



## Fractionation of a vacuum residue with a mixture of CO<sub>2</sub>-toluene as a method for characterizing heavy petroleum feedstocks

Rustam Magomedov , Artem Pripakhaylo & Tatiana Maryutina

To cite this article: Rustam Magomedov , Artem Pripakhaylo & Tatiana Maryutina (2020): Fractionation of a vacuum residue with a mixture of CO<sub>2</sub>-toluene as a method for characterizing heavy petroleum feedstocks, Separation Science and Technology, DOI: [10.1080/01496395.2020.1839098](https://doi.org/10.1080/01496395.2020.1839098)

To link to this article: <https://doi.org/10.1080/01496395.2020.1839098>



Published online: 27 Oct 2020.



Submit your article to this journal [↗](#)



View related articles [↗](#)



View Crossmark data [↗](#)



## Fractionation of a vacuum residue with a mixture of CO<sub>2</sub>-toluene as a method for characterizing heavy petroleum feedstocks

Rustam Magomedov , Artem Pripakhaylo , and Tatiana Maryutina 

Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow, Russia

### ABSTRACT

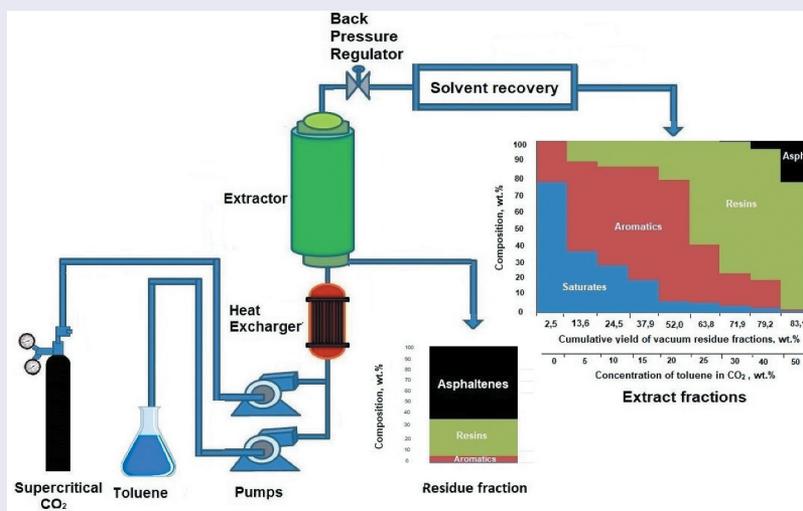
The characterization of the feedstock is an important analytical task in the modeling and development of processes for upgrading of petroleum residues. This work presents the results of fractionation of the vacuum petroleum residue by extraction using a mixture of CO<sub>2</sub> and toluene as a solvent. Fractionation was carried out by changing the ratio of components in the mixture by successively increasing the concentration of toluene in the composition of the CO<sub>2</sub> stream from 0% to 50%. As a result of separation of the vacuum residue, nine fractions of the extract with a yield of 83.1% were obtained.

### ARTICLE HISTORY

Received 10 June 2020  
Accepted 14 October 2020

### KEYWORDS

carbon dioxide extraction;  
fractionation method;  
toluene



### Introduction

Modeling the phase equilibrium in mixtures of petroleum fluids and solvent, which allows predicting the phase behavior and compositions of the phases formed, especially in the vicinity of the critical point, is an important task in the recovery and upgrading of heavy oils and natural bitumen. In this case, the use of solubility theory and equations of state (EoS) as models for predicting the phase behavior and stability of multicomponent petroleum systems has become widespread.<sup>[1–4]</sup> In particular, a group contribution pseudocomponent (PC) method based on the characterization method (CM) for petroleum fractions and the predictive Peng-Robinson 1978 (PPR78) model is promising for accurate

prediction of phase equilibrium for mixtures of petroleum fluids and solvent.<sup>[1]</sup> However, the use of EoS and this approach for petroleum residues and solvent mixtures is more challenging because characterization data are not available for the non-distillable fractions of crude oils.<sup>[2]</sup>

There are a limited number of methods for separation of the petroleum vacuum residues (VR) into narrow fractions with the possibility of subsequent analysis of the latter. One of them is the separation of VR into four to eight fractions according to their polarity using a separation procedure based on adsorption chromatography after the asphaltenes extraction from the initial sample solution. These include saturates, aromatics, resins, and asphaltenes (i.e., the typical SARA

separation). The aromatics and resins can then be separated into light, medium, and heavy components.<sup>[5]</sup> Although this approach has the advantage of providing a more defined classification, the number of fractions is limited, and it takes a long time to obtain sufficient amounts of each fraction to carry out the necessary analyses for characterization. An alternative approach is to use supercritical fluid extraction and fractionation (SFEF) to separate samples into narrow cuts in sufficient amounts needed for characterization. The narrow fractions range from light to heavy with increasing polarity and molecular weight.<sup>[4]</sup> An example of this approach is SFEF using supercritical n-pentane as a solvent. Separation occurs due to a gradual increase in the density and solvent power of n-pentane, which is achieved by a linear increase in the extraction pressure in the region of supercritical parameters for the solvent. As a result, it is possible to isolate many narrow fractions with a high total extraction yield. For example, SFEF was employed to separate four Chinese vacuum residua into 15–17 narrow fractions with total extraction yields of 71.7–87.8 wt. %.<sup>[6]</sup> However, this method requires high extraction temperatures of 240–250°C, which is associated with a rather high critical temperature of the solvent.

