

# SUPERCRITICAL FLUID EXTRACTION OF COCOA BUTTER FROM COCOA POWDER

Manuel Velásquez and Gustavo Bolaños\*

*Applied Thermodynamics and Supercritical Fluids Group  
School of Chemical Engineering, Universidad del Valle  
P.O. Box 25360, Cali, Colombia*

[gbolano@univalle.edu.co](mailto:gbolano@univalle.edu.co)

## **ABSTRACT**

We have been studying the supercritical fluid extraction of cocoa butter from cocoa powder, which is the residual cake that is obtained after defatting toasted cocoa beans by mechanical expression. Samples of cocoa powder containing 12 wt% of cocoa butter were subjected to extraction with supercritical CO<sub>2</sub> at temperatures from 35 to 50 °C, and pressures from 9.7 to 34.5 MPa in a lab-scale apparatus. For each experiment we determined the variation of the extraction yield with time, and obtained a fatty-acid profile of different samples of the extracted cocoa butter.

Our results show that it is possible to obtain cocoa powders greatly reduced in their fat content. In a typical extraction two cocoa butters with different fatty acid profiles were obtained. One that is richer in light fatty acids was obtained initially in each extraction experiment up to an extraction yield of cocoa butter in the order of 90 wt%, an another one richer in the heavier fatty acids at larger extraction yields. A new model for correlating the extraction dynamics was proposed. The model contains two adjustable parameters and represented the experimental information with an average relative deviation of 5.9%. Our results indicate that the production of cocoa butters with different properties (e.g., melting point) aimed for different applications is feasible using supercritical fluids technology.

## **INTRODUCTION**

Cocoa butter, a material that is mainly composed by triglycerides of fatty acids such as palmitic, stearic, oleic, and linoleic [1], is well known as one of the main raw materials for the manufacture of chocolate, and is responsible for some of the well appreciated characteristics of this delicacy, such as brightness, texture and, specially, melting point. In fact, one of the most pleasant characteristics of chocolate is the complete but slow melting that takes place when this material comes in contact with the human mouth, which is essentially due to the particular melting range of cocoa butter. In addition to its applications in the food industry, cocoa butter is a raw material for some pharmaceutical products, mainly as a vehicle for bioactive compounds.

Cocoa butter is obtained from the seeds of cacao (*Theobroma cacao*), which is one of the most traditional natural products of tropical countries. The extraction of cocoa butter

from *Theobroma* is a significant step for adding value to this natural raw material. This process is usually accomplished by mechanical expression of the “cocoa nib”; i.e., the cacao beans removed from the shell, and then dried and toasted. The cake obtained as a byproduct of the mechanical expression is called “cocoa powder”, and still contains a significant amount of cocoa butter. In fact, cocoa nib usually contains between 50 and 55 wt% of cocoa butter, and after mechanical expression the cake still contains about 11 wt% of cocoa butter. Because of the high value of cocoa butter (approximately 4000 US\$/ton as compared to 530 for cocoa powder and 1500 for cacao beans), there is an economical driving force for recovering the cocoa butter present in cocoa powder. In doing that, a defatted cocoa powder is also produced. This material has an increased value as raw material for the functional foods industry and its production would add value to a process for extracting cocoa butter from cocoa powder.

Extraction of cocoa butter from cocoa powder using liquid solvents such as hexane is a possible process that has been tried by some industries. However, contamination with residual solvent of both the extracted product and the cocoa powder remaining after the extraction makes this process inadmissible for obtaining products that are intended for human consumption. Thus, the use of a clean technology such as supercritical extraction to produce such materials with the necessary purity is an interesting possibility for adding value to an already economically important natural raw material.

Some efforts directed towards the supercritical extraction of cocoa butter are reported in the literature. For example, Saldaña [1] measured the solubilities of cocoa butter in supercritical ethane and in supercritical CO<sub>2</sub>, and reported on the extraction of cocoa butter from cocoa beans using these two solvents. The yields of cocoa butter obtained from the cocoa beans by extraction with supercritical ethane were reported.

