A New Industrial Process for Extracting Cocoa Butter and Xanthines with Supercritical Carbon Dioxide

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ABSTRACT: This research explores the feasibility of extracting cocoa butter and xanthines (theobromine and caffeine) from cocoa beans with supercritical CO_2. It is difficult to carry out the extraction with CO_2 alone in the temperature range 40–90°C at pressures between 80 to 300 bar. However, the addition of a polar cosolvent, such as ethanol, greatly enhances solubilities, especially that of cocoa butter. Based on experimental investigations and theoretical inference, the design of a potential industrial process for extracting cocoa butter and xanthines is proposed, in which ethanol is used as cosolvent, and distillation is used to separate and regenerate ethanol. The pressure required is much less than that for CO_2 alone as specified in the patent literature.
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KEY WORDS: Caffeine, carbon dioxide, cocoa butter, ethanol, process design, supercritical fluid extraction, theobromine, xanthines.

Supercritical fluid (SCF) extraction is a promising technology with exciting commercial potential, and CO_2 is considered to be the most suitable solvent for processing natural products. It has been used commercially for processing coffee, tea, hops, and selected spices. Attempts have also been made to obtain cocoa butter or to remove xanthines from cocoa beans by SCF extraction technology (1,2). Cocoa beans are the seeds of the tropical cocoa tree and provide the raw materials for chocolate. Cocoa beans consist mainly of cocoa butter (50–55 wt%) but also contain small amounts of xanthines (1.2–1.8 wt% of theobromine and 0.1–0.2 wt% of caffeine). The high-quality butter is used in food, cosmetic, and pharmaceutical products after removal of the xanthines, which are pharmaceutically important (3,4). Mechanical expression and solvent extraction with hexane are generally employed for obtaining cocoa butter. However, there is an increasing awareness of the health and safety hazards associated with the use of organic solvents, and expression often introduces contaminants into the butter that must be removed later. To obtain high-quality butter, Roselius *et al.* (1) describe a process in which cocoa butter is extracted from cocoa nibs with CO_2 in the pressure range of 250 to 350 bar at a temperature between 45 and 60°C. However, McHugh and Krukonis (5) found that less than 5% of the cocoa butter could be extracted, even if the extraction was carried out at 483 bar for a period of 8 h. In contrast with numerous patents for coffee decaffeination, only one patent exists for the removal of theobromine from wet cocoa beans with supercritical CO_2 (2). The question whether cocoa butter or theobromine can, in fact, be easily extracted with CO_2 thus arises. This study explores the feasibility of extracting cocoa butter and xanthines from cocoa beans with supercritical CO_2 and proposes the design of an industrial process for extracting cocoa butter and xanthines with SCF.

EXPERIMENTAL PROCEDURES

Materials and analysis. Cocoa beans and cocoa butter were supplied by Lindt & Sprüngli AG (Zurich, Switzerland). The cocoa nibs were obtained after removing the shells from the cocoa beans, which ranged in size from about 0.5 to 2 mm. The cocoa butter supplied was obtained hydraulically. The measured amounts of some selected components are as follows: theobromine, 1.44 wt%; caffeine, 0.23 wt% [ultraviolet (UV)-spectrophotometry method (6)]; cocoa butter (Soxhlet extraction method), 53.8 wt%; moisture [AOAC method (7)], 6.0 wt%. The chemicals naphthalene, theobromine, caffeine, and ethanol were supplied by Fluka Chemie AG (Buchs, Switzerland) with individual purities of 99 wt% [gas chromatography (GC)], 98% [high-performance liquid chromatography (HPLC)], 99 wt% (HPLC), and 99 wt% (GC), respectively; all chemicals were used without further purification. CO_2 was supplied by PanGas AG (Luzein, Switzerland) with a purity of 99.9%.

