Vol. 3, No. 1, 2020

Ye. Semenyshyn[1], V. Atamanyuk[1], O. Dobrovetska[1], T. Rymar[2]
Lviv Polytechnic National University,
[1] Department of Chemical Engineering,
[2] Department of Heat Engineering and Thermal and Nuclear Power Plants,
yevhen.m.semenyshyn@lpnu.ua

OIL EXTRACTION FROM THE SUNFLOWER SEEDS, MECHANISM AND KINETICS OF THE PROCESS

https://doi.org/10.23939/ctas2020.01.155

The results of the research of extraction of oil from the none-crushed and crushed sunflower seeds of different fractions by the method of extraction are presented. The mechanism of extraction and process kinetics is investigated. It has been shown that the process of extracting oil from sunflower seeds is complex and consists of both intra-diffusion and external-diffusion transfer of oil. It is stated that the process is similar to the extraction of the target components from the seeds of most types of plant raw materials. The method of experimental determination of the diffusion coefficient as the slowest stage of the process, which determines the speed of the entire extraction process, is presented. It has been shown that the extraction of oil by the extraction method can be carried out more efficiently than the pressing method, especially in cases where the oil content of the seeds is low.

Key words: extraction, sunflower seeds, extraction kinetics, n-hexane.

Introduction

The process of extraction of target components from vegetable raw materials is widely used in various industries, especially in food, pharmaceutical, chemical, petroleum and others [1, 2]. Sunflower has a great demand from agricultural businesses both in Ukraine and in other countries, which contains up to 50 % or more oil, depending on the natural conditions. Sunflower is the main agricultural crop because it contains, in addition to oil, protein and other target components [3], which are used in various industries. The biological value of sunflower oil in international units is 55.0 [3].

Worldwide sunflower processing is currently estimated at approximately 46,6 million tonnes [4]. It is worth emphasizing that Ukraine exports sunflower oil to more than 100 countries. In the structure of world exports of sunflower in 2017–2018 Ukraine occupies the first place, its share is 29 %, which is about 5 times more than in China [4]. Over the last decade, Ukraine's oil and consumer complex has been characterized by a constant increase in sunflower oil and meal production. According to theforecasts of the USA, the production of sunflower oil and meal in Ukraine in 2019–2020 will increase and will approximately amount 6.2 million tons of oil [4]. Therefore, the high demand for sunflower oil requires the use of more efficient technologies for its extraction.

Nowadays there are practically two methods of extracting oil from sunflower seeds: pressing and extraction. Each of these methods has its advantages and disadvantages. The advantage of the press method is the relatively simple technological process. The disadvantage is the high energy costs associated with the use of complicated metal and expensive equipment. In addition, the implementation of the press method results in a low oil extraction only up to 20 %, since in the meal remains up to 15 % of the oil. Significant energy costs are associated with the operation of existing complicated technological equipment, etc.

The advantage of the extraction method is the high degree of extraction of oil, which is 97–98 %, the use of simple technological equipment and lower energy costs associated with the operation of technological equipment. The disadvantages of the extraction method include the need for the usage of flammable solvents, the complexity of the process of solvent regeneration, the involvement of highly qualified service personnel, etc.

In [5] tendencies of development of the basic methods of extraction of vegetable oils with the use of hydrocarbon solvents (gasoline, hexane, heptane, etc.) are presented. Under industrial conditions, extraction of vegetable oils with alternative solvents is performed: acetone, isopropyl alcohol, ethyl alcohol, binary mixtures of organic solvents or mixtures with water, liquefied gases or supercritical liquids [6].

The use of new types of solvents is the basis for reducing the energy intensity of production. Traditionally polar organic solvents are used as solvents. H-hexane is currently the only commercially available extractant [7]. Methods of extraction of sunflower oil with ethyl alcohol are known [8], but using as an solvent in the hydromodule of absolute alcohol has three times less refining effect compared to n-hexane [7].

The use of hot pressing compared to cold requires considerable energy costs for the drying and heating of the seeds to provide a moisture content of approximately 5 % and reduce the viscosity of the oil. The availability of heat transfer equipment requires additional energy consumption and the use of more efficient drying methods [11–13].

Taking into consideration these advantages and disadvantages of traditional methods of extracting of sunflower oil from seeds, it is more effective today to combine the two methods pressing and extraction with good economic justification.

