Characterizing fractions of heavy oil by supercritical fluid extraction and fractionation using CO_2-based solvent

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Introduction

- As is known supercritical fluid extraction and fractionation (SFEF) which resembles the true-boiling-point (TBP) distillation for crude oils may serve as a powerful characterization tool for heavy oils and vacuum residues.
- Supercritical carbon dioxide ($scCO_2$) is the most common solvent for SFE processes.
- Main method allowing one to overcome the low solubility of the heavy oil components in scCO2 is an addition of organic modifiers to scCO2
- In contrast to the traditional SFEF approach based on controlling the density and solvent capacity of the solvent by changing the process parameters, selecting a suitable CO2 modifier in this case makes it possible to carry out fractionation of oil samples by simply changing the solvent composition.

Table 1. Composition and properties of heavy oil

Dynamic viscosity at 20 ^oC, cP	ASTM D 2983	2500
Hydrocarbon composition, wt % : - Saturates - Aromatics - Polar Compounds I - Polar Compounds II	IP 469	 8.1 55.5 24.9 11.5
Conradson carbon residue, wt %	ASTM D 189	9.9
Sulfur content, wt %	ASTM D 4294	4.2
Vanadium content, mg/kg	ASTM D 7876	199
Nickel content, mg/kg	ASTM D 5708	43

