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TWO-STAGE TECHNOLOGY FOR PALM OIL FRACTIONATION FOR PRODUCTION OF COCOA BUTTER SUBSTITUTES

Introduction. *Tropical oils, as the most important source of vegetable fats in the world, can be substitutes for expansive conventional raw materials in manufacturing the food stuffs that meet the global trends and requirements in the food industry.*

Problem Statement *is to study the possibility of two-stage fractionation of palm oil by the solvent method.*

Purpose *is to trial the palm oil fractionation technology for obtaining high-quality fractions of a given composition and further production of cocoa butter substitutes on its basis.*

Materials and Methods. *Refined palm oil and its fractions have been studied by thermographic, chromatographic, and standard titrimetric methods.*

Results. *The palm oil fractionation technology by using the dry method in two successive stages has been improved. Cryoscopic temperatures of 22.8 °C and 8.2 °C have been identified at a cooling rate from 0.2 to 0.8 °C/min. A palm oil fraction with a melting point of 33–39 °C, which contains 50 % of lauric acid and has a similar composition as cocoa butter has been obtained. Using the obtained mid fraction, the mix formulas for the production of substitutes, equivalents, and enhancers of cocoa butter have been designed.*

Conclusion. *The parameters of solvent palm oil fractionation for obtaining the mid fraction that meets the requirements for cocoa butter substitutes have been established.*

Keywords: fractionation, palm oil, cooling rate, mid fraction, and cocoa butter substitutes

A characteristic feature of the modern oil and fat industry is the production of special fats with given properties using technologies for their modification. One of them is fractionation by separating a mixture of triacylglycerols into fractions with different melting temperatures [1—4]. An alternative to substitution of solid hydrogenated fats in food industry is palm oil and its fractions. Palm oil is a natural solid vegetable fat that does not contain cholesterol and trans isomers of fatty acids. Since various fractions and refined forms of palm oil appeared in the world market, its production and export has been rapidly growing. Due to availability and competitive pricing of exporting countries, the market segment of palm oil has been constantly expanding.

Today, the problems related to the obtainment of fats that not only meet the requirements of regulations and standards, but also can replace the conventional types of expensive raw materials aggravate through a number of economic problems our country has faced recently.

The technology of fractionation by separating a mixture of triacylglycerols into fractions with different melting temperatures is a modern non-chemical method of fat modification. There are the following types of fractionation technology: dry fractionation (in the melt), detergent fractio-

nation (using aqueous solutions of surfactants), and solvent fractionation (using solvents). However, the technology parameters that enable to selectively influence the properties of resulting fractions and to preset their properties at an optimal output have not been found so far.

The purpose of this research is to clarify the rational parameters of palm oil fractionation to obtain high-quality fractions of a given composition with further production of high-value fat substitutes based on them. To achieve this purpose, the following tasks shall be solved in the given order:

- To study the composition and yield of palm oil fractions obtained by different methods;
- To improve the classical technology for fractionation of palm oil in the melt based on the results of thermographic analysis;
- To identify whether two-stage fractionation based on the difference in melting points of palm oil components is realizable;
- To develop the composition of cocoa butter substitutes and to establish their compliance with the standards.

MATERIALS AND METHODS

The research uses refined bleached deodorized palm oil [5]. The melting temperature is measured by the pour point method in open capillary. The fatty acid and triacylglycerol composition is determined using *Hewlett Packard HP-6890* gas chromatograph, while the acid and peroxide indexes are measured using the titrimetric method. The organoleptic properties are studied according to the standard methods [6]. The quantitative yield of the product is counted as ratio of the resulting fraction mass to the raw material one. The compatibility of substitutes with natural cocoa butter is established by the technique described in [7].

The fractionation process is a thermochemical reaction in which triacylglycerols with different melting points are divided into fractions with different crystalline structures [3, 8—11]. The more saturated triglycerols with high melting points are separated from the less saturated ones by filtration as cryoscopic temperature is reached [12, 13]. Today, the normative methods for determining the cryoscopic temperature provide for the use of a Beckmann mercury thermometer, which enables temperature measurements with an error less than 0.001 °C. However, this thermometer requires careful handling, since it contains a poisonous substance and is operated manually, which can lead to additional errors.

