

Mathematical Modeling of Technology for Disposal of Oil Sludge with the Use of Liquid and Supercritical Fluid Extraction Processes

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Abstract: The study represents the results of implementation of liquid and supercritical fluid extraction processes in order to extract oil-products from oil sludge. For modeling of periodic process of extraction the relaxation method of calculation has been used. This method is based on the equations which are written down for non-stationary conditions. Check of adequacy of mathematical model by comparison with an experiment.

Key words: Mathematical modeling, oil sludge, supercritical fluid extraction, propane-butane, adequacy

INTRODUCTION

Now for the description of processes of extraction various mathematical models are offered. So in research (Patel *et al.*, 2011) the simple mathematical model for the description of process of extraction has been offered. This model is based mainly on two mechanisms of a mass transfer: solubilities and diffusions. This model assumes division of the mode of extraction into two areas: initial with a constant speed of extraction which is controlled by solubility and the falling speed of the extraction controlled by diffusion. The data description on extraction by numerical methods with use of various models of extraction is provided in researches (Reverchon and Marrone, 2001; Cocero and Garcia, 2001; Ghoreishi and Sharifi, 2001).

The simplest model of extraction offered in (Sovova, 2005) divides an extraction curve into three main sections. The first section in which the speed of extraction is permanent is controlled by thermodynamic balance between the dissolved component and the solvent and also an external mass exchange. The last section is controlled by internal diffusion. The average section is the unique nonlinear section and represents the period when extraction process is controlled by both an internal and external mass exchange. Such model is rather good for forecasting within the first section of an extraction curve. The number of parameters of model depending on complexity of extraction to 5.

Taking into account the analysis of literature and properties of oil slime we have carried out modeling of the

extraction process within the task of oil-products detachment from oil sludge. This research is further work.

MATERIALS AND METHODS

Experimental part: Oil sludge has been used as initial waste. Some of its properties include the content of water = 0 wt% (GOST 2477-65); the content of solids = 12.05 wt% (GOST 6370-83). Propane-butane mixture has been used as an extractant, consisting of 75 wt% propane and 25 wt% butane. According to Juntarachat *et al.* (2013) the abovementioned mixture of propane-butane has the following values of critical parameters: $t_c = 386$ K ($\sim 113^\circ\text{C}$); $P_c = 4.31$ MPa. Schematic diagram of the laboratory experimental plant and results of experimental studies are in detail described in work. Kinetics of the oil yield is presented in Fig. 1.

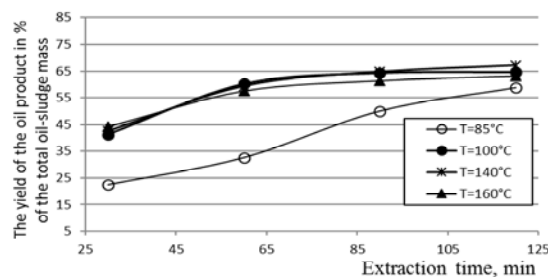


Fig. 1: Kinetics of the yield of oil-product from the sludge during the extraction process with the use of propane-butane extractant in liquid (85°C, 100°C) and supercritical fluid (140, 160°C) state: $P = 10$ MPa

RESULTS AND DISCUSSION

Theoretical part: In order to scale up the technological process of oil extraction from oil sludge a simulation of the process has been carried out.

Initial data for simulation: Propane-butane mixture has been used as an extractant, which is dispersed in the layer of the sludge. Propane-butane acts as a dispersed lighter phase whereas sludge acts as a continuous heavy phase. The extraction process takes place in an extractor. Parameters of the laboratory extractor: diameter 260 mm; height 75 mm; propane-butane disperses into sludge through the 2 mm-diameter tube with a speed of 25 g min⁻¹; temperature- 85÷100°C pressure 10 MPa; process is periodic. Kinetics of the oil yield is presented in Fig. 1. Partition coefficients for components between the continuous and dispersed phases have been determined experimentally. The coefficients obtained are generalized with the use of Lee-Kesler-Plocker model. Lee-Kesler-Plocker equation (Lee and Kesler, 1975) is an accurate common method used for calculation of non-polar components and their mixtures. Plocker and others applied the equation of Lee-Kesler relating to mixtures. In its turn Lee-Kesler equation has been obtained as a modification of the Benedict-Webb-Rubin (BWR) equation.