Recently, we have shown the possibility of fractionation of heavy crude oil sample by solvent extraction by means of changing the composition of the solvent, which is a binary mixture of carbon dioxide (CO<sub>2</sub>) and toluene. Using supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) as a solvent base makes it possible to carry out the process at low temperatures and avoid thermal decomposition of the petroleum sample components, overcoming the limitations of the distillation method.<sup>[7]</sup>

This paper will present the results of our study on the separation of a VR sample into narrow fractions using the previously proposed approach. As a result of the work, an analysis of the composition and properties of the extracted fractions and a discussion of the obtained patterns have been carried out.

## Experimental part

### Materials

For the extraction, high purity CO<sub>2</sub> (99.99%) and toluene with a purity of 99.5% were used. A VR produced at the crude distillation unit of one of the Russian refineries was used as the initial sample for separation. The composition and properties of this sample are presented in Table 1.

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

Property	Value
SARA, wt.%	
- Saturates	13.9
- Aromatics	39.0
- Resins	35.6
- Asphaltenes	11.5
CCR, wt.%	18.5
H/C atomic ratio	1.155
Nitrogen, %	0.42
Sulfur, %	4.80
Vanadium, ppm	205
Nickel, ppm	57

### Experimental apparatus and extraction technique

A supercritical fluid extraction (SFE) unit, equipped with a 1000 ml high-pressure extraction vessel and a separator for separating CO<sub>2</sub> and collecting the extract fractions, was used to fractionate the VR sample. In addition, the unit included high-pressure pumps for supplying liquid CO<sub>2</sub> and organic solvent/modifier, an electric pre-heater for heating the solvent mixture to the extraction temperature before feeding into the extractor, as well as temperature and pressure sensors, manual, and automatic valves to control process parameters.

Before the extraction, the preheated VR sample was mixed with glass balls with a diameter of 2–3 mm and loaded into the extractor. After that, the remaining free volume of the extractor was also filled with the balls. After loading the sample and sealing the setup, the extractor and preheater were heated to the set extraction temperature and CO<sub>2</sub> began to be fed at a fixed flow rate, which was monitored by a Coriolis flow meter. As the system approached the set pressure, the automatic back pressure regulator (ABPR) began to open and release a stream of solvent with extract fractions into the separator. The position of the valve needle and the maintenance of the set pressure during the dynamic extraction was carried out using a PID controller based on an electric signal from a pressure sensor inserted into the body of the ABPR. The extraction time began to be recorded from the moment the temperature and pressure reached the set values.

The first fraction was obtained using pure SC-CO<sub>2</sub> without the addition of toluene. The extraction of each subsequent fraction occurred due to a sequential increase in the concentration of toluene in the binary mixture from 5 to 50 wt. %. In this case, the toluene concentration was increased in increments of 5% in the concentration range to 30% and in increments of 10% in the concentration range from 30% to 50%. After the completion of the extraction process, the supply of solvents and heating of the vessel were stopped, followed by a slow release of pressure in the system due to the

gradual opening of the ABPR valve. After the excess pressure was released, the resulting residual solution of the last fraction of the extract was collected from the supply lines of the separator by pumping an organic solvent through them. Finally, the extraction residue, together with the glass balls, was discharged from the extractor and quantitatively collected also using a solvent (toluene). The obtained solutions of the extract and residue fractions were subjected to vacuum distillation using an IKA RV-10 rotary evaporator to remove and recover toluene.

The diagram of the SFE laboratory setup, as well as a more detailed description of its components and the extractive separation procedure can be found in our previous works.<sup>[7,8]</sup>

### **Experimental conditions**

When separating the VR, the temperature, and pressure in the extractor were set at 100°C and 30 MPa. These parameters ensured the presence of a CO<sub>2</sub>-toluene mixture in a single-phase liquid or supercritical state in the studied range of mixture compositions,<sup>[9]</sup> a sufficient decrease in the viscosity of the petroleum residue sample and overcoming diffusion limitations, as well as a high density and solvating power of the solvent mixtures. The mass of the VR sample loaded into the extractor was 120 g, and the total flow rate of the solvent mixture was maintained at 100 g/min throughout the entire time of the separation procedure. Preliminary experiments have shown that this combination of sample loading weight and solvent flow rate ensures that the solvent is saturated with soluble sample components and that the latter are not entrained by the solvent flow. In addition, the volume of the extracted fractions is sufficient for the subsequent detailed analysis of their composition, and the extraction time is acceptable for separating the sample into narrow fractions during one continuous extraction procedure. Extraction and production of each fraction separated using a fixed composition CO<sub>2</sub>-toluene mixture was carried out for about 60 minutes. This time was sufficient to achieve the exhaustion yields of the extract fractions under the specified extraction conditions.

