Middle-East Journal of Scientific Research 13 (8): 1010-1015, 2013
ISSN 1990-9233

DOI: 10.5829/idosi.mejsr.2013.13.8.3763

Supercritical Extraction of Cocoa Butter from Cocoa Seed, Using Pure Carbon Dioxide, Carbon Dioxide with Ethanol as Co-Solvent and Ethane

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Abstract: The effective parameters such as particle size, temperature, pressure and extraction time on supercritical carbon dioxide extraction of cocoa butter form cocoa seed were studied in order to find the optimum conditions for extraction. Particle size from whole cocoa nibs to one millimeter diameter, extraction temperature from 35°C to 55°C, extraction time from 2 to 8 hours and extraction pressure from 5 to 20 MPa were investigated and optimized. The optimum results (according to the limitation of the apparatus) of 5.2% extraction efficiency, suggests that pure CO_2 is not a suitable solvent for extraction of cocoa butter in the investigated range of parameters and therefore the use of a co-solvent or an entirely different solvent is indicated. Ethanol was used as co-solvent from 2% to 10% by weight and could increase the efficiency of extraction to a maximum of 16 percent, which is slightly better than pure CO_2, but not good enough to form a basis for an industrial process. Using pure ethane as solvent, we achieved 53% extraction efficiency in a single stage extraction, under the optimum conditions allowed by the limitations of our apparatus.

Key words: Supercritical CO_2 · Efficiency · Temperature · pressure · Cocoa · Ethane · Ethanol

INTRODUCTION

Cocoa butter is a valuable ingredient in food, pharmaceutical, cosmetic, health and other industries. It consists of three fatty acids: palmitic, stearic (saturated acids) and oleic (unsaturated acid). Physical properties of cocoa butter are dependant on the relative abundance of these acids in the sample. About 50% by weight of cocoa seed is cocoa butter, which at present is extracted using various methods such as mechanical extraction or solvent extraction using hexane [1, 2].

Eliminating chemical residues, decreasing negative environmental effects of solvents, lower energy requirements, better safety and quality in food processes has been a driving force in using supercritical fluids, especially carbon dioxide as extraction solvent [3,4].

In 1993 supercritical carbon dioxide was used for extraction of pepper oil [5] and from then on it has been used in many extraction processes such as caffeine from Coffee [6], cholesterol from cow brain, beef and egg [7], essential oils from basil [8] and cocoa butter from cocoa nibs [9]. In 1995 Hung *et al.* [10] could extract cholesterol with 70 percent yield by supercritical carbon dioxide. Later in 2001, Wu, *et al.* [11] achieved even a better extraction yield by optimizing pressure and temperature (55°C and 36 Mpa). Although the most common supercritical fluid is pure or modified carbon dioxide because of its low critical temperature, inertness, non-toxicity and low price, nevertheless in some cases such as polar ingredients other alternative compounds, such as nitrous oxide, ethane and water, possess critical properties that can give better results of extraction yield. D.A Saldana *et al.* [12] found that supercritical carbon dioxide without any co-solvent could not extract theobromine from cocoa seed in a suitable yield. Sh. Li, S. Hartland [13] showed that it is difficult to extract either xanthines or cocoa butter from cocoa nibs with CO_2 alone. However, the addition of polar co-solvent ethanol greatly enhances their solubility. R. S. Mohamed *et al.* [14] showed that using ethanol or isopropanol as co- solvent with supercritical carbon dioxide will increase the yield of extraction. Other n-alkanols also have been used as co-solvent with supercritical carbon dioxide [15, 16] because of their polar properties.

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To achieve better efficiency for extraction, one should either use a co-solvent together with carbon dioxide or change supercritical fluid and use another supercritical fluid, such as ethane instead of carbon dioxide. R.S. Mohamed *et al.* [17] performed Continuous extraction of cocoa beans at 343.2 K using CO_2 at pressures of 20 and 40 MPa and ethane at pressures of 15.2, 24.8 and 28.3 MPa. The extraction yields of cocoa butter obtained with ethane were much higher than those obtained with CO_2 because of the higher solubility of this fat in ethane.