$$z = z^{(0)} + \left(\frac{\omega}{\omega^{(R)}} \right) \left(z^{(R)} - z^{(0)} \right) \quad (1)$$

Compressibility factor can be determined as follows:

$$\frac{P_r V_r^{(0)}}{T_r} = 1 + \frac{B}{V_r^{(0)}} + \frac{C}{(V_r^{(0)})^2} + \frac{D}{(V_r^{(0)})^5} + \frac{c_4}{T_r^3 (V_r^{(0)})^2} \left[\beta + \frac{\gamma}{(V_r^{(0)})^2} \right] \exp \left[-\frac{\lambda}{(V_r^{(0)})^2} \right] \quad (2)$$

Where:

$$\begin{aligned} V_r^{(0)} = \frac{P_k V^{(0)}}{RT_r} &= \text{Ideal reduced volume of a simple substance} \\ V^{(0)} &= \text{Molar volume of a simple substance m}^3/\text{mol} \\ P = P/P_k &= \text{Reduced pressure} \\ P_k &= \text{critical pressure (Pa)} \\ B &= b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} + \frac{b_4}{T_r^3} \\ C &= c_1 - \frac{c_2}{T_r} - \frac{c_3}{T_r^2} + \frac{c_4}{T_r^3} \\ D &= d_1 + \frac{d_4}{T_r} \end{aligned}$$

$$\begin{aligned} \text{Coefficients} &= b_1, \dots, b_4, c_1, c_2, c_3, d_1, d_2 \\ \omega, \omega^{(R)} &= 0.3978 \end{aligned}$$

Pitzer's acentricity factor for the investigated and reference substance (octane), respectively. Mixing rule for calculation of pseudo-critical properties is as follows:

$$T_{c,m} = \frac{1}{8V_{c,m}} \sum_i \sum_j y_i y_j (V_{c,i}^{1/3} + V_{c,j}^{1/3})^3 (T_{c,i} P_{c,i})^{1/2} \quad (3)$$

$$V_{c,m} = \frac{1}{8V_{c,m}} \sum_i \sum_j y_i y_j (V_{c,i}^{1/3} + V_{c,j}^{1/3})^3$$

$$V_{c,m,i} = \frac{(0.2905 + 0.085\omega_i)RT_{c,i}}{P_{c,i}}$$

$$\omega_m = \sum_j x_j \times \omega_j$$

$$P_{c,m} = \frac{(0.2905 + 0.085\omega_m)RT_{c,j}}{V_{c,m}}$$

Where:

$$\begin{aligned} R &= \text{Universal gas constant} \\ P &= \text{Pressure} \\ P_c &= \text{Critical pressure} \\ P_r, P/P_c &= \text{Reduced pressure} \\ T &= \text{Temperature} \\ T_c &= \text{Critical temperature} \\ T_r = T/T_c &= \text{Reduced temperature} \\ V &= \text{Molar volume} \\ V_c &= \text{Critical molar volume} \\ Z &= \text{Compressibility coefficient} \\ \omega &= \text{Acentricity factor} \end{aligned}$$

Model of the flow structure and efficiency of the extractor: Solubility of components in propane-butane decreases with the increase in molecular weight of the components (Fig. 1). If a continuous phase in the extractor is completely mixed, the Peclet number $Pe_m = 0$. If there is a piston-type driving mode of a dispersed phase, $Pe_p = 8$. According to the experimental data the following parameters are found $Pe_m = 2$; $Pe_p = 55$. The degree of longitudinal mixing strongly depends on design of the apparatus and the process conditions. Longitudinal mixing is caused by turbulent diffusion of the substance along the axis of the extractor and radial diffusion caused by nonuniform distribution of velocities through the cross section of the apparatus (transverse unevenness). It is

