

## Solvent deasphalting of vacuum residue using carbon dioxide-toluene binary mixture



Rustam N. Magomedov<sup>a,b,\*</sup>, Artem V. Pripakhaylo<sup>a,b</sup>, Daniyar Sh. Dzhumamukhamedov<sup>a</sup>,  
Tatiana A. Maryutina<sup>a,b</sup>

<sup>a</sup> Moscow Institute of Physics and Technology (National Research University), Institutskiy per. 9, Dolgoprudny, 141701, Moscow Region, Russia

<sup>b</sup> Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Kosygin Str. 19, 119991 Moscow, Russia

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### ABSTRACT

Solvent deasphalting of vacuum residue using carbon dioxide-toluene mixture was studied to assess the effect of the process parameters and mixture composition on the yield and composition of deasphalted oil (DAO) produced. An insignificant effect of the toluene content in the mixture on the DAO yield was found at a concentration above 30 wt.%, which was attributed to effective anti-solvent properties of carbon dioxide. At relatively low-pressure region, an increase in temperature and the transition of the mixture to the supercritical state led to a rapid decrease in the solvent density and the DAO yield. At the same time, at pressures providing a mixture density in the region above ~0.6 g/mL, an increase in temperature above the mixture critical value was accompanied by increasing the DAO yield, even despite a noticeable decrease in the solvent density. However, conducting the extraction at temperatures near and beyond the mixture critical temperature reduces the separation selectivity at close the extraction yields due to increased solubility of metal-containing polar compounds. A proposed mixture in the single-phase liquid state can provide high DAO quality with metal and CCR removal efficiency of more than 90 and 80 wt.%, respectively.

### 1. Introduction

Due to the projected peak production of conventional oil resources and the growing consumption of liquid petroleum products, the share of heavy oils and natural bitumen involved in refinery will inevitably increase [1,2]. Taking into account falling demand and the tightening of requirements for the quality of fuel oil and bunker fuel, the cost-effective processing of heavy petroleum feedstocks (HPF) containing significant amounts of high-boiling residual fractions is possible only in the case of upgrading and complex bottoms processing with maximum distillate production [3,4].

In this regard, solvent deasphalting (SDA) processes occupy an important place in the practice of oil refining, ensuring the removal of asphaltenes or resin-asphaltene complexes and associated metals and heteroatoms, as well as reducing Conradson carbon residue (CCR), which greatly facilitates subsequent resid processing by catalytic processes. Indeed, in the hydrodesulfurization process, the deasphalted oil (DAO)

may consume only 65 % of the hydrogen required for direct hydrodesulfurization of topped crude oil [5]. Recent studies have shown that vanadium compounds in asphaltene part of HPF are most responsible for the deactivation of hydroprocessing catalysts, which makes the removal of asphaltenes an effective method of upgrading and preparing petroleum residuum for downstream fixed-bed hydrotreating and hydrocracking units [6]. For instance, DAO, extracted from vacuum residue (VR), despite the relatively high content of metals and CCR, can be effectively processed along with vacuum gas oils (VGO) in the conventional hydroprocessing reactors operated under mild hydrocracking conditions and packed with a guard-bed material [7]. In addition, the fluid catalytic cracking (FCC) yields and product qualities derived from a DAO based feed is very similar to the VGO yields from the same crude in spite of processing heavier molecules derived from the resid boiling range [8]. As a result, solvent upgrading of HPF due to asphaltene removal can eliminate the need for the use of higher cost coking and hydroconversion in ebullated bed or slurry reactors for residue processing.

**Abbreviations:** HPF, heavy petroleum feedstock; CO<sub>2</sub>, carbon dioxide; SDA, solvent deasphalting; DAO, deasphalted oil; VR, vacuum residue; CCR, Conradson carbon residue; VGO, vacuum gas oil; FCC, fluid catalytic cracking; scCO<sub>2</sub>, supercritical carbon dioxide; SFE, supercritical fluid extraction; SCF, supercritical fluid; TLC-FID, thin layer chromatography with flame ionization detection; ICP-AES, inductively coupled plasma atomic emission spectrometry; RSD, relative standard deviation; PR, Peng-Robinson; EoS, equation of state; BIP, binary interaction parameter; ARD, average relative deviation

\* Corresponding author at: Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Kosygin Str. 19, 119991 Moscow, Russia.

E-mail address: [tetrationat@rambler.ru](mailto:tetrationat@rambler.ru) (R.N. Magomedov).

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Modern SDA technologies are distinguished by a higher liquid capacity and separation efficiency of extraction units, as well as a higher yield and better DAO product quality with significantly lower specific energy consumption. This is achieved mainly due to supercritical solvent recovery, the use of state-of-the-art contacting and separation internal devices, optimal design of heat exchange systems and use of solvent in sub- and supercritical state at the extraction stage [8–11].

However, the disadvantage of existing technologies, even when using high solvent to oil ratios, is the low selectivity of C<sub>5+</sub> alkanes, which have a high dissolving ability and are used to obtain maximum amounts of DAO for subsequent transportation fuels production through processing in FCC or hydrocracking units [12–14]. In this regard, much attention is paid to the search for approaches and alternative solvents that provide the possibility of combining high solubility and selectivity and overcome the limitations associated with the physical nature of the process [15].

One of these alternative compounds is carbon dioxide (CO<sub>2</sub>), which is distinguished by its availability, fire and explosion safety. As is known, CO<sub>2</sub> can selectively extract relatively low molecular weight non-polar petroleum components with low aromaticity and act as an effective anti-solvent facilitating destabilization of the petroleum colloid system, asphaltene aggregation and precipitation [16–19]. However, the development of continuous processes of SDA using CO<sub>2</sub> as a solvent is hindered by its low dissolving ability with respect to components of heavy oils and petroleum residues containing large quantities of high molecular weight aromatic and heterocyclic compounds. The low solubility of heavy petroleum components in supercritical CO<sub>2</sub> (scCO<sub>2</sub>), including in comparison with light n-alkanes, has been repeatedly shown in a number of experimental studies of SDA and supercritical fluid extraction (SFE) processes using this solvent [20–22].

The main method for overcoming the low solubility of solutes in CO<sub>2</sub> is an addition of organic solvent modifiers, which makes it possible to increase its solvent power and adjust the selectivity towards feedstock components. Adding modifiers also leads to increase the miscibility of the feedstock components and solvent, reduce the process pressure and the amount of solvent required for extraction [23].

Toluene is known to be a promising CO<sub>2</sub> modifier for improving in solvency for heavy hydrocarbons and the extraction efficiency in the case of crude oil and bitumen extraction and liquid recovery from reservoir rocks and oil sand slurry [23,24]. The possibility of effective solvent deasphalting and demetallization of HPF using a mixture of CO<sub>2</sub>-toluene was demonstrated by us earlier in the study of the SFE process of VR [25]. It was shown that, along with other organic solvents, toluene as a CO<sub>2</sub> modifier due to strengthening van der Waals interactions through strong dispersion forces and its high ability to dissolve aromatic hydrocarbons provides a significant increase in the solvent power and extract yield simultaneously with high demetallization efficiency.

The aim of this work was to establish the influence of the process parameters (temperature, pressure and composition of the mixture) and the phase state of the solvent on the yield and composition of the extract/DAO resulting from SDA of VR using CO<sub>2</sub>-toluene binary mixture. Based on the results obtained, conditions providing a combination of high selectivity and solvent power of the solvent and, as a consequence, ensuring a high yield and quality of DAO have been determined.

## 2. Materials and methods

### 2.1. Materials

High purity CO<sub>2</sub> (99.99 %), supplied by “NII KM Ltd.”, and toluene (99.8 wt.% purity) were used for conducting the extraction experiments.

A sample of VR obtained at one of the oil refineries of the Russian Federation was used as a HPF. The composition and main properties of this feedstock are listed in Table 1.

