Thermodynamic fundamentals of extraction of hydrocarbons from oil sludge with the use of supercritical propane-butane mixture

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Abstract. Current paper represents the results of the study on phase equilibrium characteristics and thermal conductivity of some thermodynamic systems involved in the extraction of hydrocarbons from oil sludge with the use of propane-butane mixture in both liquid and supercritical (SC) states. Phase equilibria have been studied for such previously unexplored binary systems as: “naphthalene – propane/butane”, “sulfur – propane/butane”, “water – propane/butane”. The studies have been carried out with the traditional version of the static method, as well as by using an optical cell for phase equilibrium studies, designed for high pressures. Thermal conductivity of water-oil emulsion at a pressure of 0.098 MPa in the temperature range of 290 – 360 K has been investigated using the hot-wire method.

1. Introduction
Russian oil and gas enterprises have accumulated a huge amount of oil wastes. According to the most conservative estimates, the annual increase of this amount is about 3 million tons [1]. Oil-producing enterprises recently started to implement various technological solutions aimed at the disposal of oil production and treatment wastes. However, there is still a lack of a sufficiently effective and unified way of oil sludge processing for the purpose of their disposal.

As a solution to this problem the authors of this study propose the implementation of the extraction process with propane-butane extractant in liquid and SC states [2–4]. The extraction processes are carried out in the temperature range of 85–160°C and a pressure range of 5–50 MPa. The extracted oil-product is characterized by the absence of mechanical impurities, asphaltenes and a low content of water and sulfur. The effectiveness of the extraction of hydrocarbons from oil sludge as well as the content of undesirable substances in the extract, such as water and sulfur, are determined primarily by the solubility of these components in the extractant applied. As a result, the task of optimization of the proposed technological solutions for separation of hydrocarbons from oil sludge, as well as modeling and scaling of the laboratory process to a commercial level, requires the information on thermodynamic and thermophysical properties of the systems involved in the process. All the foregoing led to the formulation of the research issues of phase equilibria studies for such oil sludge components as naphthalene, sulfur and water, with the aforementioned propane/butane extractant, as well as thermal conductivity measurements of the oil-water emulsion.
2. Experimental part

2.1. Materials and methods
The applied propane – butane mixture, has a following mass composition: 46% of propane and 54% of butane. The critical parameters of propane and butane according to [5] are characterized by the following values: propane \( (T_{cr} = 369.82 \text{ K} (96.67\text{°C}), P_{cr} = 4.247 \text{ MPa}) \); butane \( (T_{cr} = 425 \text{ K} (151.85\text{°C}), P_{cr} = 3.777 \text{ MPa}) \); propane / butane mixture \( (T_{cr} = 394.24 \text{ K} (121.1\text{°C}), P_{cr} = 4.27 \text{ MPa}) \).

“Pure for analyses” grade naphthalene, meets the requirements of TU 6-09-40-3245-90 and GOST 16106-82.

Hemispherical sulfur meets the requirements of TU 2112-144-31323949-2010.

A schematic diagram of the experimental plant designed for phase equilibrium studies of binary systems using a high-pressure optical cell is shown in figure 1.

Figure 1. A schematic diagram of the experimental plant designed for phase equilibrium studies of binary systems using a high-pressure optical cell: 1 – pressure vessel; 2 – dehydration filter; 3 – pump; 4 – high-pressure optical cell; 5 – copper jacket; 6 – thermal insulation; 7 – valve for the selection of the upper (gas) phase; 8 – valve for the selection of the lower (liquid) phase; 9 – sampling instrument; 10 – constant-temperature bath; 11 – valve.

The experimental setup (figure 1) consists of pressure creating, regulating and measuring system, temperature measuring and regulating system, equilibrium vessel, evacuation system, swing unit and analytical part.

In order to provide a static experiment, the optical cell is filled with one third of the investigated substance. After that, the entire system is evacuated with a vacuum pump with the purpose to get rid of air. Next, the cell is heated to the desired temperature and supplied with the propane/butane mixture by a high-pressure pump till the required pressure is reached. In order to achieve an equilibrium in a two-phase system, the contents of the optical cell are intensively mixed. The fact of reaching an equilibrium state in a thermodynamic system is established by one or two control experiments by sampling for analysis and/or by changing the pressure of the optical cell.

The experimental plant that implements the dynamic method of SC extraction in the temperature range up to 473 K and the pressure range up to 30 MPa has been described previously [6].
The traditional variation of the static method for the study of phase equilibrium characteristics is described in [2].

The thermal conductivity measurements of heavy oil and water-oil emulsions of various concentrations have been carried out using the hot-wire method [7] with the uncertainty of the results (error) not exceeding 2%.

2.2. Results and discussion

The investigations on extraction of hydrocarbons from oil emulsions with the use of supercritical fluid extraction process have been carried out. Propane/butane mixture has been applied as an extractant. The yield of the “dehydrated” oil-product has been estimated to be up to 93% wt. of the total amount of hydrocarbons in the oil emulsion.

