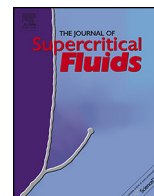




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# Solvent demetallization of heavy petroleum feedstock using supercritical carbon dioxide with modifiers

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### ABSTRACT

Possibilities of demetallization of heavy petroleum feedstocks (HPF) using supercritical fluid extraction (SFE) have been studied. Experiments with various solvent mixtures were carried out in a semibatch extractor and in dynamic mode to assess the effect of modifier type and concentration as well as extraction time on the yield of extract and content of vanadium, nickel and iron in produced phases (extract and residual phase). Vacuum residue was used as the feedstock and supercritical carbon dioxide (scCO<sub>2</sub>) was used as the primary solvent for extraction. Methanol, ethanol, acetonitrile, acetone, ethyl acetate, *n*-heptane, toluene and *o*-xylene were added to scCO<sub>2</sub> as modifiers to form the solvent mixtures. Extraction temperatures and pressures were maintained at 50 °C and 30 MPa to achieve a high density of scCO<sub>2</sub>. It has been found that methanol and *o*-xylene containing mixtures provide the highest metal content in the extract while ethyl acetate, *n*-heptane and toluene provide the lowest. Higher extract yield and the degree of metal concentration in residue were obtained with increasing both toluene concentration in scCO<sub>2</sub> and the time of dynamic extraction. The demetallization efficiency is estimated to be at a level above 95wt% at the yields of extract (demetallized oil) up to 60wt% using toluene as a modifier.

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## 1. Introduction

The depletion of deposits of light and medium-gravity oils and the growing consumption of oil and oil products will result in inevitable increasing the proportion of heavy oils involved in refining. Heavy oil and bitumen resources worldwide are estimated to be approximately 6 trillion barrels [1]. At the same time, geological reserves of highly viscous and heavy oil in Russia reach 6–7 billion tonnes (40–50 billion barrels) [2]. As the gravity of the oil increases, the amount of resin–asphaltene compounds (asphaltite), heteroatoms, and metals in it increases [3]. The presence of these components in significant quantities leads to a decrease in the H/C atomic ratio in petroleum feedstock, deterioration of its transport

properties, a decrease in stability (growth of colloidal instability) and compatibility, an increase in carbon residue, the tendency to form solid deposits, and corrosion of equipment [4].

A high content of metals, in particular vanadium and nickel, is a major problem faced in the processing of heavy petroleum feedstock (HPF) as it leads to irreversible catalyst deactivation due to metal deposition on the active surface, blocking the pore space, and degradation of the catalyst structure [4]. The metal content in the feedstock, along with group hydrocarbon composition and content of carbon residue, is the major factor that directly affects the composition and structure of the catalysts used, the maximum conversion of feedstock and hardware design process, which in turn affects plant capital cost and profitability [5–7]. In addition, inorganic vanadium compounds produced during the processing facilitate intense ash fouling and high-temperature surface corrosion of equipment, reduction in the service life of turbo-jet and diesel engines and utility boilers, gas corrosion of active elements of gas-turbine engines, and growth of environmentally harmful emissions [8,9].

Currently, in the oil refining industry, removal of metals from HPF (demetallization) is achieved during hydroprocessing, as well as in thermal and extraction processes of solvent deasphalting (SDA). As a result of these processes, the metals are removed

*Abbreviations:* HPF, heavy petroleum feedstocks; scCO<sub>2</sub>, supercritical carbon dioxide; SDA, solvent deasphalting; ROSE, Residuum Oil Supercritical Extraction; SCFs, supercritical fluids; SFE, supercritical fluid extraction; DAO, deasphalted oil; VR, vacuum residue; ICP-MS, inductively coupled plasma mass spectrometry; DE, demetallization efficiency.

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and concentrated in the composition of the carbon rich or solid carbonaceous residue, the heterogeneous catalyst or other non-catalytic solid particles performing the role of the adsorbent and the heat transfer agent [10]. Herewith extraction processes characterized by a number of obvious advantages related to the simplicity of hardware and technological design, lack of need for catalysts, adsorbents and hydrogen, by operating at relatively low temperatures and pressures, thus avoiding the formation of carbon deposits and changes in feedstock hydrocarbon composition.

The main solvents for the processes of SDA used in industry, are light *n*-alkanes with number of carbon atoms from 3 to 6, dissolving saturated and aromatic hydrocarbons with the simultaneous disruption of the oil dispersion system and precipitation of the carbon-rich components, resin and asphaltene constituents. Feedstock impurities such as sulfur and metals are concentrated in the insoluble phase [11–13]. A significant portion of the operating costs of conventional SDA technologies is the cost for regeneration of the solvent from deasphalting solution. Consequently, in advanced SDA technologies the solvent is heated to supercritical conditions to release the deasphalted oil. The main part of the solvent is recovered directly by this means, and only the small amounts associated with the product fractions are recovered by conventional stripping and condensation [14,15]. Significant savings in capital and energy costs are achieved with solvent recovery in the supercritical state. Thus, commercial plants of the ROSE process (Residuum Oil Supercritical Extraction), which is the development of KBR company, require up to 60% less energy than conventional SDA processes that use evaporation, condensation and compression of solvent in the stages of its recovery and recycling [16,17].

However in this case the supercritical state was used to reduce solubility rather than for extraction. The use of supercritical fluids (SCFs) directly in the extraction step is attractive because in the supercritical state the fluids provide a unique solvent capacity and have high diffusivity compared with conventional liquid solvents [18,19].

