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Fractionation in natural oil production tehnology. Characterization and recommendations

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Abstract

The approach from *"the natural"* perspective of food contributes to providing qualitative food products which satisfy the requests of the living cell homeostasis. In this area the *vegetable oils* are considered responsable, and that they can be, at a certain point of their existence, raw material, as well as finite product; important sources of *essential fatty acids*, that through various ways of separation which form the *"skeleton"* of the technologies of oil industry *(cold pressing, extracting)* are brought to an easily assimilated form by the human body. In the last years, the vegetable oils industry became highly attractive through the development of the newest technologies and/or through the rediscovery of the minimum processing technologies (environmently friendly, *green* technologies) through which some more "*humane*" products are obtained, easily assimilated by the human body and with increased biological activity potential. The consumer, through these information, is heading towards the consumption of vegetable oils resulted from cold pressing, persuaded by the beneficial aspects generated by the unsaturated compounds and especially of those polyunsaturated, resulted without the intervention of the chemical compounds. This constitutes an important element that characterises nutritional, structural, sensorial and functional performances of a food. The access of these "*green*" technologies (*cold pressing*) even if the extraction efficiency are poorer (absent from the technological flux of implication of exhaustive chemical reactions, that have high energy consumption and that emit effluents into the environment), but through the beneficial nature of the obtained products, contributes to a higher consumption. Also the resulted material has applications and diverse uses (pharmacy, cosmetics, medicine, food supplements etc.).

Keywords: vegetable oils, essential fatty acids, "green" technologies, unit operation, cold pressing.

1.Introduction

In recent years, the *oil press industry* has become particularly attractive by *rediscovering the minimal processing technologies* ("*environmentally friendly*", "*green*" technologies), which allow to obtain more "*humanized*" products easily assimilated by the body and with high sanogen potential. even if the separation yields are modest compared to the extraction with organic solvents. The application of the minimum processing techniques is determined by the relation: food processors - final consumer.

This, through the accessed information, is directed to the consumption of "*cold pressed*" oils, induced by the beneficial aspects generated especially by polyunsaturated compounds, without the intervention of the extraction chemicals

In the specialty literature, recognition terms such as: fat (predominantly saturated mixtures) or oil (in which the majority are unsaturated) are used. The choice of terms being conditioned by the physical state of the compound at ambient temperature, but also by tradition. In terms of specialty, lipids refer to fatty acids and their derivatives (mono-, di-,

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triglycerides and phospholipids), sterols and metabolism compounds (cholesterol).

In time, the major role in nutrition was found, being an energy source in addition to the other two basic components (carbohydrates and proteins), carriers of food utilities with beneficial effect on health maintenance (carriers of fat-soluble vitamins (A, D, E , K), essential fatty acid content (omega-3,6,9)) [1].

In certain plant and animal tissues lipids are concentrated in the proportion of 15% -60%, which allows the possibility of their separation and processing by different processes of ***dry fractionation*** (separation on physical principles (fractional crystallization conditioned by melting / solidification temperatures)), resulting in products (solid / liquid lipid fractions (stearins / oleins)), having independent characters from the raw material accessed [2].

Polyunsaturated compounds also known as "*essential fatty acids*" (compounds that cannot be metabolized naturally by the human organism, but vital for its proper functioning), are divided into three classes: **1**. omega-6 acids (cereals, eggs , poultry meat and oilseeds); **2.** omega-3 acids (alpha linoleic acid (ALA), eicosapentaenoic acid (EPA) and docohexaenoic acid (DHA); **3**. omega-9 for regulating body functions. The recommended daily dose of omega-3 acids is 1.1 -4 g, depending on sex, age and general health [17]. Lipid needs should be evaluated in terms of quantity and quality: **a**) *quantitative*, a ratio should cover 25-30% in adults, representing 1- 2 g / kg body mass / 24 hours; **b)** *qualitative*, the recommended supply of essential fatty acids must be 3-8 g / 24h [3]. The energy intake through fats should not exceed 15-17% of the caloric value of the food ration [4]. Consumption is conditioned by the physiological state of the organism and by the type of activity. It should be noted that low temperatures and high humidity require an increase in the dietary intake of lipids to 35-40% of the food ration value [5, 6]. The chemical composition of the oil has variations depending on the origin (Table 1) [7].

