Supercritical Carbon Dioxide Extraction Of Cocoa Butter: Optimization Of Operating Conditions And Sample Matrix Effect

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Key words: cocoa butter, extraction, supercritical carbon dioxide, RSM, sample matrix

Introduction

Cocoa butter, which is a yellowish white fat, is derived from the cocoa bean. After removing the shell from the bean, the remaining nib contains about 55% of cocoa butter. Unique to cocoa butter is its brittleness at room temperature and its quick and complete melting at body temperature. The special functional properties of cocoa butter make it indispensable in the food, cosmetic and pharmaceutical industries. In the food industry, cocoa butter is responsible for the smooth texture, mouth feel, flavour release and gloss of chocolate products. The customary methods of producing cocoa butter from cocoa liquor (finely ground cocoa nib) or cocoa bean at the present time are classified as hydraulic pressing, expeller pressing and solvent extraction with organic solvents. However, there is an increasing awareness of the health and safety hazards associated with the use of organic solvents; while pressing often introduces contaminants into the cocoa butter that must be removed later. These have placed new demand to develop clean and efficient technologies for obtaining cocoa butter. Supercritical fluid extraction (SFE), mainly by supercritical carbon dioxide (SC-CO_2), has been studied as a potential alternative to the current extraction method in vegetable oils extraction. The application of SC-CO_2 extraction offers the advantages of rapid, nontoxic and contamination-free extraction, less destruction of thermally labile constituents, and prevents any possible oxidation in the oxygen free extraction condition. Attempts have also been made to produce cocoa butter by SFE technology. A patent on the efficient extraction of cocoa butter from cocoa liquor and cocoa nibs with CO_2 in the pressure range from 25 to 35 MPa at a temperature between 45 and 60°C has been found. Nonetheless, other research has found that less than 5% of the cocoa butter could be extracted from nibs, even if the extraction was carried out at 48.3 MPa for a period of 8 hours at 40 to 60°C.]

Materials and MethodsMaterials

Cocoa beans and cocoa liquor with minimum 52% fat content were obtained from KL-Kepong Cocoa Products Sdn. Bhd., Malaysia. The cocoa liquor (particle size = 74 μm) was used without pre-treatment to study the optimization of operating conditions. The cocoa beans were crushed and ground to obtain particle size ranging from 4 to 6 mm and 850 μm to 1 mm. Cocoa liquor, ground cocoa nibs and crushed cocoa nibs were then used to investigate the effect of sample matrix. The CO_2 was supplied by Malaysian Oxygen (MOX) Bhd., Malaysia. The chemicals and reagents used in the study were obtained from Fisher Scientific and Sigma Chemical Co, USA, which were analytical grade and high performance liquid chromatography (HPLC) grade. SFE Apparatus and Procedure: Extraction of cocoa butter was performed by SC-CO_2 extraction. The SFE apparatus consist of Intelligent HPLC Pump Model PU-1580 (Jasco Corporation, Japan) fitted with a cooling jacket to deliver CO_2. In order to cool the pump head, ethylene glycol-deionized water mixture (50:50, v/v) was circulated through the cooling jacket using a Low Temperature Bath Circulator Model 631D (Tech-Lab Manufacturing Sdn. Bhd., Malaysia) which can deliver coolant down to –20°C. A 10 g sample was loaded into a 50mL Extraction Vessel Model EV-3 (Jasco Corporation, Japan) that was placed in Column Oven Model CO-1560 (Jasco Corporation, Japan). The column oven was used to maintain the extraction temperature. A Back Pressure Regulator (BPR) Model BP-1580-81 (Jasco Corporation, Japan) was used to control the extraction pressure. A 10 ml test tube was used as collection vessel. The sample was extracted at pressure of 10–45 MPa, temperature of 35–75°C, extraction time of 0.5-4 h, and flow rate of 2 mL/min.

