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PROCESS PARAMETERS AFFECTING THE SUPERCRITICAL FLUID EXTRACTION- A REVIEW

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ABSRTACT

Solvent extraction has major applications in extraction of vegetable oils, nuclear processing, production of fine organic compounds, processing of perfumes and other industries. But, now days, use of this method is dropping due to the solvents cost, chemical deposits and legal issues with disposal of waste after use. All these demerits are overcome by supercritical fluid extraction process. This extraction method is affected by several process parameters; those are reviewed in this paper.

KEYWORDS: Solvents, Supercritical Fluid, Carbon Dioxide, Pressure, Temperature & Extraction Time

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A Review Article

INTRODUCTION

Solvent extraction is a technique, applied to separate compounds based on their relative solubilities in two different immiscible liquids. It is also known as liquid-liquid extraction. It has major applications in extraction of vegetable oils, nuclear processing, production of fine organic compounds, processing of perfumes and other industries. In spite of the fact that the strategy can be utilized for extraction of an extensive variety of non volatile or semi volatile species utilizing just routine research facility, its utilization is diminishing as a rule, since solvents of the required immaculateness have a tendency to be costly, and can likewise cause issues with legitimate transfer after utilization. Reducing the negative ecological impacts of solvents, eliminating chemical compound deposits, lower energy requirements, better quality and safety in food processes has been a main thrust in utilizing supercritical liquids, particularly carbon dioxide as extraction solvent [3,4].

In 1993, supercritical carbon dioxide was utilized for extraction of pepper oil [5] and from that point on, it has been utilized as a part of numerous extraction procedures, for example, caffeine from coffee [6], cholesterol from beef and egg [7], basic oils from basil [8] and cocoa margarine from cocoa nibs [9]. In 1995, Hung *et al*. [10] could extricate cholesterol with 70 percent yield. Later in 2001, Wu, *et al*. [11] accomplished even a superior extraction yield by optimizing temperature and pressure (55°C and 36 MPa). Despite the fact that the most widely accepted supercritical liquid is pure or adjusted carbon dioxide due to its low critical temperature, non-harmfulness, inertness and low cost, nevertheless in some cases such as polar ingredients other alternative compounds, for example, nitrous oxide, ethane and water, have critical properties that can give better consequences of extraction yield. D.A Saldana *et al*. [12] found that supercritical carbon dioxide with no co-solvent couldn't remove theobromine from cocoa seed in an appropriate yield. Sh. Li, S. Hartland [13] demonstrated that it is hard to remove either xanthines or cocoa margarine from cocoa nibs with CO alone. Be that as it may, the expansion of polar co-solvent ethanol incredibly upgrades their solubility. R. S. Mohamed *et al.* [14] demonstrated that utilizing ethanol or isopropanol as co-solvent with supercritical carbon dioxide will increase the yield of extraction. Other n-alkanols, additionally have been utilized as co-solvent with supercritical carbon dioxide [15, 16] on account of their polar properties.

In this review, we summarize the supercritical fluid extraction process and effect of different parameters on the extraction.

SUPERCRITICAL FLUID EXTRACTION PROCESS

This arrangement must consist a pump for the CO_2, a pressure cell and gathering vessel. The fluid is heated to supercritical conditions by pumping to a heating zone. It at that point goes into the extraction vessel, where it quickly diffuses into the solid matrix and dissolves the material to be removed. The dissolved material is cleared from the extraction cell into a separator at lower pressure, and the extricated material settles out. The CO_2 would then be able to be cooled, recompressed and reused, or released to air.

