Disposal of Oil Sludge with the Use of Liquid and

Supercritical Fluid Extraction Processes with

Propane-Butane Extractant

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Abstract

The paper represents the results of implementation of liquid and supercritical fluid extraction processes for the purpose of extraction of oil-products from oil sludge. A mixture consisting of propane (75 wt%) and butane (25 wt%) has been applied as the extractant. The extraction processes have been conducted in a temperature range of 85-160°C and pressure range of 5-20 MPa.

Keywords: disposal, oil sludge, supercritical fluid, extraction

1 Introduction

Oil sludge is a multicomponent physicochemical system consisting mainly of oil-products, water and mineral supplements (sand, clay, metal oxides, etc.) [Kalimullin et al., 2003]. They are formed as a result of accidents occurring in product collection systems of wells during the processing of oil and waste water; they are also formed during mode failures at technological plants and field equipment cleaning, etc.

In recent years oil-producing enterprises implement various technological solutions aimed at disposal of wastes from oil production and processing. However, a sufficiently effective and consistent method of sludge processing for the purpose of disposal and recycling is still missing. Among the existing methods of sludge processing there are methods of centrifugation, solvent extraction, gravitational compression, vacuum-filtration, freezing and others.

Up to 85% of oil and 95% of solids can be extracted by centrifugation method with the use of flocculants. In case of reactant treatment of a sludge, water-return increases and extraction of oil-products becomes much easier. Thus, water becomes suitable for the subsequent biological purification; extracted oil is suitable for technological purposes and dewatered residue for production of construction materials. In particular, ACS 530 (US) company has developed a mobile oil-petroleum waste processing system MTU 530, implemented in the form of an installation built on the basis of an automotive platform (Rakhimov, 2014).

KHD Humboldt Wedag AG company (Germany) has suggested the technology for separation of oil sludge into phases with the subsequent combustion of residual components. The installation is equipped with the following units: device for collecting of sludge, vibrating screen for separating of solids' bulk, three-phase centrifuge, separator for purification of centrate from the centrifuge, oven. The capacity is up to 15 m^3 per hour of initial oil sludge (Rakhimov, 2014).

Several Russian oil accumulations use the installation developed by "Tatoilgas" based on the technology of "Mike" company (Germany). The technology consists in heating the sludge, treatment by demulsifiers and destruction of the emulsion in decantation tank, water and mechanical impurities separates. According to the foregoing it follows that oil sludge treatment is a complex and time-consuming

process. Moreover, among the technologies applied, there is no waste-free and cost-effective ones. Application of any of the abovementioned technologies leads to discharge of pollutants. Each of these technologies has its own wastes requiring their subsequent disposal at landfills. It is no coincidence that one of the directions in Russian petrochemical complex development policy is modernization of existing and introduction of new environmentally friendly technologies for processing and disposal of oil sludge.

Supercritical fluid extraction (SFE) technology [Gumerov et al., 2000], [Gumerov et al., 2004] for oil sludge disposal, investigated in the present paper, is extremely relevant, ecologically justified and challenging in the context of economic efficiency and profitability. It can be noted that this principle relating to oil sludge has already been implemented by "TEXACO" company (USA) in the industrial version [Cansell et al., 1995].

2 Experimental part

2.1 Materials and methods

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 (GOST, 1993), 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: $T_{cr} = 386$ K (~113°C); $P_{cr} = 4.31$ MPa.