To study the palm oil temperature behavior, the researchers used a thermocouple based complex for temperature measurement and record designed at the Department for Thermal and Refrigerating Engineering of the National University for Food Technology. The complex consists of temperature controller with a set of T-type copper-constantan thermoelectric converters (thermocouples) (measurement error of, at most, 0,05 °C), *ICP* i7018 gage, and *ICP* i7520 signal converter of *RS*-485—*RS*-232 standard. Temperature is recorded automatically, using *NDCONUTIL* v.3xx software. The system is notable for a low lag and a high reproducibility of measurement results.

THE MAIN PART

The fractionation can be divided into the three consequent stages:

- Cooling the oil through the crystallization point for creating crystal seeds as a result of overcooling;
- Gradual growth of crystals and their separation from the liquid phase;
- Separation of crystalline and liquid phases.

The composition of crystalline and liquid phases and their yield depend on process parameters. The key ones are cooling rate and temperature of fraction separation.

Palm oil cryoscopic temperature was measured by the thermal analysis method based on temperature time dependence curves. The sample temperature was derived from cooling curve when horizontal section on the isotherm was reached. Palm oil heated up to 50 °C was cooled at a rate from 0.2 to 0.8 °C/min and a temperature measurement frequency of 0.5—0.8 s (Fig. 1).

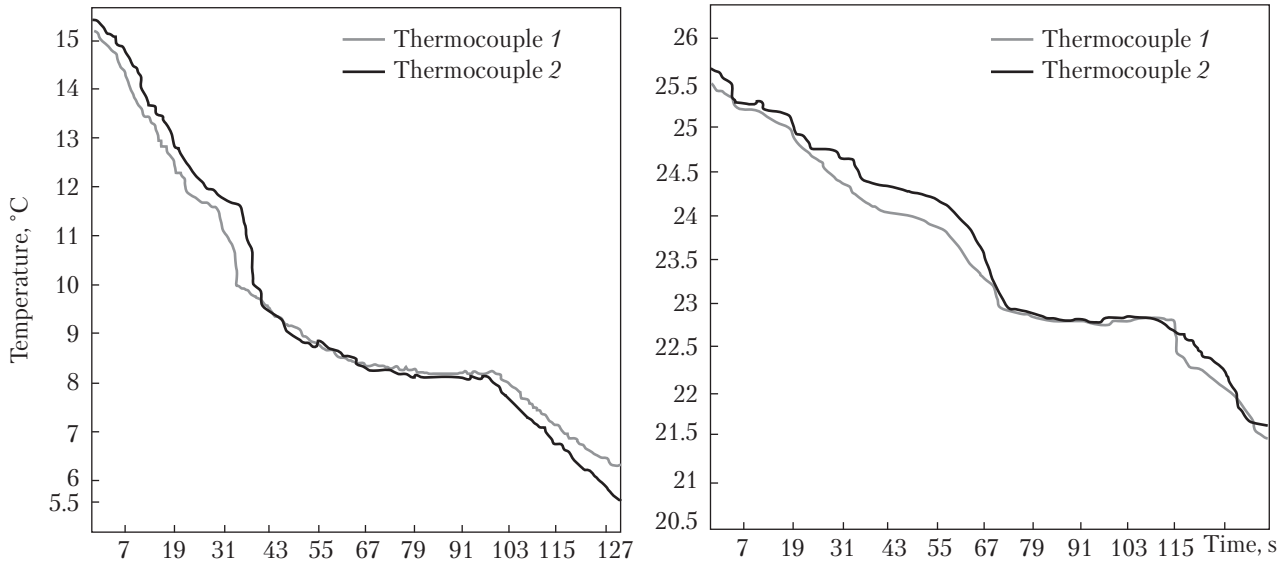

Fig. 1. Temperature curve of palm oil cooling at a cooling rate of 0.2—0.4 °C/min: *1* — first separation stage, *2* — second separation stage

The cryoscopic temperature was fixed at 22.8 °C and 8.2 °C. The characteristics and chemical composition of fractions, degree of separation of liquid and solid phases depend, primarily, on cooling technique that determines the shape and size of crystals. Fats and oils are crystallized in several polymorphic forms, as a rule, α, β, and β'. The crystallization rate of α-form is higher than that of β'-form which, in its turn, is higher than that of β-form. The rapid cooling leads to oversaturation of fatty acids of the fractions, produces a large number of hard-to-filter fine amorphous crystals. The gradual cooling entails the formation of stable β and β'-crystals that are easily filtered out from the liquid phase [12, 14, 15]. Therefore, the gradual cooling during a long while ensures a high-quality crystallization and a high effectiveness of fraction separation.

