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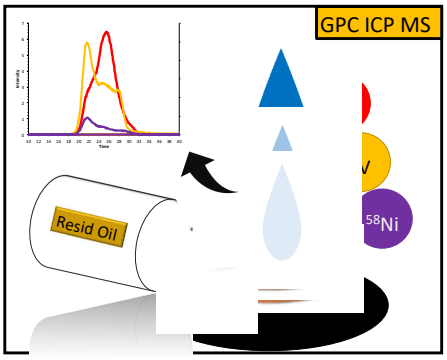
KEYWORDS: Vanadium, nickel, sulfur, demetallization, desulfurization, catalysis, residue, GPC.

ABSTRACT

This study describes the use of gel permeation chromatography inductively coupled plasma high-resolution mass spectrometry (GPC ICP HRMS) to examine and explain two important petroleum industry catalytic processes: hydrodemetallization (HDM) and hydrodesulfurization (HDS).

The sulfur, nickel and vanadium species size distributions in atmospheric residue fractions were studied to track their evolution during both catalytic processes and examine their mechanisms, especially those mechanisms linked to changes in temperature and initial deactivation via coke laydown. Chromatogram shapes as well as peak areas were used to study the V, Ni and S aggregate types and concentrations in the feedstock as well as in the product after varying the operating temperature and residence time at a constant temperature. For the V and Ni compounds, the low and medium molecular weight (LMW and MMW, respectively) aggregates are easily hydrotreated under all conditions, while the high molecular weight (HMW) compounds are more refractory. For the S compounds, a different reactivity pattern was observed whereby the LMW, MMW and HMW aggregates were more similar in their reactivity, showing that the catalyst is less selective towards a certain aggregate size for the S compounds compared to the V or Ni compounds.

TOC GRAPHIC



INTRODUCTION

Hydroprocessing atmospheric residues using fixed-bed reactors is a mature technology that has been extensively studied, and close to 100 units are in operation across the globe.[1] Most of these units are located in Asia and the Middle East, and the total catalyst demand is estimated to be approximately 50,000 tons/year. This technology is still relevant for many refineries as it can address key issues faced by the refining industry. For example, environmental specifications are getting stricter for bunker fuels as the revised MARPOL Annex VI will reduce the sulfur cap from 3.5 to 0.5 wt% from 2020 on. Furthermore, heavier crude oils are being processed, and those feedstocks require residue technologies such as atmospheric residue desulfurization (ARDS).

Among the numerous elements present in crude oil, the most abundant and undesirable elements are sulfur, vanadium and nickel,[2] which have negative effects, such as catalyst poisoning, fouling and equipment corrosion.[3,4] The presence of sulfur compounds causes environmental and health problems as well, with the emission of toxic S species into the atmosphere.[5,6] With the purpose of reducing these undesirable effects, catalytic removal of these elements is currently carried out in the industry, especially for atmospheric and vacuum residue oils, whose content of these elements is much higher.

The ARDS process will be briefly described below, but various detailed reviews and their respective references can be consulted for further information about the process and its evaluation.[1,7,8] The process consists of downflow trickle bed reactors in series with the following catalyst loading distributed across several reactors[9]: large-pore guard hydrodemetallization (HDM) catalyst (whose function is to trap V, Ni and As), a smaller-pore transition catalyst combining HDM and hydrodesulfurization (HDS) activities and a third catalyst with a higher HDS activity. The deactivation mechanisms of the catalysts in such a service have also been widely studied over the years.[10] The initial step, which is quite rapid, is mostly due to coke formation.[11] This step is followed by a slower deactivation phase during which metals gradually cover the catalyst surface.[12] The last phase is a rapid loss of activity where the metals and coke create pore plugging or restrict access to the pore structure.

Many ARDS units are operated to obtain a fixed sulfur or Conradson carbon residue (CCR) content in the product. However, due to the difficult nature of the feedstock (high amount of metals and coke precursors), many challenges are encountered: short cycle length due to high deactivation rates, pressure-drop issues due to coking, demanding catalyst unloading process, long turnarounds (typically one month), etc. To minimize these issues, it is crucial that the optimal ratio between the HDM, HDM/HDS and HDS catalysts is determined for each specific ARDS unit.

The total amounts of Ni, V or S are an important piece of information here but do not provide any information about the nature of the molecules containing these elements. Therefore, speciation of the metals in the various feedstocks is an asset in regard to understanding the feed reactivity and the influence on the various deactivation mechanisms and ultimately in optimizing the catalyst loading. One option is to use inorganic speciation in crude oil that has been

developed by using size exclusion chromatography in an organic solvent linked with a high-resolution mass spectrometer working as the detector. This technique is referred to as gel permeation chromatography (GPC) and employs an organic solvent to perform the analysis, in this case tetrahydrofurane (THF).[4] In this technique, the compounds are separated according to their hydrodynamic volumes, which in the case of these samples follow the molecular weights of the nanoaggregates and molecules that are present in the sample. By dissolving the sample in THF, it is possible to obtain a fingerprint of the molecular distribution of the species present in the sample and evaluate how the concentrations of each fraction increase or decrease as a function of the industrial process carried out.