In another paper, Venter et al. [2] proposed the use of supercritical CO<sub>2</sub> to facilitate the mechanical expression process. They injected carbon dioxide into the vegetable matrix during the mechanical expression, and observed that the expression yield increased from 63 to 79%. Apparently, this increase is due to the penetration of carbon dioxide into the vegetable matrix under the high pressure of the expression, and to the CO<sub>2</sub> dissolution in the cocoa butter, at least in the one present in extracellular spaces of the matrix. As a result, the cocoa butter density and viscosity decrease, facilitating its removal.

In a previous work by our group [3], we explored the extraction of cocoa butter from cocoa nib and powder with supercritical CO<sub>2</sub> in a range of conditions, and found sets of operating conditions where cocoa butters with different properties are produced. Such change in properties might be due to fractionation of the triglyceride mixture that conforms cocoa butter. To the best of our knowledge, studies on the fractionation of cocoa butter by supercritical fluid extraction with CO<sub>2</sub> have not been reported, as it has been the case for several other triglyceride mixtures present in vegetable matrices [4].

In this work we report on the extraction of cocoa butter from cocoa powder using supercritical CO<sub>2</sub>. Unlike previous work mentioned above, we are interested not only in extraction yields and processing conditions, but also in the process dynamics and its relation to the production of different types of cocoa butter.

## MATERIALS AND METHODS

### Materials

Cocoa powder was obtained from a local industry, and was used as received. A large sample of this material was sieved and the resulting information on particle size distribution was used to obtain an average particle size, which was 0.021 mm. The fat contents of this material was determined by Soxhlet extraction with hexane during 8 h, and was found to be 12.1 wt%. Humidity of the original cocoa powder was determined by drying and was 6.2 wt%.

CO<sub>2</sub> (purity 99.9%) was obtained from Oxígenos de Colombia S.A (Cali, Colombia). Fatty acid standards for the chromatographic work were obtained from Nuchek Inc. (Chicago, IL). Methanol (HPLC grade) was obtained from Aldrich.

### Experimental apparatus

Figure 1 shows the experimental apparatus that was used in this research. This is a laboratory scale apparatus that was designed and built in previous works [3]. In its present version, the apparatus is constituted by three sections: pumping, extraction and extract collection. The pumping section is composed of a carbon dioxide cylinder and a Williams-Milton Roy pneumatic pump (model CP250V225, rated for pressures up to 7000 psi). Because the pump operates with liquid carbon dioxide, the apparatus has a refrigeration system that allows one to maintain the pump feed in its liquid state. The refrigeration system circulates an ethylene glycol stream at -10 °C through a heat exchanger to cool the carbon dioxide before pumping.

The extraction section is composed of a cylindrical extractor fabricated in stainless steel 316, which has a useful volume of 15 cm<sup>3</sup> and is rated for pressures up to 10000 psi at 200 °C. The extractor is immersed into an isothermal water bath, which is equipped with a type-K thermocouple and a temperature controller (DISAN, Model BS 1400). The water bath and thus the extraction temperature is controlled to ± 0.3 °C.

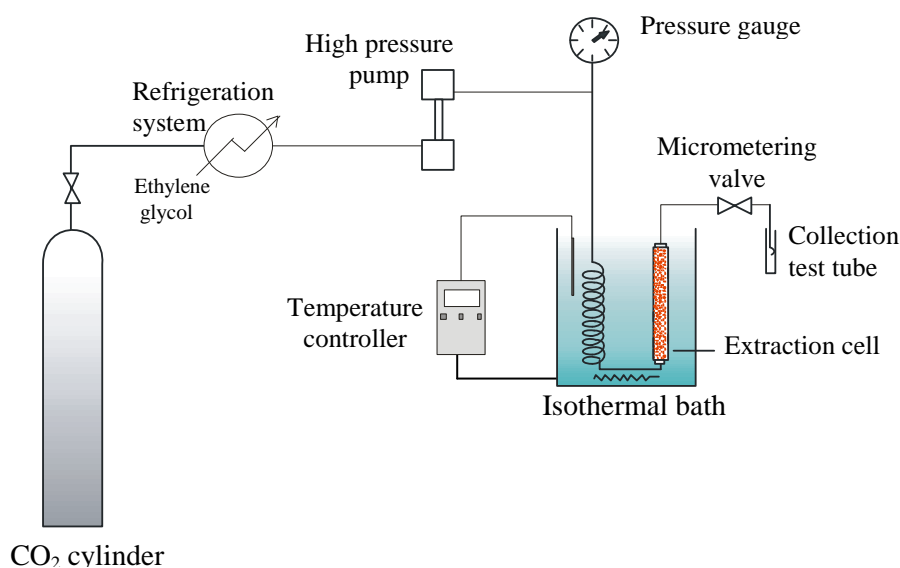


Figure 1. Experimental apparatus.