Experimental equipment and measurements. A schematic diagram of the dynamic experimental apparatus used is shown in Figure 1, which indicates the single-stage compressor (Maxitrol, Southfield, MI), pressure regulator (series 44-1100; Tescom Corp., Elk River, MN), and heated micrometer valve (SS-4MO; Nupro Co., Willonghly, OH). A detailed description of the equipment and the experimental procedures are given elsewhere (8,9). The extraction column is 4.5 cm in diameter and 31 cm long, being packed with alternate layers of the test solid and glass wool or glass beads; the glass beads were used for cocoa nibs, and the glass wool for the chemicals and cocoa butter. The inlet and outlet of the column were

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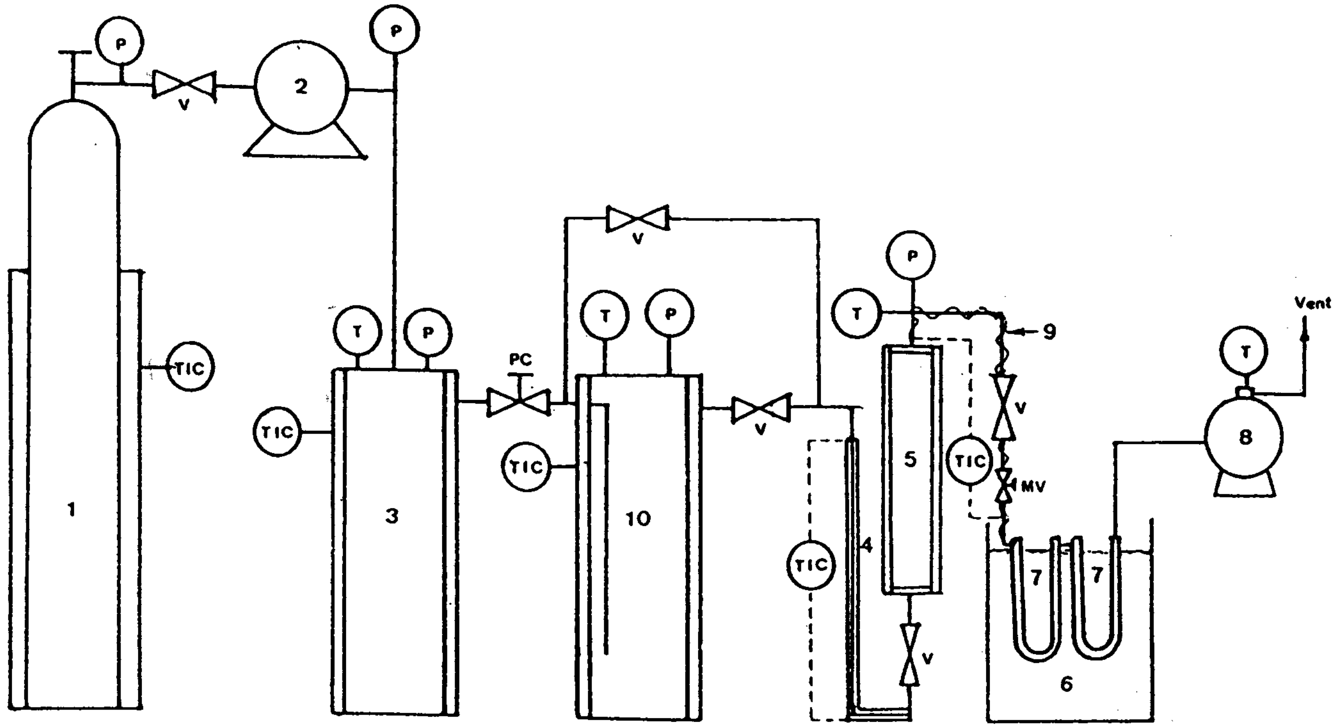

FIG. 1. Schematic diagram of experimental apparatus: (1) liquid-CO_2 cylinder; (2) compressor; (3) heated surge tank for CO_2; (4) preheater; (5) extraction column; (6) ice-water bath; (7) U-tube; (8) wet-test meter; (9) heating tape; (10) cosolvent surge tank; pressure (P) gauge; pressure control (PC) regulator; temperature (T) meter; temperature indicating control (TIC); valve (V); micrometer valve (MV).

closed by metal filter discs (threshold 7 micron) to minimize entrainment of the test solid. The temperature of both surge tanks and extraction column were monitored and controlled by thermocouples combined with proportional-integral-derivative regulators (type 070; Eurotherm, Worthing, England) to within ±1°C; the pressure was measured to an accuracy of 1% over the range.

The flow rate was controlled by a micrometer valve, varying from 0.1–0.4 standard L/min. A reliability proof test was made with the naphthalene–CO_2 system at 45°C. The measured solubility data were close to the data of Chang and Morrell (10) and within 7% of that of Tsekhanskaya *et al.* (11).