Pohl et al.[13] successfully used this method for two crude oils and two residue fractions and managed to map and fingerprint V, Ni, S, Fe, Co, Cr, Zn and Si. The distributions between high molecular weight (HMW) aggregates (possibly asphaltene structures), medium molecular weight (MMW) aggregates and low molecular weight (LMW) compounds (possibly free metal porphyrins and nonporphyrinic complexes) differ significantly between these samples, which will affect the HDM and HDS activities and their relative deactivation rates. Gascon et al.[14] used the same approach on the Saturate, Aromatic, Resin and Asphaltene (SARA) fractions of four crude oils, one atmospheric residue and one vacuum residue. The amount of each type of aggregate (HMW, MMW and LMW) was calculated, and significant variations can be observed among the four crude oils and their residue fractions. However, to understand the significance of these variations in the ARDS process, it is necessary to study not only the feedstock but also the hydrotreated product to understand the reactivity of the various types of aggregates.

With an increasing demand for low-sulfur fuel oil (LSFO), refineries are starting to consider alternative usages for their ARDS units, for example, by coprocessing vacuum residues, which

96 are typically processed in ebullated bed reactors due to the high amount of metals and
97 asphaltenes in this type of feed, which causes an extremely rapid deactivation of the catalyst. A
98 feedstock change often requires changing the operating conditions in the unit (e.g., by lowering
99 the feed rate to lower the liquid hourly space velocity) and redesigning the catalyst loading. The
100 latter is not always straightforward, as it requires a very thorough understanding of the feed and
101 its effect on the catalyst activity throughout the entire cycle to avoid untimely shutdowns. To this
102 end, a better understanding of not only the feed properties (contents of sulfur, nitrogen,
103 asphaltene, etc.) but also the molecular composition is invaluable. Thus, in this paper, two ARDS
104 pilot plant studies are reported. In study A, the temperature was adjusted from 375 to 385 °C to
105 evaluate its influence on the reactivity of the various sulfur, nickel and vanadium species. In
106 study B, the fate of sulfur, nickel and vanadium nanoaggregates was monitored under constant
107 operating conditions to examine the role of the initial coke laydown on the HDM and HDS
108 reactions.

109 **MATERIALS AND METHODS**

110 **Instrumentation**

111 A quantitative analysis of all the feedstocks was carried out with the purpose of determining
112 the mass variations of the target elements by using inductively coupled plasma mass
113 spectrometry (ICP-MS). The principle of the method is to determine the total amount of xylene-
114 soluble Ni and V compounds with inductively coupled plasma mass spectrometry (ICP-MS) after
115 suitable dilution of the petroleum/petroleum product sample by weight with xylene. The
116 vanadium and nickel contents are quantified by ICP-MS using a vanadium-isotope mass of 51
117 and a nickel-isotope mass of 60 through comparison with calibration curves obtained via 500 wt
118 ppm Conostan organometallic V and Ni standards diluted with xylene. Scandium is used as an

internal standard to correct for drift and matrix effects. The removal of molecular interferences in the ICP-MS analysis was performed with helium kinetic energy discrimination. EnviroMAT used-oil matrix reference material containing V and Ni was analyzed with each sample batch to monitor the analysis accuracy. The physico-chemical properties of the feeds and products were measured using the following standard methods: Nitrogen (ASTM D5762), Sulfur (ASTM D 4294, Hydrogen (ASTM D 7171 H), asphaltene (ASTM D6560), microcarbon residue (MCR) (ASTM D4530), specific gravity (SG) (ASTM D4052), and simulated distillation (ASTM D7169). Carbon (wt %) content was calculated by difference with 100% with N, S and H content.

All the speciation analyses were carried out with a Thermo Scientific Element XR double focusing sector field ICP-MS (Thermo Fisher, Germany) instrument accessing the spectrally interfered isotopes of ^{32}S, ^{51}V and ^{58}Ni at a resolution of 4,000 (medium resolution). The mass spectrometer was equipped with a quartz injector (1.0 mm inner diameter (i.d.)), a Pt sampler cone (1.1 mm orifice diameter) and a Pt skimmer cone (0.8 mm orifice diameter). An O_2 gas flow of 0.08 mL/min was included to avoid carbon deposition. Both the instrument and mass calibration settings were optimized daily at resolutions of 300 (low resolution) and 4,000. A medium resolution avoids the spectral interference of O_2 on the ^{32}S isotope. These optimizations were carried out using a tuning solution containing 1.0 ng g-1 of Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, In, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sc, Si, Sn, Ti, V, Zn and Y in tetrahydrofuran (THF). A mass offset was also applied to compensate for the mass drift coming from the sector field magnet.[15,16]

The mass spectrometer was equipped with a modified DS-5 microflow total consumption nebulizer (CETAC, Omaha, NE) mounted with a laboratory-made jacketed spray chamber

heated to 60 °C by a water/glycol mixture working with a temperature-controller bath circulator Neslab RTE-111 (Thermo Fisher Scientific, Waltham, MA).[17]

The chromatographic separation was carried out using three Waters (Waters Corporation, Milford, MA) styrene-divinylbenzene gel permeation columns (7.8 mm i.d. and 300 mm length). These three columns included an HR4 column (particle size of 5 µm with an exclusion limit of 600,000 Da of polystyrene equivalent), an HR2 column (particle size of 5 µm with an exclusion limit of 20,000 Da) and an HR0.5 column (particle size of 5 µm and an exclusion limit of 1,000 Da of polystyrene equivalent). A Dionex high-performance liquid chromatography (HPLC) system fitted with an UltiMate 3,000 microflow pump, an UltiMate 3,000 autosampler and a low port-to-port dead-volume microinjection valve were used to deliver the carrier solution and mobile phase. To prevent possible damage to the GPC columns, a Styragel guard column (4.6 mm i.d. and 30 mm length) was also fitted between the columns and the pumping system.

