

Considerations to the athermic fractionation (combined) to obtain lipid by-products based on natural lipids

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Abstract

Dry fractionation, as a method to separate mixtures of natural lipids by accessing athermic fractionation processes, respectively refrigeration operating temperatures, is an alternative to wet fractionation with detergent or solvent extraction. Temperature-induced changes corroborated with other operating parameters, leading to two fractions obtained by repeated thermo-mechanical separation / fractionation: solid (stearin) and liquid (olein). The paper proposes the evaluation of quality indicators of palm oil used as raw material and of liquid lipid (olein) and solid (stearin) fractions, as a result of the athermic fractionation process through vintORIZATION and centrifugation, corroborated with accessing and monitoring of the refrigeration temperatures. The results confirm how to obtain products with different characteristics from the starting mixture, with possible subsequent utilization in food domain.

Keywords: minimal processing, athermic fractionation, structured lipids, stearin, olein, vintORIZATION, centrifugation, palm oil, refrigeration

1. Introduction

The transition from a centralized, planned economy, to the market economy, gave rise to "disease of plenty" (obesity, diabetes, cardiovascular disease, osteoporosis, various cancers), which coexist with those of malnutrition, a current phenomenon in the contemporary society [1,2].

To cope with socio-economic needs and requirements in the context of globalization, each agro-food processing company sought the diversification of nutritional food, by offering of some natural products and by-products.

Techniques of athermic conducted preparation / separation on the basis of natural animal / vegetable fat, obtain by-products results with further possibilities in various food processing

technologies. In this context, from palm oil outgoing, we proceed to athermic fractionations.

Athermic fractionation implies repeating the refrigeration cycle at certain temperature, followed by mechanical separation of fluid phase or melt of solid phase [3,4]. The athermic fractionation is a physical process, considered "natural technology" or "green", which not induce structural changes compared with the chemical procedures (hydrogenation, interesterification) [5-8].

Current processing techniques (physical, chemical, biotech or combinations), allow changing in structure and properties of natural lipids, without equivalent in nature, but better adapted to technological, nutritional or prophylactic-therapeutic [9].

These products are known in literature as „modified lipids”, derived from the term „tailor-made lipids”.

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These modified lipids have following purposes [10]: obtaining lipids with different properties as raw materials; reduce the cost of report raw material / finished product; increased stability; stable crystalline structure; providing competitive nutritional products (reduced amount of trans fatty acids).

2. Materials and Method

The experiment use aromatic palm oil as raw material, processed through thermal fractionation. Table 1 shows the characterisation of this palm oil.

The equipment used for the experiment are: Centrifuge Sorvall RT6000 Refrigerated Bench Top Centrifuge (characteristics: maxim speed 6000 rot/min, maxim capacity 4x250 mL; temperature -20 +40°C; thermostat; chilled vacuum filtration installation; microscope Bötius; refractometer Abbé).

Reagents (selective presentation): 99.5% metallic iodine (CAS 7553-56-2) (Fluka Chemie); Wijs solution (CAS 7790-99-0) (Merck); standard sodium thiosulphate solution (CAS 7772-98-7) (Fluka Chemie); glacial acetic acid (CAS 64-19-7) (Sigma-Aldrich).

3. Results and Discussion

Direct separation of palm oil previously unhomogenized vintORIZED at 8°C / centrifuged 5 minutes at 2600 rot/min not led to significant results. Prior homogenization and vintORIZATION / centrifugation at 10°C, 15min at 3600 rot/min lead to two separate distinct phases: fluid ("oily"), yellow, partly cloudy at the top of the decantor and a lower solid phase with very low fluidity, white colour.

Confirming these observations with quality parameters (indices) of palm oil (Table 1) may be allowed with sufficient accuracy that the two separate fractions are: upper - mostly unsaturated lipid fraction (olein), lower - mostly saturated lipid fraction (stearin).

Based on preliminary observations and literature, we developed the following work protocol: palm oil is melted waste (75°C, 5h), to "destroy crystallization memory". The decanted oil was processed in equal amounts in two open vessels of the same size and placed in thermostat (vintORIZATION conditions 28°C, 12h), for fractional crystallization

and physical separation (settling) of the solid fraction (stearin) from the liquid fraction (olein). Further the liquid phase, yellowish, in the superiority of vessels, was decanted and recovered in another vessel and stored at refrigeration temperature of 4°C, to avoid oxidation and subsequent processing. To achieve the objectives, the two fractions are separate individual through centrifugal force field, with separate choice of operating parameters (duration, temperature) and rotation speed. Fractions were collected in sealed plastic containers and stored at refrigeration temperature of 4°C to determinate quality indicators. The separate phases through vintORIZATION and centrifugation were evaluate phzsic-chemical and chemical To implement the process to develop a block diagram of fractional athermic, by combining two athermic dry fractionation methods: vintORIZATION and spin separation achieved by the action of external forces differential acting on the phases of different densities. The separated fractions were evaluate physico-chemical and chemical (Table 1).

The Iodine number (Table 1), as a expression of the lipids unsaturation degree) shows higher values for the liquid fractions (olein) and lower for the solid fractions (sterine), due to the presence in a greater number of double ties in olein. Unfractionated sample (palm oil), has relatively high value, probably because of the number of double bonds in the raw sample. The values obtained may be due to differences in molar mass (average) of the components of these types of fractions (solid - higher concentrations of saturated compounds (higher molar mass), liquid - concentrations in unsaturated compounds (lower molar masses)).