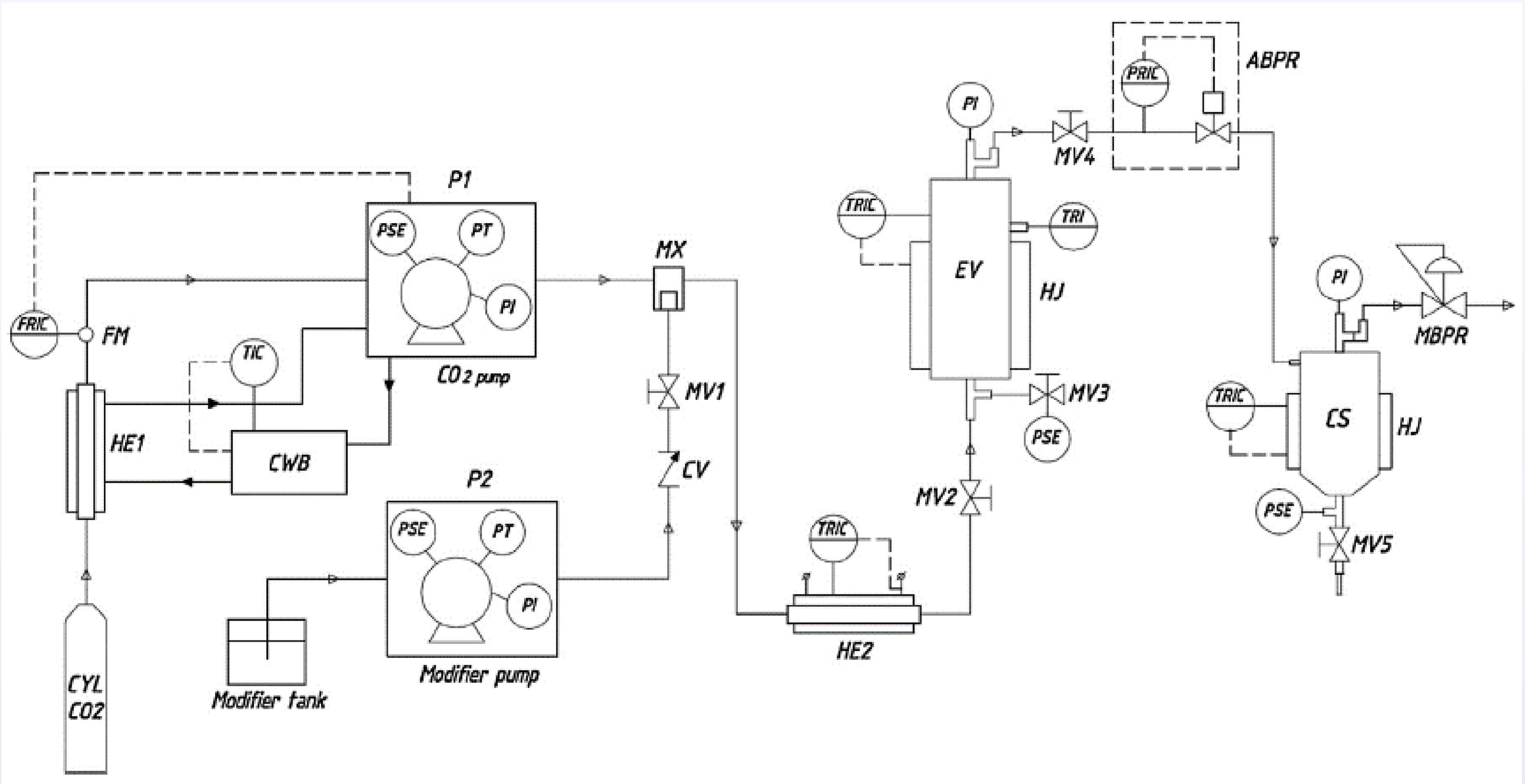

Figure 1. Process flow diagram of the laboratory-scale supercritical fluid extraction and fractionation (SFEF) system

P1, P2 –plunger pump; FM – Coriolis flowmeter; HE1 - cooler; CWB – recirculating chiller; MX – mixer; HE2 – electric heater; EV – extraction vessel; HJ – heating jacket; CS – cyclone separator; ABPR – automatic back pressure regulator; MBPR – mechanical back pressure regulator; CV – check valve; MV1 - MV5 – manual valve.

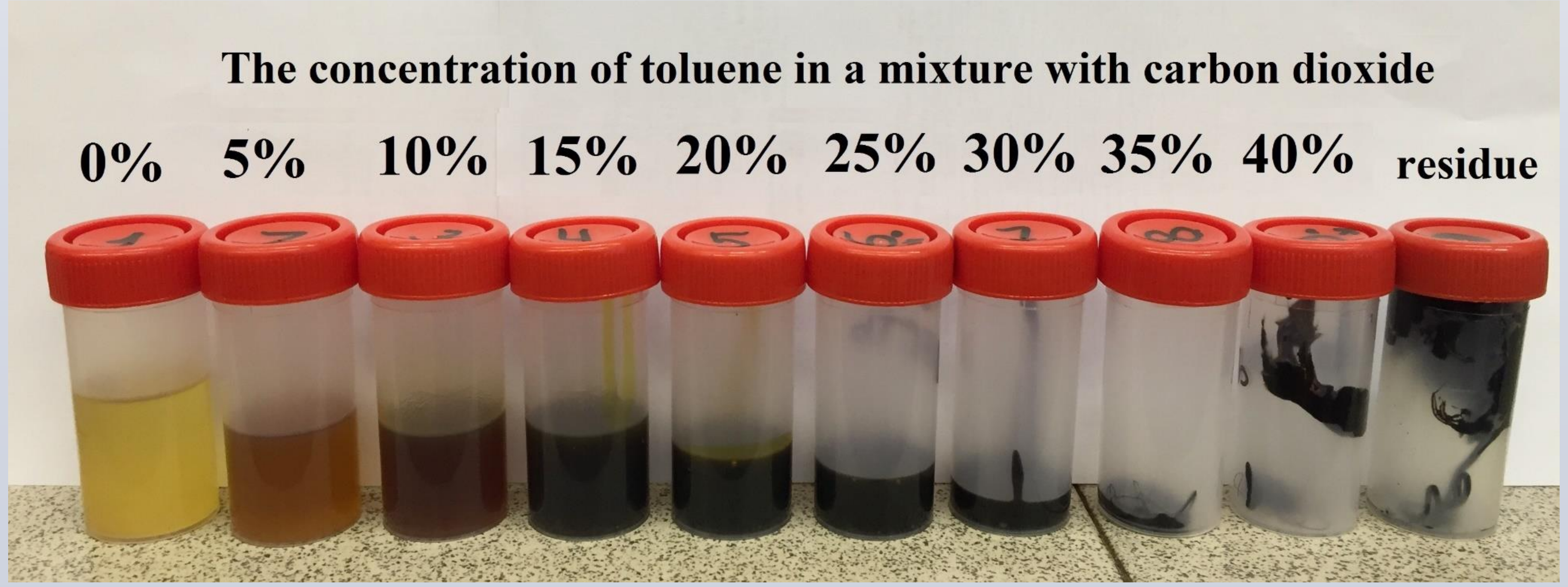

Figure 2. Narrow fractions of heavy oil obtained by SFEF using a mixture of carbon dioxide-toluene as a solvent