Methodology. One feed, which is a blend of 93% of atmospheric residue (ATM) and 7% vacuum residue (VAC), was hydrotreated under different conditions for the purpose of evaluating and understanding the removal of the target compounds by applying the method optimized by Desprez et al.[16] and Vargas et al.[18]. These researchers studied the size distributions of V, Ni and S and established the integration intervals for HMW, MMW and LMW aggregates in crude oil as follows: 1,100-1,400 s (18 – 23 mL of eluted sample) for HMW compounds, 1,400-1,600 s (23 – 27 mL) for MMW compounds and above 1,600 s (< 27 mL) for LMW compounds. The comparison of the different sizes of species will provide useful information about the removal of target compounds.

In addition, with the purpose of monitoring the stability of the ICP HR MS intensities, analysis of known crude oil samples, whose composition had been studied previously, was periodically carried out.

Reagents, samples and solutions. Tetrahydrofuran, multisolvent GPC grade, ACS, stabilized with 250 ppm of butylated hydroxytoluene (BHT) (Scharlau, Spain) to prevent the formation of peroxides, was used both for sample preparation and for chromatographic elution.

All the atmospheric residue crude oil feeds were provided by Haldor Topsoe (Denmark), and the feeds were analyzed by diluting them in THF at dilution factors of 50 for the 93% ATM/7% VAC feed blend and of 5 for the products.

Pilot plant testing. The pilot tests were performed in a once-through downflow trickle bed pilot plant located in Haldor Topsoe's R&D facilities. The unit consists of two reactors in series. The product was first separated in a high-pressure separator (HPS). The liquid product from the HPS was sent to a low-pressure separator (LPS) and to a stripper for removal of gases and other noncondensed light hydrocarbons. Nitrogen was used as the stripping agent, and once-through pure hydrogen was used. The catalyst was diluted with an inert material (mesh 60 carborundum) using a 25 vol% SiC/75 vol% catalyst ratio. The operating conditions are given in Table 1 for study A (influence of the temperature) and study B (influence of the initial deactivation). The feed properties are listed in Table 2. The results of study A are summarized in Table 3, and the results of study B are provided in Table 4. Note that the catalysts loaded were commercial catalysts used in residue service developed and produced by Haldor Topsoe A/S.

Table 1. *Operating Conditions of the Pilot Plant Tests*

Inlet pressure hydrogen (barg)	165
H_2/oil (mL/L)	550
Overall liquid hourly space	0.2

velocity (LHSV) (h^{-1})	

***Table 2**. Feed Properties*

Property	Method	Atmospheric residue (ATM)	Vacuum residue (VAC)	Blend 93 vol% ATM and 7 vol% VAC
Nitrogen, wt ppm	D 5762	2800	4500	3100
Sulfur, wt%	D 4294	3.985	5.00	4.061
Hydrogen, wt%	D 7171 H	10.75	(11.18)*	10.78
C, wt%	By difference	85.0	83.4	84.8
H/C	-	0.13	0.13	0.13
SG 60/60 °F	D 4052	0.9797	-	0.9847
Density at 40 °C, g/ml	D 4052	0.9621	-	0.9672
Nickel, wt ppm	ICP-MS	21.1	42.4	27.0
Vanadium, wt ppm	ICP-MS	61.1	121	73.0
Carbon Residue, wt%	D 4530	12.02	24.42	12.96
Asphalthenes, wt%	D 6560	5.1	11.0	6.4
Simulated Distilation	D 7169			
0.5 wt% (IBP), °C		221	415	235
5 wt%, °C		341	515	353
10 wt%, °C		378	542	388
30 wt%, °C		454	600	467
50 wt%, °C		535	649	546
70 wt%,°C		614	709	627
80 wt%, °C		665	-	676
85 wt%, °C		698	-	705
90 wt%, °C		736	-	-
95 wt%, °C		-	-	-
99.5 wt% (FBP), °C		-	-	-

**: H content back-calculated from the properties of the atmospheric residue and of the blend assuming that volume and weight fractions are equivalent as density could not be measured for the vaccum residue.*

Table 3. *Results of Study A (Influence of the Temperature)*

Sample type		Feed	Product	Product	Product
Run time, hours			1,003	1,101	1,337
Temperature of the reactor, °C			375	380	385
Sulfur, wt%	ASTM D4294	4.061	0.446	0.349	0.291
Nickel, wt ppm	ICP-MS	27	5.16	4.12	3.62
Vanadium, wt ppm	ICP-MS	73	8.61	6.65	5.85
Asphaltenes, wt%	ASTM D6560	6.4	1.4	1.2	1.6
Simulated Distillation	ASTM D7169				
0.5 wt% (IBP), °C		235	142	142	128
5 wt%, °C		353	258	244	234
10 wt%, °C		388	306	295	285
30 wt%, °C		467	399	391	394
50 wt%, °C		546	466	456	464
70 wt%,°C		627	541	532	542
80 wt%, °C		676	579	572	586
85 wt%, °C		705	603	595	612
90 wt%, °C		-	630	623	641
95 wt%, °C		-	665	658	678
99.5 wt% (FBP), °C		-	721	721	717