The dried, fried pumpkin seeds contain: 2% water, 49% fat, 15% carbohydrates and 30% protein. At a consumption of 100g, the caloric intake is on average 574 kcal. It may represent 20% of the daily value (DV) of protein, dietary fiber, niacin, iron, zinc and phosphorus. Moderate source (10-19% DV) of riboflavin, folic acid, pantothenic acid, sodium and potassium.

The main fatty acids in pumpkin seeds are: linoleic acid and oleic acid, and in small quantities palmitic and stearic acid in smaller quantities [18]. *Pumpkin oil* is obtained from pumpkin seeds (*Curcubita Pepo var. Styriaca*). The weight of the lipid material in pumpkin seeds is ≈40-50%. The lipid mixture is rich in unsaturated fatty acids, palmitic acid, proteins and vitamins (A, C, K and E). The tocopherol content (vitamin E) represents 320-520 mg / kg of oil [7]. *Vitamin K* is one of the factors involved in the blood coagulation process, is an activator of osteocalcin (a protein that plays a role in metabolism of bone synthesis), and in plants plays a role in photosynthesis [19].

The separation / fractionation operation (*cold pressing, extraction*) represents an important phase in the processing technology of oil plants. The choice of operation has a direct effect on the quality and quantity of the product (*oil + protein + accompanying substances*). In figure 1 are presented in the form of a flow, the main unit operations encountered in food manufacturing technologies.

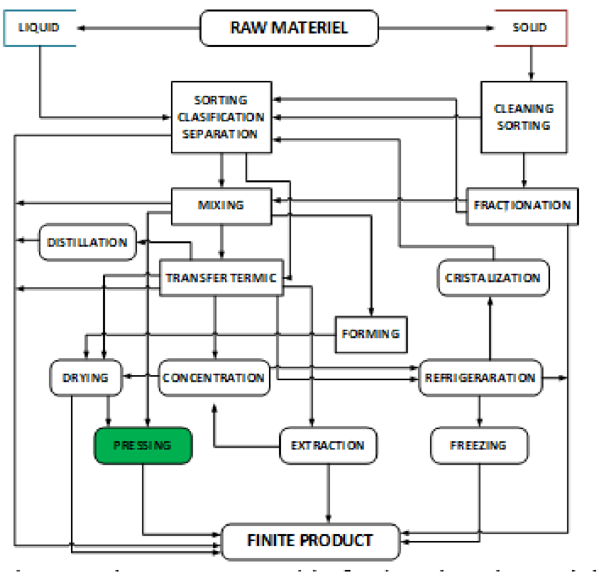

Figure 1. The main operations encountered in food engineering and their interaction.

In the specialized technique - for the case of separating the oil from the oily plant material - terms like "*pressing*" and "*extraction*" are used.

Pressing, represents the *mechanical separation* operation with reference to the separation of vegetable oils under the action of an external force (hydraulic force), whereby the liquid phase is separated from the solid phase.

Extraction is a process of partially or totally separating the liquid phase from a liquid-solid mixture by means of a *solvent*, having as a substrate the solubility difference. The operation is based on the transfer of the substance by molecular diffusion (convective or other forms) and involves two stages: **1.** the contact between the mixture and the solvent; **2**. fractionation of the resulting phases; **3**. recovery of solute and solvent [8]. In general, four basic methods are used for separating a vegetable oil (Figure 2).