The solubilities of theobromine and caffeine in CO_2 at different conditions were calculated by measuring the amount of gaseous CO_2 flow and by analyzing the amount of xanthines collected by means of UV spectrometry (6). The solubility of cocoa butter in CO_2 was measured directly by weighing. When cocoa nibs were extracted with the cosolvent ethanol, the mass of precipitated solids and liquid cosolvent collected were first weighed, then heated and vacuum-extracted to remove ethanol. Reweighing thus gave the total amount of butter and xanthines. The procedure for separation and analysis of theobromine and caffeine is similar to that used for the cocoa beans (6).

RESULTS AND DISCUSSION

Some experimental results have been reported in our previous papers (8,9), so only brief descriptions and some additional data are given here to obtain a general understanding of the design basis for the proposed potential industrial process. The experimental solubilities of cocoa butter in pure CO_2 at 40 and 60°C in the pressure range 100 to 300 bar lie between 0.05 to 0.8 wt% (Fig. 2). This is in the same order as that of soybean triglycerides measured by Friedrich and coworkers (12,13). However, above about 600 bar and 60°C, the solubility of soybean triglycerides in CO_2 rises sharply, and infinite miscibility occurs above 800 bar and 70°C. Based on these findings, they (12,13) proposed a process for single supercritical CO_2 extraction of lipids from lipid-containing materials close to infinite miscibility. This suggests that conditions used by us and those described by Roselius *et al.* (1)

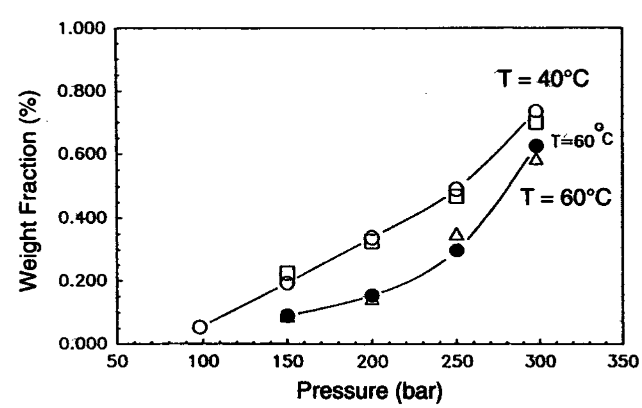

FIG. 2. Experimental solubilities of cocoa butter in supercritical CO_2; T, temperature.

(40–60°C, 250–350 bar) may be too low for the extraction of cocoa butter with CO_2.

A large solvent ratio is required to extract a significant amount of cocoa butter from cocoa beans, even when using the higher pressures investigated by McHugh and Krukonis (5) (483 bar). The pressure is often limited by the capital cost of high-pressure equipment. Selecting a suitable cosolvent to increase the solute solubility at lower pressures may provide a more economical way for extracting cocoa butter from cocoa beans.

Ethanol is one of few accepted solvents in the food industry. The CO_2–ethanol phase diagram, measured by Panagiotopoulos and Reid (14), indicates that the system critical pressure is comparable to that of pure CO_2. The solubility of ethanol in the gas phase is low in the two-phase region, but a single complete miscible phase between CO_2 and ethanol forms above the critical point.

The influence of cosolvent ethanol on the solubility of cocoa butter is shown in Figure 3. Below the critical pressure of the system (about 100 bar), only a small amount of ethanol is dissolved in the CO_2, and only a small amount of cocoa butter can be extracted. When complete miscibility between CO_2 and ethanol is attained, the concentration of ethanol is about 20 to 25 wt% under our operating conditions. The solubility of cocoa butter is greatly enhanced to about 50 wt%, and pressure has no obvious effect. Furthermore, when the extract collected in the U-tubes was taken from the ice bath and warmed to 60°C, the solid melted and two liquid phases appeared, as shown in Figure 4: liquid butter at the bottom and ethanol with some dissolved cocoa butter at the top. This means the ability to dissolve cocoa butter by supercritical CO_2 with suitable amounts of cosolvent ethanol is far larger than by either CO_2 or ethanol alone. Both ethanol and supercritical CO_2 enhance the solubility of cocoa butter.