The total mass of the obtained fractions of the extract and the extraction residue was 120 ± 1 g, which is within an error of about ± 1 wt. %. The yield of fractions was calculated as the ratio of the mass of the fraction to the mass of the VR sample loaded into the extractor. The cumulative yield of the extract fractions or cumulative extraction yield was the increasing sum of the yields of the individual fractions. To assess the repeatability of the results of the method, the extraction procedure was

carried out three times under the same extraction conditions. The relative standard deviation (RSD) for the values of the yield of the same fractions did not exceed 2%.

### **Analysis of petroleum fractions**

For characterization of the VR and narrow fractions, their elemental (CHNS analysis) and group (SARA analysis) composition, the content of heavy metals (V and Ni) and Conradson carbon residue (CCR) were determined.

The SARA analysis consisted in the initial determination of the n-heptane insoluble asphaltene content in according to IP 143 method and the subsequent separation of the maltene fraction by adsorption chromatography. Separation was carried out by sequentially eluting the group components through a glass column packed with silica gel (Silica 60) using solvents of different polarity. N-heptane, toluene, isopropanol, and their mixtures in various ratios were used as eluents for the separation. The obtained fractions were combined into the corresponding groups based on the values of their refractive index and the solvent type used. So, saturates and aromatics were usually eluted using n-heptane and heptol mixtures, while the resin fractions were eluted with toluene and toluene/isopropanol mixture.

The content of carbon, hydrogen, nitrogen, and sulfur was determined using a Flash 2000 elemental analyzer (Thermo Fisher Scientific, Great Britain). The principle of the method was to combustion a petroleum sample in an atmosphere of pure oxygen with the formation of CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>O and SO<sub>2</sub>, followed by chromatographic separation and registration using a thermal conductivity detector (TCD). The RSD of the element content in petroleum samples did not exceed 2% for the results of six parallel measurements.

The CCR content was measured according to the procedures established by ASTM D189. The accuracy of measurement was checked using standard samples with a known content of CCR. The CCR content was determined with the relative error in measurements of ±1%.

Determination of vanadium and nickel content was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) according to ASTM D 5708 after petroleum 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). The RSD for the concentration of vanadium and nickel in the samples did not exceed 3%. The calculated detection limit in determining the concentrations of both elements was approximately 0.02 ppm.

## Results and discussion

Figure 1 shows the effect of toluene concentration in a binary mixture with CO<sub>2</sub> on the total extraction yield. Pure SC-CO<sub>2</sub> without toluene addition dissolves insignificant amounts of fractions of the VR, the yield of which was about 2.5 wt. %. This is in good agreement with the available experimental data showing the low solvating power of SC-CO<sub>2</sub> in relation to the components of natural bitumen and petroleum residues, which have a high molecular weight, aromaticity, and polarity.<sup>[10–12]</sup> The addition of toluene provides a fast and almost linear increase in the cumulative yield of extract fractions, which began to slow down significantly only when the toluene concentration in the mixture was more than 40% and the extraction yield was close to 80 wt.%. Toluene is a good solvent for all components of petroleum systems and, consequently, provides a significant increase in the solvating power and solubility parameter of the solvent mixture due to strengthening van der Waals interactions.<sup>[8]</sup> Drawing an analogy with heptol, it can be assumed that with an increase in the concentration of toluene, the solvent mixture becomes more favorable for aromatic and polyaromatic molecules, which are well solvated by the solvent