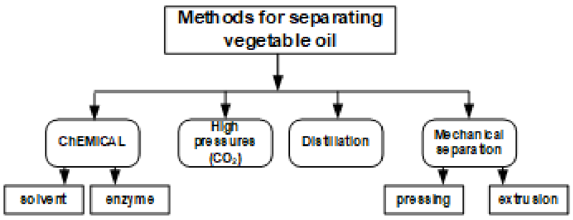

Figure 2. General methods of separating the oil from the plant material

When ***pressed***, the resulting product (*raw oil*) can be *consumed / used* as such, or processed by *dry fractionation*, when separate products (solid / liquid (stearine / olein)) are obtained, with new functions. In this area, the *hydraulic press* (England - patented in **1795** by *Joseph Bromah*) and *the screw press* (**1900**, *VD Anderson, US*) are used, which has some advantages over the hydraulic press: continuous operation, high working capacity, operation without high shocks and vibrations, easy to adjust working pressures [9, 10]. Figure 3 shows the block diagram of the oil material processing operations in order to obtain *press oil* [7, 11].

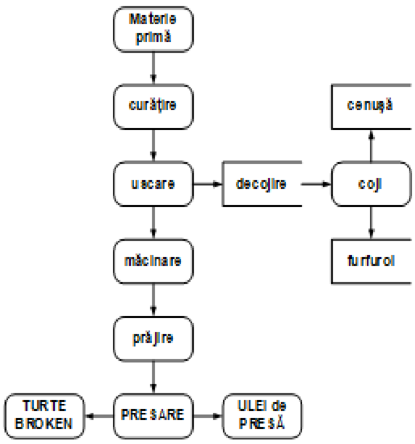

Figure 3. The block diagram of the operations for obtaining the press oil

2.Materials and methods

2.1.Materials

Dried pumpkin seeds, fried. **Method**: cold pressing. **Machine / equipment**: hydraulic press. **Reagents** (Sigma-Aldrich, Merck) of analytical purity.

2.2. Obtained results

Scakeing from the literature study, under the conditions of a family business, which sells ***raw oil*** (***cold pressing***), we proceeded to adapt / elaborate a scheme of operations for obtaining oil from pumpkin seeds (Figure 4). On the block diagram of operations the main operations that induce physico-chemical changes (drying, frying), involved in the process of obtaining the raw press oil are presented. The main operation describes the *pressing operation*, as a "*green*" operation, of ***fractionation / separation***, in which the intervention of the chemical compounds is practically absent.

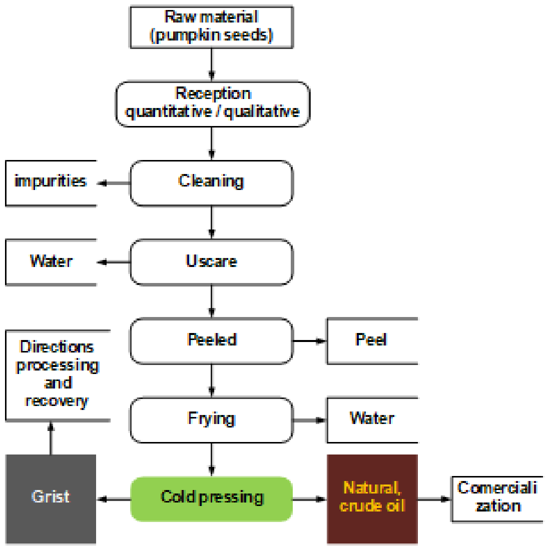

Figure 4. The block diagram of operations, proposed for obtaining the natural raw press oil (*cold pressing*).

Drying (*moisture-air balance*): the seeds should be harvested at a humidity of ≈10% in order to ensure proper transport and storage conditions. Failure to observe this value contributes to the degradation of the material, so it is necessary to periodically check and bring the material to optimum humidity. Excessive humidity reduces the oil separation efficiency [7]. The drying mode is chosen according to the processing capacity / 24h. Thermal transfer to drying is *conductive / convective*.