**Table 1**  
Composition and properties of vacuum residue.

Parameter	Measure unit	Method	Value*
Chemical group composition:	wt. %	IP 469	
- saturates			9.1 ± 0.1
- aromatics			45.2 ± 0.2
- polar compounds I			23.9 ± 0.1
- polar compounds II**			21.8 ± 0.1
Heptane insoluble (C7-asphaltenes)	wt. %	IP 143	8.2 ± 0.4
Conradson Carbon Residue (CCR)	wt. %	ASTM D 189	19.1 ± 0.2
Sulfur content	wt. %	ASTM D 4294	2.29 ± 0.03
Vanadium content	ppm	ASTM D 7876, ASTM D 5708	105 ± 3
Nickel content	ppm	ASTM D 5708, ASTM D 7876	84 ± 2
Viscosity at 100 °C	mPa·s	ASTM D 2983	1940 ± 5

\* The mean values of ten parallel measurements with respective confidence intervals (P = 0.95) are given.

\*\* This class of compounds is similar, but not identical to asphaltenes insoluble in heptane as defined in IP 143.

### 2.2. Experimental apparatus and conditions

Extraction experiments were carried out using a high-pressure laboratory setup equipped with semibatch extractor purchased from Waters company (USA, extraction system model SFE1000M1-FMC50).

Extraction vessel that had a volume of 200 mL was used for the extraction. Vessel was made of 17-4PH steel and had an internal diameter of 54 mm and a length of 193 mm. Micron size filters in the upper and lower vessel covers contributed to a more uniform distribution of solvent stream over the cross section of the vessel and prevented the entrainment of solid particles. The presence of a bottom filter also prevented the drain of the oil sample loaded into the extractor. The vessel was designed for carrying out the process in the temperature range up to 150 °C and pressures up to 60 MPa.

Before the extraction, the preheated VR sample was mixed with glass balls with a diameter of 3 mm and loaded into the extractor. After that, the remaining free volume of the extractor was also filled with the balls. In this case, glass balls acted as an inert packing, which on the one hand increased the contact surface and the efficiency of mass transfer process, and on the other hand, minimized the entrainment of the VR components by the solvent flow from the extractor, which adversely affects the separation selectivity and the quality of the DAO.

After extraction, the collected fractions of the DAO and asphaltenic residue (asphalt) solutions were distilled using an IKA RV-10 rotary evaporator to remove and recovery toluene. Vacuum distillation was carried out at a temperature of 55 °C, a pressure of 8 kPa and a rotor speed of 120 rpm. Before weighing the fractions of DAO and asphalt were dried in an oven at a temperature not exceeding 120 °C to remove any traces of solvent. The DAO yield (wt. %) was calculated as the ratio of the mass of the obtained DAO to the initial mass of the VR sample loaded into the extractor. Repeatability of the data was good and relative standard deviation (RSD) of the amount of DAO produced did not exceed 3% for constant extraction conditions.

The diagram of the laboratory setup, a more detailed description of the extraction system components and the experimental procedure as well as the accuracy of measurement of process parameters can be found in [25].

Experimental studies were carried out in dynamic mode of extraction at temperatures from 50 to 125 °C and pressures from 10 to 30 MPa. The concentration of toluene in the solvent composition was varied from 0 to 40 wt.%. The extraction time and total solvent flow rate were determined on the basis of preliminary experiments. The loading of the oil residue sample into the extractor was generally not changed and amounted to 20 g.

### 2.3. Analysis of DAO properties

The chemical group composition of DAO was determined by thin layer chromatography with flame ionization detection (TLC-FID) according to IP 469 procedure using an IATROSCAN MK6S thin-layer chromatograph (SES GmbH Analyseysteme, Germany). The TLC-FID technique, using the Iatroscan instrument, is the fastest method for analysis of chemical group composition of heavy oils and oil residues. Like SARA analysis, which implies preliminary precipitation of asphaltenes followed by separation of maltenes into fractions by liquid adsorption chromatography, this standard method determines the content of four fractions of different compound classes. However, it is not possible to define the precise composition of the four compound classes in terms of chemical types present, except for saturates. IP 469 gives the following approximate description for the separated petroleum fractions: a) Saturates – non-aromatic cyclic and acyclic hydrocarbons (naphthenes and paraffins); b) Aromatics – hydrocarbons containing one or more aromatic rings, including some sulfur-containing hydrocarbons of the thiophene or sulfide type and some low content nitrogen- and oxygen-containing compounds; c) Polars (I) – not well-defined, lower molecular mass polar compounds containing nitrogen, sulfur and oxygen; d) Polars (II) – not well-defined, higher molecular mass and polyfunctional polar compounds. Polars II is similar, but not identical, to heptane-insoluble asphaltenes as defined in IP 143. Drawing an analogy with the conventional compound classes and considering the higher content of the polars II fraction compared to C7-asphaltenes (Table 1), with some assumptions it can be stated that polars II is a mixture of asphaltene and heavy resin fractions. Whereas, polars I include lower molecular weight resin fractions.

The sulfur and CCR content in the DAO were measured according to the procedures established by ASTM D4294 and ASTM D189, respectively. The accuracy of measurement was checked using standard samples with a known content of sulfur and CCR. The sulfur content was determined with the relative error in measurements of  $\pm 1\%$ , and those of CCR measurements were also within  $\pm 1\%$ .

Determination of vanadium and nickel content was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) according to ASTM D 5708 after oil sample decomposition by closed vessel microwave oven dissolution procedure described in ASTM D 7876 and adopted for a Multiwave PRO microwave oven (Anton Paar GmbH, Austria). Digestion of the organic matrix was carried out with concentrated nitric acid and hydrogen peroxide in closed PTFE vessels. In turn, the determination of metal content was performed with a Thermo Scientific iCAP 6500 Duo spectrometer (Thermo Fisher Scientific Inc., USA). To obtain accurate results, the values of the operating parameters of the instrument were preliminary optimized. The element concentrations in the samples were found using calibration solutions containing 1, 10, 100, and 1000  $\mu\text{g/L}$  of analytes in 3 vol. % HNO<sub>3</sub>. The calibration solutions were prepared by the sequential dilution of the Multi-Element Calibration Standard-2A standard reference solution (Agilent Technologies, United States) with the addition of the required amount of an internal standard solution to create the same concentration in all the test solutions. Three consecutive measurements of metal concentrations in the solution obtained after the wet digestion were conducted to assess the reproducibility of the results. The RSD for the concentration of vanadium and nickel in the DAO samples did not exceed 3%. The calculated detection limit in determining the concentrations of both elements was approximately 0.02 ppm.

### 2.4. Phase equilibrium calculation for CO<sub>2</sub>-toluene binary mixture

The phase equilibrium and properties of the binary CO<sub>2</sub>-toluene mixture for various concentrations of toluene and component ratios were calculated in the Aspen HYSYS v.9 software. The cubic Peng-Robinson (PR) equation of state (EoS) with standard van der Waals one-fluid mixing rules was used in this study as phase equilibrium model.

The binary interaction parameter (BIP) for a pair of CO<sub>2</sub> and toluene from the Aspen database, which has a constant value of 0.0936, was used for calculations. More detailed information on the PR EoS and the phase equilibrium calculation using this property package in Aspen HYSYS is presented here [26].

## 3. Results and discussion

### 3.1. Phase equilibrium data for CO<sub>2</sub>-toluene binary mixture

PR EoS has high performance for a system comprised of CO<sub>2</sub> and small molecules. The use of the unmodified PR EoS for modeling the phase behavior of the CO<sub>2</sub>/toluene mixture provides an acceptable calculation accuracy. The absolute average relative deviations (AARD) between the calculated and experimental solubility and liquid phase density data are in the range of 10 % and 1.5 %, respectively, for the entire set of available experimental data, as shown in study [27]. In the present study, we did not adjust the BIP to tune the PR EoS to fit the experimental thermodynamic equilibrium data. A comparison of the critical properties for this binary mixture calculated by us using EoS with a predetermined BIP, with the locus of mixture critical points estimated experimentally using the peak-shape method [28], showed that ARD for the mixture critical pressure is about 10 % for the entire range of composition.