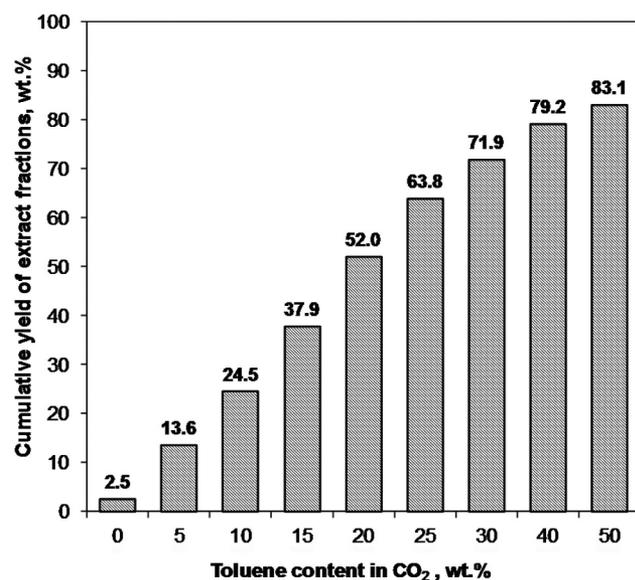


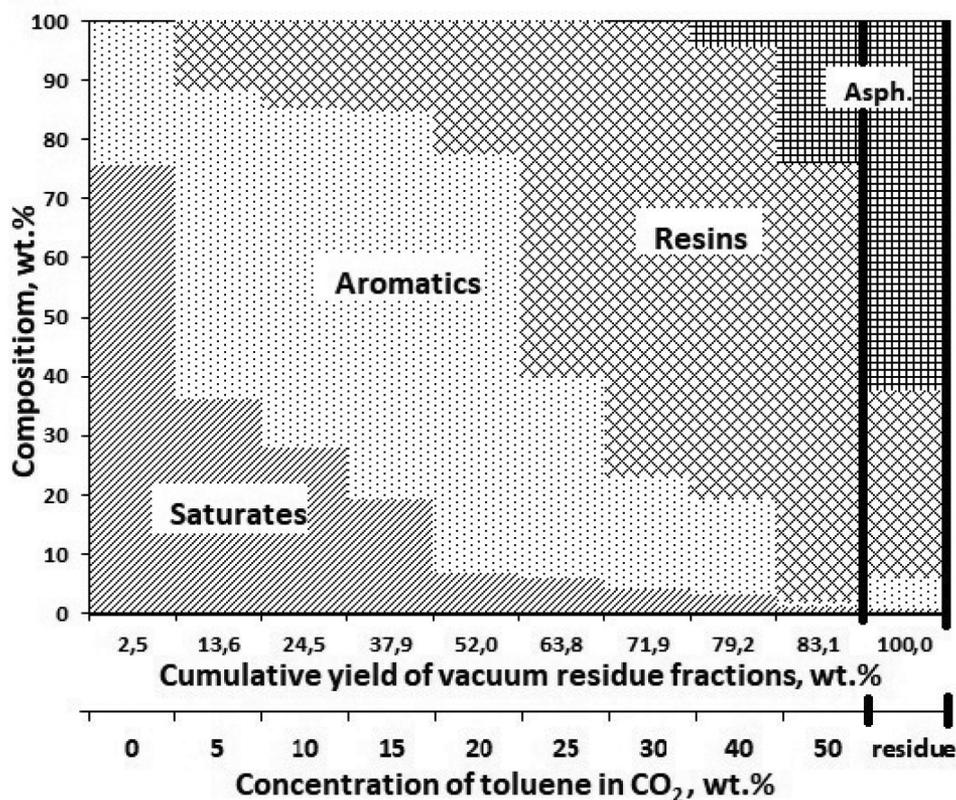
Figure 1. Effect of the concentration of toluene in a solvent mixture on the cumulative yield of extract fractions.

molecules due to similar interactions between aromatic rings in molecules.<sup>[13]</sup>

However, the observed decrease in the yield of individual fractions for mixtures with a high concentration of toluene in the region of high cumulative extraction yield indicates that CO<sub>2</sub> limits or decreases the solvating power of toluene. A similar pattern was also observed by us in the fractionation of the heavy oil sample using this binary mixture.<sup>[7]</sup> As is known, CO<sub>2</sub> is a strong precipitant for asphaltenes, the presence of which leads to a weakening of the interaction between resin and asphaltene molecules and a decrease in the solubility parameter of the hydrocarbon medium.<sup>[14–16]</sup> Moreover, CO<sub>2</sub> has a reasonable interaction coefficient with asphaltenes. A sensitivity analysis performed during modeling of asphaltene precipitation and deposition for the CO<sub>2</sub> injection scenario into oil reservoirs showed that the interaction coefficient between CO<sub>2</sub> and asphaltene is much higher than other components with asphaltene.<sup>[17]</sup> According to the authors, the main reason for the higher interaction coefficient may be that both molecules are polar. In studying the phase behavior of the solvent/bitumen systems, it was also shown that, for the CO<sub>2</sub>/bitumen system in the presence of asphaltene, CO<sub>2</sub> is more soluble in polar molecules of asphaltene because of dipole/quadrupole interactions.<sup>[18]</sup> Thus, it can be assumed that, being an effective anti-solvent, CO<sub>2</sub> prevents the dissolution and solvation of asphaltenes and other high molecular weight polar components by toluene molecules. This assumption is confirmed by the results of a study of the phase behavior of polyaromatic molecules in the presence of toluene and CO<sub>2</sub>. It was shown that at low concentration CO<sub>2</sub> acts as a co-solvent, while at higher concentration (above 40–50 wt. %), CO<sub>2</sub> acts as an anti-solvent and the polyaromatic molecule in the ternary system precipitates.<sup>[19]</sup>

In terms of selectivity, pure SC-CO<sub>2</sub> dissolves predominantly saturated hydrocarbons, whose share in the first fraction was more than 70% (Fig. 2). This is in good agreement with the available literature data on SFE of petroleum. Thus, it was found that CO<sub>2</sub> SFE selectively extracts relatively low molecular weight compounds and saturates are the dominant components in the extracts.<sup>[20]</sup>

The addition of even small amounts of toluene leads to a sharp decrease in saturates and growth of aromatics, which remain the main components of the fractions up to a concentration of toluene in a solvent mixture of 20%, as illustrated in Fig. 2. A further increase in the concentration of toluene is accompanied by a sharp increase in the concentration of resins, the content of which is close to 80% for fractions extracted with mixtures with a toluene content of 30 and 40 wt. %.