It is important to establish the parameters of the humid air (*vapor pressure, dew point, temperature*), corresponding to the degree of saturation of the contact air with the mass of water released upon drying. Under these conditions, the moisture absorbed by the material during storage must be taken into account, with negative influences on further processing [12]. Water removal from the product can be achieved by two processes [8]: **1**. *surface water vaporization* - when the water vapor pressure exceeds the vapor pressure above the product; **2**. *entrainment with air or combustion gases* - with the help of a low pressure air flow that "*washes*" the surface of the product, creates a pressure difference, thus the surface water diffuses into the air. All this implies knowledge of how the water is bound (physical (capillary), chemical, osmotic (predominantly)), which subsequently contributes to the proper choice of drying techniques and equipment, with optimal results. The mass of water present in the cells is conditioned by the chemical composition and inversely proportional to the lipid phase content [7]. The *kinetics of the operation* are mainly conditioned by the following factors: **1**. the speed, the displacement of the thermal agent, which conditions the evacuation of the water vapor formed on the surface of the material; **2**. the drying time, which is inversely proportional to the flow rate of the thermal agent. Table 2. presents the conditioning parameters for seed drying [7].

Table 2. Drying conditioning parameters of oilseed material

Speed of the thermal agent (m/s)	Drying time (min.)
0.35	20
0.37	30
0.05	52

The increase of the temperature of the thermal agent, determines the amplification of its saturation voltages, reducing the relative humidity and increasing the efficiency of the process.

Roasting - a hydro-thermal treatment, conditioned by time, with continuous mixing. *Purpose*: a) to generate physico-chemical transformations of the components and modifications of the particle structure; b) obtaining the maximum yield when pressed; c) increasing the quality of the finished products and partial deodorization. *Phases* of the operation: 1. wetting the grinding and the rapid increase of the grinding temperature; 2. drying the mixture with the required humidity and temperature for the pressing operation [11, 12].

Wetting - contributes to a series of modifications of some indicators, such as: plasticity, particle agglomeration, chemical and biochemical state changes, contributing to the separation efficiency. The frying operation induces the following changes: a) of the liquid phase - it consists in reducing the viscosity of the oil and the surface tension, as well as the evaporation of the ground water; b) modification of the gel phase - by distorting the protein substances, when the structure of the grinding becomes elastic and relaxed and favors the displacement of the oil under the action of pressure. The enzymatic activity decreases and disappears completely in the second stage of frying, because the enzymes are thermosensitive. The proper choice of operating parameters contributes to: 1. maintaining the quality of the press and the remaining oil; 2. no changes of the accompanying substances (phosphatides, vitamins, antioxidants) occur. For example, at 70˚C and at a heat flow of 3°C / s, a low acidity oil results in a twice-lower peroxide index, and the protein denaturation is 1.44-1.75%, compared to 9.33% at 110°C [12].

Pressing: defined as an operation of separating the liquid phase from the solid matrix under the action of an external force. The result is the raw oil (natural oil). Acquiring and knowing the operating parameters can contribute to advanced separation efficiency of 80-85%, the oil difference being separated by chemical extraction procedures. Operation similar to filtering: 1. both are conditioned by pressure; 2. both involve the passage of a fluid flow through a porous material. The porous material in this case is the cake [13]. The applied pressure is variable depending on the purpose and the construction of the device: from 20 kPa to 100 MPa [14]. Pressing equipment can have different names depending on the operation they serve: presses, extractors, extruders, etc. The applied pressure must overcome the resistance of the solid matrix to deformation and compaction, to create cracks at the cellular level and to compensate the pressure drops when the fluid passes through the porous layer. The efficiency of the pressing operation is dependent on the following factors:

1.The compressibility of the porous layer conditioned by its mechanical properties (rigidity, flexibility, hardness). For a ductile solid, absent of fluid, the relationship between the applied pressure and the degree of compaction (volume reduction) can be expressed with the relation for which the pressure losses required to break the cell membrane and maintain a constant fluid flow are neglected [12]:

$$\log\frac{V-V_\infty}{V_0-V_\infty} = -K_k \cdot P \qquad (1)$$

where: V – volume of compressed cake, m^3, depending on the pressure P; V_0 – volume of cake before pressing; V_∞ - the volume of cake resulting from the application of infinitely high pressure (minimum volume resulted); P – pressure applied, Pa; K_k – compressibility constant, Pa^{-1}.