Extraction of the target components from the vegetable raw material compared to the mineral raw material is a complicated process. The complexity of this process is due to the cellular structure of the raw material and the presence of a low permeable membrane in the seeds of plants. In addition, the difficulty of the process is compounded by the fact that the target component moving within the grain to the surface of the phase of contact must overcome a number of barriers that are specific to the complex grain structure. It should be emphasized that the movement of the target component in the middle of the grain to the surface of the phase of contact and from the surface of the phase of contact to the bulk of the solution is carried out at different speeds, so the whole process must be considered as a combination of intra-diffusion and external-diffusion mechanisms. It is also important that the speed of the process of extraction of the target components depends on whether the component is solid or liquid. The impellent of the extraction process depends on it.

Materials and methods of researches

To establish the mechanism of the process, experimental researches were conducted to identify the processes of moving of the components in the the grain and from the surface to the bulk of the solution. Experimental researches to establish the mechanism and kinetic regularities of the process of extraction of oil from the not grinded and grinded sunflower seeds were carried out in a Soxhlet apparatus at a boiling temperature of a solution of 65–67 °C. As the solvent was used n-hexane. Sunflower seeds were previously dried to a humidity of 3–5 %, grinded and milled into fractions with dimensions d_{midl} = 0.3 mm, d_{midl} = 0,5 mm, d_{midl} = 0,75 mm, d_{midl} = 1.25 mm. The humidity of seeds was determined by weighting method. A sample of grinded or not grinded sunflower seeds (75 g) was poured into a cartridge of filter paper, which was loaded into the extractor. The volume of the solvent was 500 ml. The extraction process was performed at the boiling temperature of the solvent.

After certain intervals of time, the extraction process was stopped and samples of the solution were taken, adding the pure solvent in the amount of taken sample, and then the mixture was again heated to the boiling temperature of the solution. Samples were filtered through a paper filter using a vacuum pump and the oil concentration was determined by weight method [14].

The results of the kinetics of the process of extraction of oil from not grinded and grinded sunflower seeds of different fractions are presented in Fig. 1.

The analysis of experimental results presented in Fig. 1, showed that the extraction process from the not grinded sunflower seeds proceeds very slowly and lasts for several days, what is explained by the complex grain structure. The movement of the target component (oil) in the grain occurs mainly by the intra-diffusion mechanism. The transfer of the substance from the grain surface to the bulk of the solvent proceeds more intensely by the external diffusion mechanism. Due to the fact that the slowest stage determines the speed of the whole process, it can be assumed that the extraction process for the not grinded sunflower seeds proceeds mainly by the intra-diffusion mechanism. As for the grinded seeds (curves 1, 2, 3, 4), the process consists of two periods, which proceed at different speeds – by internal and external diffusion mechanisms similarly to oil extraction from the other objects of plant raw material seeds [1, 2, 8–10].

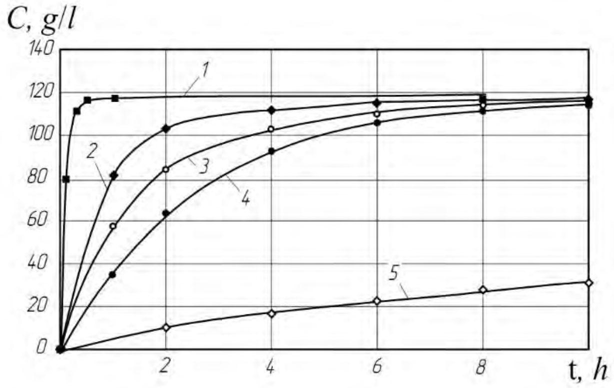

Fig. 1. Kinetics of oil extraction for not grinded and grinded sunflower seeds of different fractions with n-hexane at the boiling temperature of the solvent in the apparatus with a mixer: 1 – grinded seeds with d_{midl} = 0.3 mm; 2 – grinded seeds with d_{midl} = 0.5 mm; 3 – grinded seeds with d_{midl} = 0.75 mm; 4 – grinded seeds with d_{midl} = 1.25 mm; 5 – not grinded seeds

The exterior diffusion mechanism is characterized by a rapid increase of concentration. The first period is characterized by a slow increase of concentration, since the penetration of the target component to the surface of the phase of contact is mainly occured by internal diffusion. Thus, in general, the process of oil extraction is carried out by a mixed internal and external diffusion mechanism. That is, the reduction of grain particle size in the case of grinding approximates the kinetics of extraction to the external diffusion mechanism.