- **The use of CO_2-based solvent allows the process to be carried out at a low temperature and to avoid possible decomposition of the oil sample components.**
- **The use of toluene as a CO_2 modifier provides the high cumulative extraction yield and selective separation of heavy oil by molecular weight of fractions permitting to overcome the limitations of the distillation process.**

Table 2. Parameters of SFEF process

Temperature	^oC	50
Pressure	bar	100
Total extraction time	min	540
Oil sample loading	g	100
Solvent flow rate	g/min	100
Type of CO_2 modifier	**toluene**	
Modifier concentration in CO_2	**wt%**	**0 - 40**

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Results

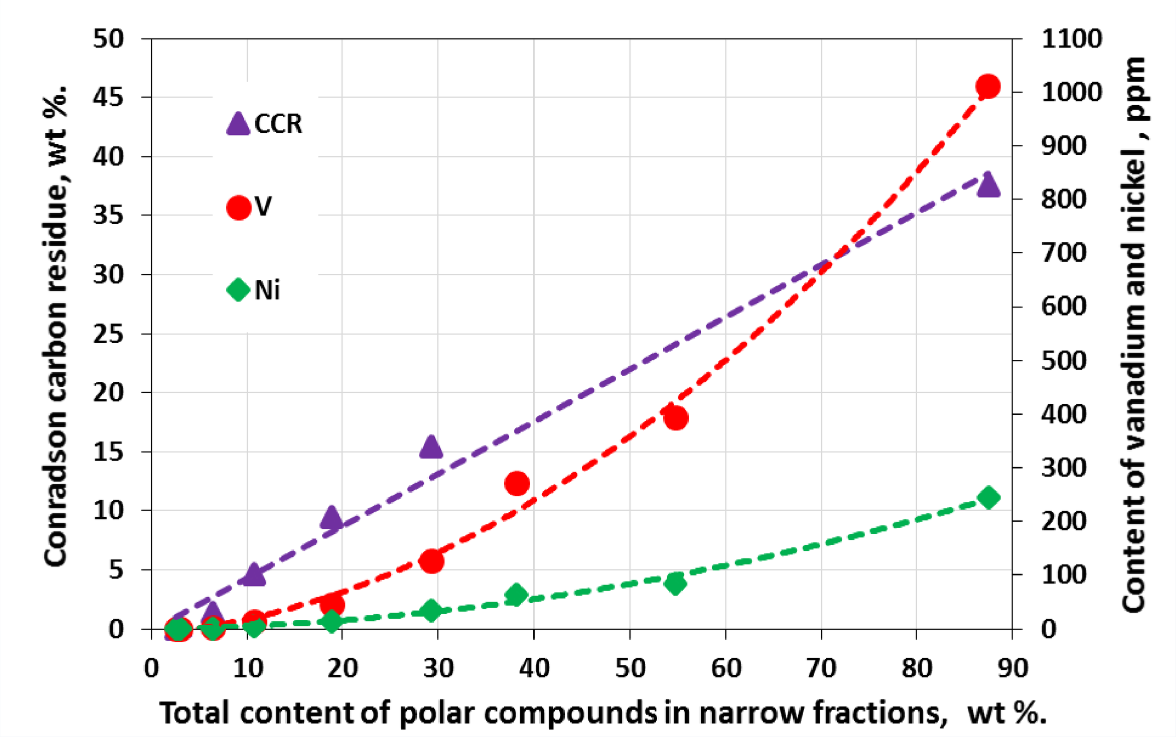

Figure 5. Content of CCR and metals versus total content of polar compounds in SFEF narrow fractions