In this work the possibility of extraction of cocoa butter from cocoa seed by supercritical fluid has been studied in three different sets of experiment, using pure carbon dioxide, carbon dioxide together with ethanol (as an effective co- solvent) and ethane as supercritical fluid. The efficiency of extraction has been determined in different conditions to find the optimum extraction conditions within the limitation of our apparatus.

We have investigated the effect of four parameters, particle size, temperature, pressure and extraction time to find the most economically and technically suitable conditions for extraction. The extraction of cocoa butter from cocoa seed by supercritical carbon dioxide has been also studied by T.J. Tan *et al.* [18] and they got nearly good results in 45Mpa, 75°C and 12 hours extraction time. Although this is acceptable at laboratory scale, but working in these conditions is not industrially and technically economic because of the high costs in high pressure industrial processes. In our work we have tried to get a good extraction yield in lower pressure and temperatures to industrialize the process as possible.

MATERIALS AND METHODS

Equipment: The extraction apparatus is built for dynamic extraction with online sampling. A schematic is shown in Figure 1. The extraction chamber is the main part and is equipped with a metal mesh basket for placing the sample and view windows for observing inside of the cell during the operation. The valves V_1 and V_2 must be opened to allow high pressure supercritical fluid enter the main chamber. An inline pump provides recirculation to ensure saturation of the solvent. An inline sampling chamber allows sampling without interruption to the extraction process. The entire apparatus is housed inside a thermostatically temperature controlled chamber.

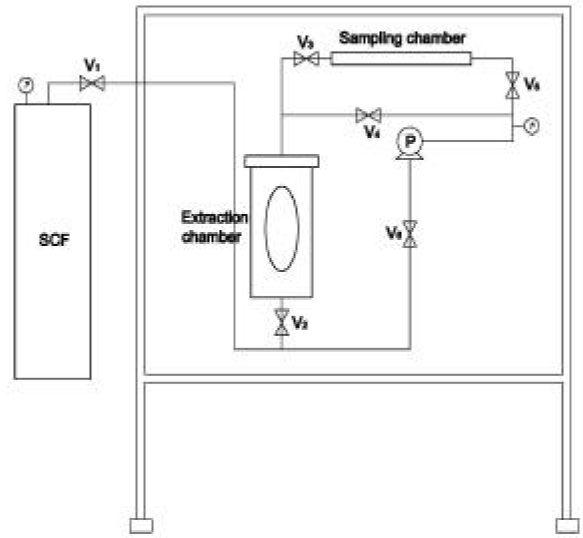

Fig. 1: Supercritical extraction equipment

Materials: Carbon dioxide with the purity of 99.5 percent is provided from Zamzam Company, Tehran Iran. Dry Brazilian cocoa seed (50.5% by weight cocoa butter content) is provided by Shirinasal Company, Tabriz, Iran. Ethanol with the purity of 99.99% is provided from Merck Company, India, Mumbai. Ethane with 99.8% purity is provided from Pars Petrochemical Industries, Tehran, Iran.

Methods: After crushing dry Brazilian Cocoa seeds (which contain 50.5 percent by weight cocoa butter), they were sorted according to particle size. (The range of assortment is shown in Table 1). A specified weight of the sample with specified particle size was put in the screen basket and set in the extraction cell and the system sealed.