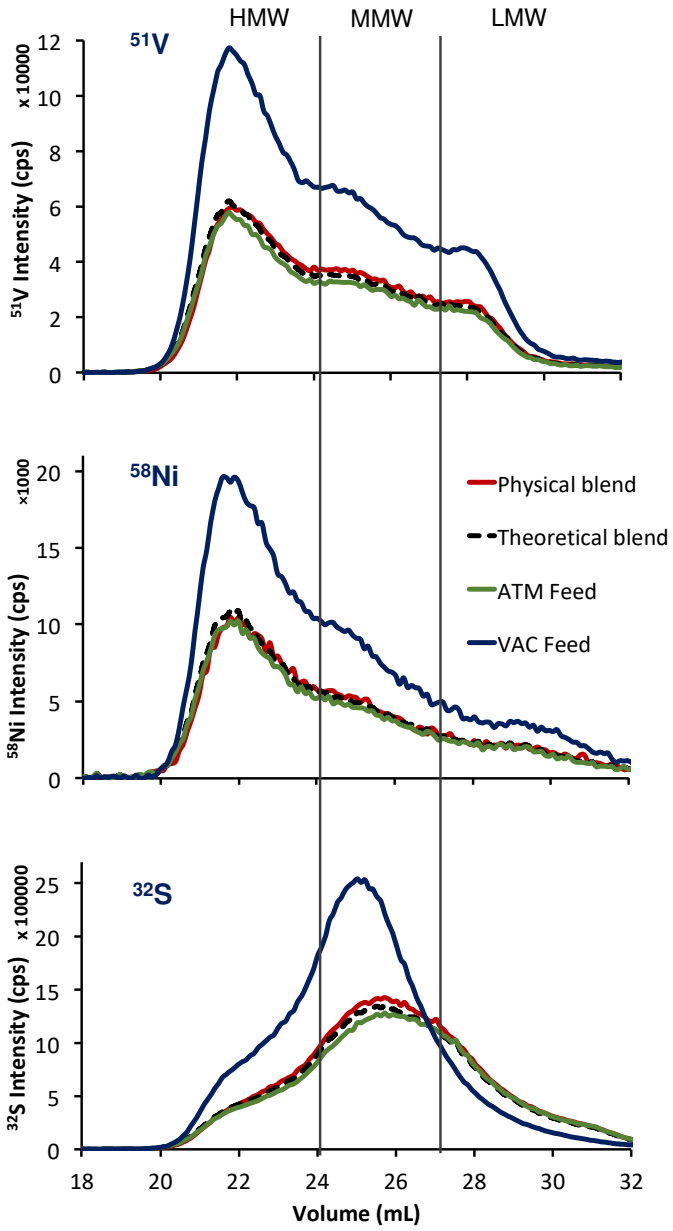
Table 4. *Results of Study B (Influence of the Initial Deactivation Due to Coke Laydown)*

Sample type		Feed	Product	Product	Product	Product
Run time, hours			23	52	76	100
Temperature of the reactor, °C			375	375	375	375
Sulfur, wt%	ASTM D4294	4.061	0.098	0.179	0.212	0.282
Nickel, wt ppm	ICP-MS	27	1.18	1.74	2.08	2.89
Vanadium, wt ppm	ICP-MS	73	2.02	2.84	3.25	4.32
Simulated Distillation	ASTM D7169					
0.5 wt% (IBP), °C		235	142	67	142	155
5 wt%, °C		353	249	247	260	272
10 wt%, °C		388	301	300	313	323
30 wt%, °C		467	407	403	415	421
50 wt%, °C		546	482	474	491	497
70 wt%,°C		627	572	553	577	583
80 wt%, °C		676	632	598	632	639
85 wt%, °C		705	675	626	668	676
90 wt%, °C		-	-	659	716	721
95 wt%, °C		-	-	702	-	-
99.5 wt% (FBP), °C		-	-	-	-	-

RESULTS AND DISCUSSION

Feedstock properties and fingerprints of the metal complexes in the feedstocks

222 The physico-chemical properties of the atmospheric and vacuum residues as well as those of
223 the blends are listed in Table 2. The properties are in line with those of the typical atmospheric
224 and vacuum residues reported in the literature.[1] It is interesting to note that there is a factor of 2
225 difference between the two residues with respect to the Ni, V, asphaltene and MCR contents.
226 When two feeds are blended, it is important to check whether aggregation phenomena occur as
227 these aggregates may influence the asphaltene stability and thereby the residue hydrotreating
228 process. As shown in Figure 1, the theoretical blend (i.e., the calculated profile based on the
229 analysis of the atmospheric and vacuum residues) and the physical blend show the same
230 distribution, indicating that no nanoaggregation occurs. It should be noted that this finding could
231 be a consequence of the fractions stemming from the same crude oil. Indeed, trimodal size
232 distributions are observed for both the V and Ni compounds present in these feedstocks, while a
233 less pronounced trimodal distribution, much richer in MMW aggregates, is observed for the
234 sulfur compounds.