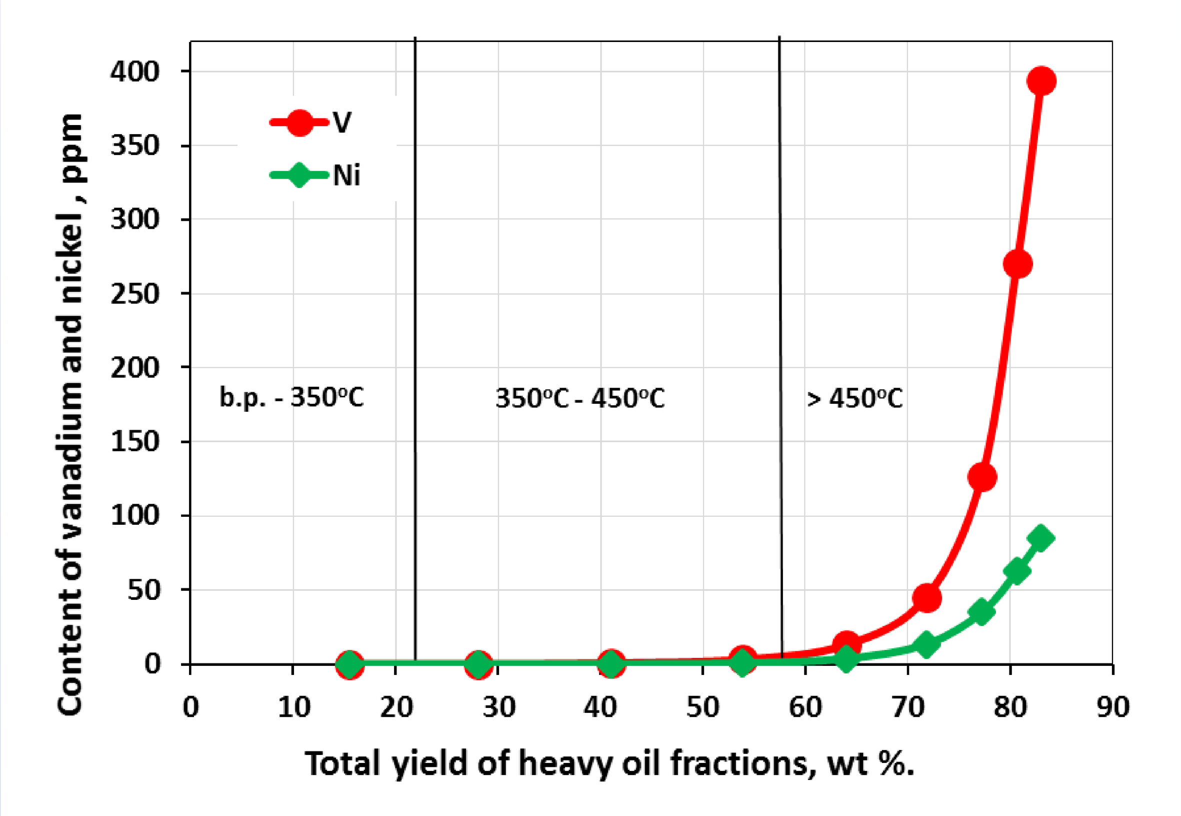

Figure 6. Vanadium and nickel concentrations of SFEF narrow fractions of heavy oil

The content of metals and carbon residue in the fractions directly correlates with the content of high-molecular polar compounds. This fact confirms high degree of aromaticity and strong binding of heavy metals in the composition of these macromolecules.

