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Julie Guillemant, Alexandra Berlioz-Barbier, Fabien Chainet, Luis de Oliveira, Marion Lacoue-Nègre, et al.. Sulfur compounds characterization using FT-ICR MS: Towards a better comprehension of vacuum gas oils hydrodesulfurization process. *Fuel Processing Technology*, 2020, 210, pp.106529. 10.1016/j.fuproc.2020.106529 . hal-02956093

HAL Id: hal-02956093

<https://ifp.hal.science/hal-02956093>

Submitted on 2 Oct 2020

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Sulfur compounds characterization using FT-ICR MS: towards a better comprehension of vacuum gas oils hydrodesulfurization process

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Abstract

Some aromatic sulfur compounds contained in vacuum gas oils are known to be very refractory to hydrotreatment. Thus, a better knowledge of these molecules would help to improve hydrodesulfurization efficiency by designing targeted catalysts or choosing adequate operating conditions for hydrotreatment process. The characterization of such compounds using advanced analytical techniques such as Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) can give more information about the aromaticity and the number of carbon atoms of these refractory molecules. One vacuum gas oil feed and six hydrotreated samples obtained from pilot plant tests at several temperatures or using different catalysts have been analyzed using APPI(+)-FT-ICR MS. The differences of the aromaticity and number of carbon atoms among the several hydrotreated samples have been investigated to identify the effects of catalysts and temperatures over hydrotreatment process. Principal Component Analysis was used to explore the obtained data and put forward the variables explaining most of the variance between the hydrotreated samples.

Keywords: Vacuum gas oils ; hydrodesulfurization ; catalysis ; sulfur compounds ; mass spectrometry ; chemometrics

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56 **1. Introduction**

57 As environmental specifications become more and more severe regarding sulfur compounds,
58 refiners need to improve hydrodesulfurization processes to reduce as much as possible the sulfur
59 content to less than 10 ppm in commercial on-road gas oils[1,2]. Such gas oils (GO) are mainly
60 obtained through conversion processes such as Fluid Catalytic Cracking (FCC) or Hydrocracking
61 (HCK) from heavier cuts such as vacuum gas oils (VGO) whose sulfur content are very high.
62 Thus, a first hydrotreatment step is often introduced before conversion processes to improve the
63 quality of the heavy cut (i.e.,VGO) before conversion into gas oil cut. However, some sulfur
64 compounds contained in vacuum gas oils are refractory to hydrotreatment and there is no
65 analytical method providing both quantitative and qualitative results to feed hydrotreatment
66 models to improve such process[3–5]. Moreover, such method would also be helpful to perform
67 catalysts screening, to go further into desulfurization mechanism comprehension as described for
68 lighter cuts such as gasoline as well as optimizing modeling processes[6,7].

69 Two-dimensional comprehensive gas chromatography (GC×GC) coupled to Sulfur
70 Chemiluminescence Detector (SCD) is mainly used to characterize sulfur compounds in gas oil
71 samples[8,9]. However, GC×GC analysis does not allow the analysis of polar compounds in
72 vacuum gas oils samples as the polar compounds are not fully resolved thus preventing their
73 quantification [10].

74 Within a mass spectrometry context, sulfur compounds are rather identified as apolar
75 compounds. [11–15]. Two ionization sources are mainly available for sulfur compounds
76 characterization: atmospheric pressure photo-ionization (APPI) and methylation of sulfur
77 compounds followed by electrospray ionization (Me-ESI). Me-ESI is more sensitive towards low
78 alkylated compounds whereas APPI ionizes a broader range of aromatic compounds[16,17].
79 Thus, APPI ionization source is preferred rather than Me-ESI to perform VGO analysis as very
80 aromatic compounds found in the VGO feedstock used to produce the hydrotreated samples
81 might not be efficiently ionized using Me-ESI without any pre-fractionation of the vacuum gas
82 oils[17].

83 Chemometric tools have been proved to be efficient to extract significant variables among
84 large FT-ICR MS datasets, especially Principal Component Analysis (PCA)[18–20]. The use of

85 such tools is then particularly suited to look for reactivity descriptors that could explain the
86 differences observed between several hydrotreated samples [21]. When vacuum gas oils matrices
87 that are more complex than gas oils matrices are considered, the number of significant variables
88 is even increased hence proving the interest of such methods [22,23].

89 This paper presents the APPI(+)-FT-ICR MS analysis of one vacuum gas oil feed and six
90 hydrotreated samples obtained from catalytic tests at several temperatures and with two different
91 catalysts. The pseudo-concentrations of each family have been followed throughout
92 hydrotreatment process for a better understanding of removal mechanisms throughout the present
93 hydrotreatment operating conditions. Finally, PCA was applied on data obtained for the feed and
94 the hydrotreated samples to explore the generated dataset.

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109 **2. Material and Methods**

110 **2.1. Vacuum gas oils**

111 6 hydrotreated samples with different hydrodesulfurization (HDS) levels have been selected for
112 this study. The samples have been produced from hydrotreating pilot tests of a VGO feedstock
113 over two different catalysts (A) and (B). The different levels of HDS have been obtained by
114 varying the reactor temperature while keeping the other operating conditions such as reactor
115 pressure, LHSV, H₂/oil ratio) constant. The S content was determined by wavelength dispersive
116 X-rays fluorescence (WDXRF) using a Panalytical Axios (Almelo, Netherlands) 4 kW equipped
117 with a Cr anode. 2 mL of the solution was introduced within a cup with a Mylar 6 μm film
118 according to an IFPEN internal method. Details about the chosen samples are given in Table 1.
119 All samples have been first solubilized in toluene to 1% w/w and further diluted in a 75%-25%
120 Toluene-Methanol solution to 0.05% v/v for FT-ICR MS analysis.