Table 1: Constants included in Eq. 5 according to the values of extraction factor ε

1/ ε	a	b	c	d	g	h
0.1	0.430	0.150	0.310	0.41	-0.305	0.073
0.2	0.470	0.210	0.485	0.59	-0.290	0.085
0.3	0.495	0.270	0.625	0.73	-0.255	0.094
0.4	0.515	0.320	0.750	0.85	-0.220	0.100
0.6	0.550	0.425	0.975	1.07	-0.150	0.115
0.8	0.580	0.520	1.160	1.25	-0.075	0.125
1.0	0.610	0.610	1.310	1.42	0.000	0.135
1.5	0.675	0.810	1.610	1.78	0.180	0.155
2.0	0.730	1.000	1.850	2.10	0.350	0.172
3.0	0.800	1.380	2.120	2.45	0.640	0.201
4.0	0.845	2.000	2.250	2.65	0.865	0.225

Table 2: Adequacy of the developed model

Temperature (°C)	Pressure (MPa)	Yield of oil in % of total oil sludge mass	
		Experiment	Model
85	10	58.3	56
100	10	65.0	63

proposed to describe the overall effect of the longitudinal mixing and transverse unevenness with the use of a single turbulent diffusion coefficient E:

$$\frac{(N_{\text{TOR}})_{\text{piston}}}{N_{\text{TOR}}} = \frac{H_{\text{piston}}}{H} = \frac{Pe_p Pe_m}{Pe_p Pe_m + \frac{HZ}{H_{\text{TOR}}}} \quad (4)$$

$$Z = aPe_m + bPe_p + c(Pe_p Pe_m)^{0.5} - d(Pe_p + Pe_m)^{0.5} + g(Pe_m - Pe_p)e^{-hH/H_{\text{TOR}}} \quad (5)$$

Where:

H_{piston} = Required height of the extractor for the predetermined extraction level under ideal counter-flow

H = Required height of the extractor for the obtaining of the same extraction level in the presence of longitudinal mixing

N_{TOR} = Number of transfer units for oil sludge

H_{TOR} = Height of a transfer unit for oil sludge

pe = VH/E - Peclet criterion for longitudinal mixing.

V = Specific load ($\text{m}^3/(\text{m}^2 \times \text{hour})$)

Constants included in Eq. 5 depend on the value of extraction factor and can be determined using Table 1. A relaxation method of calculation has been applied for the simulation of the periodic extraction process. This method is based on the equations written for the non-stationary conditions. Verification of adequacy of the mathematical model by comparison with the experiment. Adequacy of the proposed model is confirmed by the data, represented in Table 2. With an increase in diameter of the mass-transfer column apparatus, a decrease in

mass-transfer efficiency can be observed due to the so-called “scale effect”. The impact of this effect in each phase can be calculated by effective diffusivity coefficient D_x and D_y , for each phase respectively. The height of the transport unit can be determined by taking into account diffusive mixing in both phases:

$$h_{\text{ef}} = h_m + \theta \left[\frac{D_x}{\omega_x} + \frac{D_y}{\omega_y} \right] \quad (6)$$

Where:

h_m = k/ω_a partial of an effective HTU, provided by mass-transfer (actual HTU)

$\theta \leq 1$ = Coefficient depending on mass-transfer factor A

ω and ω_x = Velocities of reacting phases

The increase in effective HTU, derived from the Eq. 6, during the transfer from the column with a smaller diameter (laboratory apparatus) to the column with a larger diameter (pilot plant):

$$\Delta h = \theta \left[\frac{D_x^{\text{lab.2}} - D_x^{\text{lab.1}}}{\omega_x} + \frac{D_y^{\text{lab.2}} - D_y^{\text{lab.1}}}{\omega_y} \right] \quad (7)$$