The solubilities of theobromine in pure CO_2 were about two orders of magnitudes less than those of caffeine in the temperature range 40–95°C at pressures between 80 to 300 bar (8), even though the compounds have similar chemical

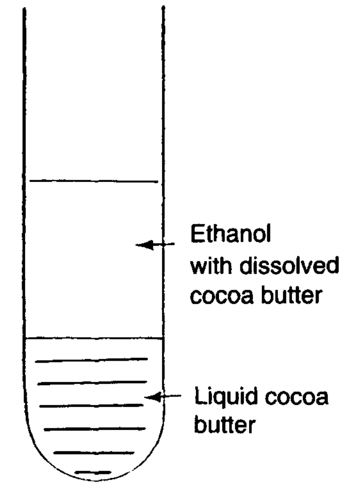

FIG. 4. Division of supercritical fluid extracts into two liquid phases at atmospheric pressure and 60°C.

structures. However, the solubility of theobromine in CO_2 in the presence of cosolvent ethanol increases greatly with the concentration of ethanol. Pressure exerts less influence than temperature, as shown in Figure 5, in which the concentration of ethanol in CO_2 is measured, according to the amounts collected in U-tubes. The amount of ethanol vapor that passes through together with CO_2 was neglected. The lower line corresponds to the measurement at 60°C and 150 bar; the upper line to 95°C and 300 bar. The measurements at other pressures lie close to these lines. The solubility enhancement of cocoa butter is mainly dependent on the cosolvent concentration in the CO_2.

However, the substances to be extracted from natural material cannot completely dissolve because they are chemically bound to their botanical matrix (5). A further investigation was carried out with 114 g of cocoa nibs at 60°C and 150 bar. The experimental results are listed in Table 1 and are shown in Figure 6, in which the amount of CO_2 flowing through is proportional to the time.

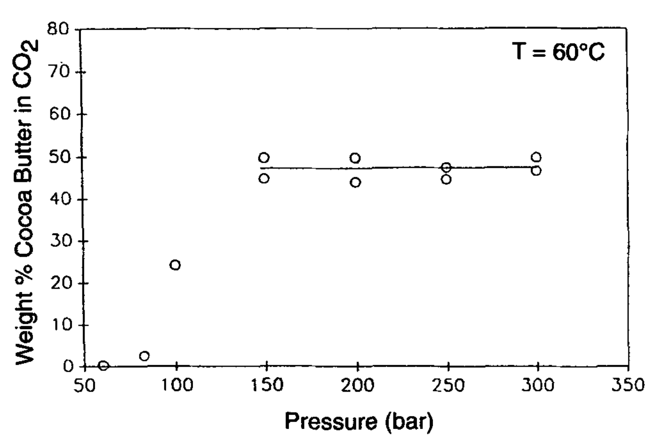

FIG. 3. Experimental solubilities of cocoa butter in CO_2 in presence of 20–25 wt% ethanol. See Figure 2 for abbreviation.

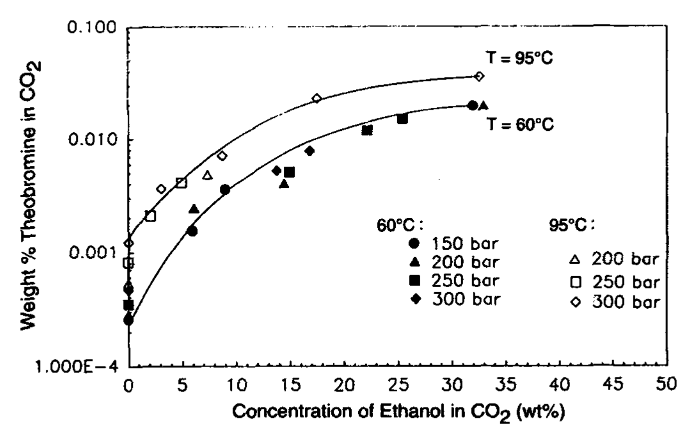

FIG. 5. Experimental solubilities of theobromine in CO_2 as function of pressure, temperature (T), and concentration of ethanol.