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236 ***Figure 1.*** *GPC ICP HR MS chromatograms of the V, Ni and S species in the atmospheric residue feedstock (ATM, green line),*
237 *vacuum residue (VAC, blue line), blend of 93 vol% ATM and 7% VAC (physical blend, red line) and theoretically reconstructed*
238 *blend of 93 vol% ATM and 7 vol% VAC (black dashed line) based on individual ATM and VAC chromatograms.*

239

240 The size distributions of different crude oils and residues were studied elsewhere,[14] showing

241 the presence of HMW, MMW and LMW nanoaggregates, and the HMW compounds were the

most abundant in Ni and V, while the MMW nanoaggregates were most abundant in S. The results obtained in this study are consistent with these previous results.

Study A – influence of the temperature

Behavior of V and Ni. The evolution of the V and Ni species present in the feed after having been through the hydrotreating process at different temperatures has been studied. The samples were hydrotreated at the three different temperatures previously mentioned: 375 °C, 380 °C and 385 °C.

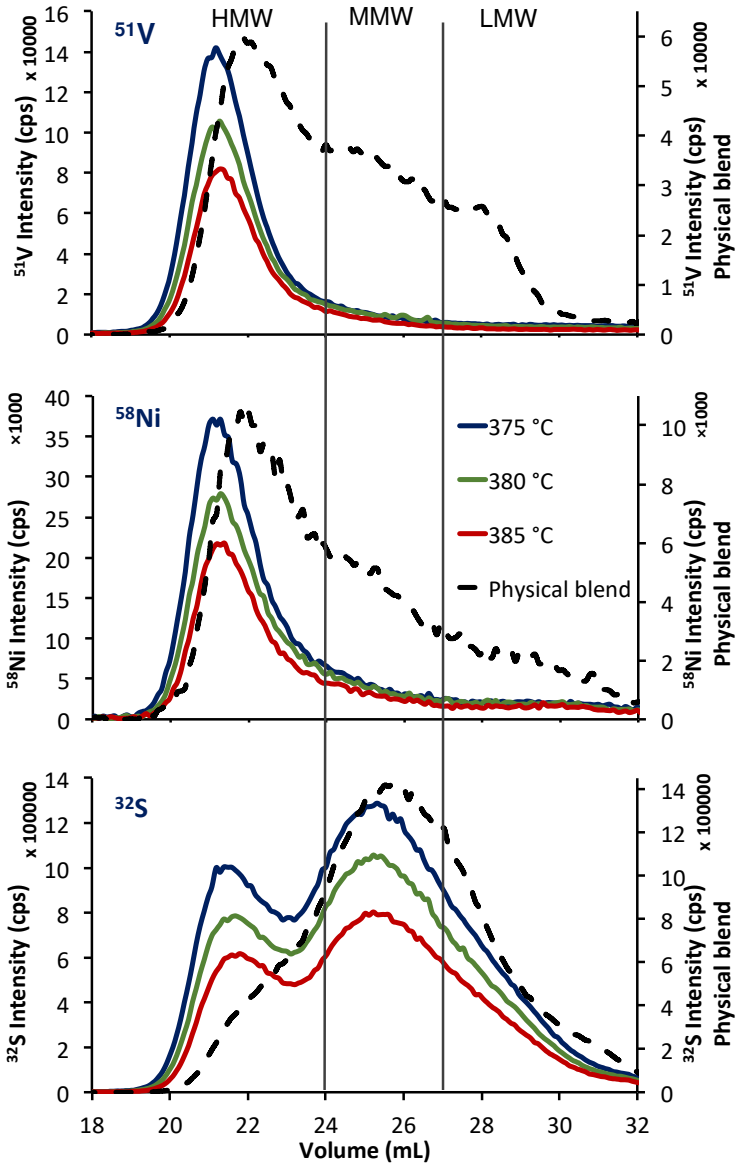
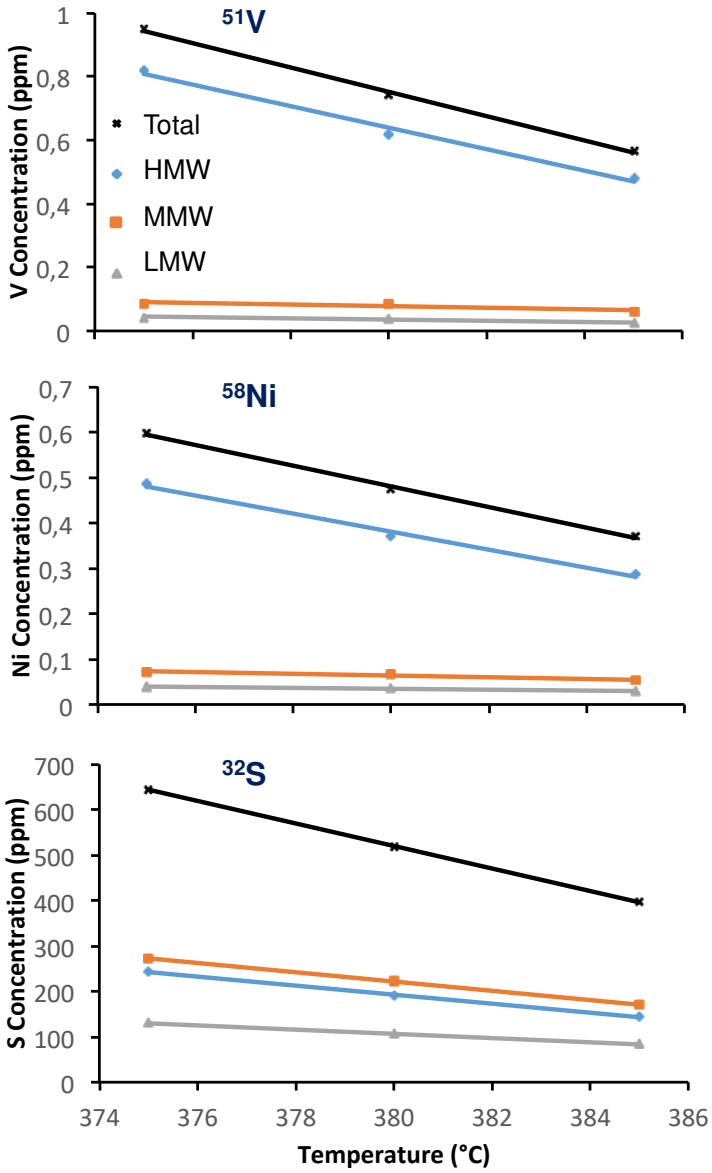