2.Fluid viscosity: both the liquid release rate and the final yield are negatively affected by a high viscosity. In most cases, the viscosity of the liquid (***oil***) is dependent on the applied pressure and the separation efficiency. Thus, the higher the separation efficiency, the higher the viscosity [15], because the composition of the oil to be separated changes depending on the size and duration of the force applied to the pressing. Frequently, the term "***premium oil***" expresses the highest quality product. *By gradual, fragmented application of different sizes of forces, different quality products and functions are obtained. This working method can be* ***associated with dry fractionation methods***.

3.The size of the pressing force is conditioned by the pressing element (piston, snail, pneumatic chamber, blades). The gradual increase of the force is recommended, because by applying a maximum force the solidification takes place with the fluid retention (=reduced separation yields). The pressing operation can be associated with the capillary filtration expressed by the relation [12]:

$$V = \frac{\pi \cdot P \cdot d \cdot \tau}{128 \cdot \eta \cdot l} \ [m^3] \qquad (2)$$

where: V - separated oil volume, m^3; P – pressure applied, daN/cm^2; l – the length of the capillaries, m; τ - duration of pressure application, s; η – dynamic viscosity, Pa·s.

Depending on the constructive-functional characteristics of the presses, the pressure P can have the following values: **a**) low capacity presses (4,16÷13,88(·10^{-3}) kg/s), P=250-280 daN/cm^2; **b**) high capacity presses (flow >0,0277 kg/s), P=400-3000 daN/cm^2 [12, 13].

4.Duration of the application of the pressing force is determined by the relationship [12]:

$$T_s = \frac{V_s \cdot E_s}{Q_V \cdot (1-\beta_s)} \ [s] \qquad (3)$$

where: V_s – the volume of free space in the press area, m^3; E_s – pressing coefficient; Q_v – the volume flow of grinding in the press, m^3/s; β_s – correction coefficient.

Depending on the constructive-functional characteristics of the press, the application time of the force is in the range 40-200s, influenced by the height of the cake, the physico-chemical characteristics of the machine, and in the case of screw presses, the speed [22].

5.Productivity is given by the relationship [12]:

$$Q = 60 \cdot V \cdot \rho \cdot \varphi \cdot n \cdot h \cdot (1-k_r) \text{ and}$$
$$V = \pi \cdot D \cdot L \cdot (1-f)$$

where: Q – productivity, kg/s; V – the free volume of the supply chamber, m^3; D – the inside diameter of the pressing chamber, m; L - the length of the grinding movement, m; f – coefficient of occupancy of space by the pressing elements (f=0,312); ρ - the density of the material at the entrance in the press, kg/m^3; φ - free volume filling with grinding coefficient; n – screw speed, rot/min; k_r – reflux coefficient.

The ***resulting raw oil*** is naturally dark brown (Figure 5) due to its carotenoid and chlorophyll content. It can be consumed as such, recommended in kidney diseases, or integrated into various bakery products. It was subsequently characterized by determining: **1**. *acidity index* (IA), mg NaOH / g product [15]; ***2***. *the peroxide index* (IP), mL Na2S2O3 0.01N / g sample [15]; 3. *Iodine value* (CI), Wijs method (iodine monochloride) (g I2 / 100 g sample) [16]. The results are shown in Figure 6.

Figure 5. Raw press oil (obtained by cold pressing).

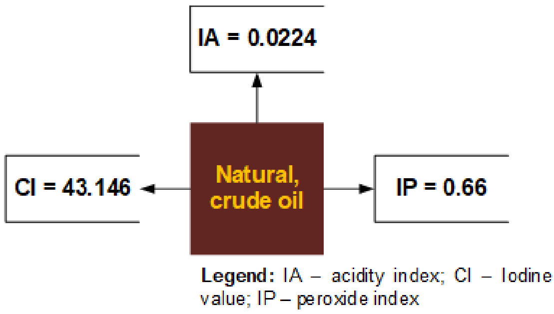

Figure 6. Presentation of results of the determinations made on the natural cold pressed oil

The values of the acidity and peroxide index (otherwise low), confirm that the presence of free acids is low, so they can be found in a higher quantity in the cake. Also the degree of unsaturation, expressed by the figure of iodine (CI), contributes to the reassessment of the process of cold separation. A continuation of this (figure 7), from which new products with technological value and nutritional-functional value are consumed, consumed or used as raw material becoming food utility carriers to emerging fields.