Values of acidity (due to the existence of free higher organic acids, basic constituents of lipids, or resulting during storage or processing): for raw material (aromatic palm oil) and lipid fractions obtained after vintORIZATION and centrifugation (I + II), are relatively low, but close (Table 1), the highest value (0.16 mg KOH/g) are for the fraction oelin II and lowest (0.10 mg KOH/g) for the control sample (aromatic oil palm). There is an approximately uniform distribution of organic higher free acids in samples.

Saponification index varies slow and does not indicate major differentiation between samples (Table 1). Thus, when the saponification index values range from 189.9 to 198.2 mg KOH/g, values were comparable between liquid and solid fractions

for control sample. The lowest values occur for the solid fractions (between 195.5 to 196.8 mgKOH/g).

Ester index (Table 2) varies according to the saponification index and can be used to determine fat fakes, if measured by high values were present.

The peroxide index (rancidity) (Table 1) is a quantitative understanding of the oxidation process in its initial phase, when food is not considered organoleptic ranced. Formation of peroxides is actually a chain reaction and existing peroxides are oxidation promoters and accelerators, highlighting their results indicate immediate consumption or processing. The peroxide index varies between 2.67 and 1.12. The highest value was recorded for the control sample, while the liquid fractions have low values in all cases. For fractions separated by vintertization / centrifugation, has in all cases lower values. Combining dry athermic fractionation techniques, corroborated by careful monitoring of operating parameters (temperature, time, rotation speed) causes a reduction of the peroxide content from the structure of a lipid modified food.

The melting temperature (Table 1), influenced by chain length and degree of unsaturation carbohydrates, exercise a direct influence on the melting temperature of the mixture triglycerides. The existence in these mixtures of triglycerides of complex fats (cholesterol, phospholipids, cephalin), has biological significance (plastic metabolic role, possibly atherogenic effect). Oleines have values of melting temperatures between 48.2°C and 13.5°C, and stearines high melting range (between 29.1°C and 59.2°C). We can say with fair accuracy that the melting temperature decreases with increasing hydrocarbon chain length and with reducing carbohydrates chain, thus reducing the degree of unsaturation.

The density (specific gravity) (Table 1) of palm oil and lipid fractions obtained from liquid and solid portions after mechanical separation, showed similar values between 0.8932 and 0.9250 g/cm³, values which are some differences between samples.

Table 1. Physico-chemical and chemical properties of palm oil as raw material and of the fractions liquid / solid which result from combined athermic fractionation

Quality indicators	Source	Dry fractionation					
	Palm oil	Vintertization		First centrifugation		Second centrifugation	
		Operating parameters		Operating parameters		Operating parameters	
		12h/28°C		4 h/3400 rot/min/18°C		4 h/3400 rot/min/10°C	
	Olein	Stearin	Olei (Soft Stearin)	Hard Stearin	Super Olein	Stearin	
CI ¹⁾ [g I ₂ /100 g]	54.6	56.5	30.5	39.6	21.3	69.4	47.3
IA ²⁾ [mg KOH/g]	0.10	0.13	0.13	0.13	0.12	0.16	0.14
IS ³⁾ [mg KOH/g]	189.9	198.2	195.5	193.7	196.4	197.9	196.8
IE ⁴⁾ [mg KOH/g]	195.4	192.7	192.23	191.5	190.3	197.1	194.7
IP ⁵⁾ [mL Na ₂ S ₂ O ₃ 0.01N/g]	2.67	2.16	2.38	1.69	2.2	1.12	1.4
PT ⁶⁾ [°C]	40.2	18.5	53	48.2	59.2	13.5	29.1
PS ⁷⁾ [°C]	38.5 ²⁾	-	-	-	-	-	-
d ₅₀ ⁸⁾ [g/mL]	0.8932	0.919	0.925	0.908	0.921	0.8781	0.8910
(n _D ⁵⁰) ⁹⁾ [-]	1.455	1.4590	1.4474	1.4510	1.424	1.4636	1.457

¹⁾CI – Iodine Number, Wijs method; ²⁾IA – Acid index; ³⁾IS – Saponification index; ⁴⁾IE – Ester index; ⁵⁾IP – Peroxid index; ⁶⁾PT – mean value from initial and final melting temperature; ⁷⁾PS – Solidification point, from literature [11]; ⁸⁾d₄₀⁴⁰ - Density, respectively relative density at 40°C; ⁹⁾n_D⁵⁰ – Refractive index at 50°C.

The refractive index (Table 1) is an important characteristic of lipids, correlated with average molecular weight and degree of unsaturation of the glycerides from lipids. Within certain limits can serve to identify different sorts of products and management of technological processes (eg catalytic hydrogenation). Refractive index has comparative values for aromatic palm oil and obtained lipid fractions (from 1.4240 to 1.4636). This is due to the presence of higher concentrations of glycerides of saturated acids with lower values for this index, compared with those corresponding to unsaturated acids. Higher values are observed for olein compared to stearine, which can be explained by the presence in the first case of higher concentrations of unsaturated compounds. Refractive index of oleines is very close to that of refined sunflower oil considered as acceptable ($n_D^{20} = 1,467 - 1,469$).

4. Conclusion

Athermic fractionation of vegetable fats (palm oil), may provide an alternative and technological perspective to wet fractionation, for diversification of physical-chemical modified/structured lipids with functional utility in food processing. There is interdependence between operating parameters and formation of the separated fractions, making difficult the isolation of their effects. However, research in the field, allowing prediction, understanding and control of lipid behavior in the desired results. Parameters operators for vintORIZATION / centrifugation (duration, rotation speed), with temperature in the refrigeration, can help optimize the operation of athermic fractionation of fat in general. Their variety with complexity of lipid system require further research.

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