TABLE 1
Experimental Data for Extraction of Xanthines and Cocoa Butter from Cocoa Nibs in the Presence of Ethanol (150 bar, 60°C)[a]

Number	W_4	W_5	W_1	W_2	W_3	W_1/WO_1%	$W_{2+3}/WO_{(2+3)}$%
1	89.442	0.058	0.0575	0.838	0.798	0.0938	0.0856
2	112.984	0.099	1.1517	1.808	2.102	0.341	0.290
3	54.613	9.284	2.3744	3.073	7.417	4.212	0.839
4	29.086	12.604	6.013	9.059	6.404	14.018	1.675
5	27.280	13.696	4.5951			21.510	2.426
6	29.673	14.444	4.7031	9.678	6.066	29.178	3.163
7	26.637	10.726	4.6788	8.755	4.545	36.806	3.859
8	26.297	10.468	3.9043			43.172	4.466
9	29.081	13.672	3.7348			49.261	5.108
10	32.480	13.488	4.1766	7.602	4.505	56.071	5.741
11	56.210	27.216	5.0122			64.244	6.732
12	39.660	17.661	5.3040	9.615	4.603	69.631	7.476
13	43.742	18.627	2.8421			74.265	8.199
14	35.840	14.895	2.4091			78.193	8.725
15	34.511	14.188	2.2744	7.247	2.609	81.901	9.241
16	45.587	17.622	2.6360			86.149	9.897
17	45.660	16.494	2.5519	8.132	3.515	90.361	10.547
18	50.955	18.140	1.8600	8.256	3.586	93.392	11.168
19	69.132	23.787	1.4467	10.070	4.592	95.751	11.935
Σ	878.470	267.170	58.726	~146	~82		

[a] W = weight in grams; 1 = cocoa butter; 2 = theobromine; 3 = caffeine; 2 + 3 = xanthines; O = feedstock cocoa nibs (114 g); WO_1 = (114 × 53.8%) = 61.322 g; $WO_{(2+3)}$ = [114 × (1.44 + 0.23%)] = 1.910 g; 4 = CO_2; 5 = ethanol.

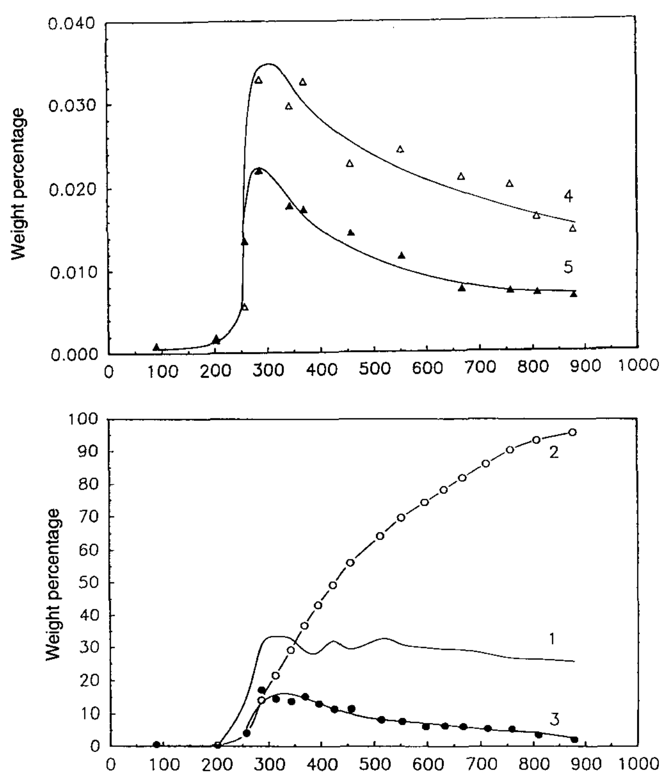

FIG. 6. Experimental investigation of extraction of xanthines and cocoa butter from cocoa nibs with supercritical CO_2–ethanol at 150 bar and 60°C: (1) concentration of ethanol in CO_2 (wt%); (2) amount of cocoa butter extracted (wt%); (3) concentration of cocoa butter in CO_2 (wt%); (4) concentration of theobromine in CO_2 (wt%); (5) concentration of caffeine in CO_2 (wt%).