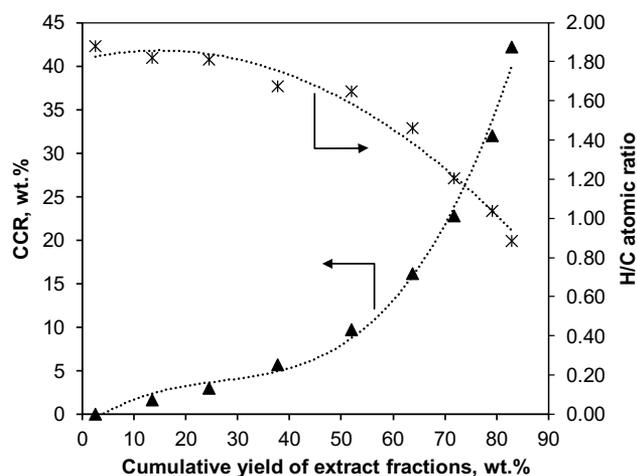
**Figure 2.** The group chemical composition of the fractions versus the cumulative extraction yield and the concentration of toluene in the binary mixture.

A change in selectivity in favor of more polar and high molecular weight fractions of resins at toluene concentrations in the mixture above 20% may indicate a sharp change in the properties of the solvent, leading to an increase in its solvating power. A sharp change in the behavior and forces of intermolecular interaction of asphaltene with a change in the composition of the heptol solvent was also observed in.<sup>[13]</sup> In this case, at toluene concentrations of less than 20%, heptol was a poor solvent, in the medium of which the attraction forces prevailed, favoring the aggregation of asphaltene molecules. However, at a concentration of more than 20%, the interaction forces changed from attractive to repulsive and heptol became a good solvent. This correlates well with the observed behavior of the CO<sub>2</sub>-toluene mixture and the active dissolution of the resin fractions when the toluene content is above 20%.

The asphaltene content in the fractions begins to increase markedly only for mixtures with a toluene content of more than 30% and was 24 wt. % for the last fraction extracted with a mixture with an equal (50/50) content of CO<sub>2</sub> and toluene. Based on the results obtained in<sup>[19]</sup>, it can be assumed that, at a concentration of 50%, CO<sub>2</sub> begins to exhibit the properties of a co-solvent, contributing to the dissolution of

asphaltene fractions. Despite this, asphaltene are almost completely concentrated in the extraction residue, being the main component of the latter with a content of more than 60 wt. % (Fig. 2).

An increase in the content of aromatic type components in the fractions leads to the expected increase in their CCR and a decrease in the H/C atomic ratio with an increase in the cumulative extraction yield, as presented in Fig. 3. Moreover, a rapid change in these properties correlates well with the rapid increase in resin content in fractions, which was observed for solvent mixtures with a toluene content above 20% and corresponds to a cumulative yield of more than 50 wt. %, respectively. Resins as well as asphaltene have condensed aromatic and naphthenic ring systems, which gives them high aromaticity and explains the obtained dependencies. According to available data, the H/C atomic ratio of resin fractions as a rule does not exceed 1.6, which corresponds to the H/C values for the obtained fractions with a high resin content, which were lower than 1.5. The decrease in H/C for fractions obtained with a solvent with 40% and 50% toluene content lower than 1.2 is in good agreement with the appearance of asphaltene, for which the H/C ratios are normally in the range of 0.9–1.2.<sup>[5]</sup> At the same



**Figure 3.** CCR and H/C atomic ratio of extract fractions versus the cumulative extraction yield.

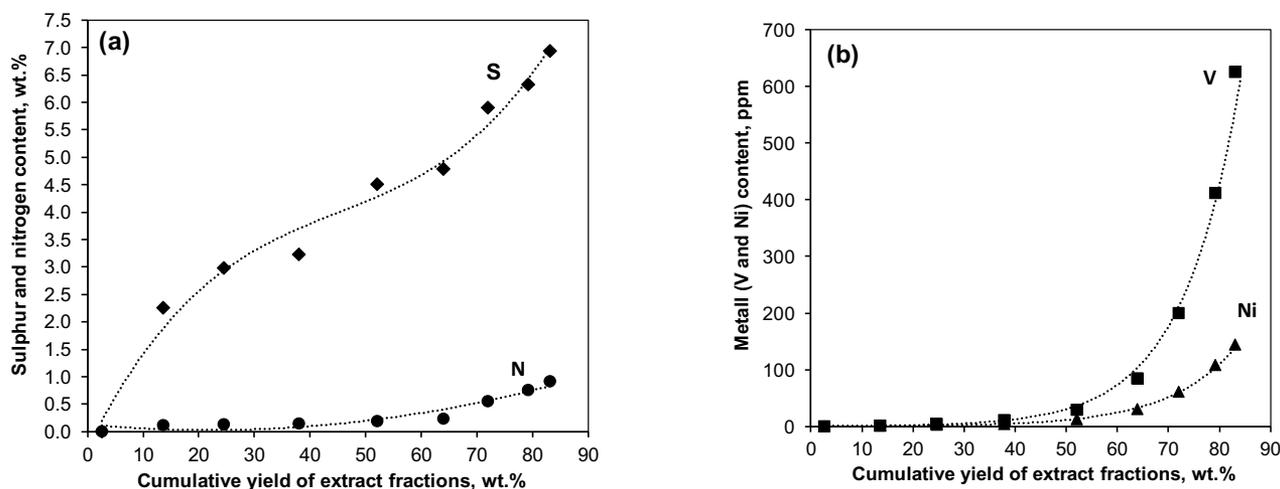
time, the carbon residue for various resin sub-fractions varies in the range from approximately 22 to 43 wt. %, <sup>[5]</sup> which also finds confirmation in the obtained fractionation results. An increase in the concentration of toluene in the mixture from 30% to 50% led to an increase in the CCR of the extract fractions containing about 74–76% resins, from about 23 to 42 wt. % (Fig. 3).