Schematic diagram of the experimental plant, allowing implementation of extraction process with propane-butane extractant in liquid and supercritical fluid (SCF) state, is presented in figure 1.
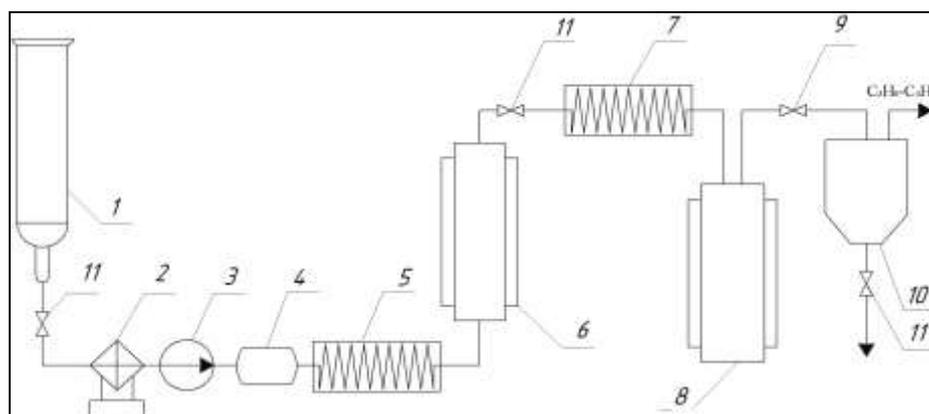

Fig. 1. Schematic diagram of the extraction plant: 1- reservoir for C_3H_8; 2 - refrigeration unit; 3- pump; 4 – receiver tank; 5 – heat exchanger; 6 - extractor; 7 – heat exchanger; 8 – separation vessel; 9 – control valve; 10 – heated separator; 11 – valve

2.2 Results and discussion

Figure 2 represents the yield of oil-products from oil sludge during the process of extraction with propane-butane extractant in a wide range of regime parameters (P, T, τ) of the process. Relative error of the experimental data varies in the range from 5.4% to 8.3%. Since the effectiveness of extraction is determined by the solubility of extracted component, the further discussion of yield character is based on the solubility concept for substances in various solvents and in particular state [Gumerov et al., 2000], [Chernishov et al., 2013] and even despite the fact that in this case the dissolved substance represents a mixture with composition that constantly changes depending on conditions of the extraction process. Taking into account that solubility measurements of pure substances in solvents which change their state from liquid, including subcritical, to supercritical fluid state, are extremely rare, this paper includes the results of solubility behavior studies of naphthalene in carbon dioxide appearing in various phase states (Fig. 3).
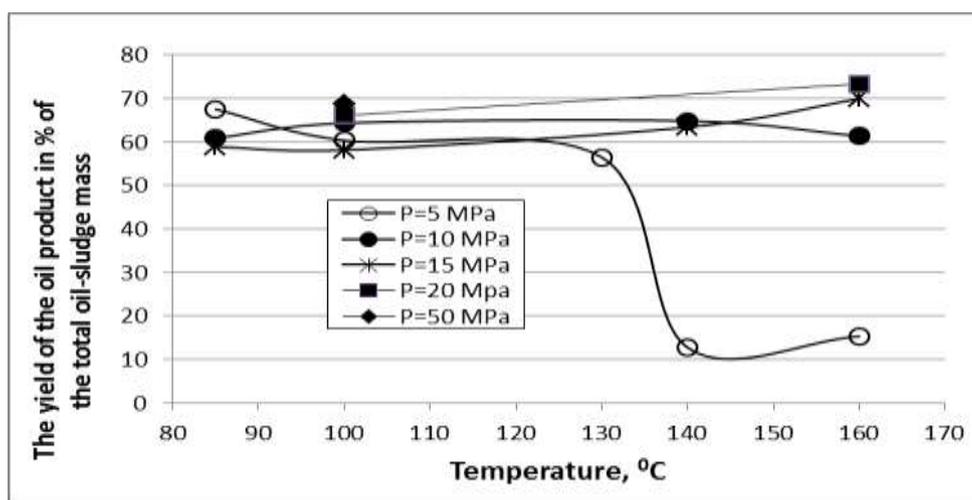

Fig. 2. The yield of oil-product from the sludge during the extraction process with propane-butane extractant in liquid (85°C, 100°C, 130°C) and supercritical fluid (140°C, 160°C) state: duration of the process is 60 minutes