Curve 1 shows the concentration of ethanol in CO_2. After an initial incubation period, the amount of ethanol in the CO_2 increased rapidly to a maximum and then remained almost constant at about 25–33 wt%. Curve 2 shows the amount of cocoa butter extracted. Only about 900 g of CO_2 and less than 300 g of ethanol were needed to extract about 95 wt% of the cocoa butter. Curves 3, 4, and 5 show that the concentration of cocoa butter, theobromine, and caffeine in the CO_2 have similar shapes.

Variation in the selectivity with the amount of cocoa butter extracted is shown in Figure 7, in which the selectivity (S) of CO_2 for the cocoa butter relative to xanthines in the presence of ethanol is defined in Equation 1.

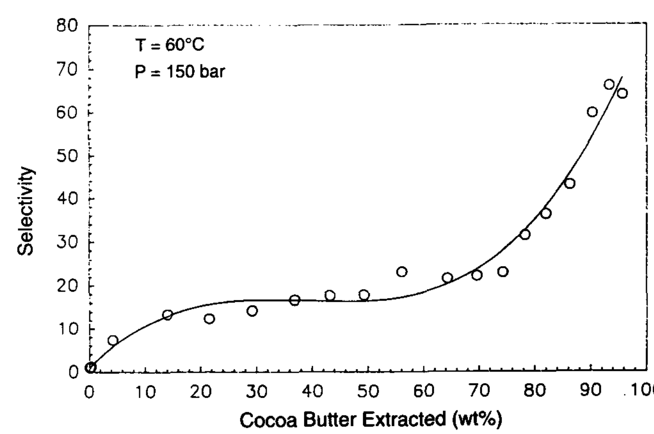

FIG. 7. Selectivity of supercritical CO_2 for cocoa butter relative to xanthines in processing cocoa nibs in the presence of ethanol (25–33%) at 150 bar pressure (P) and 60°C temperature (T).

$$S_{1/(2+3)} \frac{(x_1)_f}{(x_1)_s} \Bigg/ \frac{(x_{2+3})_f}{(x_{2+3})_s} \qquad [1]$$

The x denotes composition (wt%); subscript 1 denotes cocoa butter; subscripts 2 and 3 denote theobromine and caffeine, respectively; subscripts f and s denote the fluid and solid phases. The selectivity (S) of CO_2 for cocoa butter relative to xanthines in the presence of ethanol rises markedly with the amount of cocoa butter extracted. Only about 10 wt% of the total amount of xanthines was extracted when about 95 wt% of the cocoa butter was extracted. Cocoa butter is extracted faster than the xanthines, especially theobromine.

Process design. When a suitable cosolvent is added, the solubility of solute can be markedly enhanced compared with a single SCF alone under the same pressure and temperature, even when the pressure is low. However, the separation of solute from the solvent and solvent regeneration will not be as easy as for an SCF without cosolvent. Classical separation methods, such as distillation or evaporation, are needed to obtain the desired products and regenerate the solvent.

Supercritical CO_2 is a nonpolar solvent. However, it has a strong homogenizing action (15). It is miscible with low-molecular-weight organic solvents (such as methanol, ethanol, acetone, and benzene) at moderate pressures and room temperature, and the concentration of these cosolvents in the SCF can be varied.

At least four components are involved in SCF extraction in the presence of cosolvent, and quasi-ternary phase diagrams may be used to qualitatively describe the equilibrium. The solubilities of theobromine and cocoa butter have been shown in Figures 3 and 5, and the binary phase equilibrium for CO_2–ethanol (14) may be used to explain SCF extraction in the presence of cosolvent, as shown in Figure 8. If the extraction solvent CO_2 contains 30 mol% ethanol, and the extraction conditions are 150 bar and 65°C, a single miscible phase (point A) exists. If we reduce the pressure to 80 bar, the two-phase region (point B) is entered. According to the lever rule, about 47 mol% of the total amount of CO_2–ethanol (in which 60 mol% is ethanol, shown in point C) will liquify, while about 53 mol% of the total amount of CO_2–ethanol (in which ethanol is about 2–3 mol%, shown in point D) is in the vapor state. If we reduce the pressure further (e.g., 50 bar, point H), still about 2–3 mol% ethanol is in the vapor state (point G). Reducing the pressure can thus increase the vapor amount but not change the vapor composition; most of the ethanol will liquify; and hence, most extracts will be precipitated. If we choose 80 bar and 35°C as extraction condition (point B), which is still a miscible single phase, the two-phase region can be reached by changing the temperature to 60–65°C at the same pressure, and less energy is needed compared with separation by pressure reduction.

