Monitoring the behaviour and fate of nickel and vanadium complexes during vacuum residue hydrotreatment and fraction separation

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ABSTRACT

The size distribution of nickel and vanadium complexes was monitored by Size Exclusion Chromatography separation (SEC) and Inductively Coupled Plasma Mass Spectrometry (ICP/MS) detection, at different steps of a vacuum residue fractionation and hydrotreatment. Sample preparation includes asphaltene/maltene separation, and asphaltene fractionation by cross-flow ultrafiltration. The asphaltene fractionation gives asphaltene fractions enriched in low and high molecular weight compounds. The impact of asphaltene's size on hydrotreatment reactivity was investigated. Finally, a vacuum residue was reconstituted in order to monitor and control the fate of nickel and vanadium complexes through hydrotreatment. Results show that metals in the asphaltene fraction are associated with molecules that present a complex continuum of polydispersed compounds, with a majority of metal complexes found at 15 kDa polystyrene equivalent. Nickel is generally present in higher molecular weight compounds than vanadium. The size of the metal compounds impacts significantly their reactivity during hydrotreatment; metals present in high molecular weight compounds are the most refractory to conversion. Only the light metal complexes were easily converted during hydrotreatment.

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1. Introduction

One of the characteristics of heavy petroleum fractions named vacuum residues (boiling point over 500 °C) is their high concentration of impurities such as heteroatoms (sulphur, nitrogen) and metals, especially vanadium (V) and nickel (Ni). The concentration of Ni and V can range up to several hundred parts per million (ppm) in heavy crudes, depending on their geological origin [1,2]. These metals are known to be poisons of catalysts during refining processes, and a better characterisation of their distribution in residues can improve oil refining strategies. Thus, several research groups have developed their own techniques for the characterization of metal complexes in petroleum products; Chevron has used gas chromatography (GC) coupled with Inductively Coupled Plasma Mass Spectrometry (ICP/MS) in order determine the volatile fraction of Ni and V in crude oil [3]. Petrobras has used High-Performance Liquid Chromatography (HPLC) with reversed phase and elution gradient to quantitate V and Ni as metallic tetrapyrrole complexes [4]. More recently, Thin Layer Chromatography (TLC) was used to elute fractions containing Ni, V and sulphur compounds and Laser Ablation–Inductively Coupled Plasma High Resolution Mass Spectrometry (LA–ICP/HRMS) was used for metal analysis [5].

However, no further investigation was carried out with unconverted effluents for the understanding of the relation between metal complexes and their reactivity during hydrotreatment. This information should be useful for the understanding of hydrotreatment reactions and also for the design of high performance hydrotreatment catalysts [6–8].

To fill this gap, we used a hyphenated technique based on Size Exclusion Chromatography separation (SEC) and ICP/MS detection developed in a previous work [9], and applied it to access the size-distribution of nickel and vanadium complexes in petroleum products after fraction separation and hydrotreatment. The hyphenated technique was used on an Arabian heavy vacuum residue and its fractions. Residues are complex and polydispersed mixtures, therefore a preliminary step of matrice simplification was achieved in order to isolate subfractions of common characteristics, more easily analysable. As heteroatoms and metals are mainly concentrated in the most polar fraction (asphaltenes), residues were subfractionated by polarity. The two fractions obtained, the maltene and asphaltene fractions, were analysed for metal size distribution. The asphaltenes were then further fractionated by cross-flow ultrafiltration to obtain asphaltenes respectively enriched in low and high molecular weight compounds [10,11]. Model feedstocks were then reconstituted, and SEC–ICP/MS was used to monitor the reactivity of vanadium and nickel during hydrotreatment of these feedstocks. The impact of asphaltene's size on hydrotreatment reactivity is also discussed.

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2. Experimental section

2.1. Sample fractionation

Fig. 1 presents a simplified scheme of sample preparation. The feed used in this study was an Arabian heavy vacuum residue (VR). The main properties of the VR are summarized in Table 1.

Asphaltenes of this VR were recovered from the partial VR flocculation in contact with the paraffinic solvent n-heptane. The flocculated fraction is called asphaltenes ($IAsC_7$) and the soluble fraction is called maltenes. The n-heptane from the maltenes fraction was eliminated by vacuum evaporation to recover the DeAsphalted Vacuum Residue (DAVR).

An aliquot of these asphaltenes ($IAsC_7$) was then physically fractionated by cross-flow membrane ultrafiltration. The experimental set-up consisted on a filtration cell housing flat membrane sheets. It allowed a continuous operation and displays 280 cm^2 of active filtration surface. This device contained a 140 ml hold-up volume and recycled the retentate stream at 500 L/h. The polyethersulfone porous membranes used presented a 20 kDa molecular weight cut-off (MWCO) (UP020 membrane produced by NADIR and provided by Alting, Hoerdt France). Membranes were calibrated by the supplier using polysaccharide and polyethylene glycol. Membrane conditioning was first performed using toluene, at 10 bars and 25 °C. Toluene Normapur TM 99.5% VWR was used after distillation and water elimination using a 3 Å molecular sieve VWR Prolabo. The asphaltene sample was then dissolved in toluene (2 wt.%) and filtered until asphaltenes were no longer found in the permeate stream. During operation the asphaltene concentration in the retentate was maintained between 1 and 2 wt.% by controlling the toluene make-up. Passed 40 h, membranes were replaced in order to verify if fouling occurs. The filtrate and retentate fractions were recovered and toluene was then removed by vacuum evaporation. Two samples were obtained: a Low Molecular Weight C_7 asphaltene fraction ($LMwAsC_7$) that represented 22 wt.% of the $IAsC_7$ and a High Molecular Weight C_7 asphaltene fraction (HMwAsC7) which represented 78 wt.% of the $IAsC_7$. Asphaltene fractions were characterized as described elsewhere [10,11].