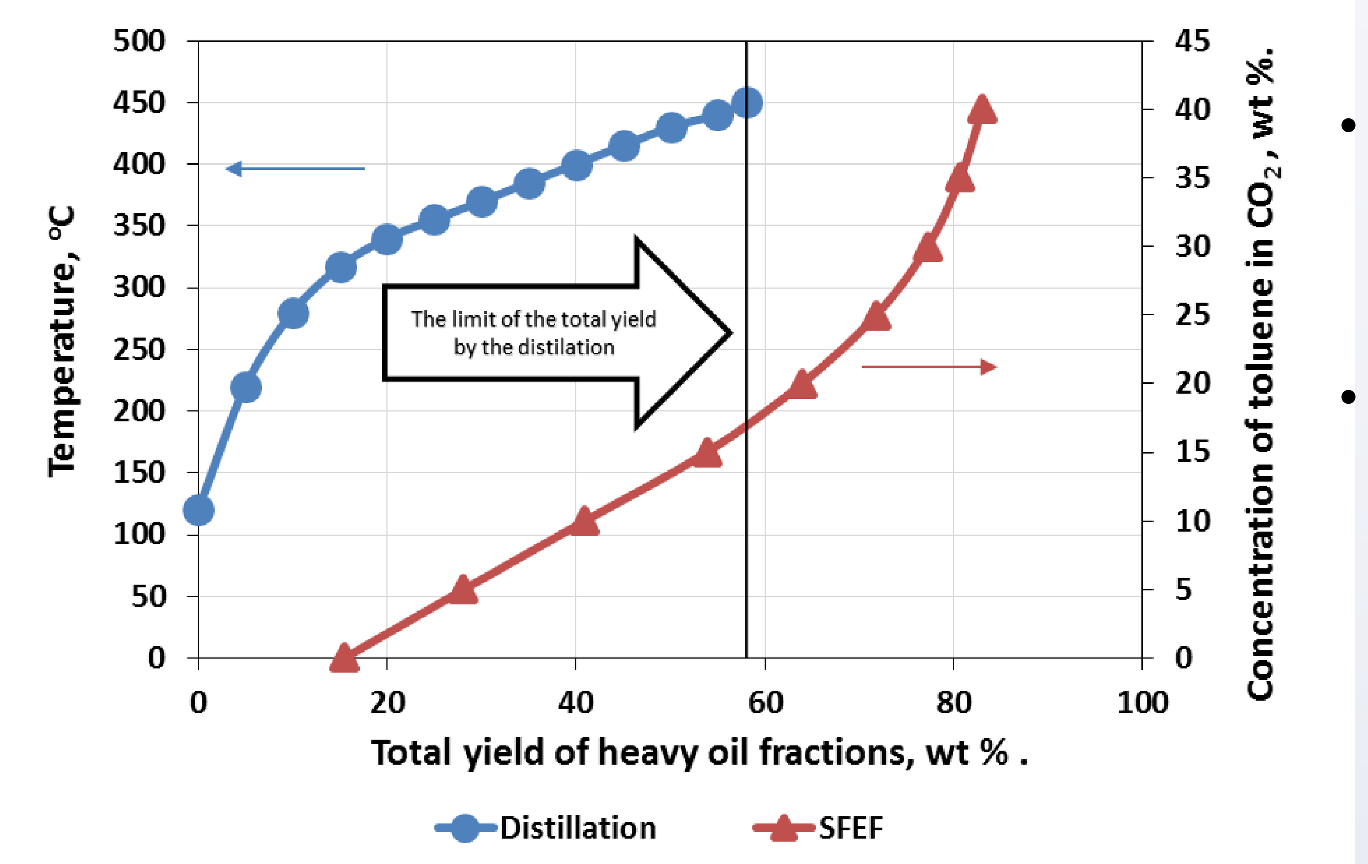

Figure 3. Comparison of the depth of the separation of heavy oil into fractions by the distillation method and SFEF

- For the first time the possibility of deep separation and fractionation of heavy oil in the SFEF process by changing the solvent composition based on CO_2 has been shown
- The analysis of the composition and properties of narrow fractions allows us to investigate the distribution of hydrocarbon components, elements and trace elements among fractions from heavy oil and to assess the relationship between them

The increase in cumulative yield and molecular weight of the extracted fractions with an increase in the concentration of toluene in CO_2 is accompanied by the redistribution of the group hydrocarbon components in their composition. In the area of yields of distillate fractions the content of saturates is decreased due to an increase in the proportion of aromatic hydrocarbons. While the extraction of vacuum residue fractions (b.p. >450°C) leads to a rapid increase in the content of high molecular weight resinous compounds (polar I). Asphaltenes (polar II) are concentrated in the extraction residue.