Table 1 presents the comparative characteristics of the initial oil sludge and the oil-product obtained from oil emulsion sample with a water content of 30% wt. using the SC extraction process with propane-butane extractant \((t = 130^\circ C, P = 10 \text{ MPa})\).

| No. | Characteristic                           | Testing technique             | Initial oil sludge | Oil-product |
|-----|-----------------------------------------|--------------------------------|--------------------|-------------|
| 1   | Water content, % wt.                    | GOST 2477-65                  | 30                 | 2.35        |
| 2   | Density at 20°C, kg·m\(^{-3}\)          | GOST 3900-85                  | 960.5              | 877.5       |
| 3   | Sulfur content, % wt.                   | GOST R 51947-02               | 4.498              | 2.498       |
| 4   | Kinematic viscosity, mm\(^2\)·sec\(^{-1}\) | GOST R 33-00                  | 3010.1             | 374.1       |
| 5   | Mechanical impurities content, % wt.    | GOST 6370-83                  | 7                  | 0.0073      |
| 6   | Chloride salts concentration, mg·dm\(^{-3}\) | GOST 21534-76              | 20                 | 13          |
| 7   | Asphaltenes content, % wt.              | GOST 11851-85                 | 5.7                | 2.7         |

The mass content of sulfur, chloride salts and asphaltenes in the oil product, separated by the discussed extraction process, is approximately two times lower than the values presented in the original sludge. At the same time, kinematic viscosity in the framework of this comparison is reduced by almost 10 times. Water content reduced from 30% wt. to 2.35% wt. That is a good result. Moreover, these characteristics can be reduced even more by defining of the optimal thermodynamic conditions for the extraction process. Particularly for this purpose the phase equilibrium studies for the “naphthalene – propane/butane”, “sulfur – propane/butane”, and “water – propane/butane” systems have been carried out.

Naphthalene is an aromatic hydrocarbon that is part of oil sludges. As a result of the phase equilibrium study of “naphthalene – propane/butane” system carried out in the present research using a high-pressure optical cell, it has been established that it belongs to phase behavior of the type I [8]. The characteristics of “liquid – vapor” phase equilibrium for this system are in fact represented only by binodals, eventually forming a kind of a continuous critical curve, and the concept of solubility in SC solvent is simply absent. This state of affairs fully explains and confirms the previously established preference for using SC extraction process (in opposition to liquid extraction) [9] in cases where the “soluble – extractant” is a system with a continuous critical curve. The results of the phase equilibrium study carried out at a temperature of 130°C are presented in figure 2. It is notable that the binary system “naphthalene – CO\(_2\)” refers to the phase behavior of type V with a discontinuous critical curve. The uncertainty of phase equilibrium measurements for “propane/butane - naphthalene” system varies from 0.5 to 2.2%.
During the extraction of hydrocarbons from oil sludge, sulfur and its compounds in various concentrations, determined by the operating parameters of the process, are presented in the composition of the extracted oil-product. Reliable data on the phase behavior of this system can indicate the conditions for minimizing this undesirable substance in the resulting oil-product. The results of the phase equilibrium study for “sulfur – propane/butane” system are presented in figure 3.

Phase behavior of the binary system “sulfur – propane/butane” refers to the behavior of type V [8]. As a consequence, in the supercritical area of parameters for the propane/butane mixture, the phase boundary is maintained and there is a possibility for studying the solubility of sulfur in supercritical propane/butane. The results of the study on solubility of sulfur in propane/butane, carried out at temperatures of 130°C and 150°C, are presented in figure 4.

The crossover behavior of the solubility isotherms is clearly observed. Along with this, the presented point of intersection of the corresponding isotherms refers to the second or upper crossover point [10]. The uncertainty of phase equilibrium measurements for “propane/butane – sulfur” system varies from 0.55 to 3.72%.
The phase behavior of the “water – propane/butane” binary system also refers to type V behavior [8]. The results of the study on solubility of water in SC-propane/butane, carried out on isotherms of 130°C and 150°C in the pressure range 5–22 MPa, are presented in figure 5. The uncertainty of solubility measurements of water in propane/butane varies from 0.8 to 7.1%.

![Figure 5. The results of the study on solubility of water in SC-propane/butane.](image)

It should be noted that phase equilibria for the abovementioned systems are investigated for the first time.

![Figure 6. Thermal conductivity of water-oil emulsion at pressure of 0.098 MPa at various concentrations of water: 1 – heavy oil; 2 – 10% emulsion of heavy oil; 3 – 30% emulsion of heavy oil; 4 – 40% emulsion of heavy oil.](image)

With an increase in water concentration (figure 6), the heat conductivity also increases proportionally, the temperature dependence is poorly indicated. The presence of water changes the slope of the temperature dependence of thermal conductivity from negative (dehydrated oil, 1st curve in figure 6) to positive (curves 2–4 in figure 6). Thermal conductivity measurements are limited to a temperature of 353 K and a water concentration of 40%, since a further increase in temperature and concentration of water leads to separation (demixing) of the aqueous emulsion.
3. Conclusion
Current research represents the results of the study on separation of hydrocarbons from oil emulsions using a supercritical fluid extraction process with propane/butane extractant. The yield of the “dehydrated” oil-product reaches the value of 93% wt. of the total amount of hydrocarbons in the oil emulsion.

In the frames of the phase equilibrium study carried out for “naphthalene – propane/butane” system, its affiliation to behavior of type I is established. The phase equilibria of “sulfur – propane/butane” and “water – propane/butane” systems refer to behavior of type 5.

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