The extract collection section is constituted by a micrometering valve (High Pressure, model 1511AF1-REG) with which we manually control the extraction pressure and the exit flow rate. The extract is collected after the micrometering valve in a 10 mL test tube, fitted with a soft rubber stopper to protect the tube in case of a sudden pressure increase during sample collection.

The operating pressure was determined with a Bourdon pressure gauge (Ashcroft, model 3005HL, 0 to 5000 psi, with marks every 100 psi) placed in the extractor feed line. The pressure readings have a precision of  $\pm 50$  psi. The exit line is wrapped with an electric resistance to prevent plugging due to freezing of the extract or CO<sub>2</sub> as a consequence of the cooling produced by the fluid expansion in the valve. The CO<sub>2</sub> flow rate is controlled by the micrometering valve and was set to 0.56 kg/h.

### **Experimental procedure**

In an extraction experiment, cocoa powder was loaded into the extractor, which was then introduced into the isothermal bath. After thermal equilibration, carbon dioxide was pumped with the micrometering valve fully closed until the desired pressure was reached. At this moment, the micrometering valve was slowly opened, so that steady values of the pressure inside the extractor and the exit flow rate were obtained. For each experiment, a sample of the extract was collected each 10 to 20 minutes and was weighed. The extraction run was stopped when no new extract was detectable in the collection vial in a 40 min period.

An experimental plan was prepared to explore the effect of extraction temperature and CO<sub>2</sub> density on the yield and chemical composition of the cocoa butter extracted from cocoa powder. The extraction yield is defined as the percentage of cocoa butter in the raw material that is extracted by the supercritical fluid. The experimental runs were organized according to an augmented 2<sup>2</sup> factorial experiment in which temperatures between 35 and 50 °C, and CO<sub>2</sub> densities between 0.7 and 0.9 g/cm<sup>3</sup>, were used as the conditions for the factorial experiment. At each one of the 4 possible combinations of these conditions one experimental run was made. One more run was planned at 42.5 °C and 0.8 g/cm<sup>3</sup> (i.e., the so called “augmentation”). For each combination of temperature and CO<sub>2</sub> density, we used the Bender equation of state [5] to calculate the pressure at which the corresponding run was to be made. The mentioned values of temperature and density were chosen such that they rendered pressures in the range of the operational capacity of our apparatus.

Samples of the extracted cocoa butter were dissolved in analytical-grade hexane and a fatty acid profile was obtained by gas chromatography, following a standard procedure [6]. The melting point of the extracted cocoa butter was measured by introducing a sample of this material into a capillary, and subjecting it to slow heating in a water bath until complete melting was visually detected. The melting point that was reported was the average of three replicates.

## **EXPERIMENTAL RESULTS**

Figure 2 shows the variation of extraction yield of cocoa butter with time in the SCF extraction of cocoa powder at different conditions. Extraction yield is defined as the

mass percent of cocoa butter extracted as related to the initial content present in the cocoa powder. The linear tendency that was obtained is typical of extractions controlled by solubility at least until 90 wt% extraction yield. After this value the extraction yield changes more slowly and asymptotically to 100 wt%, indicating that a different mechanism acts in this region as a limiting step in the extraction. The figure indicates that cocoa powder greatly reduced in their content of cocoa butter is obtained at 0.9 g/cm<sup>3</sup> and 50 °C in 70 min of extraction, and at longer times at other conditions. As mentioned before, defatted cocoa powder has added value for the functional foods industry.

All the extractions that were performed behaved in a similar way with time, the slope of the linear part being the main difference. The slope increased with increasing CO<sub>2</sub> density at constant temperature, and also with increasing temperature at constant density. Presumably, because at temperatures above 35 °C cocoa butter is a liquid, it easily flows from the vegetable matrix with increasing temperature. Higher CO<sub>2</sub> densities not only favor the solubility of cocoa butter in supercritical CO<sub>2</sub>, but also the higher pressures at which this occurs increase the solvent permeability in the matrix.