Table 1: Effect of particle size on extraction efficiency for three different temperatures (P=10MPa, 6 hrs extraction time) using pure CO_2 as supercritical solvent

Particle Size (mm)		Uncrushed Particles	2-4	1-1.4	0. 5-1	0.25-0.5
Efficiency (%)	T= 30°C	0	2.3	2.7	2.85	2.9
	T= 40° C	0	2.5	2.8	3	3
	T= 50° C	0	2.6	2.85	3.2	3.25

The air bath door is closed and air thermostat set to the desired temperature. Valve (V_1) is opened to allow high pressure supercritical fluid into the system. The main chamber door is closed and the hot air circulation bath is turned on and sufficient time is allowed for the entire system to come to thermal equilibrium. The outlet valve of supercritical fluid (V_2) is opened. Supercritical fluid enters the extraction chamber and causes the pressure to rise to the desired point. Valves V_1 and V_2 are closed and the inline pump is turned on to circulate the fluid during the extraction process.. The extraction chamber is immediately depressurized and opened. The cocoa sample is removed and analyzed for butter content. At the end of the experiment fresh solvent is used to wash the apparatus. The extraction efficiency is then calculated by:

$$Y = \frac{\text{Extracted butter weight}}{\text{Butter content of the sample}} \times 100$$

RESULTS AND DISCUSSION

Pure Carbon Dioxide:

The Effect of Particle Size: As shown in our experiments and also previously reported by T.J. Tan *et al.* [9], the amount of oil extracted from whole cocoa beans using SC CO_2, in the temperature and pressure ranges used in these experiments, is too small to form a basis for a commercial extraction process. A slow increasing trend in extraction efficiency is observed when using particles with smaller size. It is likely that the oil is trapped within the cell walls and does not come into contact with the supercritical solvent. When crushed, some cell walls are ruptured and therefore the oil within them becomes available for extraction.

The effect of particle size in three different temperatures (15 MPa and 6 hours extraction time) is shown in Table 1.

All further experiments are carried out using particles with below 1 mm diameter.

The Effect of Pressure: 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 Figure 2.

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.

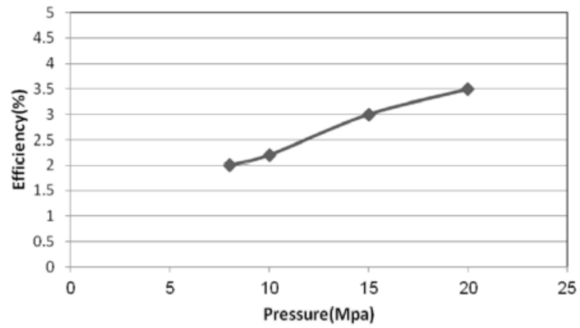

Fig. 2: Effect of pressure on efficiency for pure CO_2 as solvent (T = 40°C d<1 mm extraction time 6 hrs)

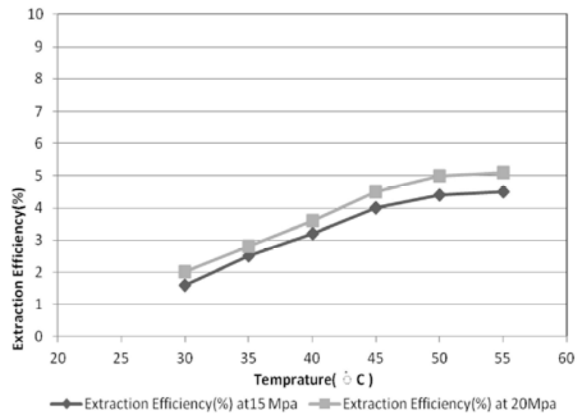

Fig. 3: Comparing the effect of temperature on the efficiency (P=20 and 15Mpa d<1 mm extraction time 6 hrs, Solvent: SC CO_2)

The Effect of Temperature: 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 are shown in Figure 3. Due to an increase in solubility in higher temperatures, the efficiency of extraction rises slowly as the temperature increases. In higher pressure the efficiency is slightly better.