Reconstituted vacuum residues (RVR) were created by mixing the different fractions (*i.e.* $IAsC_7$, $LMwAsC_7$ or $HMwAsC_7$) with DAVR. Since the quantity of $LMwAsC_7$ was limited, RVR were reconstituted with 5.8 wt.% of asphaltenes.

2.2. Hydrotreatment catalytic test

The catalytic test was carried out in an isothermal 300 ml batch reactor operated in fixed bed conditions. A simplified scheme of the
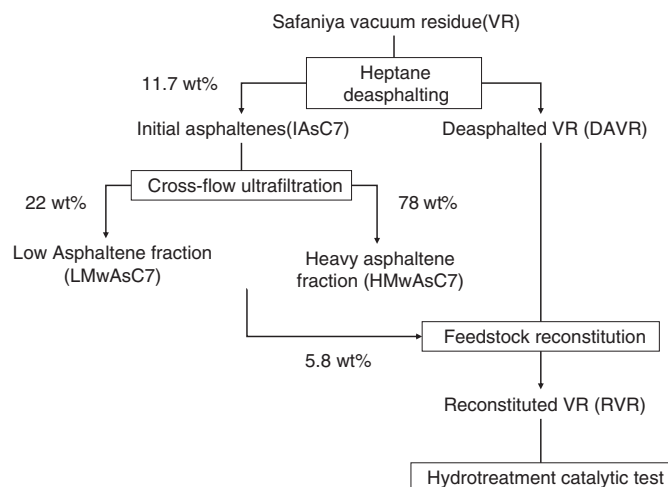

Fig. 1. Scheme of sample preparations.

Table 1
Characterization of Safaniya vacuum residue.

Density (15 °C)	1.029
Viscosity 100 °C (cSt)	1678
Viscosity 125 °C (cSt)	407.5
Conradson carbon (wt.%)	19.66
Elemental analysis	
S (wt.%)	5.11
N (wt ppm)	3665
Ni (wt ppm)	43
V (wt ppm)	145
H (wt.%)	10.11
SARA analysis	
Saturates (wt.%)	11.2
Aromatics (wt.%)	40.3
Resins (wt.%)	33.9
C_7 Asphaltenes (wt.%)	12.4

batch reactor is presented elsewhere [6]. The catalysts were composed of NiMoP on an alumina support.

The catalyst was introduced inside a stationary perforated basket with a hollow stirrer placed in the centre. A catalyst volume of 10 ml (catalyst sulfided *ex-situ*) was used for treating 60 ml of feedstock. The hollow stirrer rotated at 800 rpm for temperature and composition homogenization and also for promoting the contact between gas–liquid phases.

The reactor was first purged with hydrogen in order to eliminate the air and was then pressurised with hydrogen to 40 bar and heated up from room temperature to the test temperature (370 °C) at 20 °C/min in a reproducible way. The pressure was generated by the temperature increase and was maintained constant during the test by a hydrogen make-up. The catalytic test was performed for 2 h at constant temperature (370 °C) and pressure (9.5 MPa).

At the end of the test, the reactor was cooled down using an air vortex cooling system, which allowed decreasing temperature from 370 °C to 150 °C in less than 5 min.

Nickel, vanadium, sulphur and nC_7 asphaltenes conversion (HDNi, HDV, HDS, $HDAsC_7$) were defined as following:

$$HDX = \frac{m_{feed}[X]_{feed} - m_{product}[X]_{product}}{m_{feed}[X]_{feed}} \times 100. \qquad (1)$$

[X] stands for Ni, V, S or C_7 asphaltene content in the feedstock ($[X]_{feed}$) and in product ($[X]_{product}$). m stands for the mass of feed (m_{feed}) and product ($m_{product}$).

2.3. Analytical conditions

Elemental analyses of samples for Ni, V and S content were performed by Wavelength Dispersive X-Ray Fluorescence method according to a IFPEN standard (IFPEN 9422) and for C, H and N by combustion method according to ASTM D5291 [12].

The instrument used for SEC–ICP/MS analysis was an Ultimate 3000 binary HPLC pump (LC Packings, Amsterdam, The Netherlands) connected to an Elan 6000 ICP mass spectrometer (PE-SCIEX, ON, Canada). The SEC was achieved with three polystyrene-divinylbenzene columns of increasing porosity (100 Å, 1000 Å and 10,000 Å). The mobile phase was THF with a flow rate of 0.7 mL.min^{-1} and the injection volume was 20 μL [9]. SEC separation was performed at ambient temperature. All VR and asphaltene samples were diluted 160-folds in THF before analysis with SEC–ICP/MS.

The columns were calibrated with polystyrene standards, to get a scale of molecular weight function of the retention time [9].