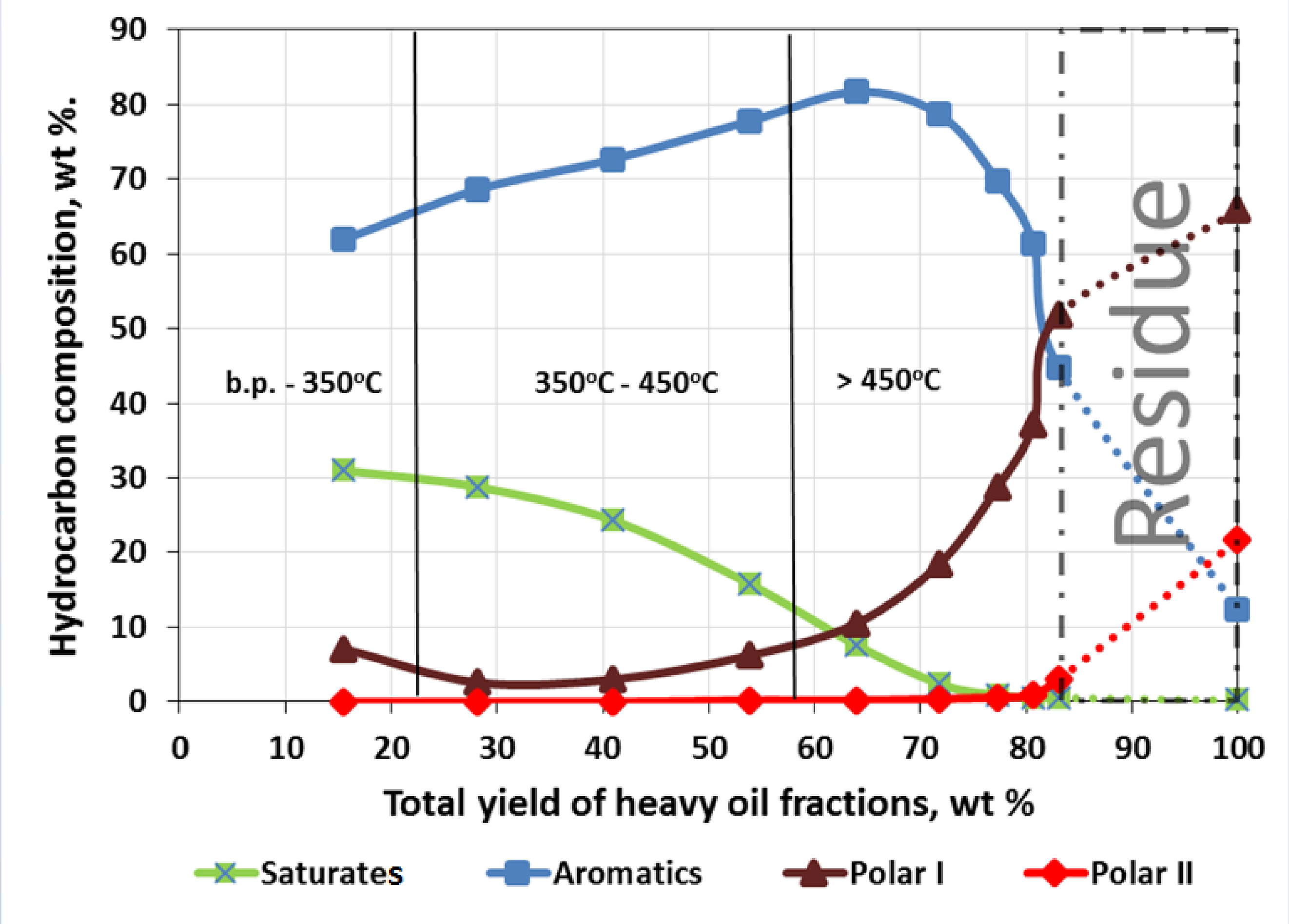

Figure 4. Saturates, aromatics, polar I and polar II percentages of SFEF narrow fractions of heavy oil