The established polymorphic transformation of crystalline structures is in good agreement with data of [1, 16, 17] obtained by the differential scanning calorimetry method. The formation of stable coarse crystals at a temperature of 22.8 °C and 8.2 °C, when the heat-resistant components are quite easily separated into individual phase enables fractioning in two consecutive stages with a new product (the so-called mid fraction) obtained. The proposed process scheme is shown in Fig. 2.

The described fractionation from melt is based on oil cooling under controlled conditions without introduction of any chemical substances. The liquid and solid phases are separated by filtering. The manufacturers of equipment for dry fractionation [7] recommend the technique for dry separation from melt and state that this technology does not require any additional substances and has the following advantages:

- Physiologically neutral products, no risk of contamination with artificial impurities;
- A high operating reliability, the technology does not use any flammable or explosive solvents;
- No additional environment impact;
- Fully computerized manufacture;
- A high flexibility of cooling profile.

Among the disadvantages of dry fractionation method there are a low crystallization rate, a complicated separation of phases because of a high viscosity of oil at low temperature, and mixed crystals formed during crystallization, which as a result of further recrystallization weep low-melting acylglycerols as liquid phase. Thus, the dry fractionation is environment friendly modifica-

tion of specialized fats, which does not require any catalysts or chemically active substances and is based on physical phenomenon of crystallization.

Table 1 shows the properties of palm oil obtained by its dry fractionation under established parameters. Both palm stearin and palm olein meet the requirements of applicable standards in terms of melting points [18, 19]. The most valuable is the palm oil fraction with a melting point of 33—39 °C. It contains about 50% lauric acid and can be used as raw material for cacao butter substitutes.

Natural cacao butter is used as fat base for in confectionary (chocolate), in fragrance and pharmaceutical industries. The interest in cacao butter substitute is caused by the following factors:

- A high price for cacao butter and its disposition towards substantial qualitative changes;
- Instable composition and properties of cacao butter;
- Special conditions for heat pretreatment of cacao butter and chocolate products in order to get a stable crystalline structure;
- Instable luster of finished chocolate products;
- Sophisticated manufacturing process for manufacture of chocolate products.

Since the second half of the 20th century, several types of cacao butter substitutes have been developed, with the following world classification [20, 21]:

- cacao butter equivalents (CBE);
- cacao butter improvers (CBI);
- non-lauric cacao butter replacers (CBR); and
- lauric cacao butter substitutes (CBS).

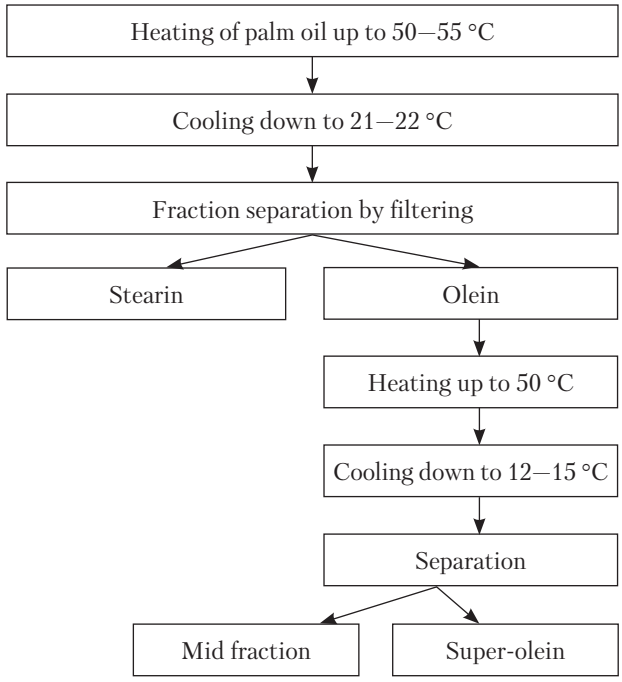

Fig. 2. Flowchart of two-stage palm oil fractionation by the dry method

The cacao butter equivalents are non-hydrogenated vegetable fats based on the same fatty acids and the same symmetric monounsaturated triglycerides, as CB [20, 22, 23]. This leads to them to having also very similar physical properties and to being compatible with CB in all proportions without any significant effect on the chocolate behavior. They can be mixed in any proportions for manufacturing chocolate blends