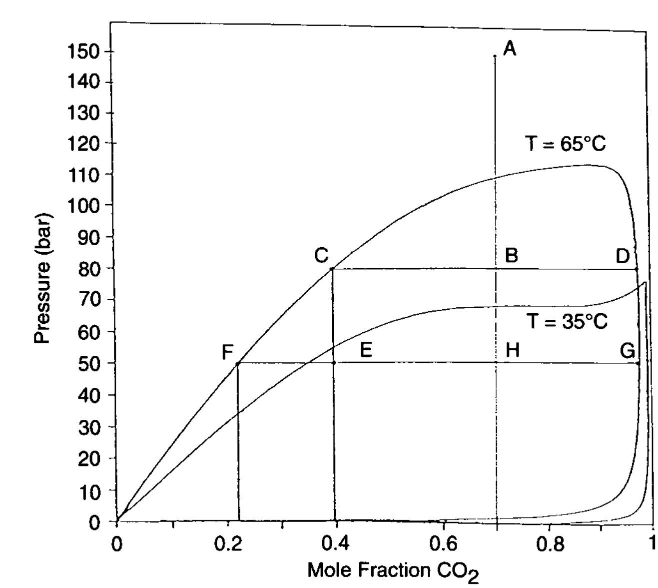

FIG. 8. Schematic description of supercritical fluid extraction and separation with CO_2–ethanol. See Figure 7 for abbreviation.

The following results suggest that it may be possible to design a new industrial process for extraction of cocoa butter and xanthines with supercritical CO_2 in the presence of ethanol with low capital and operating costs: (i) Ethanol is a better cosolvent for extracting cocoa butter than for theobromine in the SCF extraction with CO_2. (ii) The solubility of theobromine in CO_2–ethanol is mainly dependent on the concentration of ethanol and is lower than the solubility of theobromine in pure ethanol, which is about 5.10^{-4} g/g solvent at room temperature (16); no data can be found that suggest that theobromine can dissolve in cocoa butter. Therefore, xanthines extracted will mainly dissolve in liquid ethanol when separation is performed by reducing pressure or increasing temperature. (iii) The separation of cocoa butter from solvent CO_2–ethanol is easier by pressure reduction or changing temperature to reach such a level in which the single-fluid phase will split into two phases, and most of the cosolvent ethanol is liquified. Most of the liquid cocoa butter will precipitate at the bottom of the separator. (iv) Distillation can be used for separating ethanol as a top product. Concentrated crude xanthines will be obtained as bottom product, and further refinement is possible because there is a large difference in melting point and other properties between xanthines and cocoa butter.

Based on the above considerations, a proposed industrial process is shown in Figure 9. CO_2 with a suitable amount of cosolvent ethanol (20–30 wt%) is first mixed (1) before entering the column (2) where the cocoa nibs are extracted at 60 or 65°C and 150 bar. Supercritical CO_2 plus cosolvent in a single fluid phase extracts cocoa butter and xanthines from the cocoa nibs before entering the separator (3), where the pressure can be reduced to 80 bar or less at 65°C.

Under these conditions, CO_2–ethanol splits into two phases. Most of the ethanol is liquified, and gaseous CO_2 containing a small amount of ethanol can be recirculated. Cocoa butter is in the liquid state, and most of it precipitates so that it can be withdrawn easily.