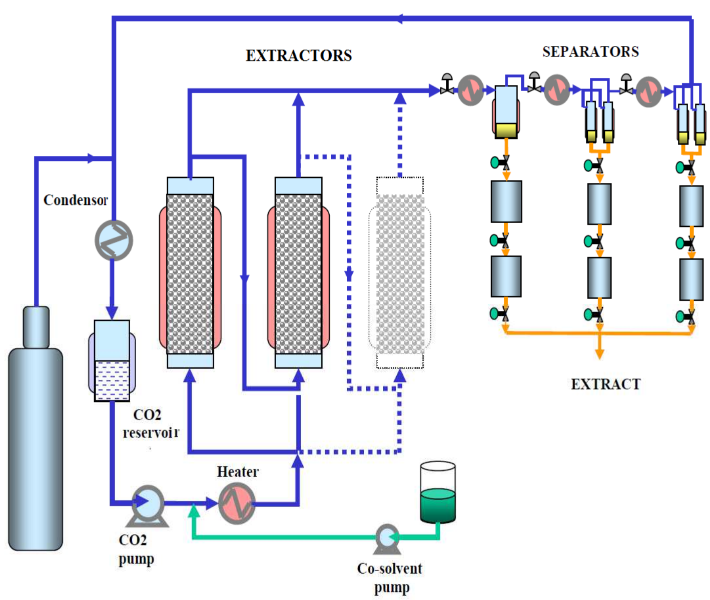

Figure 1: SCFE Processing Unit

PARAMETERS AFFECTING THE SUPERCRITICAL FLUID EXTRACTION- REVIEW

In spite of the fact that the choice of the supercritical solvent to be utilized might be imagined as the most-impacting parameter in the extraction, there are various critical parameters that will altogether influence the extraction process. These parameters are described here.

Effect of Particle Size

T.J. Tan *et al.* [9] had done a research on extraction of oil from whole cocoa beans using SC-CO_2 as solvent. They observed that there was a slow increasing trend in extraction efficiency, when using particles with smaller size. It is likely that the oil is caught inside the cell walls and does not come into contact with the supercritical solvent. Whenever pulverized, some cell walls are cracked and subsequently, the oil inside them ends up noticeably accessible for extraction. The effect of particle size in three unique temperatures (15 MPa and 6 hours extraction time) is appeared in Table 1.

Table 1: Effect of Particle Size on Extraction Efficiency for Three different Temperatures (P=15 MPa, 6 Hrs Extraction Time) Using Pure CO_2 as Supercritical Solvent

Partical Size (mm)	Uncrushed Particles	2-4	1-1.4	0.5-1	0.25-0.5
Efficiency (%)	0	2.3	2.7	2.85	2.9
T=30° c	0	2.5	2.8	3	3
T=40° c T=50° c	0	2.6	2.85	3.2	3.25

Li *et al*. [17] investigated SC-CO_2 extraction of black pepper at 16–26 MPa, temperature of 308–323 K, and solvent flow rate from 0.2–0.4 m^3/h, and diameter of ground material of 20–50 meshes. They concluded that the extraction rate increased with increasing particle size, due to intraparticle diffusion resistance was smaller for smaller particle size, because of shorter diffusion path. Essential oil obtained by SC-CO_2 extraction had higher levels of sesquiterpenes and monoterpenes.

Effect of Pressure

Increases in extraction pressure increase yield in lycopene recovery (Nobre *et al*. 2009, Yi *et al*. 2009; Lenucci *et al*. 2010, Huang *et al.* 2008, Rozzi *et al*. 2002, Baysal *et al*. 2000), while applications employing pressure values ranging between 200 and 450 bar produce optimum results depending on other process parameters, especially extraction temperature, and/or type and features of product. Optimum pressure parameter in lycopene recovery through SFE method are generally reported between 300 and 400 bar; however, especially 400 bar was set out as the optimum process parameter with different extraction temperatures ranging between 40°C and 100°C (Ciurlia *et al*. 2009, Topal *et al*. 2006, Huang et al. 2008, Yi *et al.* 2009, Saldana *et al*. 2010).

Solubility of oil increased with increase of the pressure, because of the solvent density increase. It was possible to identify the constant extraction rate period in the extraction curves as well as the falling and diffusion rate period. When the yield of the SC-CO_2 extraction was compared with that of steam distillation, it can be concluded that SFE was an efficient process for black pepper oil extraction. Perakis *et al*. [4] showed the results of the SC-CO_2 extraction of ground black pepper, they examined effect of process parameters, namely pressure (9, 10, 15 MPa), temperature (313, 323 K) on extraction rate.

Salajegheh *et al*. (2013) investigated SC-CO_2 extraction of Cocoa Butter from Cocoa seed, keeping other conditions constant (40°C temperature, 6 hours extraction time and particles smaller than 1 mm), the effect of pressure was investigated. The results are reflected in, as one might expect, higher pressures result in higher density of solvent which increases the solvent power, and therefore an increasing trend of higher extraction efficiency is observed. The highest efficiency observed is at 20 MPa, which is the pressure limit for the equipment used in these experiments.