The addition and subsequent increase in toluene in the composition of the solvent mixture also leads to an increase in the polarity of the fractions, which can be observed by the rapid increase in sulfur content, as illustrated in Fig. 4. Pure CO<sub>2</sub> dissolved mainly nonpolar hydrocarbon components, while the growth of the sulfur content in the fractions was from 2.3% to 6.9% with an increase in their cumulative yield for extraction by the mixtures with toluene content from 5% to 50% (Fig. 4a). Unlike sulfur, which is the predominant heteroatom and

more evenly distributed between the petroleum constituents, nitrogen began to grow rapidly only in fractions with a predominance of resins and asphaltenes. A similar observation of the correlation between the nitrogen and resin content in the fractions was made in the study of SFEF of the bitumen pitch using n-pentane. According to the data obtained, the resins were associated with as much nitrogen as the end-cut, or asphaltene component. <sup>[21]</sup> In this regard, it should be noted that the resins have a lower molecular weight than the asphaltenes but may be equivalent in polarity. According to infrared spectroscopic investigations, the resin constituents are made up of a variety of functional groups, including bands in the spectra that are assigned to N-H functions in pyrrole(s) or indole(s). <sup>[5]</sup>

The concentration of heavy metals shows a rapid exponential growth in the region of cumulative yields corresponding to a sharp increase in the resin content and the subsequent appearance of asphaltenes in fractions (Fig. 4b). As is known, vanadium and nickel are concentrated in the polar fractions of resins and asphaltenes, which explains the obtained dependences. <sup>[22]</sup> Moreover, the observed correlation between the nitrogen and metal contents in the fractions may indicate that a significant proportion of vanadium and nickel are present in the VR in the form of bound porphyrin compounds.

Table 2 presents the properties of the extraction residue. The insoluble fraction of the extraction residue has a higher CCR, the content of metals and heteroatoms, and is also characterized by a lower H/C atomic ratio compared to the fractions of the extract. This is a consequence of the concentration in this fraction of asphaltenes, which have the highest molecular weight,



**Figure 4.** The content of heteroatoms (a) and heavy metals (b) in fractions versus the cumulative extraction yield.

**Table 2.** Properties of the extraction residue.

Property	Value
CCR, wt.%	44.6
H/C atomic ratio	0.877
Nitrogen, %	1.03
Sulfur, %	6.95
Vanadium, ppm	667
Nickel, ppm	183

polarity, and aromaticity among other petroleum components.

## Conclusions

In this study, a characterization of the vacuum residue was carried out using a new approach consisting in the extractive separation of the sample due to a change in the composition of the solvent, which is a mixture of CO<sub>2</sub> and toluene. As a result of fractionation, nine narrow fractions were extracted using SC-CO<sub>2</sub> and mixtures with a toluene content from 5 to 50 wt. %. The results showed that toluene has a strong effect on the solvent power and selectivity of the solvent mixture. Mixtures with a toluene content of up to 20 wt.% extract mainly aromatic hydrocarbons, while at higher concentrations of toluene in the solvent, the main components of the extracts are resins. A rapid increase in the concentration of resins and subsequent extraction of part of the asphaltenes led to a corresponding increase in the polarity and aromaticity of the fractions, as evidenced by the rapid growth of heteroatoms and metals in the fractions, as well as an increase in CCR and a decrease in the H/C atomic ratio.

Fractionation of the VR under the specified extraction conditions ensured the achievement of a total extraction yield of 83 wt.%, which is comparable to the SFEF method with supercritical n-pentane (72–88 wt. %). However, in addition to a lower extraction temperature in comparison with the well-known SFEF method, the use of a binary CO<sub>2</sub>-toluene mixture opens the possibility of further increasing the separation depth by using the toluene-rich mixtures. It has been established that CO<sub>2</sub>, which is an effective anti-solvent at high concentrations in the mixture, at a concentration of 50% begins to exhibit the properties of a co-solvent, contributing to the dissolution of asphaltene fractions. This makes it possible to separate into fractions not only resins but also asphaltene components of petroleum residues.