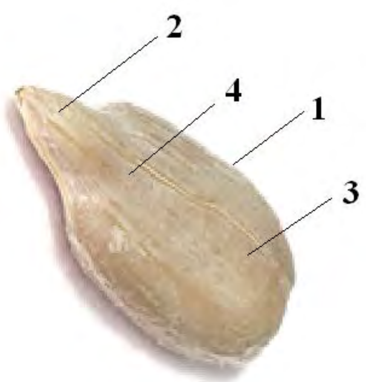

Fig. 2. The structure of the section of sunflower: 1 – membrane partition; 2 – embryo; 3 – perisperm; 4 – cell

It is important to note that the internal-diffusion transfer is caused mainly by the complex grain structure, its thin film, which resists the penetration of the target component to the surface of the phase of contact. The complexity of the grain structure of vegetable raw materials can be confirmed by similar grain structure shown in Fig. 2, in the form of section.

Results and discussion

To study and establish the mechanism and theoretical foundations of the process of extraction of oil from sunflower seeds, we use the equation obtained by the method of integral relations for the extraction processes of the target components of both mineral and vegetable raw materials, in which the target components can be solid (sulfur) and liquid (oil). For mathematical description of the extraction process with some assumption, a physical model of grain in the form of a sphere (Fig. 3) is adopted, in the pores of which the target component is subjected to be extracted [1, 2, 8–10].

$$\tau = \frac{t}{T} = \frac{1 - 3\cdot\varphi_0^2 + 2\cdot\varphi_0^3 + \frac{6}{\varepsilon}\cdot(1-\varphi_0) + \frac{2}{Bi}\cdot(1-\varphi_0^3)}{1 + \frac{6}{\varepsilon} + \frac{2}{Bi}}, \quad (1)$$

where τ – dimensionlesstime; *t* – the running time of extraction; *T* – time of complete extraction of the target component; φ_0 – the dimension lessradius of a poro us grain particle (weassume approximately that thegra in look slikeasphere), in which the target component is placed; $\varphi_0 = \frac{r_0}{R}$, where r_0 – the radius of the sphere in which the target component is located; *R* – the radius of the grain; $Bi = \frac{K\cdot R}{D}$ – Bio criterion; *K* – masstransfer coefficient; $\varepsilon = \frac{K_{r_0}\cdot R}{D}$ – chemical interaction criterion; K_{r_0} – chemical interaction constant; *D* – diffusion coefficient.

The values of the Bio criterion and ε can be determined from the equations obtained on the basis of the method of linearization of equation (1).

The value of $\varphi_0$corresponding to a specific extraction time *t* is determined from the material balance:

$$G_0 = (1-\varphi_0^3) = W\cdot C, \quad (2)$$

where G_0 – theinitialmassoftheoilinthegrain, g; W – volume of solvent in the extractor, l; C – the concentration of oil in solution, g/l.

The value of φ_0 varies from 0 to 1.

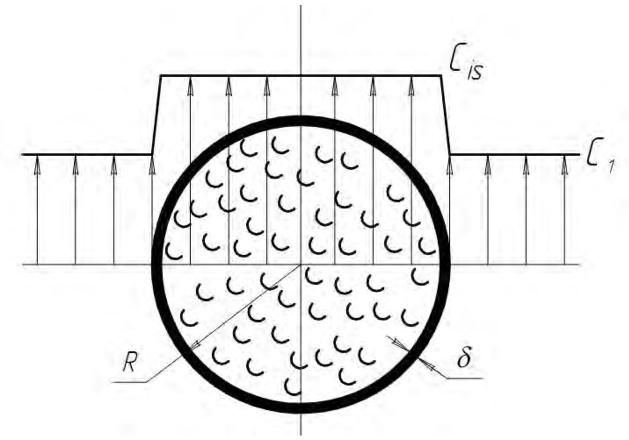

Fig. 3. Scheme of a simplified physical model of extraction of target components from sunflowers eeds (δ – film thickness, C_1 – the concentration of oil in the main mass of solution, kg/m^3; C_{is} – the initial concentration of oil in the seed, kg/m^3)

For the conditions of extraction of oil from sunflower seeds three mechanisms are possible: internal-diffusion ($\varepsilon = \infty$, $Bi = \infty$), external-diffusion, for which ($\varepsilon = \infty$, $Bi \geq 1$); mixed external diffusion and internal diffusion ($\varepsilon = \infty$).