From Figures 6 and 7 the following are observed: management of the process of obtaining the oils in their natural state, by physical processing techniques, cleaning (cold pressing) can be controlled, subsequently conducted, through a detailed study of the influencing factors that compete with the mode of final application of the operating parameters on each operation.

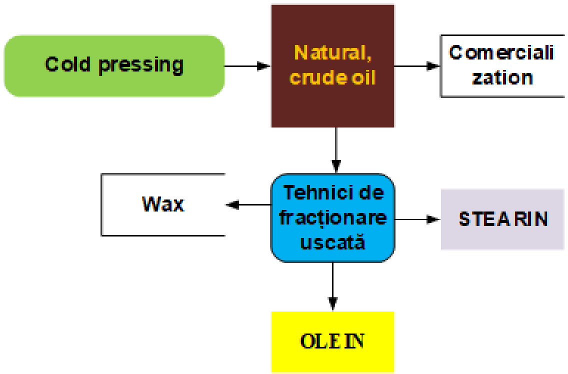

Figura 7. Block diagram, proposed to continue the recovery by means of ***dry fractionation*** techniques of the raw oil.

Finally, based on the block diagram of operations (Figure 4), the balance of materials was prepared on each phase, for the processing of a mass of 10000 kg pumpkin seeds, centralized in Table 3, considering the following technological data: the remaining shell content in the core following peeling is 2.4%; the content of botanical shell in seeds 14.3%; the existing shell content in the technological fraction called eliminated shell, 97.4%; initial seed moisture, 10.7%; after the drying operation the seed moisture is 5.1%; the oil content of pumpkin seeds is 49%; the oil content that remains in the brochure resulting from pressing is 19.41%; the yield of the pressing operation is 84%; losses during the cleaning operation, 2.8%.

Table 1. Chemical composition of some oilseeds

Surce	Skin [%]	Chemical composition [%]					
		humidity	Raw oil	protein	NES[1)]	cellulose	ash
Sunflower	14-28	9-11	44-48	18-20	10-15	14-18	2-2
Soy	7-12	11-13	17-19	33-36	20-23	3-6	3-5
Flax	4-6	9-11	35-38	25-27	20-23	4-5	3-4
Colza	4-6	6-8	23-42	25-28	17-20	4-6	3-5
Pumpkin	24	9-11	35-54	28-30	15-20	13-20	4-5

[1)] NES - non-nitrogenous extractive substances

Table 3. Total material balance.

Input materials			Output materials		
Crt.no.	**Name**	**Mass (kg)**	**Crt.no.**	**Name**	**Mass (kg)**
1	Pumpkin seeds	10000	1	***Press oil***	**2894.77**
			2	Impurities	280
			3	Evaporated water (drying)	574
			4	Shell	1145.65
			5	Evaporated water (frying)	116.31
			6	***Groats***	**4989.27**
Total		**10000**	**Total**		**10000**

4.Conclusions

In general, the consumption of crude press oil is of particular importance through the bioactive compounds that support and regulate the functions of the body while maintaining the health status, which contributes to the development of this branch of the food industry. The evolution of the contemporary human being conditioned by the severity of the nutritional disorders, metabolism (obesity, diabetes, cardiovascular diseases, osteoporosis, different types of cancer, malnutrition), has led to the *rediscovery of the processing technologies on physical principles* resulting in products with high bioavailability. These technologies are simple, easy to access and "*environmentally friendly*".

This paper brings to attention the operation of *cold pressing*, a physical, independent process, which allows the unaltered preservation of the compounds, even if the separation yields are modest. This shortcoming can be compensated by the detailed, combined analysis of the influence factors and the operating parameters (nature of the material, temperature, humidity, calculation of the pressing force, time, the advance velocity of the pressing element). The resulting product, by knowing the *physical properties* (melting / solidification interval), can be further processed by physical modification / formulation procedures (*dry fractionation*), which would increase the economic value, the technological and nutritional utility and functionality.

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human / or animal subjects (if exist) respect the specific regulation and standards.

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