## Acknowledgements

The authors thank the Engineering Center of the Moscow Institute of Physics and Technology (MIPT Center for

Engineering and Technology) for the opportunity to use research equipment under the Agreement on Scientific and Technical Cooperation of March 2, 2015, as well as its staff for their help in analyzing the properties of samples of petroleum fractions.

## Funding

This work was financially supported by the Russian Foundation for Basic Research, project No. 18-33-00716 mol\_a “Development of a new method for the fractionation of heavy oils and oil residues based on the process of supercritical fluid extraction (SFE).”

## ORCID

Rustam Magomedov  <http://orcid.org/0000-0002-1682-7024>

Artem Pripakhaylo  <http://orcid.org/0000-0001-5902-8954>

Tatiana Maryutina  <http://orcid.org/0000-0002-5591-2133>

## Declaration of interest statement

The authors declare that they have no competing interests.

## Abbreviations

EoS	equations of state
PC	pseudocomponent
PPR78	predictive Peng-Robinson 1978
VR	vacuum residues
SARA	saturates, aromatics, resins and asphaltenes
SFE	supercritical fluid extraction
SFEF	supercritical fluid extraction and fractionation
ABPR	automatic back pressure regulator
CO <sub>2</sub>	carbon dioxide
SC-CO <sub>2</sub>	supercritical carbon dioxide
CCR	Conradson carbon residue
RSD	relative standard deviation

## References

- [1] He, P.; Ghoniem, A. F. A Group Contribution Pseudocomponent Method for Phase Equilibrium Modeling of Mixtures of Petroleum Fluids and a Solvent. *Ind. Eng. Chem. Res.* **2015**, *54*, 8809.
- [2] Díaz, O. C.; Modaresghazani, J.; Satyro, M. A.; Yarranton, H. W. Modeling the Phase Behavior of Heavy Oil and Solvent Mixtures. *Fluid Phase Equilib.* **2011**, *304*, 74. DOI: [10.1016/j.fluid.2011.02.011](https://doi.org/10.1016/j.fluid.2011.02.011).
- [3] Punnapala, S.; Vargas, F. M. Revisiting the PC-SAFT Characterization Procedure for an Improved Asphaltene Precipitation Prediction. *Fuel.* **2013**, *108*, 417. DOI: [10.1016/j.fuel.2012.12.058](https://doi.org/10.1016/j.fuel.2012.12.058).
- [4] Zhao, S.; Wang, R.; Lin, S. High-Pressure Phase Behavior and Equilibria for Chinese Petroleum Residua and Light Hydrocarbon Systems. *Pet. Sci. Technol.* **2006**, *24*, 297.