Most of the xanthines extracted will be dissolved in

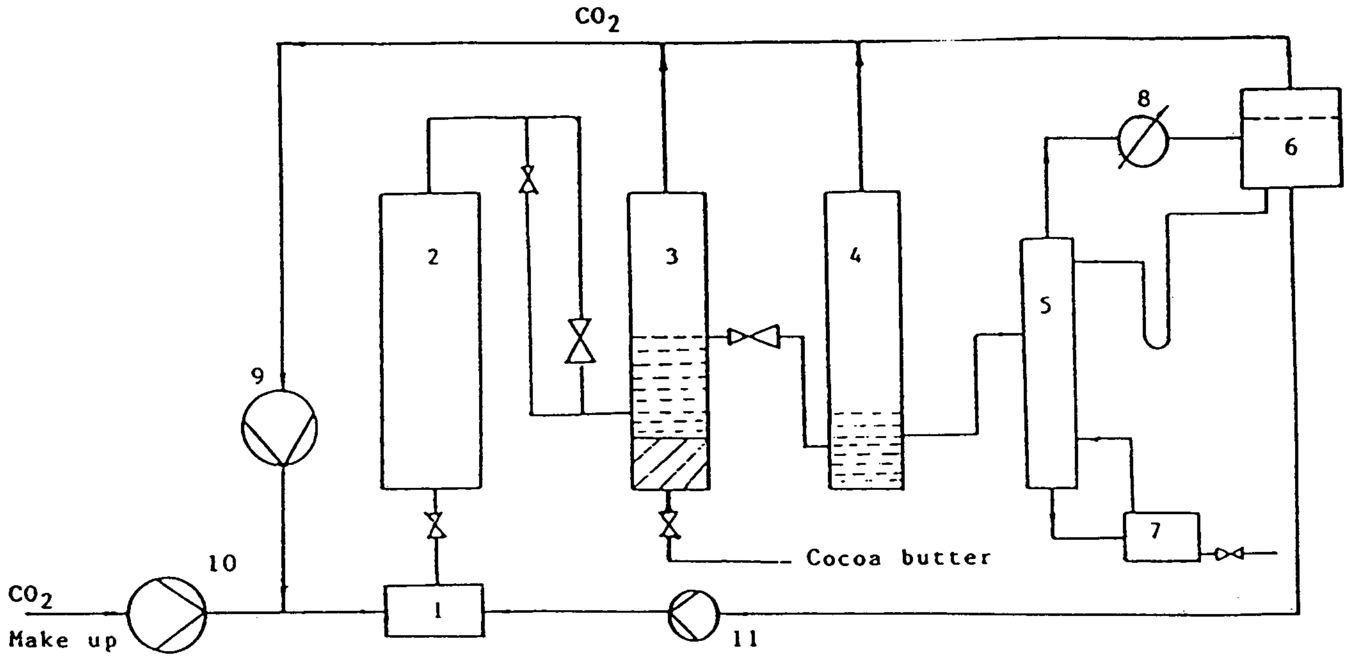

FIG. 9. Proposed industrial process for extraction of cocoa butter and xanthines: (1) mixture; (2) extraction column; (3) + (4) separators; (5) distillation column; (6) cosolvent surge tank; (7) reboiler; (8) condenser; (9) + (10) compressors; (11) metering pump.

ethanol–liquid CO_2 solution, which is lighter than liquid cocoa butter and flows under liquid level control to a second separator (4), where further pressure reduction vaporizes most of the CO_2 and a small amount of ethanol, which is recirculated together with the vapor from the first separator. The ethanol solution is then sent to the distillation column (5), where ethanol is recovered and returned to the storage tank (6) for reuse. Concentrated xanthines are filtered from the bottom of the reboiler (7). To obtain pure xanthines, further investigation is needed: this may be done by water washing at low temperature because cocoa butter is insoluble in water. After filtering, pure xanthines dissolved in water can then be obtained by evaporation. Other methods, such as ion exchange or adsorption, are also possible. The extraction conditions may also be carried out at 35°C and 80 bar, and the first separator is maintained at 65°C and 80 bar by only increasing the temperature followed by pressure reduction in the second separator as described above.

Table 2 compares our results with those of other workers. It shows that the pressure required in our process design is much less than that for CO_2 alone or combined with water.

Further experimental work is needed to optimize the operation conditions. However, solubility enhancement and lower pressures are attractive advantages. Using a suitable cosolvent in combination with traditional separation methods is a promising way to expand the application of SCF technology.

TABLE 2
Comparison of Supercritical Fluid Extraction Under Different Conditions

	Patent 1		Patent 2	
	Roselius *et al.* (Ref. 1)	McHugh and Krukonis (Ref. 5)	Margolis *et al.* (Ref. 2)	Present work
Solvent CO_2		CO_2	CO_2 Feed + water	CO_2 + Ethanol
Extracts	Cocoa butter	Cocoa butter	Theobromine	Cocoa butter Theobromine
Extraction temperature (°C)	40–60	60	80–100	60 (or 35)
Extraction pressure (bar)	250–400	482	250–350	150 (or 80)

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