P-T phase diagrams for CO<sub>2</sub>-toluene mixtures with toluene content from 10 to 40 wt. % are presented in Fig. 1.

An increase in the toluene concentration in the mixture leads to an increase and expansion of the two-phase region to the region of higher temperatures and pressures (Fig. 1). The position of the critical point in the diagram also depends on the composition of the mixture. With an increase in the concentration of toluene from 10 to 30 wt. % the critical point moves upward along the bubble point locus, approaching the point of maximum pressure on the curve (cricondenbar or maxcondenbar), and only at a concentration of 40 wt. % almost coincides with the point of maximum pressure. The mixture is characterized by unusual phase behavior and phase transitions when the system parameters change. So, when moving direct or opposite direction along isobars (heating or cooling) and isotherms (compression or throttling) near the critical point, the mixture crossing the bubble point or dew point locus can transit from a one-phase to a two-phase region and back, i.e. the vapor or liquid phases may appear and then disappear. These effects are known as retrograde vaporization/condensation [30]. Experimental phase transition data for CO<sub>2</sub>/toluene mixture with a toluene content of about 19 wt.% (0.1 mol fraction) are in acceptable agreement with the phase boundaries calculated by PR EoS with a predetermined BIP, as illustrated in Fig. 1.

Thus, when mixing CO<sub>2</sub> and toluene, depending on the ratio of components and process parameters (temperature, pressure), the resulting mixture can be either single-phase, being in a different aggregate state (liquid, vapor, SCF), or divided into two phases (liquid-vapor). In this study, a mixture of CO<sub>2</sub>-toluene, acting as a solvent in the SDA process, was, as a rule, in a single-phase liquid or supercritical state.

### 3.2. Preliminary experiments

Preliminary experiments were carried out in order to determine the extraction time and total solvent flow rate, ensuring the achievement of exhaustion DAO yield and thermodynamic equilibrium between the contacting phases at the solvent exit from the extractor under various extraction conditions. Fig. 2 shows the dependence of the DAO yield on the time of dynamic extraction carried out at various pressures and temperatures, as well as changing the concentration of toluene in the solvent and loading the VR sample into the extractor.

At the initial period, lighter and less polar VR components, which have high solubility, are extracted. This is followed by a rapid increase in the DAO yield. Subsequently, the rate decreases due to increasing the molecular weight and polarity of the remaining part of the residue and slowing down diffusion of its components into the solvent phase. It

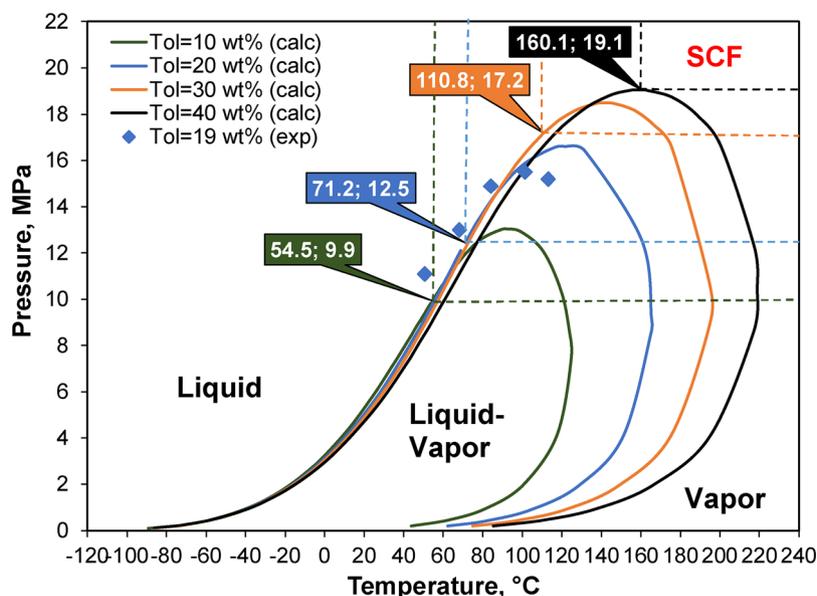


Fig. 1. Phase diagrams for a mixture of CO<sub>2</sub>-toluene with different toluene contents, obtained by the calculation method using PR EoS with standard van der Waals one-fluid mixing rules and BIP value for a pair of CO<sub>2</sub> and toluene of 0.0936 (experimental data are from the literature [29]).

should be noted that an increase in the extraction pressure and temperature, as well as the concentration of toluene in the solvent is accompanied by an increase in the DAO extraction rate at the initial periods of time. As can be seen from Fig. 2, regardless of the extraction conditions at times above 240 min. for a given solvent flow rate the DAO extraction rate decreases almost to zero and the total DAO yield changes insignificantly, reaching its exhaustion value. As a consequence, further experimental studies were carried out at an extraction time of 260 min for a total solvent flow rate of 30 g/min or a total solvent mass passed through an extractor of 7.8 kg, ensuring that the solubility of the VR components and the DAO yield is close to exhaustion or limiting values.

The dependence of the DAO yield, as well as the average linear velocity of the solvent flow, calculated on the free cross section of the extractor, on the flow rate of the solvent under various extraction conditions is shown in Fig. 3.

In this case, during the experiments, the mass of the solvent pumped through the extractor, or the mass ratio of the solvent to the loaded VR sample was maintained at a constant level by changing the extraction time. The experiments were carried out at three different combinations of temperature and pressure, providing different densities and transport

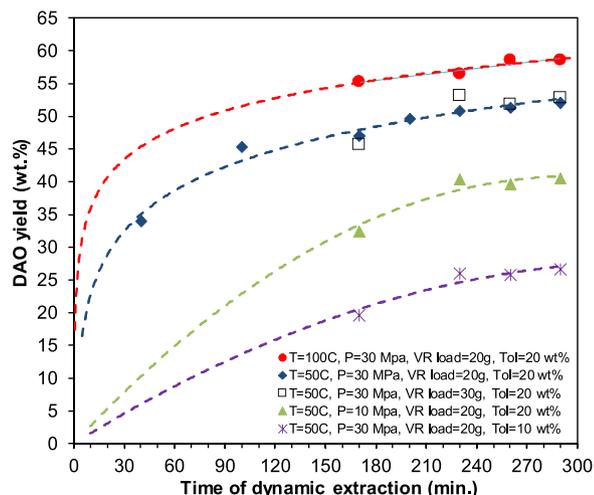


Fig. 2. Effect of extraction time on the DAO yield in the SDA of VR using a mixture of CO<sub>2</sub>-toluene under various process conditions (total solvent flow rate - 30 g/min).

properties of the solvent due to changes in its phase state, as well as different viscosity of the feedstock, which made it possible to assess the influence of entrainment effects and mass transfer limitations under various process conditions.

In the range of low flow rates and linear velocities of the solvent in the extractor, regardless of the process conditions, an increase in the yield of DAO was observed, indicating the presence of mass transfer limitations and a low rate of diffusion processes (Fig. 3a). The increase in the linear velocity can increase the diffusion rate of soluble VR components into the solvent phase and the DAO yield, which according to the film theory of mass transfer can be associated with a decrease in the film thickness of the boundary layer existing next to the interface [31]. If the solvent is in a liquid state and the VR has a high viscosity ( $T = 50\text{ }^{\circ}\text{C}$ ,  $P = 10\text{ MPa}$ ), the DAO yield reaches its maximum value at a solvent flow rate of 30 g/min and with a further increase in flow rate to 50 g/min and a decrease in the phase contact time, respectively, is reduced by approximately 10 wt. %. This may indicate that these extraction conditions are characterized by low mass transfer coefficients and high diffusion resistances in the boundary film both from the side of the solvent phase and from the VR phase, preventing the achievement of thermodynamic equilibrium between the phases in the region of small ( $< 30\text{ g/min}$ ) and a sufficiently high solvent flow rates ( $> 30\text{ g/min}$ ). However, at very close average linear velocities and contact times between phases the DAO yield remains almost unchanged in the flow rate range from 20 to 70 g/min for extraction conditions providing transition of the solvent mixture in supercritical region and the viscosity reduction of the VR ( $T = 100\text{ }^{\circ}\text{C}$ ,  $P = 25\text{ MPa}$ ) (Fig. 3). Thus, in this case, we can talk about an increase in the diffusion rates and the absence of mass transfer limitations in a wide range of solvent flow rates.

