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# Deacidification of crude low-calorie cocoa butter with liquid–liquid extraction and strong-base anion exchange resin

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ABSTRACT

A feasible and novel deacidification process for the production of refined low-calorie cocoa butter by liquid–liquid extraction and anion exchange resin was investigated. The results showed that ethanol was a better solvent for extraction than methanol and isopropanol. The commercially available anion exchange resin D202 used in the experiments had a maximum adsorption capacity of 223.71 mg/g. With a two-stage extraction using 85 vol.% aqueous ethanol and an interaction time with resin of 4 h under the optimum conditions, low-calorie cocoa butter with an acid value of 0.81 mg KOH/g was obtained. Stable and qualified final products were acquired from 10 batches, indicating that the integrated process had no significant tendency to change the characteristics of low-calorie cocoa butter. The D202 anion exchange resin was regenerated and reused in 38 consecutive batches.



## 1. Introduction

Transesterification is one of the most promising methods for modification of oils and fats. It is well known that cocoa butter, providing 7 kcal per gram, is the primary high-energy constituent of chocolate. Hence, partial reduction in the calorie content of cocoa butter is desired and could be accomplished by enzymatic transesterification. However, transesterification inevitably yields crude low-calorie cocoa butter with substantial free fatty acids (FFAs) [1]. Therefore, deacidification is a necessary process for the production of refined low-calorie cocoa butter.

The refinement of crude oils and fats with high FFAs content has long posed economic challenges. Traditional alkali neutralization leads to high losses of neutral oil and large amounts of soap, whereas physical refinement is energy intensive [2,3]. Recent investigations have therefore focused on the development of potential deacidification processes to remove FFAs effectively without deteriorating the quality of oils and fats [4]. Liquid–liquid extraction, which employs an appropriate solvent for the possibility of restraining the losses of neutral oil and nutraceutical compositions, is recommended as an alternative deacidification approach [5–13]. However, solvent extraction is not directly applicable to the deacidification of crude low-calorie cocoa butter with high acidity because of the high solvent consumption of this tedious extraction procedure [6–8].

Since the development of synthetic ion exchangers, ion exchange resins have not been limited to the fields of water purification and demineralization, as they have been shown to have a number of potential applications to food production in aqueous systems [14–21], as well as in non-aqueous systems [2,13]. There are relatively few studies regarding resin employed in non-aqueous systems in the literature: for instance, Jamal and Boulanger successfully reduced the FFAs content of soybean oil from 5 to 0.35 wt.% using anion exchange resin [4]. However, taking the objective of this study into consideration, ion exchange resins have no capacity to remove a majority of FFAs from crude low-calorie cocoa butter. As a result, a union route, including liquid–liquid extraction and ion exchange resin treatment, should be developed to eliminate large-scale FFAs from crude low-calorie cocoa butter.

The aim of this work was to assess the industrial applicability of this new deacidification method. The appropriate extractant and resin were screened for the union process according to their deacidification capacities. The optimum liquid–liquid extraction and adsorption conditions were investigated for preparation of low-calorie cocoa butter with low acidity. Scale-up batches were attempted on the basis of the optimized processing parameters. Finally, the micrography surface of D202 resin was investigated

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by scanning electron micrography (SEM). This novel union process showed promise for refined products because recycling ion exchange resin dramatically reduced costs and solvent consumption.

## 2. Materials and methods

### 2.1. Materials

Cocoa butter with an acid value (AV) of 3.16 mg KOH/g was supplied by Shangke Food Co., Ltd. (Wuxi, China). Lipozyme TL IM (product number: LA35017103, enzyme activity: 250 IUN/g) was purchased from Novozymes A/S (Bagsvaerd, Denmark). Caprylic acid and behenic acid were obtained from Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China) and Sipo Chemical Co., Ltd. (Sichuan, China), respectively. The commercially available resins with different matrices and functional groups, including 7 anion exchange resins (D201, D202, D280, D290, D318, D319 and IRA402), 3 cation exchange resins (D001, D113 and D732) and 3 macroporous adsorption resins (X-5, DA-201 and AB-8), were supplied by Shanghai resin factory Co., Ltd. (Shanghai, China), Rohm and Haas Company (Philadelphia, USA), Chemical Plant of Nankai University (Tianjin, China) and Haiguang Chemical Co., Ltd. (Tianjin, China), respectively. The characteristics and specifications of these resins are listed in Table 1. The aqueous methanol, ethanol and isopropanol (65, 70, 75, 80 and 85 vol.%) for liquid–liquid extraction were prepared by blending absolute alcohols with different volumes of deionized water. Standards of 1,3-palmitin-2-olein (purity: 99.0%, CAS Number: 2190-25-2), 1,3-stearin-2-olein (purity: 99.0%, CAS Number: 2846-04-0), 1,3-behenin-2-olein (purity: 99.0%, CAS Number: 82056-35-7), 1,3-caprylin-2-olein (purity: 99.0%, CAS Number: 322456-95-1), 1-palmitin-2-olein-3-stearin (purity: 99.0%, CAS Number: 2190-27-4), 1-palmintin-2-linolein-3-stearin (purity: 99.0%, CAS Number: 2190-12-7) and triolein (purity: 99%, CAS Number: 122-32-7) for our analyses were purchased from Larodan Chemicals (Malmö, Sweden). Unless indicated otherwise, the solvents were analytical grade and were used as received.

