essential oil extracted by using the distillation process. Several anti-oxidant substances can now be isolated and made in higher concentration due to the availability of the supercritical extraction method.

3.4 Pharmaceutical and Biomedical Processing:

There are two ways in making a sustainable product: sourcing from nature or by synthetic means. Several drugs and extremely high cost molecular compounds obtained by synthesis have now found natural sources as replacements. In the past, the extraction was a problem if not by supercritical condition, as the compound can easily oxidize just by exposure to air. However, by processing it in CO2 supercritical condition, the drugs or natural extract remain intact, for the benefit of the consumer. This approach leads to great cost saving in principle. In addition, the SFE process uses much lower energy consumption and does no generate any wastes.

3.5 Other Potential Uses in Phase of Experimentation:

Water oxidation in supercritical condition (waste water), water hydrolysis of biomass, converting biomass into cellulosic sugar, nuclear power generation in a supercritical condition vessels, industrial production of biodiesel in a continuous process through supercritical conditioning have found great acceptance in the industry especially in large quantities [2-5].

4.0 HOW SFE WORK

Figure 1 shows the diagram of the 'conversion' of carbon dioxide where the critical temperature for carbon dioxide is 31.1°C, and the critical pressure is 73 atm. Whereby beyond this critical temperature, the fluid is called super-critical fluid [6].

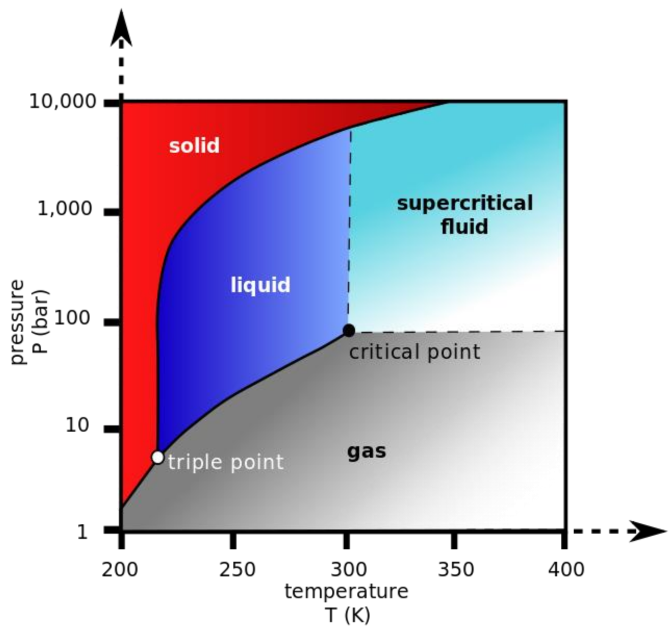


Figure 1 Phase diagram for carbon dioxide [6]

In the aforementioned condition, the carbon dioxide is neither a solid, nor gas or liquid; it is a supercritical fluid that has a particular property with no surface tension and has the same solvency power as a non-polar organic solvent (typically used in distillation, i.e. hexane and petrol ether) [7]. The advantage of the SFE is that the pressure is indeed high, but the temperature is very low, where it can be as low as 31.1°C, versus in distillation where the pressure may not be not high but the temperature is much higher, at least 100° Celsius and this will lead to many natural chemical compounds to decompose or to deform into something different and often unwanted.

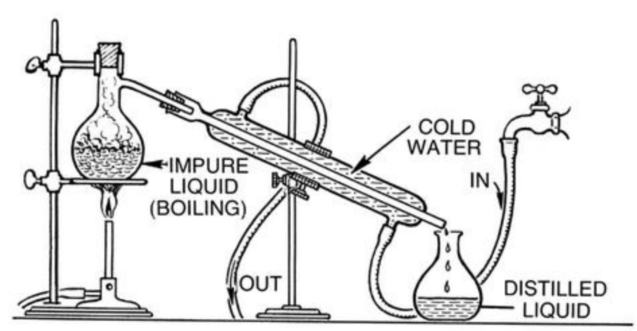


Figure 2 A typical distillation process [8]

Another advantage of the SFE, is the separation process, where in distillation (refer to Figure 2) requires a cooling circuit to bring down the temperature to condensation point (or dew point). This implies the use of energy twice; firstly heat to boiling point then distillation, and secondly to cooling down in order to condense the distillate.

At this point the distillate is certainly of good concentration but there will be some contaminant (water) and unless is fractionally distillate, will take only a part of the distillate and recycle the others back (refer to Figure 3). Both of these processes will use energy twice or create waste water particularly in the process of condensation.