For the internal-diffusion mechanism conditions, equation (1) is reduced to the form:

$$\frac{t}{T} = 1 - 3\cdot\varphi_0^2 + 2\cdot\varphi_0^3. \tag{3}$$

For the diffusion dissolution conditions, equation (1) is reduced to the form:

$$\frac{t}{T} = 1 - \varphi_0. \tag{4}$$

Equation (4) holds for chemical interaction and externally-diffusion dissolution, since formally $\varepsilon = \infty$ for particles of spherical form $Bi << 1$ and this condition is not realizedBut in the case of chemical interaction, provided that $\varepsilon = \infty$ and $Bi \leq 1$ give curves of the same nature.

For mixed-diffusion conditions, the equation is reduced to the form:

$$\frac{t}{T} = \frac{1 - 3\cdot\varphi_0^2 + 2\cdot\varphi_0^3 + \frac{2}{Bi}\cdot\left(1-\varphi_0^3\right)}{1 + \frac{2}{Bi}}. \tag{5}$$

To establish the extraction mechanism, it is necessary to identify the experimental data from the kinetics of extraction as a function $C = f$ (t) with the theoretical (equation (3)) as a function $\Phi = f$ (t) $(\Phi = 1 - 3\cdot\varphi_0^2 + 2\cdot\varphi_0^3)$ Fig. 4.

$$D = \frac{R\cdot C}{\rho\cdot\eta}, \tag{6}$$

where ρ – densityoftheparticle, kg/m^3; R – the particle radius, m; η – the oil content per unit mass.

The determined diffusion coefficients for sunflower oil in the studied range of change of initial parameters are $1.5\cdot10^{-11} - 10^{-12}$ m^2/s.

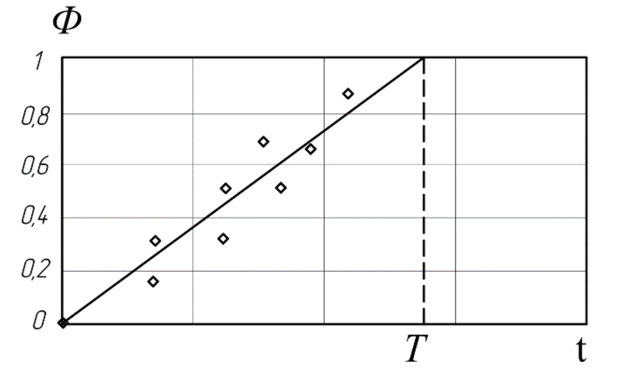

Fig. 4. Determination of the diffusion coefficient D

Such a model does not claim high accuracy, since the structure of the seeds is much more complex (Fig. 2 where show sections of grain sunflower).

Analysis of researches of the mechanism and kinetics of oil extraction from sunflower seeds showed that the speed of the extraction process also depends on the size of the grain. Therefore, the grinding processes associated with energy consumption should be taken into account in the technological schemes of extraction of components in the form of the effect of dispersion on the kinetics of the process.

Assuming that the mass of the oil contained in the grinded seeds is removed by the internal- M_2 and external-diffusion M_1 mechanism, then at time t will be extracted the mass of the component M:

$$M = M_0 - (M_1 + M_2) = \\ = M_0\cdot\left[1 - \varphi_{\text{dis}}^3\cdot\alpha - (1-\alpha)\cdot\varphi_e^3\right], \tag{7}$$

$$\alpha = \frac{M_1}{M_0}, \quad M_1 = \frac{\pi\, d_0^3}{6}\cdot\rho_0\cdot n, \quad M_2 = \frac{4\pi\, R^3}{3}\cdot\rho\cdot m,$$

where ρ_0 – oildensity, kg/m^3; n – the number of particle sonwhichsur faceis the oil; ρ – the amount of oil per unit volume of particle, kg/m^3; m – the number of particles in the pores of which there is oil, d_0 – the initial diameter of the particle, m, M_0 – initial oil content, kg.