The Effect of Extraction Time: Figure 4 shows the result of varying extraction times in 20 MPa, 50 °C and particle size of smaller than 1 mm diameter. Extraction efficiency increases 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 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

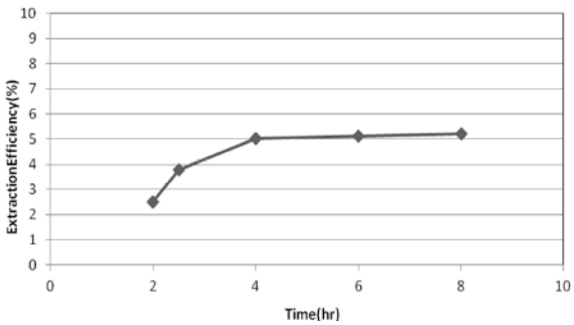

Fig. 4: The effect of extraction time on efficiency (T = 50°C P=20 Mpa d<1mm, Solvent: SC CO_2)

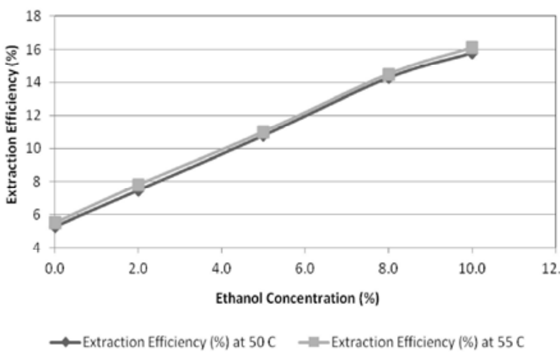

Fig. 5: The effect of ethanol percentage as co-solvent on the efficiency for extraction. D= 1 mm P =20 Mpa, Extraction Time =8 hrs, Solvent: SC CO_2

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. Figure 5 presents a summary of these results. 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 (Figure5).

Within the limits of parameters investigated, the optimum extraction efficiency of 16.1% was obtained at 55°C, 20 MPa, 8 hour extraction time and particle size of less than 1 mm diameter. This is an improvement over the best results obtained using CO_2 as pure solvent (5.3% extraction efficiency) but hardly a basis for an industrial process. In section 3.3 we discuss using pure ethane as a solvent.

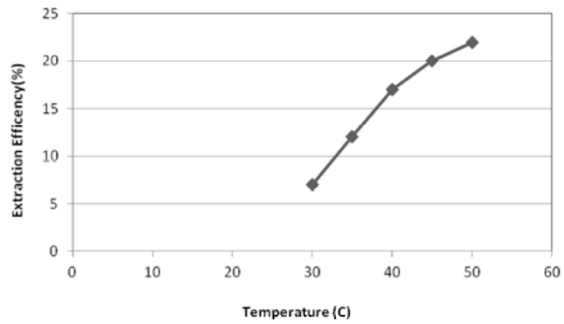

Fig. 6: Effect of temperature on efficiency p=15 Mpa D < 1 mm, Extraction Time =8 hrs, Solvent: Ethane

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 D. A. *et al.* used ethane as supercritical solvent for extraction of cocoa butter [17].The extraction of cocoa butter from cocoa beans were performed with ethane at 323.2 and 343.2 K, pressures of 15.2, 24.8 and 28.3 MPa and 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.

Effect of Temperature: Supercritical ethane proved to be a more effective solvent than CO_2 for extraction cocoa butter, In 20 MPa pressure, 6 hours extraction time and particle size of less than 1 mm diameter. Different temperatures from 30 °C to 50 °C were conducted with results shown in figure 6. As it is expected, the extraction has improved due to increasing temperature. Changing temperature from 20 °C to 55 °C showed that extraction yield would increase with increasing temperature but more than 50 °C increasing is not noticeable, so 50 °C is the optimum temperature.