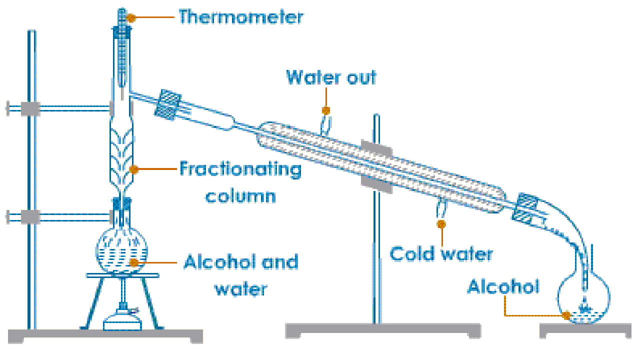


Figure 3 Fractional distillation process [9]

The AFE process instead is much more efficient as it will use energy only once and much less in comparison to distillation. The carbon dioxide used is supplied already in compressed cylinder at an average pressure of 57 bar at 20° C and is in a liquid form. Unfortunately the pressure is not in a supercritical level yet, therefore there is a need to compress it further a bit more which requires a multistage gas compressor to achieve the supercritical stage. The SFE process is conceptually fairly simple, but the equipment involved is a bit more complicated (refer to Figure 4).

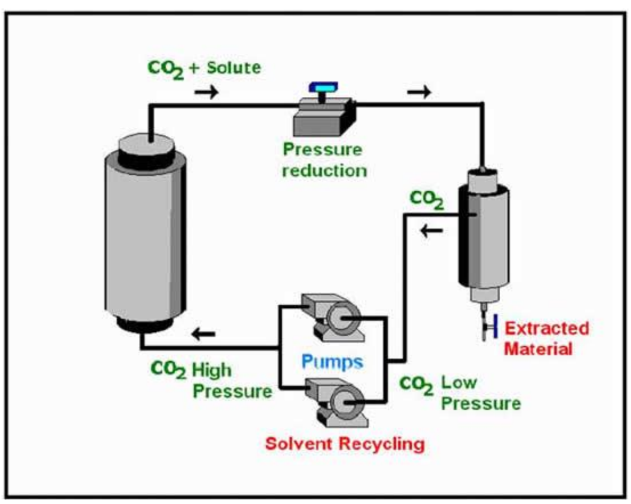


Figure 4 SFE process [10]

In principle, the carbon dioxide is reused many times in the cycle after releasing the pressure into another vessel the liquid solution is the extracted material. The carbon dioxide is a gas, perfectly non miscible, and with a certainly huge gravity difference, so that the gas will rise to the top of the vessel and the liquid remains at the bottom. Subsequently, with no energy requirement at all, the gas (carbon dioxide) is re-compressed into supercritical pressure (above 73 atm) and then reused.

The major advantage are such that the compound extracted via SFE has a much higher yield, predominantly in selected essential oils has a total yield of 10 times in some cases [11, 12], or even more as compared with traditional distillation process. This factor is not due to the solvency issue, but instead the temperature, where the aromatic compounds by nature decompose due to its own instability to high temperature and or light. Whereas in the SFE process, the factor of temperature is not affecting the extracted product as it operates at ambient temperature or in some cases at max 60°C only. In line with the aforementioned advantages of SFE, it have to be highlighted that the residence time or processing time is the most gain, usually with SFE the processing time is around 20 to 30 minutes per batch in industrial scale, while in distillation we are at in the range of hours and one batch per day at its best. In addition, the carbon dioxide is reused several times in the process, and can be released to the atmosphere as it is an inert gas, thus make more financial sense to reuse it several times after all.

■5.0 WHY IS THE INDUSTRY STILL USING DISTILLATION?

Distillation is still a more approachable technology and much older than SFE. Thus it is not a surprise to hear that SFE is not known by most individuals, probably because it is a rather advanced technology versus distillation which is commonly used in domestic applications. The first evidence of distillation comes from Greek alchemists working in Alexandria in the 1st century AD [13]. It is certain that distillation in some culture in the West is associated with fermentation and is a common practice in daily life like the production of wines, whiskey, brandy and or many other alcoholic beverages, this bringing a very wide familiarity with this process. As such, the industry has adopted it much earlier than SFE. Another factor that is probably the prime deterrent is the cost. An SFE industrial plant is costly as initial investment to procure the system and to operate it due to the high pressure vessels (73 atm and above) and fittings requirement s well as the need for a dedicated and trained personnel who is hard to find.