Considering the above conditions, it is possible to obtain the equation in the form:

$$C = \frac{M_0}{W}\cdot\left[1-\alpha\left(1-\frac{t}{T_{\text{dis}}}\right)-(1-\alpha)\times\right.$$
$$\left.\times\left\{\frac{1}{2}\pm\cos\left[60^0+\frac{1}{3}\arccos\pm\left(1-2\frac{t}{T_e}\right)\right]\right\}^3\right]. \quad (8)$$

The equation is valid for conditions of constant impellent ΔC = const ($\Delta C = C_{\text{eq}} - C_1$).

In Fig. 5 the effect of grain particle size on the mechanism of the process is shown. In Fig. 5 the following areas are available: α = 1 is characterized by the mechanism of exterior diffusion extraction; α = 0 is characterized by the mechanism of internal-diffusion extraction.

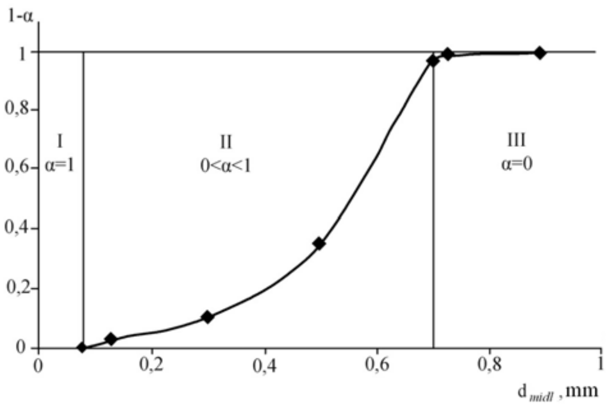

Fig. 5. The influence of the size of the raw material grinding on the degree of extraction of oil, in the form of dependence $1-\alpha = f(d_{\text{midl}})$

According to the results of experimental researches of the process of extraction of sunflower oil from grinded seeds, in particular, for the investigated range of fraction 0.3 mm < d_{midl}< <0.75 mm, it is characteristic that the process proceeds by a mixed (external and internal diffusion) mechanism, so a compatible process of dissolution and extraction occurs, for what mass fraction of the oil in the raw material extracted by a mixed mechanism for which α lies within 0 <α <1.

For the fraction sunflower seeds with size d_{midl} = 1.25 mm, the extraction process proceeds mainly by the intra-diffusion mechanism, that is, for which α = 0. For the fraction sunflower seeds with size d_{midl} < 0.3 mm, the extraction process proceeds mainly by the externally-diffusion mechanism, that is, for which α < 1.

Conclusions

Consequently, the researches confirmed that the process is similar to the extraction of the target components from the seeds of most types of vegetable raw materials. The kinetics of the mass transfer process of extraction of sunflower oil from grinded and not grinded seeds has been investigated. The analysis of the process indicates that one of the most influential factors in the process of intensification of internal transfer is the grinding of grain, the purpose of which is to break down the barriers of penetration of the component. For the investigated range of the fraction d_{midl}> 0.3 mm is characterized by the fact that the process proceeds by a mixed (exterior and intra-diffusion) mechanism, so a compatible process of dissolution and extraction occurs.

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Є. М. Семенишин[1], В. М. Атаманюк[1], О. Я. Добровецька[1], Т. І. Римар[2]
Національний університет "Львівська політехніка",
[1] кафедра хімічної інженерії,
[2] кафедра теплоенергетики, теплових та атомних електричних станцій,
yevhen.m.semenyshyn@lpnu.ua

ЕКСТРАКЦІЙНЕ ВИЛУЧЕННЯ ОЛІЇ З НАСІННЯ СОНЯШНИКА, МЕХАНІЗМ ТА КІНЕТИКА ПРОЦЕСУ

Наведено результати досліджень вилучення олії з неподрібненого та подрібненого насіння соняшника різних фракцій методом екстрагування. Досліджено механізм екстрагування та кінетику процесу. Показано, що процес вилучення олії з насіння соняшника складний і складається із внутрішньо-дифузійного і зовнішньо-дифузійного перенесення олії. Вказано, що процес є аналогічним екстракційному вилученню цільових компонентів із насіння більшості видів рослинної сировини. Наведено методику експериментального визначення коефіцієнта дифузії як найповільнішої стадії процесу, яка визначає швидкість всього процесу екстрагування. Показано, що вилучення олії методом екстрагування можна здійснити ефективніше порівняно з методом пресування, особливо у тих випадках, коли вміст олії в насінні низький.

Ключові слова: екстрагування, насіння соняшника, кінетика екстрагування, н-гексан.