Effect of Pressure on Efficiency: The effect of pressure on extraction efficiency was investigated by changing the pressure from 5 MPa to 20 MPa at 50°C with 8 hours extraction time on particles of less than 1 mm diameter. The results are shown in Figure 7. The efficiency of extraction would increase by increasing pressure from 5 MPa to 20 MPa which is the limit of the equipment used for these experiments. To achieve 53%extraction yield in 20 MPa pressure is nearly a good result in a single stage extraction.

Comparison of Extraction Efficiency Between Carbon Dioxide and Ethane as Supercritical Solvent: Keeping other conditions the same for ethane and carbon dioxide

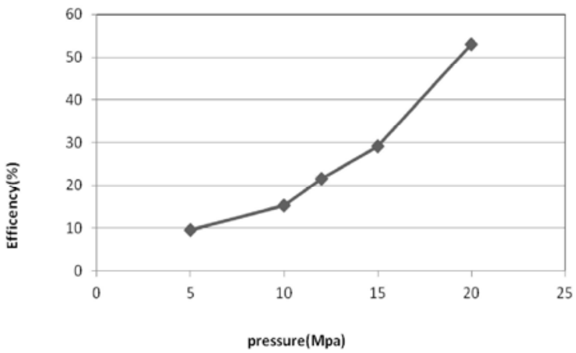

Fig. 7: Effect of pressure on efficiency T =50°C D< 1mm T =8 hrs Solvent: Ethane

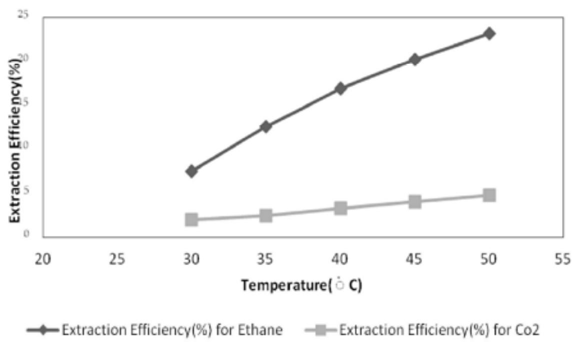

Fig. 8: Extraction efficiency for Ethane and CO_2 in different temperatures D<1mm Extraction Time= 8 hrs P=15 Mpa

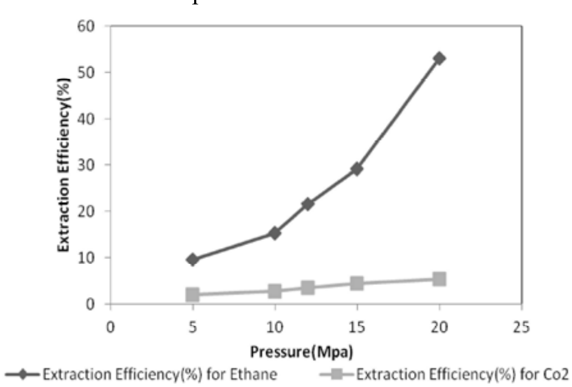

Fig. 9: Extraction efficiency for Ethane and CO_2 in different Pressures D<1mm Extraction Time= 8 hrs T=50°C

(D<1 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 degree centigrade and then in constant temperature (50°C) from 5 Mpa to 20 Mpa. The results are shown in figures 8 and 9. 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

The main parameters of the supercritical extraction process, i.e. particle size, pressure, temperature and extraction time behaved as expected. However, even under the optimum conditions(according to the limitation of our apparatus), i.e. particle size of less than 1 mm diameter, 20 MPa pressure and 50 C temperature, we were unable to extract any more than 5% of the oil extractable by traditional methods of supercritical extraction, using pure supercritical carbon dioxide. Therefore we conclude that within the limits of the parameters that were explored in this work, pure supercritical CO_2 is not a suitable solvent for the extraction of cocoa butter from cocoa beans. 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 (for 10 percent by weight ethanol) for a single pass, which is a significant improvement over use of pure CO_2, but perhaps not sufficient for an industrial process.

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 8 hours extraction time for particles with diameters less than 1 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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