Li *et al.* [17] investigated SC-CO_2 extraction of black pepper at 16–26 MPa, temperature of 308–323 K, solvent flow rate from 0.2–0.4 m^3/h, and diameter of ground material of 20–50 meshes. They concluded that the extraction rate was higher at higher pressure, because of the fact that at constant temperature, the density of the solvent increases with pressure increase and the vapor pressure of the solute decrease with pressure increase.

Effect of Temperature

The temperature used in extraction process varies within a wide range like 50-110°C is considered as optimum.

However, most frequently reported value is 80°C as optimum (Egydio *et al*. 2010, Vagi *et al*. 2007, Sabio *et al*. 2003, Cadoni *et al*. 2000). Number of studies indicating temperature esteems over 80°C as an optimum is limited (Yi *et al*. 2009, Topal *et al*. 2006, Rozzi *et al*. 2002, Ollanketo *et al*. 2001). No relation could be found between this value and characteristics of material.

Salajegheh *et al.* (2013) investigated SC-CO_2 extraction of Cocoa Butter from Cocoa seed, two temperature series from 30°C to 55°C (at pressures of 15 MPa and 20 MPa) were conducted, both with 6 hour extraction time and particle size of less than 1 mm diameter. The results showed that an increase in solubility in higher temperatures, the efficiency of extraction rises slowly as the temperature increases.

Li *et al*. [17] investigated SC-CO_2 extraction of black pepper at 16–26 MPa, temperature of 308–323 K, and solvent flow rate from 0.2–0.4 m^3/h, and diameter of ground material of 20–50 meshes. They concluded that the extraction rate increases with an increase in temperature at 25 MPa and decreases with an increase in temperature at 10 MPa. This behavior could be explained by appearing so call "cross-over" pressure between this two values of pressure, which means that than exists two competing effects of reduction in solvent density and the increase in solute vapor pressure with increase in temperature. The fact is that at lower pressure, the change of the solvent density is more efficient than that of solute vapor pressure, as extraction rate increases with decrease in temperature. However, at higher pressure (25 MPa) the extraction rate is dependent on the solute vapor pressure and it increase with an increase in temperature. The optimal process condition of the supercritical fluid extraction for pepper oil was at 22–26 MPa, 318 K, and 0.3–0.4 m^3/h.

Shi *et al*. [18] utilized different temperatures from 40 to 70 °C in the SC-CO_2 extraction of carotenoids from pumpkin. They found that carotenoid yield increased with increasing temperature. The highest extraction yield (6.1 mg/100 g matrix d.m.) was obtained at 70 °C and 35 MPa. At the point, when the extraction temperature was raised from 40 to 70 °C, the (9 + 13) - Z-β-carotene isomers increased considerably from 10.3% to 12.7% at 25 MPa and from 8.0%–12.5% at 35 MPa. What's more, when the extraction temperature was increased from 50 to 80 °C at a constant pressure of 25 MPa, there was a decrease in carotenoid yield from 132.2 to 44.6 mg/100 g d.m. also, the ratios of Z-β-carotene/ carotenoids increased from 13.7% to 24.5%.

Effect of Extraction Time

Salajegheh *et al.* (2013) investigated SC-CO_2 extraction of Cocoa Butter from Cocoa Seed, the result of varying extraction times at 20 MPa and 50^0 C increases extraction efficiency significantly up to 6 hours, and then remains fairly unchanged up to 8 hours because the system reaches the equilibrium state.

Use of Ethanol as Co-Solvent

Ethanol is the commonly used co-solvent with the usage rate ranging between 5.0% and 16.0% (Saldana *et al*. 2010, Shi *et al*. 2009a, Kassama *et al*. 2008, Baysal *et al*. 2000) for the effectiveness of extraction, while organic solvents like chloroform (Cadoni *et al*. 2000), tetrahydrofluran (Ciurlia *et al*. 2009), and acetone (Ollanketo *et al.* 2001) as well as vegetable oils like olive oil (Shi *et al.* 2009a), canola oil (Saldana *et al*. 2010) and hazelnut oil (Vassapollo *et al*. 2004) were also employed for this purpose. An increase in the ratio of modifier or co-solvent increases yield (Shi *et al*. 2009a). For the usage as modifier, various optimum ratios and types were reported like 5.0% ethanol (Baysal *et al*. 2000), 10.0% vegetable oil (Vasapollo *et al.* 2004), 5.0% olive oil + 5.0% ethanol (Shi *et al*. 2009a) and 14.0% ethanol (Kassama *et al*. 2008). It is believed that the use of vegetable oil (for example hazelnut oil) contributes to solubility of lycopene in solvent