There is an evident analogy in behavior of the solubility of naphthalene in CO2 (Fig. 3) and the yield of the product (Fig. 2) within the propane-butane extraction process.
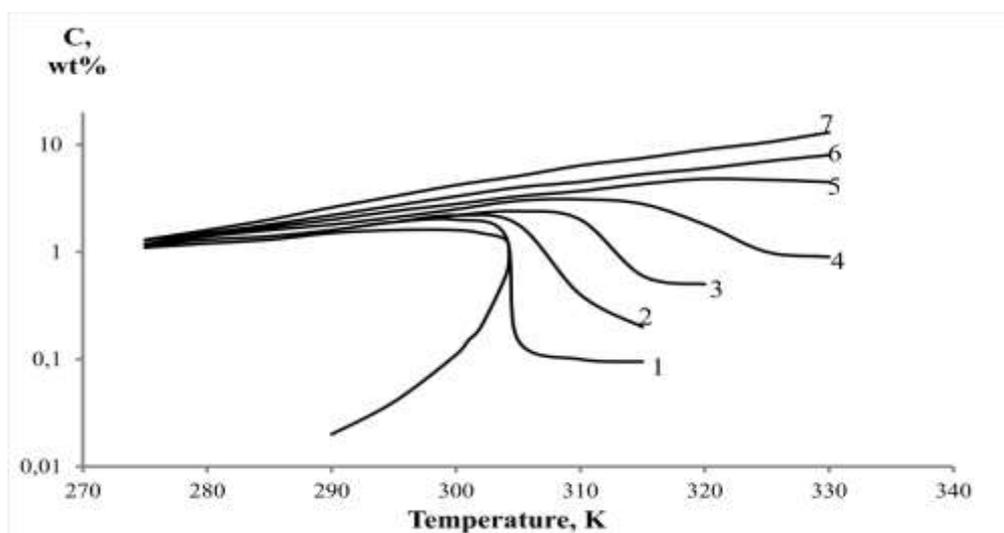
Fig. 3. Solubility of naphtalene in carbon dioxide (T_{cr} = 304.14K, P_{cr} = 7.378 MPa (Gumerov, 2000)) for liquid, sub- and supercritical fluid states of the solvent (Mc Hugh, 1994): 0.1-7 MPa, 0.2 - 8 MPa, 0.3 - 9 MPa, 0.4 - 10 MPa, 0.5 - 12 MPa, 0.6 - 15 MPa, 0.7 - 30 MPa

A highly profitable "ROSE" process for deasphaltizing of oil-products that has been already implemented in the industry is based on the sharp decrease in solubility (Fig. 3) and yield of the oil-product (Fig. 2) at low pressures (7-9 MPa for carbon dioxide and 5 MPa for propane-butane) in the area of solvent's transition from liquid to supercritical fluid state [Gumerov et al., 2000]. Another example is the study of SCF-impregnation process of carbonate rock proposed by the authors [Gumerov et al., 2014].

At the same time, it should be noted that the required decrease in dissolving capacity necessary for the aforementioned processes can be also obtained at "high pressures". In the first case, it was necessary to increase the temperature of the solvent/extractant at a certain low pressure, in the second case, a certain "high pressure" (isobar P = 30 MPa in Figure 3) requires decreasing of the temperature. This situation can be defined and explained by the presence of so-called crossover points (upper and lower [Mukhopadhyay et al., 2000] or first and second [Gumerov et al., 2015]) located on isotherms of solubility of substances in SCF solvents. Figure 4 shows the behavior of the oil-product's yield in the extraction process with propane – butane extractant in liquid (85°C, 100°C, 130°C) and supercritical fluid (140°C, 160°C) states, presented in the form of corresponding isotherms.
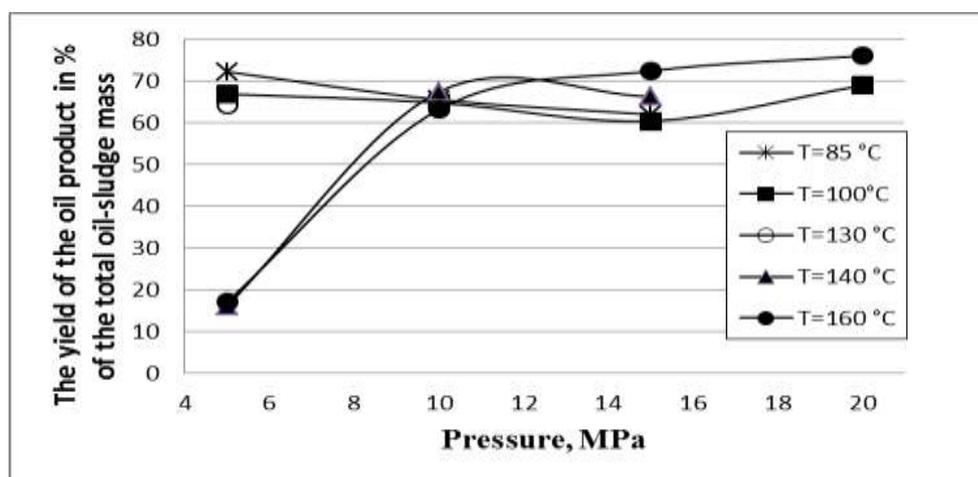
Fig. 4. The yield of oil-product from the sludge during the extraction process with the use of propane-butane extractant in liquid (85°C, 100°C, 130°C) and supercritical fluid (140°C, 160°C) state: duration of the process is 120 minutes