To assess the effect of solvent flow rate on the entrainment of VR components, experiments were carried out at a relatively low viscosity of the residue and a low density of the solvent being in a supercritical state ( $T = 100\text{ }^{\circ}\text{C}$ ,  $P = 15\text{ MPa}$ ). In the range of solvent flow rates from 20 to 50 g/min and average linear velocities up to 5 cm/min, a slight change in the DAO yield was observed. A further increase in flow rate and linear velocity above 50 g/min and 5 cm/min, respectively, despite a decrease in contact times between phases, was accompanied by some increase in DAO yield. So, increasing the flow rate from 50 to 100 g/min, the DAO yield increased from about 14 to 18 wt. %, which may indicate the presence of entrainment of the VR components in this flow rate range, reducing the selectivity of extraction (Fig. 3). This was also confirmed by an increase in the metal content in DAO, in particular, the

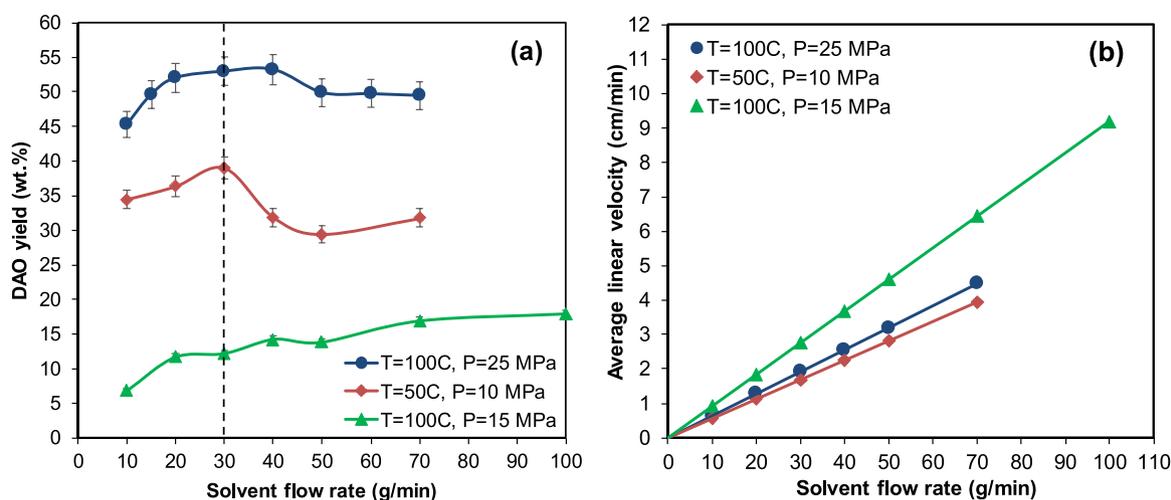


Fig. 3. Effect of total solvent flow rate on the DAO yield (a) and the average linear velocity of the solvent flow in the extractor (b) in the SDA of VR using a mixture of CO<sub>2</sub>-toluene with a toluene content of 20 wt.% under various extraction conditions (the total mass of solvent passing through the extractor during the experiment is constant and equal to 7.8 kg).

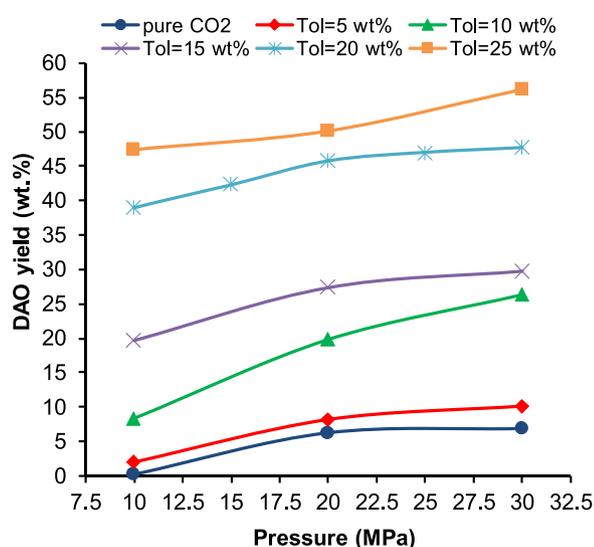


Fig. 4. DAO yield as a function of the pressure for various concentrations of toluene in the solvent ( $T = 50\text{ }^{\circ}\text{C}$ , total solvent flow rate - 30 g/min, extraction time - 260 min).

concentration of vanadium increased from 6 to 9 ppm with an increase in flow rate up to 100 g/min.

Thus, based on the results obtained, further studies were carried out at a total solvent flow rate of 30 g/min. This flow rate ensured that there was no influence of the entrainment effect on the extraction process. Experimental results also suggest that operating at 30 g/min the system seems to be approaching thermodynamic equilibrium, and the solvent flow leaving the extractor is saturated with the soluble fractions of VR.

### 3.3. Effect of solvent composition and process pressure

A rapid increase in the yield and production rate of the extract with an increase in the concentration of toluene in the composition of CO<sub>2</sub> at solvent demetallization of VR, carried out at a temperature of 50 °C and a pressure of 30 MPa, was shown by us recently [25]. As part of the present study, the influence of the solvent composition on the yield and composition of DAO was also studied at a temperature of 50 °C, ensuring that the CO<sub>2</sub>-toluene mixture was preferably in the liquid state, regardless of the ratio of components in the mixture in the investigated pressure range. The dependences of the DAO yield on the process pressure obtained for

mixtures with different toluene concentrations are shown in Fig. 4.

Without the addition of toluene, pure scCO<sub>2</sub> has an extremely low dissolving power with respect to VR components. So, the DAO yield using scCO<sub>2</sub> as a solvent did not exceed 0.2 wt. % at a pressure of 10 MPa. The increase in pressure and density of scCO<sub>2</sub> contributes to an increase in its dissolving ability and DAO yield, which reached about 7 wt.% at a pressure of 30 MPa. The results obtained are in good agreement with the available literature data on the low solubility of high molecular weight petroleum components with high degrees of molecular condensation in scCO<sub>2</sub>, which extracts predominantly only volatile compounds of small molecular weight [16,17,20–22]. The addition of 5 wt.% toluene to the composition of CO<sub>2</sub> slightly changes the solvent capacity and the yield of DAO, which increased only to 10 wt.% at a pressure of 30 MPa. While a further increase in the concentration of toluene in the mixture was accompanied by a rapid increase in the solubility of the VR components and the DAO yield. So, at a concentration of toluene of 25 wt.% and pressures above 20 MPa, the DAO yield exceeded 50 wt. %, increasing by about five times with a five-fold increase in its content in the solvent (Fig. 4). However, it is necessary to note the uneven increase in the DAO yield with an increase in the toluene concentration in the mixture, which indicates the uneven change in the energy of the intermolecular interaction of the VR and solvent components with a change in the composition of the latter. As can be seen from the presented dependences, the yield growth significantly slowed down with an increase in toluene concentration from 10 to 15 % and from 20 to 25 %. At concentrations of toluene in the solvent above 15 wt.% an increase in pressure in the studied range slightly increased the DAO yield, which confirms the presence of CO<sub>2</sub>-toluene mixtures of given composition in a liquid state, which is characterized by low compressibility and, as a consequence, a weak dependence of density and dissolving ability on pressure. While for mixtures with a toluene content of less than 15 %, the rate of change in the DAO yield increases significantly and the dependence on pressure is more drastic. According to the phase diagram, at a temperature of 50 °C and pressures above 10 MPa a mixture with a toluene content of 10 wt.%, despite the liquid state, is in the vicinity of its critical point ( $T_{cm} = 55\text{ }^{\circ}\text{C}$ ,  $P_{cm} = 9.9\text{ MPa}$ ) and the transition region (Fig. 1). As is known, in this case the liquid substance is in the subcritical state, in which it begins to acquire the properties of SCF [32]. As a result, for this mixture (CO<sub>2</sub>/toluene = 90/10), an increase in pressure in the studied range from 10 to 30 MPa led to a rapid increase in density of the solvent mixture from 0.6 to 0.9 g/mL and the DAO yield from 8 to 26 wt.% (Fig. 4).