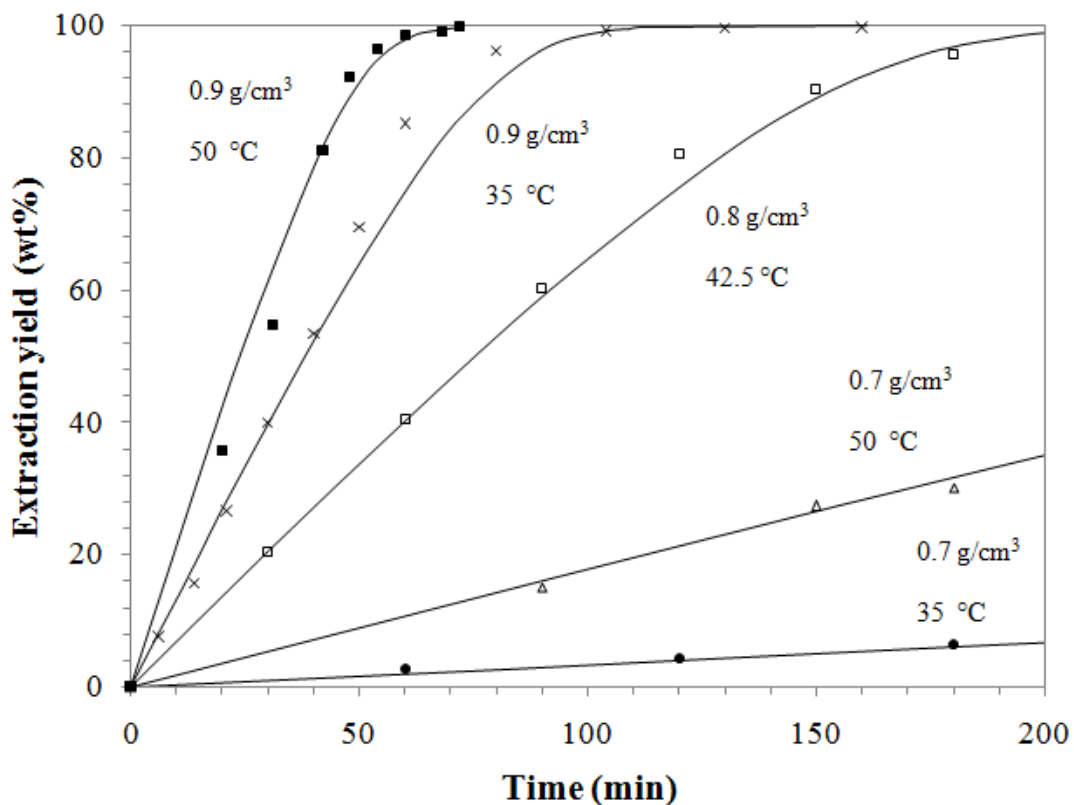


Figure 2. Variation of extraction yield of cocoa butter with time in the SCF extraction of cocoa powder at different conditions. Continuous lines correspond to a model that is described in the text.

Table 1 shows the fatty acid composition and melting point of cocoa butters extracted at different conditions. To differentiate between the cocoa butter extracted in the linear region (i.e., up to 90 wt% extraction yield) from the one extracted in the asymptotic

region (extraction yield above 90 wt%), we designated those cocoa butters as A and B, respectively. Notice that the composition and thus the melting point of the cocoa butters A and B differ somewhat from each other. Cocoa butter A has larger percentage of lighter fatty acids such as palmitic, oleic and linoleic, and as a result, its melting point is slightly lower than that of cocoa butter B. This small difference in melting point, however, is determinant in the use of cocoa butter by the food industry [7].