In figure 4 it can be seen quite clearly how the temperature dependence of the yield changes in a variety of pressure ranges. In particular, for the range of P = 6.5-12 MPa the yield drops as the temperature increases, whereas at P > 12.5 MPa, the opposite trend can be observed, namely, with the increase in temperature the yield also increases. According to the results above, taking into account the measurement errors, the first and the second crossover points correspond to the pressures of 5-6.5 MPa and 11-12 MPa, respectively.

Modeling of any process, and in this case the extraction of oil-products from oil sludge, requires an investigation on kinetics of the corresponding process. The results of the kinetics investigation for the process under discussion in a wide range of regime parameters are presented in figures 5-8.

The yield of oil product from the sludge is determined by its solubility in the extractant, even though the dissolved substance is a mixture. In its turn, the value of solubility is determined on the one hand by the dissolving capacity of the extractant (propane-butane), which largely depends on its density, and on the other hand by saturated vapor pressure of the solute (oil-product) under the corresponding thermodynamic conditions. Table 2 shows the density behavior of propane-butane mixture with the corresponding composition.

According to table 2, propane-butane at pressure of P=5 MPa in supercritical fluid state (140°C and 160°C) has a much lower density than the values typical for the extractant in liquid state (85°C and 100°C). This determines the lower yield of oil-product provided by SCF extractant at P=5 MPa (Fig. 5). At the same time, the practical equality of the oil-product's yields at two different supercritical temperatures means that the pressure of 5 MPa is a characteristic of abovementioned first or lower crossover point. Regarding liquid state of the extra-

ctant (85°C, 100°C and 130°C) at P=5 MPa, it is necessary to note the following: the highest yield of oil-product takes place at T= 85°C, indicating that under these conditions temperature dependence of density of the extractant
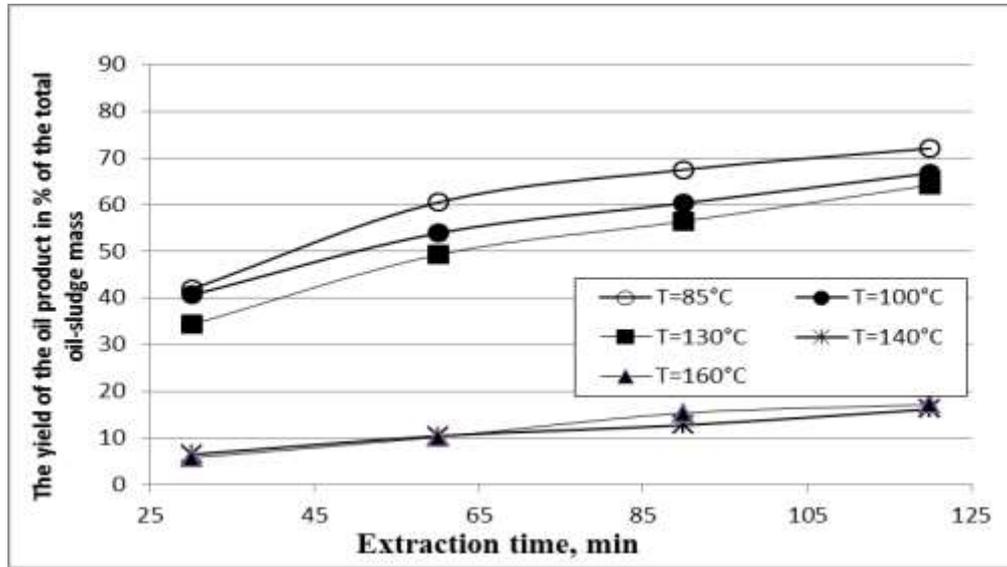