An increase in the DAO yield, achieved as a result of an increase in the concentration of toluene in the composition of the solvent,

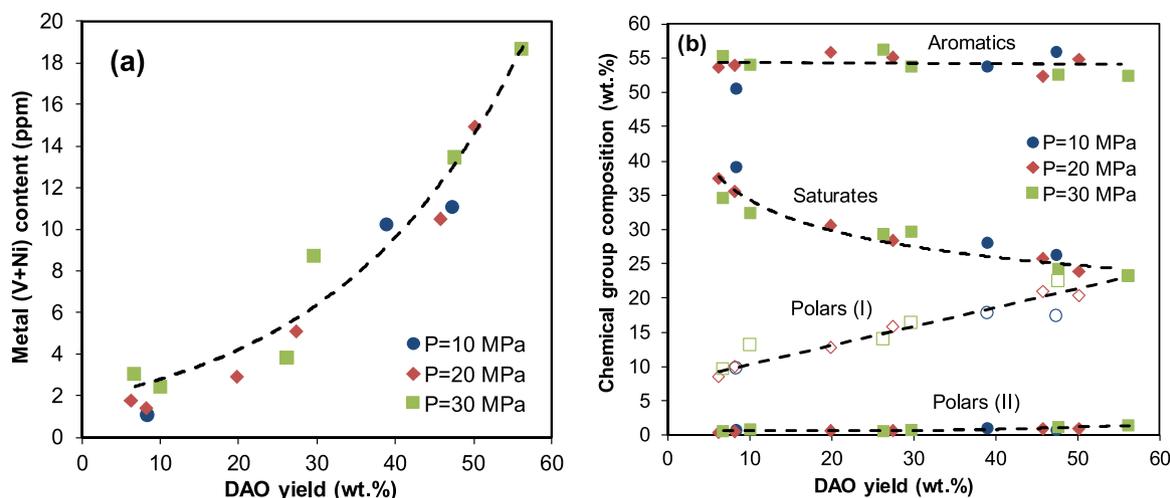


Fig. 5. Vanadium and nickel content (a) and chemical group composition (b) in DAO versus DAO yield produced from extraction of VR using a mixture of CO<sub>2</sub>-toluene at different pressures ( $T = 50^{\circ}\text{C}$ , total solvent flow rate – 30 g/min, extraction time - 260 min). The DAO yield at a given pressure was varied by changing the composition of the mixture in the range of toluene concentrations from 0 to 25 wt.%.

regardless of the process pressure, was accompanied by exponential increasing the metal content in the extracted DAO product (Fig. 5a). The increase in metal content is associated with a change of chemical group composition of DAO. In particular, increasing the DAO yield as a result of the use of CO<sub>2</sub>-toluene mixtures with a higher toluene content led to an increase in the fraction of polar compounds I, represented mainly by resin fractions, due to the predominant decrease in the content of saturated hydrocarbons in the DAO (Fig. 5b). At the same time, the share of aromatic hydrocarbons and high molecular weight polar compounds II, including asphaltenes of the feedstock, in this range of DAO yields and compositions of the solvent used, respectively, varied slightly. Thus, an increase in the share of polar compounds, in particular resins, that along with asphaltenes are metal concentrators in the petroleum residues, is accompanied by a rapid increase in the metal content in DAO, which is also observed for SDA processes using light alkanes with increasing their molecular weight and solvent power [14]. Despite the decrease in the selectivity of the solvent with respect to the oil components of VR with increasing toluene content in the mixture, the content of high molecular weight polar compounds II in the DAO did not exceed 1.5 wt.%, which can indicate the low solubility of asphaltenes and high deasphalting efficiency using this solvent in the studied range of its compositions.

The process pressure also slightly affected the group composition of

the DAO obtained (Fig. 5b). It can be concluded that the pressure is a parameter that affects the density and solvent power of the solvent, but almost does not affect its selectivity and the composition of the separation products at their given yield.

### 3.4. Effect of process temperature

A study of the effect of extraction temperature on the yield and composition of DAO was carried out for a mixture of CO<sub>2</sub>-toluene with a toluene content of 20 wt.% ( $T_{\text{cm}} = 71^{\circ}\text{C}$ ,  $P_{\text{cm}} = 12.5\text{ MPa}$ ). The obtained isotherms in the dependences of the DAO yield on the process pressure and solvent density are shown in Fig. 6.

As noted earlier, the pressure insignificantly affects the dissolving ability and the DAO yield at a temperature of 50 °C and liquid phase state of the solvent. In turn, an increase in temperature above the critical temperature for a given mixture in the pressure range of less than 20 MPa led to a rapid decrease in solvent density and DAO yield. Based on Fig. 6, an increase in temperature from 50 to 125 °C at a pressure of 15 MPa is accompanied by a decrease in the density of the solvent from 0.83 to 0.36 g/mL and a corresponding decrease in the yield of DAO from 42 to 3 wt. %. Such a sharp change in the properties and solvent power of the solvent following the transition to the SCF region, observed for this mixture in the region of relatively low pressures, is in

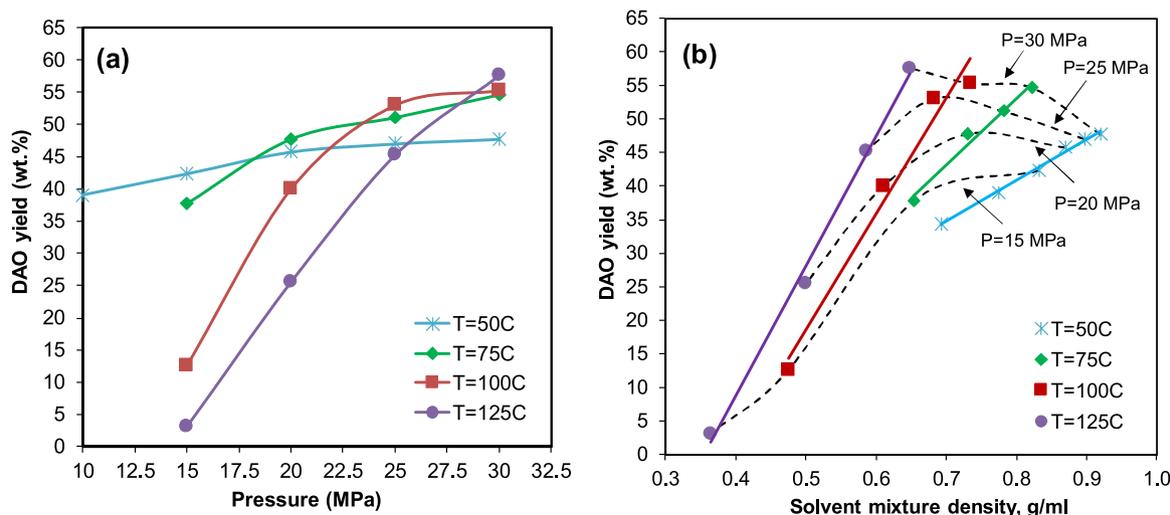


Fig. 6. DAO yield as a function of pressure (a) and solvent mixture density (b) in the SDA of VR using a mixture of CO<sub>2</sub>-toluene with a toluene content of 20 wt.% for various extraction temperatures (total solvent flow rate – 30 g/min, extraction time - 260 min).

good agreement with the phase behavior of the individual compounds and is widely used in practice for DAO product separation and solvent recovery in SDA process technologies [9].