(Ciurlia *et al*. 2009). Furthermore, it was reported that there is a synergic effect between concentration of modifier and extraction temperature, while it does exist between pressure and modifier concentration (Kassama *et al*. 2008); however, there are researchers reporting that the use of a modifier like ethanol, water, and olive oil increases lycopene yield independently from variations in temperature and pressure (Shi *et al*. 2009a).

Salajegheh *et al.* (2013) investigated SC-CO_2 extraction of Cocoa Butter from Cocoa seed, ethanol was chosen as a co-solvent for our extractions because of its “Generally Regarded as Safe (GRAS)” status in The Food and Drug Administration of USA (FDA), polar nature and the significant impact that it has on the polarity of CO_2 solutions. It is readily available in food grade and therefore there are no concerns regarding residual amounts left in the cocoa butter. Using the best conditions found for pure supercritical carbon dioxide, i.e. particle size of less than 1 mm, extraction time of 8 hours, pressure of 20 MPa and temperature of 50°C, we carried out a series of extractions using ethanol as co solvent in various concentrations. There was Single pass extraction efficiency rises to 15.8% at 10% ethanol concentration. This is an almost 200% improvement on the results obtained using pure CO_2 as the extraction solvent. Another series of extractions were carried out using the same conditions, but at 55°c. The results indicate that slight increase in extraction efficiency can be achieved using higher temperature.

Using Ethane as the Extraction Solvent

Ethane is an easily available and non contaminating solvent with readily achievable supercritical properties (305.4K and 48.8 bars). Marleny *et al.* (2001) used ethane as supercritical solvent for extraction of cocoa butter. The extraction of cocoa butter from cocoa beans were performed with ethane at 323.2 and 343.2 K, pressures of 18.2, 24.8 and 28.3 MPaand ethane flow rate of 0.9 gm min^{-1}. They found that extraction yields of cocoa butter using ethane, has an order of magnitude higher than obtained with CO_2.

Comparison of Extraction Efficiency between Carbon Dioxide and Ethane as Supercritical Solvent

Salajegheh *et al*. (2013) investigated SC-CO_2 extraction of Cocoa Butter from Cocoa seed, keeping other conditions same for ethane and carbon dioxide (D<I mm, extraction time 8 hours) the difference between ethane and carbon dioxide was investigated once in constant pressure (20 MPa) in different temperatures from 30 to 55 ^{0}C and then in constant temperature (50°C) from 5 MPa to 20 MPa. As it is expected, in each case the extraction yield for ethane is much greater than carbon dioxide (more than 5 times) and in some cases *(55°C* and 20 MPa the degree of magnitude is quite noticeable (53% for ethane but 5.2% for carbon dioxide).

CONCLUSIONS

It is concluded that the main process parameters affecting the supercritical extraction process are particle size, pressure, temperature and extraction time. As the pressure, temperature and extraction time increases, the extraction efficiency increases. But, decrease in particle size increases extraction efficiency. In some researches, it was unable to extract any more than 5% of the oil by traditional methods of supercritical extraction, using pure supercritical carbon dioxide. In order to achieve acceptable extraction efficiencies, a suitable co-solvent or an entirely different solvent is needed. Using ethanol as co solvent, would increase the efficiency of extraction up to 16 percent (for10 percent by weight ethanol) for a single pass, which isa significant improvement over use of pure CO_2, Using pure ethane as the supercritical extraction solvent showed efficiencies as high as 53% extraction in a single pass, under optimum conditions in the range investigated (20 MPa pressure, 50 °C temperature and 8hours extraction time for particles with diameters less than1 mm).

These results could be a good basis, as the first step of the industrial process of cocoa butter extraction from cocoa beans.

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