Figure 2. *GPC ICP HR MS chromatograms of the V, Ni and S species in the feed (black dashed line) and the product after having been hydrotreated at different temperatures (the hydrotreatments at 375 °C, 380 °C and 385 °C correspond to the blue, green and red lines, respectively).*

Figure 2 shows that, as expected, at higher temperatures, more V, Ni and S species are removed. For V and Ni, the LMW and MMW aggregates are easily hydrotreated even at low temperatures, and as the temperature is increased, only the remaining HMW aggregates are hydrotreated. This phenomenon can be quantitatively observed in Figure 3, where the concentration of each nanoaggregate size is determined based on the areas of the peaks (details of the integration method are available in the open literature).[15] The concentration of LMW and MMW aggregates is negligibly small at all temperatures, while the concentration of HMW aggregates shows a linear decrease as a function of the temperature. The correlation coefficient of the slope is better for the regression of the HMW nanoaggregates compared to those of the MMW and LMW nanoaggregates, confirming that the temperature is driving the HMW hydrotreatment. From the slopes of these linear trends, as listed in Table 5, it can be readily observed that the HMW V aggregates are hydrotreated faster than the Ni aggregates. This observation is in agreement with previous results in the open literature.[19]



267

268 ***Figure 3.*** *The concentrations of V, Ni and S (total in black, HMW in blue, MMW in orange and LMW in gray) in the products that*
269 *were hydrotreated at different temperatures quantified based on the total concentration and the GPC ICP HR MS*
270 *chromatograms.*

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Table 5. *Slopes and Regression Coefficients for the Variation in V, Ni and S Concentrations vs. Temperature*

	Total		HMW		MMW		LMW	
	Slope	r^2	Slope	r^2	Slope	r^2	Slope	r^2
V	-3.82 E-02	0.998	-3.39 E-02	0.988	-0.25 E -02	0.733	-0.19 E -02	0,965
Ni	-2.28 E-02	0.998	-1.98 E -02	0.992	-0.19 E -02	0.957	-0.10 E -02	0,879
S	-24.84	0.999	-9.955	0.997	-10.21	0.999	-4.678	0,999

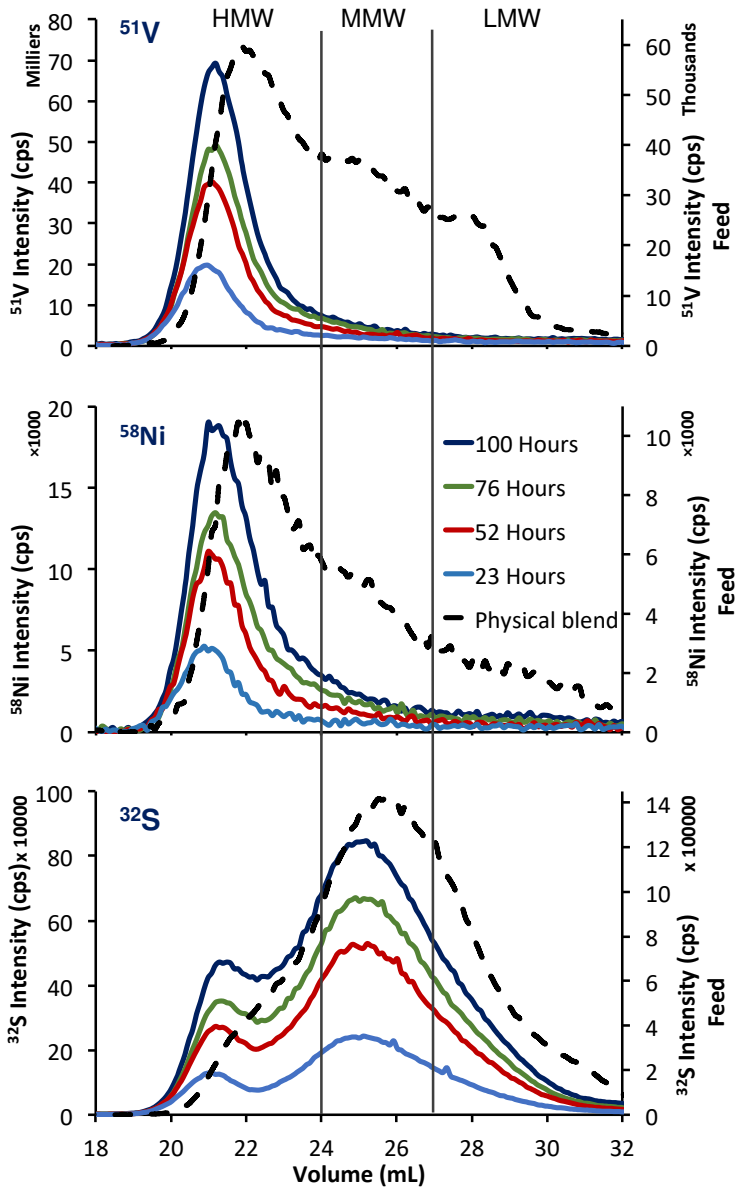
Behavior of S. Interestingly, the fate of the S aggregates differs from that observed for the V and Ni aggregates. Figures 2 and 3 show that the LMW and MMW S aggregates are not fully hydrotreated at the lowest temperatures. This phenomenon indicates that these LMW and MMW compounds are more refractory compared to the size-similar V and Ni compounds. It is also worth noting that a bimodal HMW-MMW S distribution is observed in the hydrotreated products, while this distribution was not clearly present in the feedstock. It is likely that a trimodal distribution occurs in the feedstock but is hidden due to the high concentration of aggregates eluting in the MMW range. These results show that S compounds/nanoaggregates with molecular weights between HMW and MMW are more easily removed, indicating that the catalyst possesses a higher efficiency for these kinds of nanoaggregates.

