MATHEMATICAL MODELING OF OIL EXTRACTION FROM WALNUT CRUMBS WITH SUPERCRITICAL CO_2

Jenac A.
Migalatiev O., Caragia V.

Scientific and Practical Institute of Horticulture and Food Technologies
Jenac A.: e–mail: ana.jenac@mail.ru

Abstract: In this article are presented the results of scientific research on the CO_2–extraction of oil from walnut crumbs. The walnut oil was extracted at different parameters of temperature (35–55°C), pressure (10–40MPa) and time (20–150 min.). Using the central rotational program of planning experiments it was established that it is necessary to perform 20 experiments (in parallel) so that the data obtained can be processed mathematically. It was established that the CO_2–extraction of oil from walnut crumbs is adequately described by a polynomial of second degree. The most significantly parameter that influence the extraction process is the pressure. The maximum yield of oil was obtained at 40 MPa, 55°C and 120 minutes.

Keywords: walnut crumbs, CO_2–extract, mathematical design of experiments, response surface

Introduction

The carbon dioxide is the most widely used solvent for the extraction, because it is almost completely eliminated from the obtained products, it has a wide range of extraction of chemical compounds (carotenoids, diglycerides, monoglycerides, sterines, tocopherols, terpenes, organic acids, glycosides, minerals, phenols, tannins, etc.) and it's harmless to the environment.

This method of extraction features similar yields to conventional extraction techniques (extraction with hexane, dichloromethane, butane), but require specific conditions, such as extraction pressure, temperature, particle size and fluid flow rate [1].

The walnut crumbs, are derived from mechanical breakage of the walnut shell and are sized from 2 to 5–6mm. Following this process, it obtains up to 30–40% of walnut crumbs which are used for industrial purposes: in confectionery, bakery or for oil production. Given that walnut crumbs are remnants of walnut processing that quickly alters, a solution of their efficient utilization is the extraction of their lipid fraction with supercritical carbon dioxide. The raw material, crumbs of walnut kernel was provided by "Prometeu–T" a walnut processing plant.

In this context, the aim of researches is to determine the optimal parameters of oil extraction from walnut crumbs with supercritical CO_2, but also to obtain functional relations between the yield of walnut oil at 30, 60, 90 and 120 minutes of extraction time and process parameters such as pressure and temperature.

The parameters of extraction were choosing taken into account the technical characteristics of extractor, the needed parameters to ensure the supercritical state of carbon dioxide, and that these parameters do not affect negatively the quality of obtained products, but also that the obtained data can be mathematically processed for the purpose of optimizing the extraction process.

The extractor HA 120–50–01C allows the extraction at maximum pressure –

40MPa and the maximum temperature – 75˚C, so from the economic and technological points of view it was decided that the experiments will be performed to the pressure range – 10–40MPa, temperature range 35–55 ˚C and time range – 30–120 minutes.

Preparation of the experimental matrix

Planning experiments means accurate the form of program matrix. Following the strategy of full factorial experiments, we get a structured data table showing all the possible combinations between the levels of influence factors. These data define the program matrix of planned experiments. The matrix includes (in coded form) the experimental conditions for each of the N conducted experiences; for a full factorial experiment, the matrix comprising a number of experiments $N=2^k$, $k=3$. This type of matrix is shown below.

To obtain a second–order mathematical model is used the factorial design of experiments, the most important designs are the central composed programs. In formulating the mathematical model for polynomial of second degree, the numbers of factors cannot be limited to two. For the cases with 3 or 4 levels the programs are uneconomical or impractical due to the very high number of determination. In this context, it can get a program with fewer measurements than 3^k program, if a 2^k program is supplemented with specific points in the factorial space. This results that:

$$N = N_c + N_\alpha + N_0 \qquad (1)$$

where: N – the total number of determinations;
N_c – the number of determinations of the "sphere" points;
N_α – the number of "star" points;
N_0 – the number of points in the center.

The method of the rotatable central composite design is made in regard to complete the main matrix 2^k with a additional number of experiments ($N_\alpha = 2^k$), while the other factors are at the minimum and maximum levels, and with N_0 experiences at the center of the experiment.
Under these conditions the total number of experiments is:

$$N = 2^k + 2k + N_0 \qquad (2)$$

For the rotatable central composite design is attached following mathematical expression [2]:

$$y = b_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2 + b_{11}x_1^2 + b_{22}x_2^2 \qquad (3)$$

It were performed in parallel 20 experiments to the minimum, maximum, center and to the calculated values in „star” and „sphere” points of the extraction parameters so that results can be processed according to the selected mathematical model. The obtained data are presented in table 1.