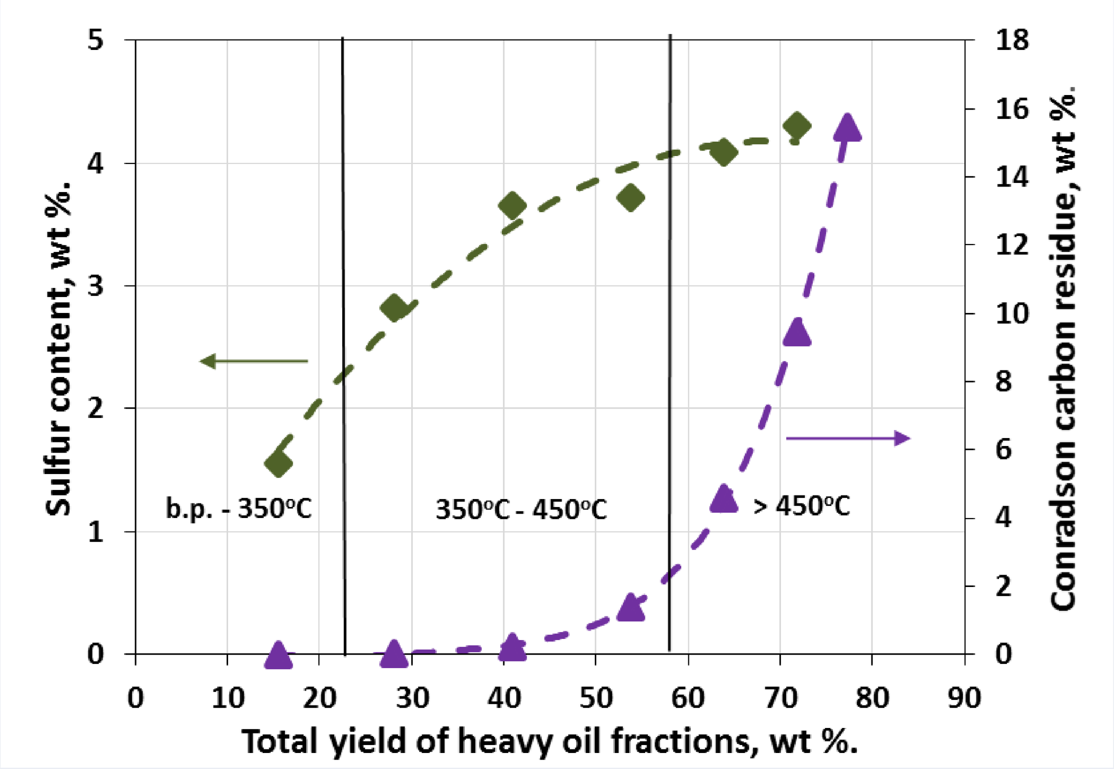

Figure 7. The content of sulfur and CCR of SFEF narrow fractions of heavy oil

The sulfur concentration increases monotonously with increasing the total yield of fractions indicating quite uniform distribution of sulfur compounds between fractions of heavy oil.

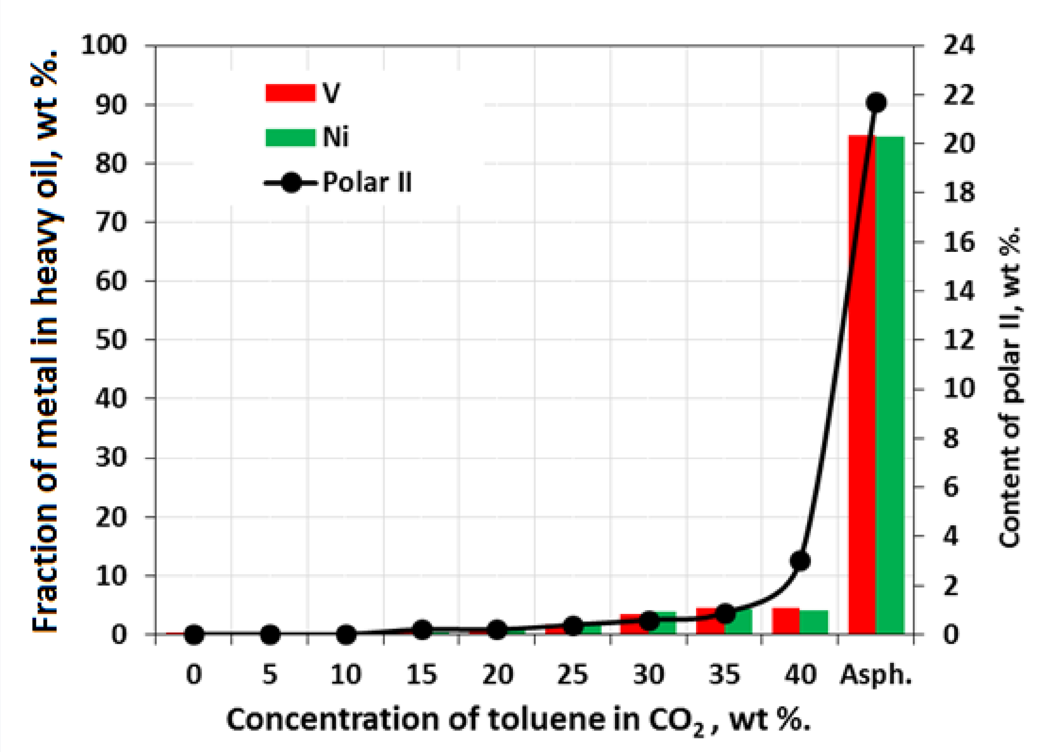

Figure 8. Distribution of metals and content of polar II in SFEF narrow fractions of heavy oil

Vanadium and nickel are almost completely concentrated in the extraction residue and mainly associated with asphaltenes (polar II).