Tabla 3. Fatty acid composition and melting point of cocoa butters (A and B) extracted at different conditions

Fatty acid		Extraction conditions					
		0.8 g/cm <sup>3</sup> 42.5 °C		0.9 g/cm <sup>3</sup> 35 °C		0.9 g/cm <sup>3</sup> 50 °C	
		A	B	A	B	A	B
C12:0	Lauric						
C14:0	Miristic	0.07		0.06		0.04	
C16:0	Palmitic	27.92	13.45	30.69	15.08	28.16	17.20
C16:1	Palmitoleic	0.18		0.23	0.08	0.19	0.11
C18:0	Stearic	34.28	47.36	31.33	46.74	34.03	44.16
C18:1	Oleic	33.32	32.72	33.27	33.08	33.28	32.88
C18:2	Linoleic	2.93	2.25	3.19	2.06	2.98	2.24
C18:3	$\alpha$ -Linolenic	0.18		0.13		0.09	
C18:4n-3	Parinaric						
C20:0	Arachic	0.85	2.97	0.74	2.17	0.94	2.39
C20:1					0.08		
C22:0	Behenic	0.08	0.63	0.11	0.35		0.46
C22:6n-3		0.18	0.19	0.25	0.11	0.28	0.19
C24:0			0.42		0.25		0.37
	Total	100.0	100.0	100.0	100.0	100.0	100.0
	Melting point (°C)	38.6	42.3	38.1	42.3	38.6	42.3

Conceivably, cocoa butter A might be essentially extracellular and is extracted by the supercritical fluid in a relatively easy way, with dissolution rate as the controlling step. Cocoa butter B is definitely a different one and its removal from the vegetable matter is controlled by another mechanism, perhaps its diffusion through the vegetable matrix. We speculate that cocoa butter B might be intracellular. Important to observe, however, that these results indicate that cocoa butters aimed for different applications, as deduced from their different melting points, can be extracted from cocoa powder.

## MATHEMATICAL MODEL

Several mathematical models have been presented in the literature to represent the dynamics of the supercritical extraction of natural matter. Among them, the one referred as VTII [5], and the one developed by Sovova [8], are well known. The VTII model is expressed as two partial differential equations with three adjustable parameters. The Sovova model, in turn, is expressed as four partial differential equations with also three adjustable parameters. To represent the extraction yield as a function of time in supercritical fluid extraction of a natural matter such as cocoa butter, these models have to be numerically integrated by using an appropriate routine. In this work we propose a simple model that has two adjustable parameters and explicitly expresses the relation between extraction yield and time; i.e., no differential equations are present in the final expression.

We represent the cocoa powder as a set of solid particles, each one with successive layers of cocoa butter molecules adsorbed to its surface. Then, there is an initial monolayer that is physisorbed directly to the solid particle, and successive layers of molecules adsorbed on already adsorbed molecules. We thus start by using the well known BET adsorption isotherm, which represents this physical situation for the adsorption of an ideal gas, by the equation [9]:

$$N_A = \frac{N_m CX}{(1-X)[1+X(C-1)]} \quad (1)$$

where  $N_A$  is the total number of molecules of substance A adsorbed on the solid,  $N_m$  is the number of molecules of A adsorbed on the first monolayer,  $C$  is the ratio between the adsorption equilibrium constants of A in the first monolayer and that in subsequent layers, and  $X$  is the product between the adsorption equilibrium constant and pressure.

This equation is simplified by considering  $C=1$ ; i.e., the adsorption equilibrium constants for the first monolayer and for subsequent layers are identical, to give:

$$N_A = \frac{N_m X}{1-X} \quad (2)$$

We know transform this equation, which is valid for adsorption of a pure ideal gas, to consider the case of adsorption of a solute from a solution in a supercritical fluid. As for a pure gas  $X=KP$ , where  $K$  is the adsorption constant and  $P$  is the total pressure of the pure gas, we replace this property for the fugacity of solute A in the supercritical solvent as given by the Lewis rule, to obtain:

$$N_A = \frac{N_m K y_A f_A^0}{1 - K y_A f_A^0} \quad (3)$$

where  $y_A$  is the concentration of A in the solvent and  $f_A^0$  is the fugacity of pure A.

The adsorption constant can be obtained from this equation by considering that when the solvent is saturated with the solute, the number of molecules adsorbed on the solid becomes very large (i.e., infinity). By taking the appropriate limits the adsorption constant is obtained. By replacing it into equation 3 we obtain after some rearrangement:

$$m_A = \frac{m_m y_A}{y_A^{Sat} - y_A} \quad (4)$$

where  $m_A$  is the total mass of adsorbate A,  $m_m$  is the mass of adsorbate on the first monolayer, and  $y_A^{Sat}$  is the solubility of A in the solvent.