Table 1. The central rotational programming matrix

N	**X_0**	**X_1**	**X_2**	**X_3**	**X_{12}**	**X_{13}**	**X_{23}**	**X^2_1**	**X^2_2**	**X^2_3**	**Ym***
1	+	+	+	+	+	+	+	+	+	+	77.47
2	+	–	+	+	–	–	+	+	+	+	74.86
3	+	+	–	+	–	+	–	+	+	+	2.09
4	+	–	–	+	+	–	–	+	+	+	2.85
5	+	+	+	–	+	–	–	+	+	+	61.66
6	+	–	+	–	–	+	–	+	+	+	59.55
7	+	+	–	–	–	–	+	+	+	+	7.5
8	+	–	–	–	+	+	+	+	+	+	1.92
9	+	+1.682	0	0	0	0	0	2.829	0	0	68.9
10	+	–1.682	0	0	0	0	0	2.829	0	0	54.12
11	+		+1.682	0	0	0	0	0	2.829	0	70.9
12	+	0	–1.682	0	0	0	0	0	2.829	0	2.09
13	+	0	0	+1.682	0	0	0	0	0	2.829	55.5
14	+	0	0	–1.682	0	0	0	0	0	2.829	29.4
15	+	0	0	0	0	0	0	0	0	0	63.4
16	+	0	0	0	0	0	0	0	0	0	63.4
17	+	0	0	0	0	0	0	0	0	0	63.4
18	+	0	0	0	0	0	0	0	0	0	63.4
19	+	0	0	0	0	0	0	0	0	0	63.4
20	+	0	0	0	0	0	0	0	0	0	63.4

**Y_m – the average value of the response (the oil yield reported to the oil content of the raw material).*

Calculation of regression coefficients

The regression coefficients were calculated according to the expressions:

$$b_0 = c_1 \sum Y_u - c_2 \sum_{i=1}^{k} \sum X_{iu}^2 Y_u \tag{4}$$

$$b_i = c_3 \sum X_{iu} Y_u \tag{5}$$

$$b_i = c_4 \sum (X_i X_j)_u Y_u \tag{6}$$

$$b_{ii} = c_5 \sum X_{iu}^2 Y_u + c_6 \sum_{i=1}^{k} \sum X_{iu}^2 Y_u - c_2 \sum Y_u \tag{7}$$

According to Box and Hunter (1957) for 2^3 factorial experiments the c_n coefficients are:

$c_1 = 0.16634$. $c_2 = 0.05680$. $c_3 = 0.07322$. $c_4 = 0.125$. $c_5 = 0.0625$. $c_6 = 0.00689$

According to formula (4)–(7) we obtained the following values of the regression coefficients:

$b_0 = 63.7$; $b_1 = 2.52$; $b_2 = 27.45$; $b_3 = 5.16$; $b_{12} = -0.0125$; $b_{13} = -0.73$;
$b_{23} = 4.45$; $b_{11} = -2.75$; $b_{22} = -11.58$; $b_{33} = -9.48$

It was calculated that $b_{12} = -0.0125$ is insignificant regression coefficient and was eliminated from the final regression equation.

The second order equation which describes the CO_2 extraction process

After processing the results and eliminating the insignificant coefficients we obtained the following second order regression equation:

$$Y = 63.7+2.52X_1+27.45X_2+5.16X_3-0.73X_1X_3+4.45X_2X_3-2.75X^2_1- -11.58X^2_2-9.48X^2_3 \quad (8)$$

Were the parameters of extraction process are coded according to the equations:

$$X_1=(T-T_0)/\Delta T;\ X_2=(P-P_0)/\Delta P;\ X_3=(t-t_0)/\Delta t \quad (9)$$

According to the verification it is seen that the extraction process is adequately described by this second order equation and corresponds to the real result obtained from the experiments. The second order equation can be represented by a response surface:

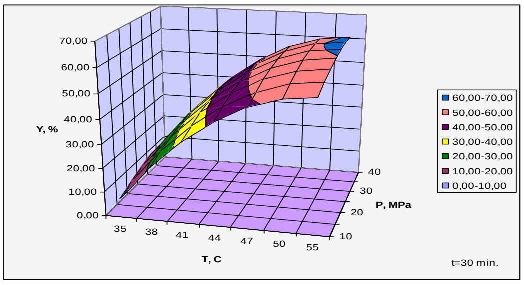

Fig. 1. The response surface characterized by the polynomial of second degree that describes the CO_2–extraction of oil from walnut crumbs (t = 30 min.)

Conclusions

1. By the programming of experiments it was determined that we need 40 experiments (20*2) in order to obtain the equation of second order.

2. It was established the final form of second order regression equation characterizing the CO_2–extraction of oil from walnut crumbs, which is: $Y=63.7+0.25(T-45)+1.83(P-25)+0.115(t-75)-0.00008(T-45)(P-25)-0.0016(T-45)(t-75)+ +0.0066(P-25)(t-75)-0.03(T-45)^2-0.05(P-25)^2-0.005(t-75)^2$.

3. According to obtained polynomial the most influencing parameter of the extraction process is the pressure.

References

1. OLIVEIRA, R., RODRIGUES, M. F., BERNARDO–GIL, M. G., *Characterization and supercritical carbon dioxide extraction of walnut oil, JAOCS, Vol. 79, no. 3, 2002*
2. CLOCOTICI. V. *Introducere in statistica multivariată: note de curs.* Universitatea “Alexandru Ioan Cuza”, Iaşi, 2007
3. BARBU A. *Testul Fisher F cu valori semnificative mici in eşantioane de volum redus. Studiu de caz.* Romanian Statistical Review nr. 4/2011