Table 1

Properties of Palm Oil Fractions Obtained by Two-Stage Fractionation

Stage of separation	Temperature of separation, °C	Palm oil fraction					
		Stearin		Mid fraction		Super-olein	
		$T_{m.}$, °C	Yield, %	$T_{m.}$, °C	Yield, %	$T_{m.}$, °C	Yield, %
1	22.8	+48	35.0	—	—	—	—
2	8.2	—	—	+34	28.0	+15.0	35.0
Average value		+46.5	36.5	+33	27.0	+14.75	34.5
Value as per DSTU		+44—50	—	+32—37	—	+13—16	—

Table 2

Estimated Composition of Fat Mixes

№	Group			
	CBE	CBI	CBR	CBS
1	cacao butter 80 %; shea butter 10 %; mid fraction 10 %	mid fraction 60 %; pork fat 40 %	mid fraction 100 %	coconut oil 100 %
2	pork fat 80 %; shea butter 20 %	olein 40 %; cacao butter 60 %	stearin 60 %; olive oil 40 %	coconut oil 60 %; stearin 40 %
3	cacao butter 50 %; stearin 50 %	shea butter 40 %; pork fat 60 %	palm oil 60 %; olive oil 40 %	
4	stearin 60 %; shea butter 40 %		stearin 60 %; sunflower oil 40 %	
$T_{melting}$., °C	33—36	36—45	32—41	20—44
Compatibility, %	60—85	90—95	10—20	2—5

Table 3

Organoleptic, Physical and Chemical Properties of Cacao Butter Substitutes

Property	Standard			
	CBE	CBI	CBR	CBS
Taste and odor	Typical for de-identified fat, flavorless and odorless			
Color	From white to cream			
Body at a temperature:				
18 °C	Homogeneous, solid or soft flexible			
40 °C	Fluidal			
Transparency at a temperature 50 °C	Transparent liquid			
Moisture content, wt. %, at most	0.2			
Acid index, mg KOH/g, at most, or	≤0.2	≤0.3	≤0.3	≤0.4
Content of free fatty acids (determined by oleic acid), at most				
Peroxide index, mmole/kg, at most	≤0.07	≤0.11	≤0.11	≤0.14
Fatty acid content, wt. %				
$C_{8:0}$	—	—	—	1—6
$C_{10:0}$	—	—	—	2.0—8.0
$C_{12:0}$	0—0.5	0—0.5	0—0.7	44—60
$C_{14:0}$	0.1—0.5	0.1—0.5	0.6—1.5	14—23
$C_{16:0}$	24—40	15—35	12—40	6—12
$C_{16:1}$	0—0.5	0—0.5	0.3—0.7	—
$C_{18:0}$	22—35	25—60	3—14	5—22
$C_{18:1}$	30—37	30—40	48—76	0—7.0
$C_{18:2}$	0.1—5	0.1—4	0.4—7.0	0—1.0
$C_{18:3}$	0.—1.0	0.—1.0	0.1—0.6	0—0.6
=> $C_{20:0}$	0.1—1.0	0.1—1	0—0.5	0—0.5
Compatibility of substitute with cacao butter in blend, %	0—100	0—100	15—20	Incompatible

[24]. The main disadvantages of cacao butter equivalents are low affinity to milk fat, insufficient stability at a high temperature, and disposition towards fat bloom.

Unlike the CBE, the cacao butter substitutes have physical properties similar to those of cacao butter, but completely different fatty acid composition [4, 25, 26].

Based on fatty acid composition of palm oil and its fractions their optimal blends with conventional oils, which meet requirements for cacao butter substitutes have been proposed; 4 CBE formulations, 3 CBI formulations, 4 non-lauric CBR formulations, and 2 lauric CBS formulations have been designed (Table 2).

The physical and chemical properties of cacao butter substitutes must meet the requirements listed in Table 3.

In terms of fatty acid composition all mentioned products comply with standards [23] on the content of saturated fatty acids and their proportions to mono- and polyunsaturated acids. The designed formulations of cacao butter substitutes cover the whole range of mentioned groups (equivalents, improvers, and replacers) and comply with requirements for compatibility with natural cacao butter [23]. The substitutes that are highly compatible with natural cacao butter are used for confectionery glazes as main type of confectionery fat. The substitutes that are partially compatible with natural cacao butter can be used in recipes for confectionery products containing cocoa powder and a small amount of cocoa solids. These oils are suitable for confectionery glaze, tablets, bars, and hollow figurines. The cocoa butter substitutes are recommended to be stored in original packaging at a temperature under 20 °C and a relative humidity up to 60%.