Experimental Design

The optimization was carried out using response surface methodology (RSM). Pressure (P), temperature (T) and extraction time (t) that were the important operating parameters involved in cocoa butter extraction using SC-CO_2, were the independent variables. Three levels of each of the three variables were chosen and coded as -1 (lowest), 0 (middle) and 1 (highest). For each of the experiments done, the total fat content (%) was determined by gravimetry and triglyceride profile of cocoa butter was determined by HPLC.

Results and DiscussionOptimization of Operating Conditions

The percentage of total fat content extracted by SC-CO2 was greatly influenced by pressure, temperature and extraction time. Increment in pressure, temperature and extraction time up to 45 MPa, 75oC and 4 hours gave the highest value of total fat content (31.89%). The lowest value of total fat content was observed at 10 MPa, 35oC and 0.5 hour, with only 1.20%. The effects of pressure (P), temperature (T), extraction time (t) and interactions of P and t, T and t contribute significantly to the extraction efficiency of cocoa butter, with R^2 of 0.985 and significance P values of 0. The R^2 more than 0.75 is statistically

considered accurate for developing a model or equation. In order to describe how the test variables affect the response, contour plots for response were generated by the RSM model using ECHIP software. The predicted total fat content (%) extracted by $SC\text{-}CO_2$ as a function of pressure and temperature at constant extraction time of 0.5, 2.25 and 4 hours, respectively. The contour plots demonstrate that total fat content (%) increased with increasing pressure, temperature and extraction time. This may be due to the solubility of a given solute tends to increase with the operating pressure and temperature. Meanwhile, as expected the total fat content (%) increased in longer extraction time. Optimum conditions of pressure, temperature and extraction time were determined by overlapping the contour plots and predict the optimum operating condition from superimposed region of the three contour plots. It is apparent that optimum conditions for cocoa butter extraction by $SC\text{-}CO_2$ are pressure, 45 MPa, temperature, 75°C, and extraction time, 4 hours, with 30.63% of predicted total fat content. However, the practical limits of each variable are governed by different factors. Temperature must be kept below a level where the material begins to suffer thermal degradation. Pressure and extraction time are more related to economic considerations, as construction and operating costs increase with higher system pressure and longer extraction time. Response surfaces can also be visualized as three-dimensional plots by presenting the response in function of two factors and keeping the others constant. The response surface showed a strong degree of curvature, where the optimum can be readily determined (the point marked by arrow). The temperature had a weak influence on the yield of total fat content that indicate the less importance of this factor, while the pressure had a major effect

The Effect of Sample Matrix

The rate of removal of a solute from a matrix using SFE is a function of its solubility in the fluid media and the rate of mass transport of the solute out of the sample matrix. The physical morphology of the sample matrix can have a profound effect on the yield that obtained by $SC\text{-}CO_2$ extraction. The effect of sample matrix with different particle sizes on extraction of cocoa butter by $SC\text{-}CO_2$ at optimum conditions that had been obtained by optimizing the operating conditions. It is obvious that the smaller the particle size of sample, the higher the total fat content will be extracted by $SC\text{-}CO_2$. This effect may be due to the shorter internal diffusional path lengths over which the extracted solutes must travel to reach the bulk fluid phase. Studies have shown that the geometric size of the matrix particles can influence the speed and completeness with which a SFE can be conducted. Our results confirm the value reported by Rossi *et al.*, who suggested that the low extraction yields observed from the nibs (particle size ranging from 2-4 mm) were caused by the lipid-bearing cells remaining intact in the nib, and concluded that extraction of cocoa butter appears to be more of a leaching phenomenon

Triglyceride profiles of cocoa butter extracted by $SC\text{-}CO_2$

The effects of various operating conditions namely pressure, temperature and extraction time to triglyceride profiles of cocoa butter extracted from cocoa liquor are given in Table 5. It can be seen that triglyceride profiles of cocoa butter extracted using $SC\text{-}CO_2$ contain mono-unsaturated triglycerides (e.g. POP, POS, SOS, SOA and PLiP) and di-unsaturated triglycerides (e.g., POO, PLiO). The results demonstrated POP (C_{50}), POS (C_{52}) and SOS (C_{54}) were the major triglycerides in the extracted cocoa butter, whereby POS was the highest component which was more than 30% for all treatment. The sample matrix effect on triglyceride profiles of cocoa butter extracted using $SC\text{-}CO_2$ is shown that cocoa butter extracted from various sample matrix had similar triglyceride profile to that of typical cocoa butter.