- [5] Andersen, S. I.; Speight, J. G. Petroleum Resins: Separation, Character, and Role in Petroleum. *Pet. Sci. Technol.* **2001**, 19(1–2), 1. DOI: [10.1081/LFT-100001223](https://doi.org/10.1081/LFT-100001223).
- [6] Shi, T.-P.; Hu, Y.-X.; Xu, Z.-M.; Su, T.; Wang, R.-A. Characterizing Petroleum Vacuum Residue by Supercritical Fluid Extraction and Fractionation. *Ind. Eng. Chem. Res.* **1997**, 36, 3988. DOI: [10.1021/ie970152b](https://doi.org/10.1021/ie970152b).
- [7] Pripakhaylo, A. V.; Magomedov, R. N.; Maryutina, T. A. Separation of Heavy Oil into Narrow Fractions by Supercritical Fluid Extraction Using a CO<sub>2</sub>-toluene Mixture. *J. Anal. Chem.* **2019**, 74(4), 401. DOI: [10.1134/S1061934819040105](https://doi.org/10.1134/S1061934819040105).
- [8] Magomedov, R. N.; Pripakhaylo, A. V.; Maryutina, T. A. Solvent Demetallization of Heavy Petroleum Feedstock Using Supercritical Carbon Dioxide with Modifiers. *J. Supercrit. Fluids.* **2017**, 119, 150. DOI: [10.1016/j.supflu.2016.08.022](https://doi.org/10.1016/j.supflu.2016.08.022).
- [9] Wu, W.; Ke, J.; Poliakoff, M. Phase Boundaries of CO<sub>2</sub> + Toluene, CO<sub>2</sub> + Acetone, and CO<sub>2</sub> + Ethanol at High Temperatures and High Pressures. *J. Chem. Eng. Data.* **2006**, 51, 1398. DOI: [10.1021/jc060099a](https://doi.org/10.1021/jc060099a).
- [10] Lodi, L.; Cárdenas Concha, V. O.; Medina, L. C.; Maciel Filho, R.; Wolf Maciel, M. R. An Experimental Study of a Pilot Plant Deasphalting Process in CO<sub>2</sub> Supercritical. *Pet. Sci. Technol.* **2015**, 33, 481. DOI: [10.1080/10916466.2014.988871](https://doi.org/10.1080/10916466.2014.988871).
- [11] Deo, M. D.; Hwang, J.; Hanson, F. V. Supercritical Fluid Extraction of a Crude Oil, Bitumen-derived Liquid and Bitumen by Carbon Dioxide and Propane. *Fuel.* **1992**, 71, 1519. DOI: [10.1016/0016-2361\(92\)90229-H](https://doi.org/10.1016/0016-2361(92)90229-H).
- [12] Rose, L.; Svrcek, W. Y.; Monnery, W. D.; Chong, K. Fractionation of Peace River Bitumen Using Supercritical Ethane and Carbon Dioxide. *Ind. Eng. Chem. Res.* **2000**, 39, 3875. DOI: [10.1021/ie000320r](https://doi.org/10.1021/ie000320r).
- [13] Wang, S.; Liu, J.; Zhang, L.; Masliyah, J.; Xu, Z. Interaction Forces between Asphaltene Surfaces in Organic Solvents. *Langmuir.* **2010**, 26(1), 183. DOI: [10.1021/la9020004](https://doi.org/10.1021/la9020004).
- [14] Dashtia, H.; Zanganeh, P.; Kord, S.; Ayatollahi, S.; Amiri, A. Mechanistic Study to Investigate the Effects of Different Gas Injection Scenarios on the Rate of Asphaltene Deposition: An Experimental Approach. *Fuel.* **2020**, 262, 116615. DOI: [10.1016/j.fuel.2019.116615](https://doi.org/10.1016/j.fuel.2019.116615).
- [15] Fang, T.; Wang, M.; Li, J.; Liu, B.; Shen, Y.; Yan, Y.; Zhang, J. Study on the Asphaltene Precipitation in CO<sub>2</sub> Flooding: A Perspective from Molecular Dynamics Simulation. *Ind. Eng. Chem. Res.* **2018**, 57(3), 1071. DOI: [10.1021/acs.iecr.7b03700](https://doi.org/10.1021/acs.iecr.7b03700).
- [16] Headen, T. F.; Boek, E. S. Molecular Dynamics Simulations of Asphaltene Aggregation in Supercritical Carbon Dioxide with and without Limonene. *Energy Fuels.* **2011**, 25, 503. DOI: [10.1021/ef1010397](https://doi.org/10.1021/ef1010397).
- [17] Zanganeh, P.; Dashti, H.; Ayatollahi, S. Visual Investigation and Modeling of Asphaltene Precipitation and Deposition during CO<sub>2</sub> Miscible Injection into Oil Reservoirs. *Fuel.* **2015**, 160, 132. DOI: [10.1016/j.fuel.2015.07.063](https://doi.org/10.1016/j.fuel.2015.07.063).
- [18] Azinfar, B.; Haddadnia, A.; Zirrahi, M.; Hassanzadeh, H.; Abedi, J. Effect of Asphaltene on Phase Behavior and Thermophysical Properties of Solvent/Bitumen Systems. *J. Chem. Eng. Data.* **2017**, 62(1), 547. DOI: [10.1021/acs.jced.6b00836](https://doi.org/10.1021/acs.jced.6b00836).
- [19] Soroush, S.; Breure, B.; de Loos, T. W.; Zitha, P.; Peters, C. J. High-pressure Phase Behaviour of Two Poly-aromatic Molecules in the Presence of Toluene and Carbon Dioxide. *J. Supercrit. Fluids.* **2014**, 94, 59. DOI: [10.1016/j.supflu.2014.05.019](https://doi.org/10.1016/j.supflu.2014.05.019).
- [20] Ni, H.; Hsu, C. S.; Lee, P.; Wright, J.; Chen, R.; Xu, C.; Shi, Q. Supercritical Carbon Dioxide Extraction of Petroleum on Kieselguhr. *Fuel.* **2015**, 141, 74. DOI: [10.1016/j.fuel.2014.09.126](https://doi.org/10.1016/j.fuel.2014.09.126).
- [21] Zhao, S.; Sparks, B. D.; Kotlyar, L. S.; Chung, K. H. Correlation of Processability and Reactivity Data for Residua from Bitumen, Heavy Oils and Conventional Crudes: Characterization of Fractions from Super-critical Pentane Separation as a Guide to Process Selection. *Catal. Today.* **2007**, 125, 122. DOI: [10.1016/j.cattod.2007.05.025](https://doi.org/10.1016/j.cattod.2007.05.025).
- [22] Yakubov, M. R.; Sinyashin, K. O.; Abilova, G. R.; Tazeeva, E. G.; Milordov, D. V.; Yakubova, S. G.; Borisov, D. N.; Gryaznov, P. I.; Mironov, N. A.; Borisova, Y. Y. Differentiation of Heavy Oils according to the Vanadium and Nickel Content in Asphaltenes and Resins. *Pet. Chem.* **2017**, 57(10), 849. DOI: [10.1134/S096554411710019X](https://doi.org/10.1134/S096554411710019X).