Study B - initial deactivation due to coke laydown

The initial and fast deactivation during ARDS tests is due to coking and, more specifically, the strong initial adsorption of polyaromatic compounds, including N-containing molecules onto the surface of the catalyst.[11] In commercial units, the impact of the initial coke laydown on HDS and HDM is not simple to evaluate. For some units, it is clear that the HDM activity is more affected than the HDS activity during the first hundred hours. For other units, the initial deactivations of

295 the HDS and HDM activities are equal, which depends on the catalyst loading, feed properties
296 and operating conditions. Therefore, the goal of this study was to evaluate how the initial
297 deactivation (which is due to coke laydown) affected the hydrotreatment rates of the various
298 aggregates and if certain differences between the initial deactivations of HDM and HDS could be
299 observed, which could be related to the aggregate distribution. For this purpose, the temperature
300 of the process was kept constant at 375 °C to evaluate the changes due to the initial catalyst
301 deactivation (at 23, 52, 76 and 100 run hours).

302 ***Behavior of V and Ni.*** The evolution of the V and Ni species present in the feed after having
303 been through the hydrotreating process at different times has been studied. As shown in Figure 4,
304 initially, the concentration of V and Ni species is very low, but during the first hours of the test, a
305 steady increase in the total concentration of V and N is observed. Figure 5 shows the quantitative
306 description of this increase. This increase is almost entirely ascribed to an increase in the HMW
307 fraction. It should be noted that most of the LMW and MMW aggregates are removed
308 throughout the test despite the increasing deactivation (Table 6) of the catalyst, as indicated by
309 the total product Ni and V contents listed in Table 4.



310

311 ***Figure 4.*** *GPC ICP HR MS chromatograms of the V, Ni and S species in the feed (black dashed line) and the product for different*
312 *run times after having been hydrotreated at the same temperature (the run times of 23 h, 52 h, 76 h and 100 h correspond to*
313 *the light blue, red, green and blue lines, respectively).*

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319 ***Table 6.*** *Slopes and Regression Coefficients for the Variation in V, Ni and S Concentration vs. Run Time (Hours).*

	Total		HMW		MMW		LMW	
	Slope	r^2	Slope	r^2	Slope	r^2	Slope	r^2
V	4.96 E-03	0.991	4.44 E-03	0.987	0.38 E -03	0.989	0.14 E -03	0,997
Ni	3.66 E-03	0.993	2.98 E -03	0.989	0.46 E -03	0.997	0.22 E -03	0,966
S	6,22	0.994	2.19	0.994	2.87	0.990	1.16	0,995

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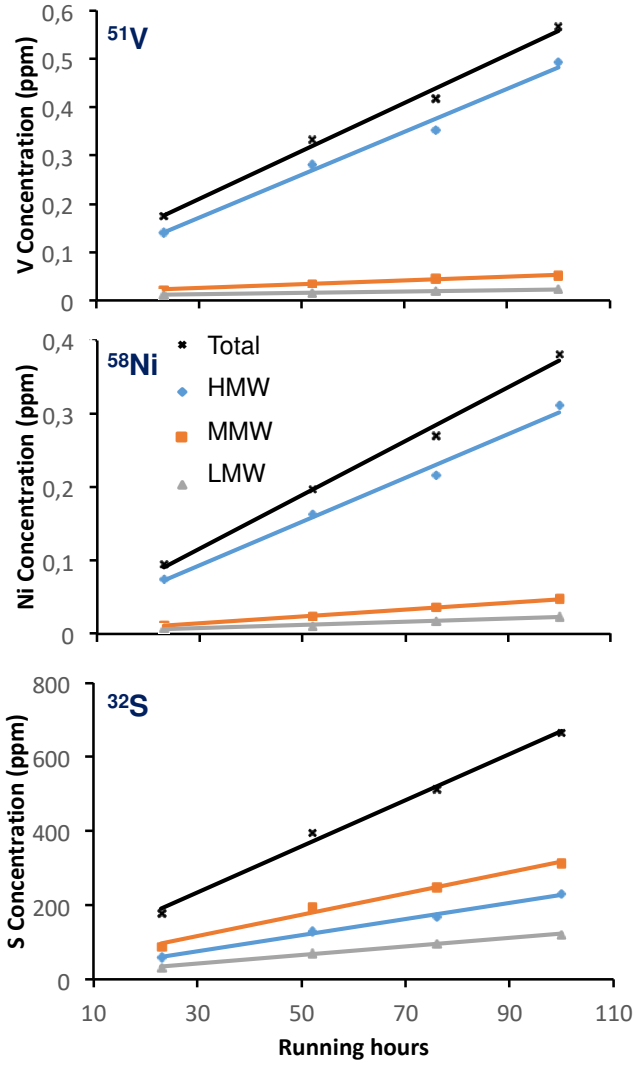
321