### 2.2. Preparation of crude low-calorie cocoa butter

Crude low-calorie cocoa butter was prepared using the method of Fomuso and Akoh [22] with some modifications. Briefly, 1.0 kg cocoa butter and 0.1 kg behenic acid were placed into a 2 L round bottom flask. Until these two materials thoroughly melted in a water bath of 80 °C, 0.5 kg of caprylic acid was slowly added into the flask. The flask was then moved to a thermostatic water bath with a magnetic stirrer, and the substrates were stirred at 60 °C for 30 min. Finally, Lipozyme TL IM (96.0 g, 6.0 g immobilized enzyme/100 g substrates) and 3Å molecular sieve (80.0 g, 5.0 g molecular sieve/100 g substrates) were loaded. Transesterification was implemented at 60.0 °C, 120 rpm for 12 h. Crude product was obtained by filtration to separate the lipase through glass-sintered filters with filter papers. Three subsamples were taken for analytical determination. The rest of the product was kept in a deep-freeze refrigerator at −20 °C before deacidification by the union process.

### 2.3. Deacidification of crude low-calorie cocoa butter by liquid–liquid extraction

Laboratory scale multi-stage liquid–liquid extraction was carried out according to the method of Kale et al. [9] with minor modifications. Fully melted crude low-calorie cocoa butter was mixed with alcoholic solutions (methanol, ethanol and isopropanol) in 250 mL separatory funnels with a mass ratio of 1:1. After 10 min of vigorous shaking, the mixtures were then left still for 30 min for complete phase separation at 40 °C. The raffinate phases (oil phase) at the bottom of the funnels were carefully transferred to other funnels with the same mass of fresh solvent. The extraction process was repeated as described above until the last stage of extraction. The upper phases (extract phase) were collected for recovery of FFAs. The raffinates from the last extraction were collected for AV determination after removal of alcohols by rotary evaporation under reduced pressure (85 kPa).

### 2.4. Resin pretreatment

Ion exchange resins were pretreated according to the following procedures: soaked in 4 volumes of deionized water for 24 h, decanted water, and rinsed in 4 volumes of 95 vol.% aqueous ethanol for 24 h, washed with deionized water three times. Resins were then soaked in 4 volumes of 1 mol/L NaOH for 24 h and washed with deionized water to neutral pH. Subsequently, resins were immersed in 4 volumes of 1 mol/L HCl for 24 h and then washed with deionized water to neutral pH. Finally, resins were washed to neutral pH and dried at 35 °C after resins were immersed in 5 volumes of 1 mol/L NaOH for 24 h.

To pretreat macroporous adsorption resins, resins were firstly washed several times with deionized water to eliminate impurities, decanted water, rinsed in 4 volumes of 95 vol.% aqueous ethanol for 6 h, washed three times with deionized water and dried at room temperature for deacidification.

### 2.5. Deacidification of low-calorie cocoa butter by resins

The low-calorie cocoa butter used in this process was deacidified by two-stage solvent extraction unless indicated otherwise.

#### 2.5.1. Selection of resins

Low-calorie cocoa butter was mixed with each resin in a 50 mL screw cap glass flask with a mass ratio of 1:2, together with the addition of hexane. The adsorption was carried out in a temperature-controlled water bath with a magnetic stirrer at 30 °C, 150 rpm for 6 h. The mixture was collected using vacuum filtration to separate resin after the adsorption equilibrium was achieved. Hexane was evaporated and recovered via reduced vacuum distillation, and refined product was obtained for further determination.

#### 2.5.2. Effects of processing parameters

The effects of processing parameters, such as resin load, duration of deacidification and solute concentration in hexane, were investigated to obtain the optimized conditions for crude low-calorie cocoa butter deacidification. The factor of resin load (1.5, 3.0, 4.5, 6.0, 7.5, 9.0, 10.5 and 12.0 g) was studied at 30 °C for 6 h with 3.0 g low-calorie cocoa butter in 30 mL of hexane, whereas the parameter of solute concentration in hexane (71, 77, 83, 91, 100, 111, 125, 143, 167 and 200 mg/mL) was investigated at 30 °C for 6 h with an employment of a 1:2 mass ratio of solute to resin.

In addition, the AV of low-calorie cocoa butter as a function of reaction time was determined at 30 °C when the solute concentration was fixed at 100 mg/mL and the mass ratio of solute to resin was 1:2. Aliquots of 20 mL solutions were taken for AV determination at regular intervals.

#### 2.5.3. Regeneration and recycle of D202 anion exchange resin

A series of experiments was designed to investigate the regeneration and reusability of D202 anion exchange resin. First, 3.0 g of low-calorie cocoa butter in 30 mL of hexane was interacted with 6.0 g of D202 resin in a 50 mL screw cap glass flask with magnetic stirring at 30 °C for 6 h. Separation of solution and resin was accomplished by vacuum filtration. The deacidified sample was