Fig. 5. Kinetics of the yield of oil-product from the sludge during the extraction process with the use of propane-butane extractant in liquid (85°C, 100°C, 130°C) and supercritical fluid (140°C, 160°C) state: P = 5 MPa

Table 2. Density of $propane_1$/$butane_2$ mixture (x_1=0.7308, x_2=0.2692) under conditions of the experiments carried out [Miyamoto et al., 2008], $kg \cdot m^{-3}$.

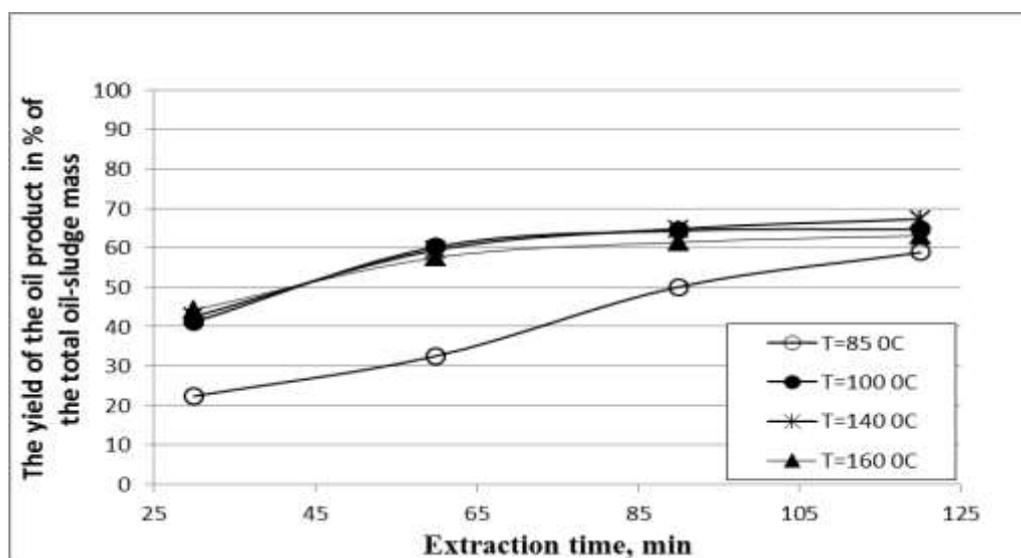| T, °C (K) / P, MPa	85 (358)	100 (373)	140 (413)	160 433)
5	432,3755	316,1102	302,511	255,8818
10	459,6025	432,8735	359,3068	322,5788
15	475,266	452,992	391,7253	360,6488
20	490,9295	473,1105	424,1438	398,7188
50	541,0635	529,2038	498,1778	483,3127

Fig. 6. 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, 130°C) and supercritical fluid (140°C, 160°C) state: P = 10 MPa

prevails over temperature dependence of saturated vapor pressure of the solute. In other words, as the temperature increases density of the extractant, and, accordingly, its solvent capacity decreases significantly more than increases the vapor pressure of the dissolved oil-product, thereby increasing the solubility.