CONCLUSIONS

Process parameters for palm oil fractionation have been elaborated. The first stage of crystallization has been established to be held at a temperature of 22—23 °C for 60 min, while the second one at a temperature of 8—9 °C for 30 min. The cooling rate for both stages shall not exceed 0.2—0.4 °C/min. Under the mentioned conditions, high-melting (melting point +46.5 °C) and low-melting (melting point +14.75 °C) palm oil fractions have been obtained. The properties of these fractions correspond to those of palm stearin and palm super-olein. The mid fraction of palm oil with a melting point of +32—36 °C has been extracted. It is advisable to use it for manufacturing the fatty products meeting the requirements for cacao butter substitutes.

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ТЕХНОЛОГІЯ ДВОСТАДІЙНОГО ФРАКЦІОНУВАННЯ ПАЛЬМОВОЇ ОЛІЇ ДЛЯ ВИРОБНИЦТВА ЗАМІННИКІВ КАКАО-МАСЛА

Вступ. Олії тропічних рослин, як найбільш значиме джерело рослинних жирів у світі, можуть замінити традиційні види високовартісної олійної сировини у виготовленні харчових продуктів, що відповідатимуть світовим стандартам і вимогам харчової галузі.

Постановка завдання. Виявити можливість двостадійного фракціонування пальмової олії сольвентним методом.

Мета. Апробація технологій фракціонування пальмової олії для отримання високоякісних фракцій заданого складу з наступним виробництвом на їх основі замінників какао-масла.

Матеріали й методи. Рафіновану пальмову олію та її фракції досліджено термографічними, хроматографічними та стандартними титрометричними методами.

Результати. Удосконалено технологію фракціонування пальмової олії сухим методом для здійснення фракціонування двома послідовними стадіями. Встановлено наявність кріоскопічних температур — 22,8 і 8,2 °С при швидкості охолодження від 0,2 до 0,8 °С/хв. Одержано фракцію пальмової олії з температурою плавлення 33—39 °С, що містить 50 % лауринової кислоти й за своїм складом наближається до характеристик какао-масла. Розроблено склад сумішей із застосуванням одержаної середньої фракції для виробництва замінників, еквівалентів та поліпшувачів какао-масла.

Висновки. Встановлено режими сольвентного фракціонування пальмової олії для одержання середньої фракції, яка відповідає вимогам замінників какао-масла.

Ключові слова: фракціонування, пальмова олія, швидкість охолодження, середня фракція, замінники какао-масла.

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ТЕХНОЛОГИЯ ДВУХСТАДИЙНОГО ФРАКЦИОНИРОВАНИЯ ПАЛЬМОВОГО МАСЛА ДЛЯ ПРОИЗВОДСТВА ЗАМЕНИТЕЛЕЙ КАКАО-МАСЛА

Введение. Масла тропических растений, как наиболее значимый источник растительных жиров в мире, могут заменить традиционные виды дорогостоящего сырья при производстве пищевых продуктов, отвечающих мировым стандартам и требованиям пищевой отрасли.

Постановка задачи. Выявить возможность двухстадийного фракционирования пальмового масла сольвентным методом.

Цель. Апробация технологий фракционирования пальмового масла для получения высококачественных фракций заданного состава с последующим производством на их основе заменителей какао-масла.

Материалы и методы. Рафинированное пальмовое масло и его фракции исследованы термографическими, хроматографическими и стандартными титриметрическими методами.

Результаты. Усовершенствовано технологию фракционирования пальмового масла сухим методом для осуществления фракционирования в две последовательные стадии. Установлено наличие криоскопических температур — 22,8 °С и 8,2 °С при скорости охлаждения от 0,2 до 0,8 °С/мин. Получено фракцию пальмового масла с температурой плавления 33—39 °С, которая содержит 50 % лауриновой кислоты и по своему составу приближается к характеристикам какао-масла. Разработан состав смесей с применением полученной средней фракции для производства заменителей, эквивалентов и улучшителей какао-масла.

Выводы. Установлены режимы сольвентного фракционирования пальмового масла для получения средней фракции, которая соответствует требованиям заменителей какао-масла.

Ключевые слова: фракционирование, пальмовое масло, скорость охлаждения, средняя фракция, заменители какао-масла.