Conclusions

The optimization of $SC\text{-}CO_2$ extraction of cocoa butter from cocoa liquor was measured as total fat content (%), as a function of pressure, temperature and extraction time at constant flow rate. Increment in pressure, temperature and extraction time increased the total fat content (%) extracted from cocoa liquor. Pressure had a strong effect on the yield of total fat content compared to temperature. The optimum conditions for cocoa butter extraction using $SC\text{-}CO_2$ were 45 MPa, 75°C and 4 hours. Sample matrix had significant effect on $SC\text{-}CO_2$ extraction of cocoa butter. The results indicated POP (C_{50}), POS (C_{52}) and SOS (C_{54}) were the major triglycerides in the extracted cocoa butter, whereby POS was the highest component for all treatments studied. The triglyceride profiles of the extracted cocoa butter complied with the typical triglyceride profile of cocoa butter.

Benefits from the study

Malaysia has been known to have high-melting point cocoa butter which is very much in demand by the world market. The current technology (hydraulic / screw press) being practiced by cocoa grinders is such that some of the cocoa butter is still remained in the cocoa powder; the technology is capable of producing maximum of 10% fat-cocoa powder. Organic solvent can be used to extract all the cocoa butter in the powder; however the resultant powder cannot be used for human consumption. Furthermore, because cocoa powder is used mainly for beverages, the presence of the extra cocoa butter does not give any advantage (fatty drink is not preferred by customers) to the product. In this study Supercritical Fluid Extraction Technology will used to extract the maximum level of fat from cocoa liquor or cocoa powder. However, further work is needed to optimize the operating conditions, which may be the key to expanding the application of $SC\text{-}CO_2$ extraction on cocoa butter extraction

Patent(s), if applicable:

Nil-

Stage of Commercialization, if applicable:

Nil-

Project Publications in Refereed Journals:

Nil

Project Publications in Conference Proceedings

1 Tan, T. J., **Jinap**, S. and Asep, E. K. (2002). Effects Of Temperature, Pressure And Extraction Time On Extraction Of Cocoa Butter From Cocoa Liquor Using Supercritical Carbon Dioxide. Oils and Fats International Congress 2002. Kuala Lumpur, Malaysia: 7-10 October, 2002.

2 Asep, E. K., **Jinap**, S. and Tan, T. J. (2002). Effects of Particle Size, Fermentation and Roasting on Cocoa Butter Extraction Using Supercritical Fluid Extraction Carbon Dioxide. Oils and Fats International Congress 2002. Kuala Lumpur, Malaysia: 7-10 October, 2002.

3 Tan, T. J., **Jinap**, S. and Asep, E. K., Harcharan, S., Rusly, A. R., Nazimah, S.A.H. (2002). Supercritical Carbon Dioxide Extraction Of Cocoa Butter: Optimization of Operating Conditions And Sample Matrix Effect. Malaysian Science and Technology Congress 2002. Kuching, Sarawak, Malaysia: 12-14 December, 2002.

Graduate Research

	Name of Graduate	Research Topic	Field of Expertise	Degree Awarded	Graduation Year
1	**Asep Edi Kusnadi**	Effect of sample preparation on cocoa butter extraction by supercritical fluid and modeling	Extraction of cocoa butter by supercritical fluid extraction (SFE)	PhD	On going
2	**Tan Teng Ju**	Effect of co-solvent on cocoa butter extraction by supercritical fluid	Extraction of cocoa butter by supercritical fluid extraction (SFE)	Master	On going

IRPA Project number01-02-04-0512
UPM Research Cluster:AFF