Implementation of the extraction of oil-product from oil sludge at pressure of P = 10 MPa produces the following picture: the efficiency of solvent extraction at T = 100°C is not effected by the increase in pressure from 5 MPa to 10 MPa; the possibilities of supercritical fluid extractant are significantly increased by 6-8 times, moreover isolines characterized by temperature values of 140°C and 160°C match together again; kinetics analysis of the oil sludge's yield applied to the P = 15 MPa allows to suggest that the aforementioned coincidence is a sign that the pressure of 10 MPa is the pressure of the second or upper crossover point, because at higher pressures, e.g. at P = 15 MPa type of the temperature dependence of the oil-products' yield changes on the opposite and, in particular, as the temperature increases the oil-products' yield in supercritical fluid area begins to increase (see. fig. 7). And yet, it is necessary to comment the increase in oil-product's yield for SCF extractant up to the level of the extractant in liquid state. In principle, there is nothing surprising in this, if the density of SCF extractant equals to the density of the extractant in liquid state. However, in this case (see. Table. 2) it is not so (the density of SCF extractant substantially lower than the density of propane-butane mixture at T = 100°C: 322.58 kg·m^{-3} and 359.31 kg·m^{-3} against 432.87 kg·m^{-3}). Apparently, this result is achieved due to the fact that in the case of SCF extractant the sludge processing takes place throughout the whole volume of the sample, the phase contact area of between the phases, and thus the mass transfer is significantly higher, while the liquid processing of solid matrices, and it is a well-

known fact, has only a "shell" nature [Gumerov et al., 2015], [Gumerov et al., 2012]. The argument above is a good explanation of the trends observed in Figure 7. Finally, it is impossible not to draw attention to a sharp reduction in the product's yield for the process carried out at a temperature of 85°C, with the pressure increase from 5 MPa to 10 MPa. And this is despite the fact that there is no such a trend for the process carried out at T = 100°C. This can be explained by the fact that with the increase in pressure, in this case 85°C, viscosity of liquid propane-butane significantly increases and the processing capabilities of solid matrix dramatically worsen, whereas in case of 100°C similar tendency is poorly noticeable, since viscosity of propane-butane mixture at 100°C is lower than viscosity that takes place at 85°C. Table 3 contains properties of the oil-product produced with the use of extraction process and propane-butane extractant at temperature T=140°C and pressure P=10 MPa.
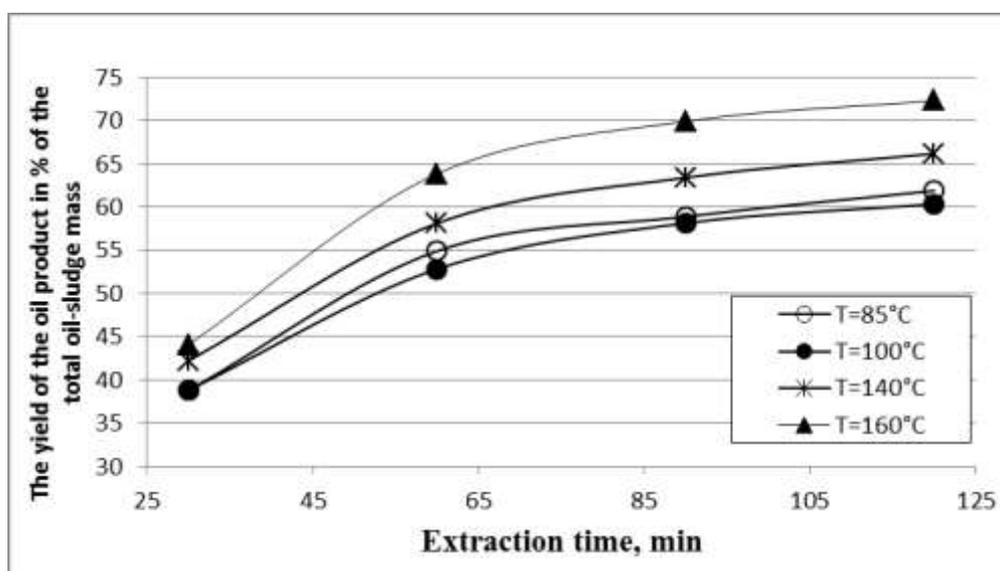

Fig. 7. Kinetics of the yield of oil-product from the sludge during the extraction process with the use of propane-butane extractant in liquid (85°C, 100°C) and supercritical fluid (140°C, 160°C) state: P = 15 MPa

Table 3. Characteristics of the oil-product produced with the use of extraction process carried out at T=140°C and P=10 MPa.