Values of D_x and D_y coefficients, can be calculated with use of the diffusion model (Eq. 8). All the missing data for the diffusion model can be taken from the experiment with laboratory extractor:

$$\begin{cases} \frac{D_y V}{L_y} \cdot \frac{d^2 y}{dz^2} - H \frac{dy}{dz} = N_{0y} (y - y^*) \\ -\frac{D_x V}{L_x} \cdot \frac{d^2 x}{dz^2} + H \frac{dx}{dz} = N_{0y} (y - y^*) \end{cases} \quad (8)$$

With an increase in diameter of the extractor from 75-130 mm, almost twofold increase in HTU is expected. It means that to maintain the efficiency of the extractor its height should be increased by 2 times (in the presence of four sources/spreaders of the dispersed phase (propane-butane)). Reduction of the “scale effect” influence can be achieved by sectioning the column, by installing partition-walls (Fig. 2).

It is important to estimate the impact of a “scale effect” on the efficiency of extraction, i.e., to carry out two experimental runs: with partition-wall; without partition-wall. It is expected that the extractor’s height of 300 mm should be sufficient for the partition-wall variant. It is also important to evaluate the influence of quantity of the spreaders. For this reason two experimental runs should be carried out: with four spreaders (Fig. 2) with eight spreaders of the dispersed phase (propane-butane).

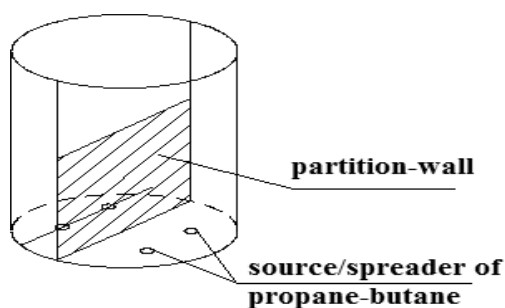


Fig. 2: Schematic illustration of the column with partition-walls

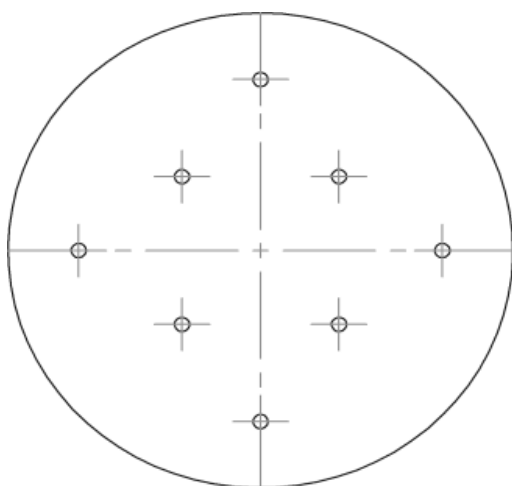


Fig. 3: Allocation of spreaders for propane-butane at the bottom of the extractor

The increase in diameter of the extractor from 75-130 mm will allow 4 times increasing in productivity of the extractor both in continuous phase (oil sludge) and dispersed phase (propane-butane). This will affect the influence of the scale effect thus the height of the extractor should be increased to 500 mm. However, the discussed above structural measures are not able to increase the height of the extractor significantly (up to 300 mm). Actions for the improvement of the extraction efficiency for the pilot plant extractor:

- Sectioning of the extractor (assembling of the partition-walls)
- Increasing of spreaders number for propane-butane up to 8 pieces (Fig. 3)

Parameters of the laboratory extractor 1 and pilot plant extractor 2 are hurred together in Table 3.

Table 3: Optimal geometric characteristics and thermodynamic parameters

Extractor	Ø (mm)	Height (mm)	No. of spreaders	Volume (L)	Effective section (m ²)
1	75	260	1	1.00	0.004 42
2	130	500	8	6.64	0.013 27

Temperature/pressure: 85°C/10MPa

CONCLUSION

For the purpose of scaling of the developed technology solutions, taking into account results of experimental studies on laboratory installation, it was carried out mathematical modeling of process of extraction is carried out. By results of mathematical modeling of process of extraction optimum geometrical characteristics (height, diameter and volume) of pilot plant extractor are determined.

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