■6.0 RISK FACTOR IN SFE VERSUS DISTILLATION

SFE being a high pressure system certainly has a great risk as all the vessels need to withstand such pressures which are somehow dangerous compounded by the possibility of spillage or leakage of the carbon dioxide. Thus, it is important to have a good ventilation system in the premise otherwise the risk of asphyxiation could occur as the concentration of CO2 will drastically increase the atmosphere of the premise. This could cause even death if not taken under consideration. Pressure risk is mostly related with explosion, which in the case of distillation may not involve much pressure but the outflow of solvent and solvate in the ambient could cause a serious danger since both are highly flammable and sources of ignition like heat or fire are readily available in the premise. The abundance of burners used to transfer heat to the distillation vessel is a major risk. While in the SFE no organic solvent are used, this risk is drastically minimized.

In the distillation process, fire hazard, explosion hazard, exposure to such organic solvent is another medium and long terms hazard to the operator, while in the SFE the aforementioned hazards do not exist at all. Continuous distillation is already being used particularly in the oil and gas industry, while in SFE continuous processing is theoretically possible but practically not being exploited yet. The possibility to process continuously in SFE is close to success.

7.0 SFE TRENDS IN THE FUTURE

Every now and then there are publications coming up on SFE, which clearly portrays wider application in analysis and industrial uses. Referring to current driving force of carbon foot print in many industrial processes, the tendency to steer away from organic solvent and distillation is getting much influence. Indeed, the sources of many substances are now required to be from sustainable source, therefore reducing the usage of fossil fuels. SFE has a great role in this aspect, since distillation has proven to be much poorer in terms of efficiency, ability to extract lower amount and lower quality of essential substances, uses more energy and in some cases being even unprofitable as some essential oils yield less than 1% of extracted oil. On the other hand, SFE is the opposite, with an additional advantage the CO2 which can be reused many times over, this increases the sustainability of the final product and reduces its carbon footprint. One should take consideration the residence time which in the case of SFE is about 10 times faster in comparison to distillation. Strong environmental demands make SFE to be seen as a "cleaner" process than distillation [14]. The question often posed is, when will SFE substitute most of the distillation processes? It will eventually happen, as the initial cost of SFE and poor familiarity with this concept may not prevail as a deterrent in the long run.

Undeniably, there are now SFE pilot plants from 5 to 60 liter processing vessel at prices from 70.000 to 180.000 USD available online. The next question is, is this still "expensive"?

8.0 SUPERCRITICAL FLUIDS OTHER THEN CO2

As shown in Figure 5, there are several other critical property including CO2. Which ones work best depends on many factors including cost and material.

CRITICAL PROPERTIES OF SELECTED SOLVENTS

Solvent	T_c (K)	P_c (atm)	V_c (cm/mol)	Molecular Weight	ρ_c (g/cm^3)
CO_2	304.2	72.8	94.0	44.01	0.47
C_2H_6	305.4	48.2	148	30.07	0.20
C_3H_8	369.8	41.9	203	44.10	0.22
n-C_4H_{10}	425.2	37.5	255	58.12	0.23
n-C_5H_{12}	469.6	33.3	304	72.15	0.24
CH_3-O-CH_3	400	53.0	178	46.07	0.26
CH_3CH_2OH	516.2	63.0	167	46.07	0.28
H_20	647.3	12.8	65.0	18.02	0.33
C_2F_6	292.8	30.4	22.4	138.01	0.61

Figure 5 Other critical properties of selected solvents [15]

Notably, here it can be contemplated that not only CO2 have the supercritical properties, this may be remark that there are other substances being tested in this field. However CO2 is one of the lowest in temperature and pressure most importantly the most stable and inert gas, other substances are indeed super fluid solvent with higher temperature or pressure make only few being potentially the choice for analytical and industrial applications.

9.0 CONCLUSION

What drive the SFE after we have seen so many potentials uses in analysis, production of drugs, chemical synthesis decaffeination, essential oils and many more, it is the changing of the environment and the advancement of technology associated with the efficiency that are driven by the carbon foot print reduction. In substance the SFE have some weak point in comparison with solvent extraction widely used due to very much earlier discovery. SFE have the necessity to have a compressor which is not a common machine like any other compressor, is a multistage piston compressor very high pressure 5000 psi is very unpopular equipment and very special that only few manufacturers have in their production range. Particularly in Asian region the SFE seems to be quite new, distillation is still largely used, without concern of related risk and poor yield. Lack of availability of services dedicated to supercritical fluids; lead the industry to still rely on distillation. Financially it is not really unreachable, but being poorly understood, may slow the implementation in the field of herbal, and or essential oils extraction. More discoveries are on the research table, not completed, one day or another will be the major choice for many products like biodiesel. By using modular system is possible to process in closed loop [16] the equipment are available and at a very reasonable financial burden. Being able to break the taboo in the SFE will certainly lead to have a change on this. Hopefully the industry will hang on it.

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