This is also expressed as:

$$y_A = \frac{m_A y_A^{Sat}}{m_m + m_A} \quad (5)$$

We now use a material balance to represent the change of the concentration of solute A in the fluid in the axial direction of the extractor:

$$u_z \varepsilon \frac{\partial y_{Af}}{\partial z} = k(y_A - y_{Af}) \quad (6)$$

where  $u_z$  is the velocity in the z direction,  $\varepsilon$  is the porosity of the packed bed,  $y_{Af}$  is the concentration of A in the bulk of the fluid at position  $z$ ,  $k$  is a mass transfer coefficient, and  $y_A$  is the concentration of A in the fluid, which is in equilibrium with that adsorbed on the solid.

After taking the usual limits for a packed extractor, this equation is integrated to obtain:

$$y_{Af} = \frac{y_A}{1 + \frac{u_z \varepsilon}{kz}} \quad (7)$$

or, for the full length L of the extractor:

$$y_{AfL} = \frac{y_A}{1 + \frac{u_z \varepsilon}{kL}} \quad (8)$$

where  $y_{AfL}$  is the concentration in the fluid at the exit of the extractor.

We now use a material balance of A in the solid packed in the extractor, which is given by:

$$\frac{\partial m_A}{\partial t} = -\dot{m}_B \frac{y_{AfL}}{1 - y_{AfL}} \quad (9)$$



where  $\dot{m}_B$  is the mass flow rate of the solvent and  $t$  is time.

After replacing 5 in 8 and 9, integrating the resulting equation, and some rearrangement we finally obtain:

$$t = \frac{1}{\dot{m}_B y_A^*} [x_A - x_m \ln(1 - x_A)] \quad (10)$$

where:

$$y_A^* = \frac{y_A^{Sat}}{1 + \frac{u_z \mathcal{E}}{kL}} \quad (11)$$

$x_A$  is the extraction yield of A; i.e., the ratio between the mass of A extracted and the mass of A originally present in the extractor.  $x_m$  is the ratio between the mass of A adsorbed in the first monolayer and the mass of A originally present in the extractor.  $\dot{m}_B$  is the mass flow rate of the solvent divided by the initial mass of A in the extractor.

Equation 10 expresses a relationship between time and extraction yield, and has two adjustable parameters,  $y_A^*$  and  $x_m$ . Notice that according to Equation 11, for situations where diffusional limitations are negligible (i.e.,  $u_z \rightarrow 0$ ,  $L \rightarrow \infty$ , or  $k \rightarrow \infty$ ),  $y_A^* \approx y_A^{Sat}$ , and in these cases, knowing the solubility of A in the solvent would reduce the number of adjustable parameters to one. A detailed derivation of this model is presented elsewhere [10].

Table 4. Values of the adjustable parameters that were obtained\*

Operating conditions		Adjustable parameters	
Density (g/cm <sup>3</sup> )	Temperature (°C)	$y_A^* \times 10^5$	$x_m$
0.7	35	4.26	
0.7	50	18.10	
0.8	42.5	78.70	0.129
0.9	35	173.00	
0.9	50	7950.00	

\* average absolute deviation =  $\sum \frac{1}{n} \sum \left| \frac{t^{\text{exp}} - t^{\text{cal}}}{t^{\text{exp}}} \right| = 5.90\%$

The model was used to correlate the data of extraction yield vs. time for the supercritical extraction of cocoa butter that were presented. Table 4 shows the values of the adjustable parameters that were obtained. A single value of  $x_m$  was obtained to represent the whole set of data because it was observed that this parameter does not

strongly depend on the operating conditions since it is related to a property of the solid-solute pair. An average absolute deviation of 5.90% was obtained for the 54 data that were measured. As indicated by this value, and by the continuous lines that are shown in Figure 2, this model makes a reasonable correlation of the data.

## CONCLUSIONS

Supercritical fluid extraction allows one not only to recover the valuable cocoa butter present in cocoa powder, but also to produce a cocoa powder greatly reduced in its fat content, which has an important potential for the functional foods industry. We showed that two different types of cocoa butters are obtained during the extraction. They differ in their chemical composition and thus in their melting point. These cocoa butters might thus be aimed for different applications in the chocolate industry. A mathematical model that adequately correlates the experimental data with only two adjustable parameters was developed on the basis of the BET adsorption theory.

## ACKNOWLEDGEMENTS

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