322 ***Behavior of S.*** In Figure 4, it is observed that the sulfur species follow a different evolution. A
323 bimodal distribution of the HMW and MMW peaks is observed, and its ratio has been calculated,
324 resulting in an almost constant value. As shown more clearly in Figure 5, the increase in S
325 species is similar for the three groups of hydrodynamic volume distributions, which could
326 indicate either a higher preference of the catalyst for the HMW species (if we compare the
327 behavior of S with the behavior of V and Ni) or a more refractory behavior from the S species
328 with the catalyst.



329

330 ***Figure 5.*** *The concentrations of V, Ni and S (total in black, HMW in blue, MMW in orange and LMW in gray) in the products that*
331 *were hydrotreated for different run times quantified based on the total concentration and the GPC ICP HR MS chromatograms.*

332

333 **CONCLUSION**

334 This study has provided innovative and valuable information related to the size distributions of
335 the different species present in atmospheric residue feedstocks and how these distributions vary
336 during HDS and HDM processes. Obtaining fingerprints of the metal aggregates in these
337 feedstocks has provided us with a better understanding of their speciation in S, Ni and V. For the

Ni and V aggregates, it was found that the HMW compounds are more refractory compared to the LMW and MMW compounds, which are removed at low temperatures or even after long run hours.

For the S aggregates, a slightly different behavior was observed whereby the LMW and MMW aggregates are not as easily hydrotreated, and in fact, the MMW nanoaggregates/compounds are slightly less easily hydrotreated compared to the HMW aggregates. This phenomenon illustrates the inherent difference in chemical composition of the metallo-organic compounds compared to the sulfur-containing compounds and their reactivity. In a previous study[15,20,21] free porphyrinic compounds were easily removed, possibly via easy access of the molecules to the catalyzer. Of the HMW nanoaggregate part, only a small portion can be easily removed, which can be the porphyrins linked at the surface of the nanoaggregates,[15] but the Ni and V compounds that are located deeper in the nanoaggregates are more difficult to remove as the shell of the nanoaggregates has to be removed first before the V and Ni compounds can access the catalyst. In regard to the S compounds, the observed behavior seems to me driven more by the types of S compounds than by the aggregation states of the S compounds. Here, the molecular conformation of the S compounds needs to be studied. More in-depth molecular studies have to be conducted.

Nevertheless, this study provides insights into the catalyst preference towards these compounds/nanoaggregates, which is an important factor for future optimization of the balance between the HDM and HDS catalysts for those ARDS units processing different feedstocks with different V, Ni and S nanoaggregate distributions.

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434 **TABLE CAPTIONS**

435 **Table 1.** Operating Conditions of the Pilot Plant Tests

436 **Table 2.** Feed Properties

437 **Table 3.** Results of Study A (Influence of the Temperature)

438 **Table 4.** Results of Study B (Influence of the Initial Deactivation Due to Coke Laydown)

439 **Table 5.** Slopes and Regression Coefficients for the Variation in V, Ni and S Concentrations vs.

440 Temperature

441 **Table 6.** Slopes and Regression Coefficients for the Variation in V, Ni and S Concentration vs.

442 Run Time (Hours)

443

FIGURE CAPTIONS

Figure 1. GPC ICP HR MS chromatograms of the V, Ni and S species in the atmospheric residue feedstock (ATM, green line), vacuum residue feedstock (VAC, blue line), blend of 93 vol% ATM and 7% VAC (physical blend, red line) and theoretically reconstructed blend of 93 vol% ATM and 7 vol% VAC (black dashed line) based on individual ATM and VAC chromatograms.

Figure 2. GPC ICP HR MS chromatograms of the V, Ni and S species in the feed (black dashed line) and product after hydrotreatment at different temperatures (the hydrotreatments at 375 °C, 380 °C and 385 °C correspond to the blue, green and red lines, respectively).

Figure 3. The concentrations of V, Ni and S (total in black, HMW in blue, MMW in orange and LMW in gray) in the products that were hydrotreated at different temperatures quantified based on the total concentration and the GPC ICP HR MS chromatograms.

Figure 4. GPC ICP HR MS chromatograms of the V, Ni and S species in the feed (black dashed line) and the product for different run times after having been hydrotreated at the same temperature (the run times of 23 h, 52 h, 76 h and 100 h correspond to the light blue, red, green and blue lines, respectively).

Figure 5. The concentrations of V, Ni and S (total in black, HMW in blue, MMW in orange and LMW in gray) in the products that were hydrotreated for different run times quantified based on the total concentration and the GPC ICP HR MS chromatograms.