However, the temperature has a different effect on the solubility of the VR components in the solvent and the yield of DAO in various pressure ranges. The mixture in the supercritical state provides an increase in the DAO yield relative to the solvent in the liquid state in the region of higher extraction pressures exceeding a certain boundary value. Moreover, this boundary value of pressure, above which the solubility increases, enhances with increasing temperature of extraction. So, if for a temperature of 75 °C this pressure is approximately 18 MPa, then for a temperature of 125 °C it is about 25 MPa (Fig. 6a). In the SCF region, an increase in temperature also led to some increase in the DAO yield when a certain boundary pressure or otherwise the crossover pressure was exceeded. Such retrograded behavior of solubility is typical for SFE especially occurring in a solid-fluid binary system and explained from the point of view of the competing effect of solvent density and volatility of the solute [32]. In our case of supercritical extraction of VR using a mixture of 20 wt.% of toluene in CO<sub>2</sub> increasing the temperature from 75 to 125 °C at pressure of 30 MPa resulted in an increase in DAO extracted from about 55 to 58 wt. % (Fig. 6a). A slight increase in the DAO yield beyond the crossover pressure can be explained by the low vapor pressure of the VR components in the studied temperature range.

The dependences of the DAO yield on the solvent density obtained at different temperatures are almost linear in the investigated pressure range (Fig. 6b). Moreover, an increase in temperature and the transition of the solvent to a supercritical state due to an increase in compressibility leads to a substantial increase in the rate of change in the yield of DAO with a change in pressure and density, respectively. At process pressures providing a solvent density in the region above ~0.6 g/mL, an increase in temperature above the critical value for the mixture is accompanied by an increase in the DAO yield, even despite a noticeable decrease in the density of the mixture. So, at a pressure of 30 MPa, a temperature increase from 50 to 125 °C resulted in an increase in the DAO yield from 48 to 58 wt. % while reducing the density of the solvent from 0.92 to 0.65 g/mL (Fig. 6b). That is, in this case, the decrease in density, which is the physical characteristic of the solvent, is apparently compensated by the increase in the energy of intermolecular interaction as a result of the phase transition. A similar effect of compensating for a decrease in density due to enhanced solvating power of the solvent near the solvent critical temperature was observed in the study of the SFE process of various petroleum feedstocks using propane and CO<sub>2</sub> as solvents [21]. In this work, the authors also observed an increase in extraction yields at lower values of the solvent reduced density when the extraction temperatures were in the vicinity of the critical temperature of the solvent. Thus, during the propane extraction of bitumen-derived liquid the temperature increase from 38 °C ( $T_r = 0.84$ ) to 107 °C ( $T_r = 1.03$ ) at constant pressure (10.3 MPa), despite the decrease in the reduced solvent density from 2.92 to 2.11, led to an increase in the total yield of the extract by approximately 10 wt.% at the maximum cumulative volume of solvent pumped. Confirmation of an increase in the solubility of HPF components in the solvent when it is in a sub- and supercritical state, which compensates for the effect of a decrease in the density of SCF, can also be found in [33], in which the SDA of a VR using supercritical propane conducted in a semibatch extraction unit was investigated. In this case, at a pressure of about 10 MPa, an increase in temperature near the critical point ( $T_c = 97$  °C) from 66 to 107 °C had practically no effect on the extract yield, despite the reduction in propane density from 0.47 to 0.38 g/mL. Thus, it can be stated that in the SDA process with a CO<sub>2</sub>-toluene binary mixture, the solvent density is not the only parameter that determines its dissolving ability, which also largely depends on the extraction temperature, especially near and beyond the solvent critical temperature.

The chemical group composition of DAO obtained at extraction temperatures from 50 to 125 °C and a constant pressure of 25 MPa using a mixture with toluene content of 20 wt.% is shown in the histogram of Fig. 7.

At a given pressure in the temperature range studied, the DAO yield

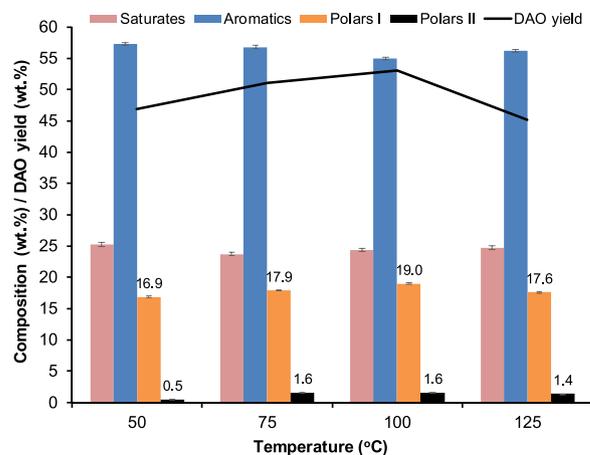


Fig. 7. Chemical group composition and the yield of DAO formed at different temperatures in the extraction of VR using a mixture of CO<sub>2</sub>-toluene with a toluene content of 20 wt.% (P = 25 MPa, total solvent flow rate – 30 g/min, extraction time – 260 min).

varied in a narrow region from about 45 to 53 wt. %. An increase in temperature and the transition of the solvent mixture to the supercritical state also affects the selectivity of the extraction, contributing to an increase in the solubility of higher molecular weight polar compounds in the solvent phase. As a result of extraction using a supercritical CO<sub>2</sub>-toluene mixture, the content of polar I and polar II in the composition of DAO increased by about 1–2 and 1 wt.%, respectively, compared with this mixture in the liquid state (T = 50 °C) (Fig. 7). An increase in temperature from 75 to 125 °C in the supercritical region for the mixture, considering some change in the yield, slightly affects the group composition of the DAO at a given process pressure. It should be noted that an increase in the solubility of heavier compounds of petroleum feedstock and a change in the quality of the extract with an increase in the extraction temperature above the solvent critical temperature were also observed in several previous studies. For instance, in the already mentioned work [21], it was found that extracts obtained from crude oil under conditions ensuring the presence of CO<sub>2</sub> in a supercritical state (T = 38 °C, P = 17.2 MPa) contained heavier compounds compared to extracts obtained using liquid CO<sub>2</sub> as a solvent (T = 24 °C, P = 10.3 MPa). An experimental study of SDA of VR using propane in a sub- and supercritical state showed that the DAO of the subcritical process had a lower molar mass, as well as the content of asphaltenes and metals, compared with the DAO formed in the supercritical process. When using subcritical propane, the content of asphaltenes in DAO did not exceed 0.1 %, while in the case of supercritical propane it reached 1.16 % [34].

An enhanced solubility of polar resin and asphaltene fractions in the CO<sub>2</sub>-toluene beyond the mixture critical point contributed to an increase in the content of metals in the DAO with increasing the extraction temperature and a decrease in the demetallization efficiency, respectively. In the vicinity of the critical temperature for this mixture (T = 75 °C), the metal content change insignificantly with respect to the mixture in the liquid state (T = 50 °C), while a further increase in temperature leads to increased vanadium and nickel concentrations in the composition of DAO at its fixed yield. For instance, an increase in temperature from 50 to 125 °C at the DAO yield of about 45 wt. % increased the vanadium and nickel content from about 11 to 16 ppm, as illustrated by Fig. 8.

While the sulfur and carbon residue contents in the DAO are less sensitive to changes in the extraction temperature in the studied range and the transition of the solvent mixture to a supercritical state (Fig. 9). An increase in the DAO yield with increasing extraction pressure is accompanied by an increase in CCR content of extract produced, which can be associated with observed growing the share of resin fractions (polars I) in the DAO, that have the high degree of aromaticity (Fig. 9a). It is important to note that the sulfur content in the DAO in the yield region up to 60 wt.