Characteristics defined	Standardized document for a test technique	Results
Content of chlorine salts, mg·dm^{-3}	GOST 21534-76	30
Density of the oil at 20°C, kg·m^{-3}	GOST 3900-85	880,0
Content of water, wt%	GOST 2477-65	0
Content of sulfur, wt%.	GOST 51947-02	2,831
Content of solids, wt%	GOST 6370-83	0,0090

Table 3. (Continued): Characteristics of the oil-product produced with the use of extraction process carried out at T=140°C and P=10 MPa.

Kinematic viscosity, mm^2·sec^{-1}	GOST 33-00	73,75
Yield of fractions: initial boiling temperature, ^{0}C at temperature 100°C, % at temperature 150°C, % at temperature 200°C, % at temperature 250°C, % at temperature 300°C, % at temperature 325^{0}C, % final boiling temperature, ^{0}C	GOST 2177-99	43.6 2.5 3.5 4.5 7 17 19 325

One of the most important features of the discussed process is the intensity of desorption of the extractant from the oil-product. Thus, the presence of extractant, especially in SCF state can multiply (up to 4-5 times (Gumerov, 2000)) decreases viscosity of the oil, which in its turn is very important for technical and economic parameters of the process. Figure 8 shows the results of the investigation on kinetics of desorption for propane-butane mixture from oil-product produced during the processes of liquid (85°C, 100°C) and supercritical fluid (140°C) extraction in the framework of the present research.
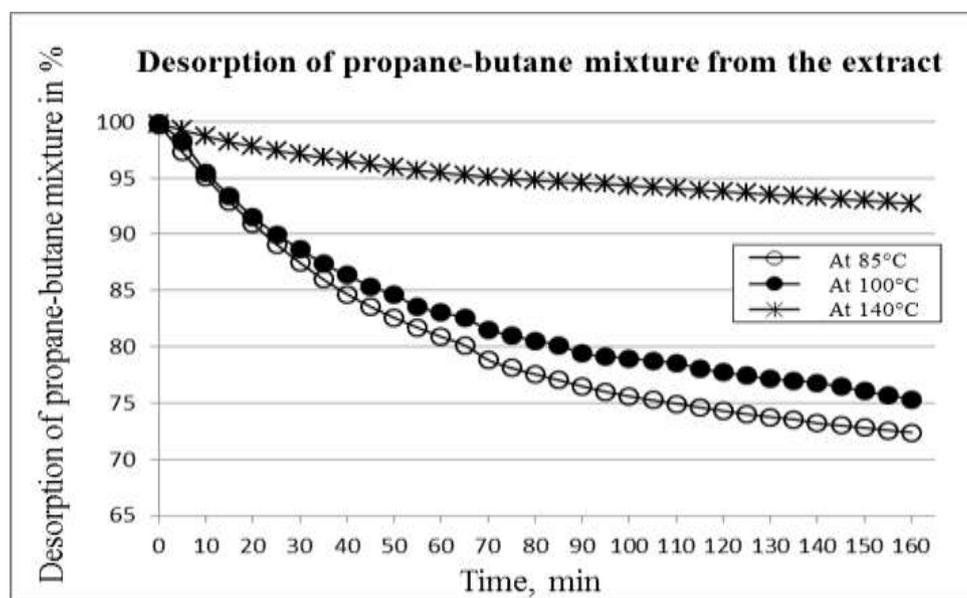

Fig. 8 Kinetics of desorption for propane-butane mixture from an oil-product produced during liquid (85°C, 100°C) and supercritical fluid (140^{0}C) extraction/

3 Conclusion

Current paper has determined the efficiency and preferability of supercritical fluid extraction process with propane-butane extractant within the task of extracting oil-product from oil sludge. Here are also presented the results of indirect estimation of short pressure ranges for the first (5-6.5 MPa) and the second (11-12 MPa) crossover points on the solubility isotherms of the investigated oil-products in propane-butane solvent.

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