Along with development and research on the use of organic solvents for conducting of supercritical fluid extraction (SFE) with respect to the recovery and refining/upgrading of HPF [20–24], the use of inorganic and readily available solvents such as carbon dioxide (CO<sub>2</sub>) and water attracts much attention. Supercritical carbon dioxide (scCO<sub>2</sub>) is the most common solvent for SFE processes because it is inexpensive, nonflammable, nonexplosive, noncorrosive, nontoxic and available in large quantities [25].

As is known, CO<sub>2</sub> in sub- and supercritical state is used to extract oil and petroleum products from porous solid matrices that resulted its widespread use as a flooding agent in the tertiary methods of enhanced oil recovery [26–28]. Intensive research is carried out in the use of scCO<sub>2</sub> and scCO<sub>2</sub> mixed with organic modifiers as a solvent to extract the oil components from various types of reservoir rocks [29,30] and bitumen from oil sands [31–33].

The use of CO<sub>2</sub> as a solvent for deasphalting of petroleum feedstocks in the refining processes currently has not found a proper application. So, Lodi et al. [34] used scCO<sub>2</sub> as a solvent in the deasphalting of atmospheric and vacuum residues in an extraction vessel with a volume of 3 L under batch conditions. This process results in a high degree of demetallization of petroleum residues. For instance, vanadium and nickel contents in deasphalted oil (DAO) extracted from an atmospheric residue were less than 1 ppm. However, the yield of DAO was at a very low level of about 1% vol. that was associated with low selectivity of scCO<sub>2</sub> in relation to high molecular weight components of heavy petroleum residues. Low solubility of oil components in scCO<sub>2</sub> at equilibrium conditions was also observed in [35]. According to [35] at a pressure of 16.1 MPa and a temperature of 75°C, the solubility of oil in scCO<sub>2</sub> did not exceed 5wt %, and the average molecular weights of the extracted oil components was significantly lower than that of the crude oil.

Main method allowing one to overcome the low solubility of the components of crude oil in scCO<sub>2</sub> is an addition of organic modifiers to scCO<sub>2</sub> that enables to increase its solvent power and to adjust selectivity for group components of the petroleum feedstock [25]. There are published data describing the effect of adding a series of modifiers (*n*-hexane, toluene, chloroform, acetonitrile, methanol, diethyl sulfide) on solvent strength and selectivity of scCO<sub>2</sub> towards group components of distillation residue derived from Venezuelan heavy crude [36]. It has been shown that the use of diethyl sulfide possible to obtain a maximum yield of extract (25.9%), after diethyl sulfide in order of decreasing yield was followed by hexane (21%), chloroform (20.9%), acetonitrile (18.8%), methanol (16.4%) and finally pure scCO<sub>2</sub> (14%). Some patents [37,38] describe the methods of extraction separation, purification and isolation of resins and asphaltene from petroleum feedstock by using as the solvent sub- and supercritical CO<sub>2</sub> adding liquid and gaseous organic modifiers.

Samedova et al. [39–41] propose to apply the method of deasphalting of crude oil and residua using scCO<sub>2</sub> as a solvent as an alternative to existing standard methods of separation of asphaltenes in the determination of their content according to IP 143 and GOST 11851-85 as well as industrial SDA processes using large volumes of light hydrocarbon solvents. According to the proposed method, a weighed sample prior to charging into the extractor is diluted with a light hydrocarbon solvent (e.g., *n*-heptane) in the solvent to sample mass ratio of 0.7:1 to 1:1. At the given supercritical parameters, CO<sub>2</sub> circulates over 4 h in the system extractor-separator-compressor-extractor. After that, the CO<sub>2</sub> circulation is stopped, and asphaltenes are allowed to precipitate from the solution for 4 h. Despite the high values of DAO yield at the level of 95–96wt % and the degree of concentration of metals in the asphaltite phase, the efficiency of the demetallization remains at a low level. So, according to [41] efficiency of vanadium, iron and nickel removal for vacuum residue was 16, 18 and 34%, respectively, i.e. the main part of the metals was transferred to DAO fraction. Besides, considering the very high DAO yields and a relatively low density of CO<sub>2</sub> under process conditions, it can be assumed that CO<sub>2</sub> performs the function of an anti-solvent and/or drags out components of petroleum residue from the extractor rather than dissolves them in this case.

Thus, in the literature there is a small number of experimental data obtained in different conditions, which do not give possibility to evaluate efficiency of the use of solvents based on CO<sub>2</sub> to remove the metals from HPF in SDA process. The objective of this work was to assess the efficiency of solvent demetallization of vacuum distillation residue using scCO<sub>2</sub> as the primary solvent. Supercritical extraction experiments were conducted in semibatch extractor and in dynamic mode. Due to the low solubility of the HPF components in scCO<sub>2</sub> the approach taken to achieve the above objective involves the addition of various modifiers to CO<sub>2</sub>. The effect of the resulting mixtures, which include various types of modifiers in CO<sub>2</sub> will be compared to establish best possible modifier/solvent combinations for the demetallization of vacuum residue. In addition, the influence of concentration of selected organic modifier in scCO<sub>2</sub> and time of dynamic extraction on the yield of products and the concentration of the main trace elements in their composition will be discussed.

## 2. Experimental part

### 2.1. Materials

High purity carbon dioxide (99.99%), supplied by “NII KM Ltd.”, was used for conducting the experiments. Heteroorganic compounds and hydrocarbons used as modifiers had the following purity: toluene (99.5wt%), acetone (99.75wt%), *n*-heptane

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