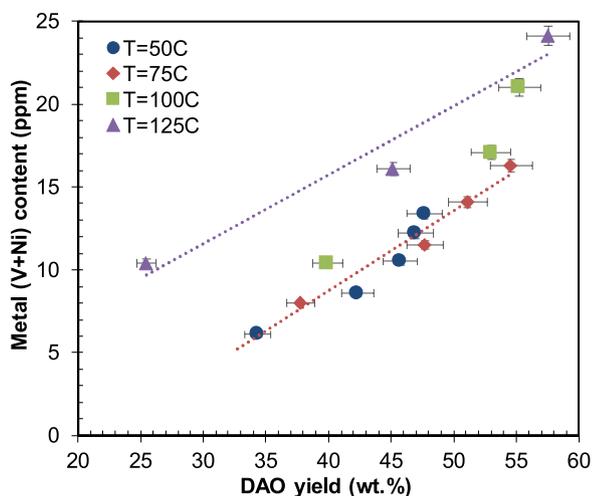


Fig. 8. Vanadium and nickel content in DAO versus DAO yield produced from extraction of VR using a mixture of CO<sub>2</sub>-toluene with a toluene content of 20 wt.% at different temperatures (P = 10-30 MPa, total solvent flow rate – 30 g/min, extraction time - 260 min).

% varies slightly, as presented in Fig. 9b. It may indicate a more complex distribution of sulfur compounds between the chemical group components of the VR, as well as the binding of a significant proportion of sulfur in the composition of asphaltene molecules that are mainly concentrated in the process residue (asphalt) regardless extraction temperature.

It can be concluded that temperature is an important parameter of the deasphalting process, since it significantly affects the physico-chemical properties of the CO<sub>2</sub>-toluene mixture, its dissolving ability and selectivity, especially near and beyond the critical temperature of the solvent.

### 3.5. Effect of phase transitions and extraction temperature for various solvent composition

To study the effect of temperature on the yield and composition of DAO formed during the SDA of VR using CO<sub>2</sub>-toluene mixtures of various compositions, experiments were carried out at two different temperatures of 50 and 100 °C for mixtures with a high toluene content of 20, 30, and 40 wt.%, differing in critical point parameters, accordingly (see Fig. 1). A histogram of the obtained DAO yield values for these CO<sub>2</sub>-toluene mixtures at extraction temperatures of 50 and 100 °C is shown in Fig. 10.

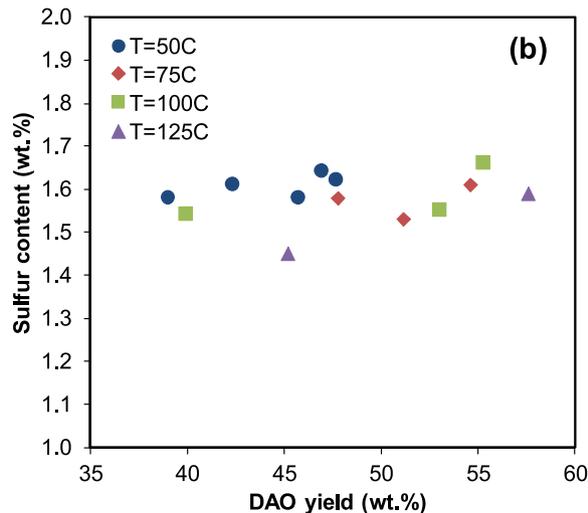
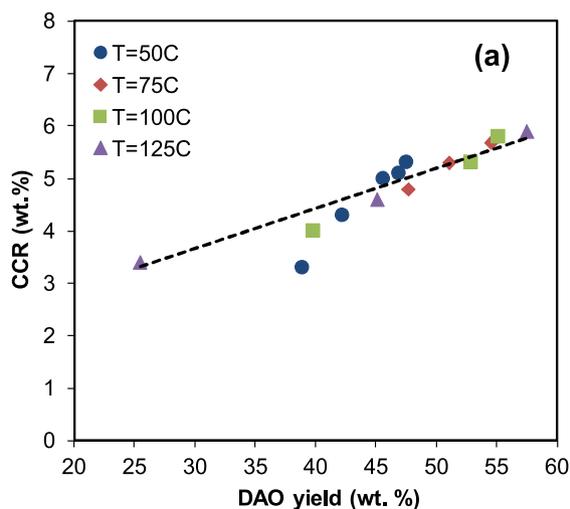


Fig. 9. CCR (a) and sulfur (b) content in DAO versus DAO yield produced from extraction of VR using a mixture of CO<sub>2</sub>-toluene with a toluene content of 20 wt.% at different temperatures (P = 10-30 MPa, total solvent flow rate – 30 g/min, extraction time - 260 min).

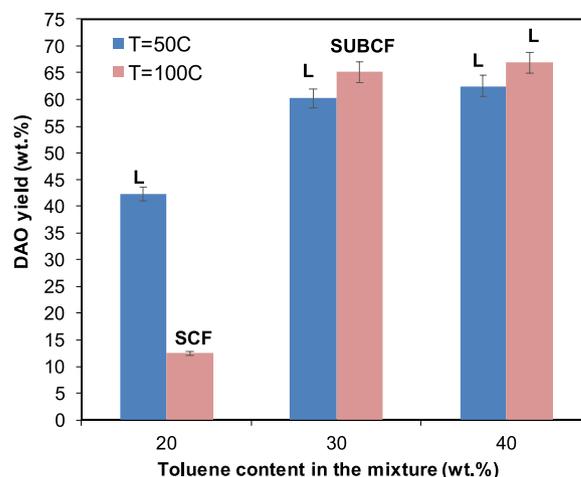


Fig. 10. DAO yield produced from extraction of VR using a mixture of CO<sub>2</sub>-toluene with various toluene concentrations and extraction temperature (P = 15 MPa, total solvent flow rate – 30 g/min, extraction time - 260 min): L – liquid; SUBCF – subcritical fluid; SCF – supercritical fluid.

As shown previously, an increase in the concentration of toluene in the mixture above 5 wt.% leads to a rapid increase in the solubility of VR components and the DAO yield. When the mixture is in a liquid state (T = 50 °C), an increase in the concentration of toluene from 20 to 30 wt.% in the composition of CO<sub>2</sub> is also accompanied by a significant growing the yield of DAO from 42 to 60 wt.%. While a further increasing the toluene content in the mixture has little effect on the solvating power of the solvent. Thus, in the case of liquid extraction using a mixture with a toluene content of 40 wt.%, the DAO yield increased only by 3%, reaching 63 wt.%, as reported by Fig. 10. We also observed a slowdown in the growth of extract production rate at toluene concentrations in the solvent composition of more than 30 wt.% when studying the process of solvent demetallization of VR with a mixture of CO<sub>2</sub>-toluene [25]. A similar slowdown in the growth of the extraction efficiency of crude oil from dolomite rock with an increase in the concentration of toluene in the composition of CO<sub>2</sub> was previously noted during SFE using CO<sub>2</sub> with chemical modifiers [23]. It can be assumed that in this case, CO<sub>2</sub>, being an effective anti-solvent and a coagulant of asphaltenes in petroleum systems, limits the growth of the solvent power of the mixture, preventing the dissolution of high molecular weight polar compounds by toluene. A study of the phase behavior of two poly-aromatic model molecules in the presence of toluene and CO<sub>2</sub> showed that, at high concentrations in the mixture (above

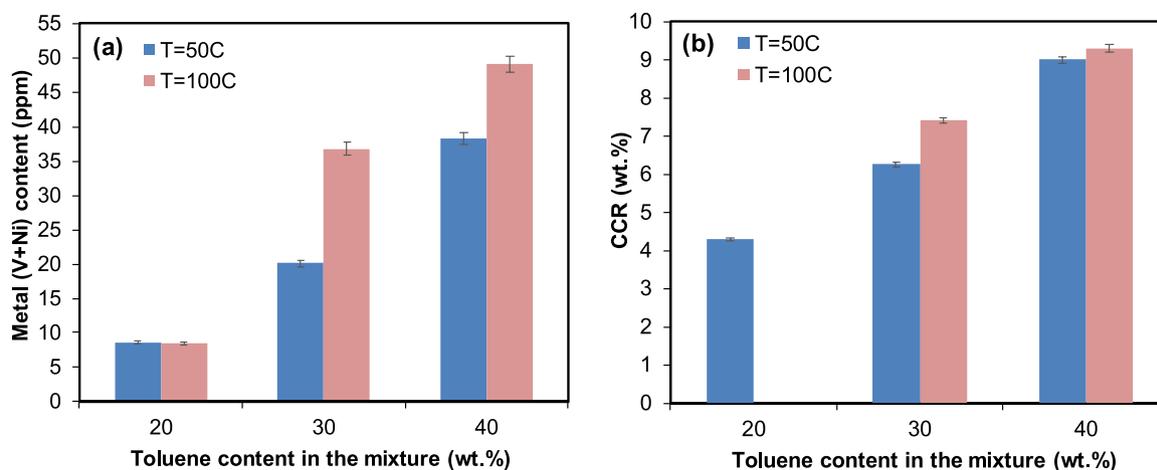


Fig. 11. Vanadium and nickel (a) and CCR (b) content in DAO produced from extraction of VR using a mixture of CO<sub>2</sub>-toluene with various toluene concentrations and extraction temperature (P = 15 MPa, total solvent flow rate – 30 g/min, extraction time - 260 min).

50 wt.%), CO<sub>2</sub> begins to act as an anti-solvent, leading to the precipitation of poly-aromatic molecules from the solution [35].

An increase in the extraction temperature to 100 °C for a CO<sub>2</sub>-toluene mixture with a toluene content of 20 % leads to its transfer to the SCF region, a sharp decrease in the density of the solvent and the DAO yield, which drops to 12 wt.%. While for mixtures with a toluene content of 30 and 40 %, carrying out the process at 100 °C ensures that the mixtures are in the region of the critical point or subcritical state and liquid state, respectively. In the latter case, a slight increase in the solvent power and the DAO yield was observed for both mixtures, as presented in Fig. 10. Fig. 11 shows the content of metals and CCR in the composition of the DAO produced during the extraction process using the abovementioned mixtures.

When the mixture is in a liquid state (T = 50 °C), an increase in the concentration of toluene from 20 to 30 % and the DAO yield was accompanied by increasing the metal and CCR content in DAO composition that however remained at a sufficiently low level. Thus, the metal and CCR content was about 20 ppm and 6 wt.%, which corresponds to the removal efficiency of these unwanted components or impurities of more than 90 and 80 wt.%, respectively. This pattern is in good agreement with the change in the group composition of DAO observed with increasing toluene content in the solvent, namely, a decrease in the content of saturated hydrocarbons and an increase in the content of resins (polars I) (Fig. 12).

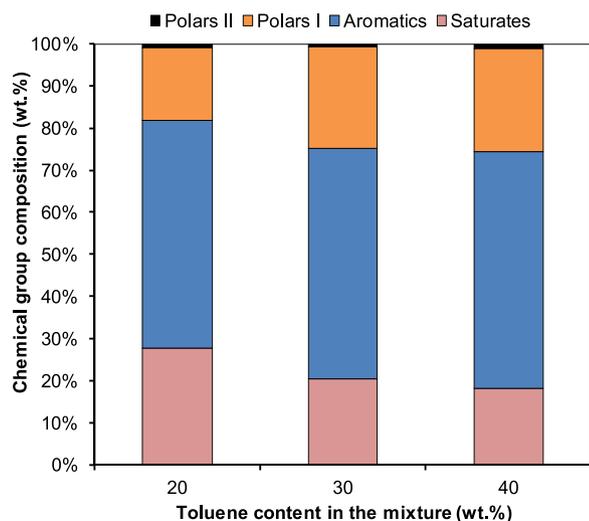


Fig. 12. Chemical group composition of DAO produced from extraction of VR by CO<sub>2</sub>-toluene mixture with different toluene content (T = 50 °C, P = 15 MPa, total solvent flow rate – 30 g/min, extraction time - 260 min).

At the same time, a further increase in the concentration of toluene in CO<sub>2</sub> to 40 %, slightly affecting the yield of separation products, leads to a significant decrease in selectivity and a deterioration in the quality of DAO. Carrying out the extraction using this mixture increased the metal concentration in DAO almost twice to 38 ppm and the CCR content by approximately 3 wt.%, as illustrated in Fig. 11. Such a deterioration in the quality of DAO when using a mixture with a high toluene content (40 %) may be associated with some solubility enhancement for heavy resin and/or asphaltene fraction in the solvent phase, as can be seen from some increase in the share of polar compounds II in DAO (Fig. 12).

SDA of VR using a CO<sub>2</sub>/toluene mixture with a component ratio of 70/30 at increased extraction temperature of 100 °C which corresponds to being in the vicinity of the mixture critical point (T<sub>cm</sub> = 111 °C, P<sub>cm</sub> = 17.2 MPa) was accompanied by growing the metal and CCR content in DAO simultaneously with increasing the solvating power of the solvent. As in the case with a mixture with a toluene content of 20 %, such a decrease in the selectivity when the mixture is located near the critical temperature is apparently associated with enhanced solubility of resin and asphaltene constituents, as evidenced by an increase in the polar compounds content in the composition of the DAO obtained. It is interesting to note that an increase in temperature for a mixture with a toluene content of 40 %, despite a sufficient distance from the critical temperature (T<sub>cm</sub> = 160 °C) and its presence in the liquid state, also led to decreasing the DAO quality due to increased content of polar compounds and associated heavy metals (Fig. 11).

#### 4. Conclusions

The influence of process parameters and solvent composition on the yield and composition of the DAO produced from extraction of VR with a mixture of CO<sub>2</sub>-toluene has been established. The obtained experimental data and the observed behavior of the solvent are in good agreement with phase equilibrium data for CO<sub>2</sub>-toluene mixtures obtained using PR EoS.

When the mixture is in a liquid state, process indicators are determined mainly by the composition of the solvent. An increase in toluene content in the region up to 30 wt.% leads to a rapid increase in the solvent power and the yield of DAO, as well as decreasing the content of saturated hydrocarbons and an increase in the share of resin fraction (polar compounds I), metal and CCR content in its composition. Pressure is a parameter that affects the density and solvent power of the solvent, but almost does not affect its selectivity and the composition of the separation products at their given yield. While temperature is an important parameter of the deasphalting process, since it significantly

affects the physicochemical properties of the CO<sub>2</sub>-toluene mixture, its dissolving ability and selectivity, especially near and beyond the critical temperature of the solvent. An increase in temperature and the transition of the CO<sub>2</sub>-toluene mixture to the supercritical state leads to a rapid decrease in the solvent density and the DAO yield. At the same time, at process pressures providing a solvent density in the region above ~0.6 g/mL, an increase in temperature above the critical value for the mixture is accompanied by an increase in the DAO yield, even despite a noticeable decrease in the density of the mixture.

Taking into account a sharp slowdown in the growth of solvent power and a decrease in the DAO quality due to enhanced solubility of heavy resin and/or asphaltene fraction at toluene content above 30 wt. %, the most optimal mixtures for the SDA process are that containing from 20 to 30 wt.% of toluene and providing a sufficiently high solvent capacity and selectivity. Conducting the process at temperatures higher than critical for these mixtures necessitates a significant increase in the process pressure in order to maintain an acceptable solvating power of the solvent mixture and/or reduces the separation selectivity and DAO quality due to increased solubility of metal-containing polar compounds. As a result, temperatures from 50 to 75 °C and pressures from 10 to 15 MPa, which ensure the presence of the solvent in the liquid phase state depending on the composition of the mixture, are apparently the optimal parameters for SDA.

Thus, a mixture of CO<sub>2</sub>-toluene can act as an effective solvent for the SDA of HPF, removing heavy resin and asphaltene fraction that ensures high metal and CCR removal efficiency and DAO quality. To assess the prospects of using this solvent in practice, pilot tests are required to evaluate the necessary solvent to feed ratios, extraction efficiency and product quality in the continuous process mode.

#### CRedit authorship contribution statement

**Rustam N. Magomedov:** Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing, Visualization, Supervision. **Artem V. Pripakhaylo:** Methodology, Validation, Investigation, Visualization. **Daniyar Sh. Dzhumamukhamedov:** Methodology, Software, Formal analysis. **Tatiana A. Maryutina:** Writing - review & editing, Project administration, Funding acquisition.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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