121 **Table 1. Vacuum gas oil samples characteristics**

Sample	Reactor Temperature	Sulfur content (ppm)	Boiling Point Ranges (°C)	Catalyst
Feed (85% Arabian Light + 15% Irak)	-	18921	394-580	-
A-1	Low temperature (1)	1251		A
A-2	Middle temperature (2)	693		A
A-3	High temperature (3)	334		A
B-1	Low temperature (1)	949		B
B-2	Middle temperature (2)	483		B
B-3	High temperature (3)	200		B

122

123

124 2.2. FT-ICR MS analysis

125 VGO samples were analyzed in APPI(+)-FT-ICR MS considering 6 technical replicates to assess
126 the ionization repeatability of the analysis. Mass spectrometry (MS) analyses were performed
127 using a LTQ FT Ultra Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR
128 MS) (ThermoFisher Scientific, Bremen Germany) equipped with a 7T magnet (Oxford
129 Instruments) and with APPI source (Syagen Technology, Tustin CA, USA) used in positive
130 mode. Mass range was set to m/z 98-1000. 4 μ -scans, 70 scans and an initial resolution set to
131 200,000 (transient length of 1.6s) at $m/z=500$ (center of average vacuum gas oil mass
132 distribution) were recorded for each sample. Transient signal was recorded to enable further data
133 processing. Tube lens, capillary voltage and vaporization temperature were fixed to 70 V, 30 V
134 and 250°C respectively. Sheath gas was 20 a.u. and auxiliary gas was 5 a.u.. Nitrogen was used
135 in both cases. External mass calibration was performed using a home-made sodium formate
136 clusters solution (sodium formate from VWR, Fontenay-sous-Bois, France) from about 90 Da to
137 1000 Da.

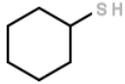
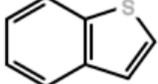
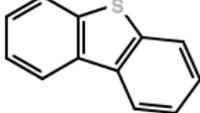
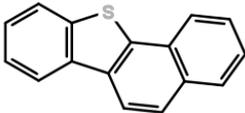
138 2.3. Spectral data processing

139 Spectral data were processed using several softwares. More details about full data processing are
140 available elsewhere[24] leading to a resolution of about 445,000 at m/z 498 sufficient to resolve
141 the 3.4 mDa difference between C_3 and SH_4 . Molecular formula assignment conditions were the
142 following ones: $C_{0-100}H_{0-200}O_{0-5}N_{0-5}S_{0-5}$ with maximum content of heteroatoms of 5 for the
143 vacuum gas oils samples. The error between the theoretical and experimental masses was set to 1
144 ppm after iterative mass recalibration based on S1 family (most abundant family)[25]. S1 family
145 corresponds to radicalar ions and was supposed to contain all elementary sulfur as only a small
146 percentage of protonated cations were observed and they would be more likely to correspond to
147 fragments rather than precursors Relative intensities were calculated by multiplying the
148 compound absolute intensity by 100 and divided by the sum of all S1 absolute intensities.
149 Pseudo-concentrations in sulfur were obtained by multiplying relative intensities by the amount
150 of sulfur in the sample. Families were attributed regarding values of Double Bond Equivalent
151 (DBE) with $DBE = c - h/2 + n/2 + 1$ where c corresponds to the number of carbon atoms, h to the
152 number of hydrogen atoms and n to the number of nitrogen atoms. As FT-ICR MS does not

153 allow isomers identification, the types of structures most likely to correspond to molecules with
154 the indicated DBE are available in Table 2 [17,26].

155

156 **Table 2. Types of sulfur compounds found in crude oils and their corresponding DBE.**

Thiols DBE 1-2	Thiophenes (T) DBE 3-4-5	Benzothiophenes (BT) DBE 6-7-8	Dibenzothiophenes (DBT) DBE 9-10-11	Naphthobenzothiophenes (NBT) DBE 12-13-14
				

157

158 2.4.Principal Component Analysis

159 As this study focuses on sulfur compounds contained in VGO, only molecular formulas
160 containing a single atom of sulfur were taken into account for spectral analysis. The six different
161 replicates were used as single samples to assess the repeatability of the FT-ICR MS analysis
162 through PCA. The data formatting has been described and successfully applied on gas oil
163 matrices elsewhere[21] and adapted here to VGO data. Briefly, APPI-FT-ICR MS data was re-
164 arranged into a 42×2500 matrix where 42 correspond to the 7 samples times 6 replicates and
165 2500 to the possible combinations of DBE (from 1 to 25) and carbon number (from 1 to 100).
166 The relative intensities of the peaks have been considered as variables and the matrix has been
167 mean-centered prior to statistical analysis.

168 All models were developed with the PLS_Toolbox version 8.6 for Matlab version R2018b
169 (Eigenvector Research Inc, Wenatchee, WA, USA). Replicates from sample A-3 were used for
170 validation and all other samples were used for performing PCA. The optimization of the model
171 was performed with venitian-blinds cross-validation (10 data splits, 20 samples per blind, 20
172 maximum principal components). Optimal number of components for PCA was chosen based on
173 % explained cumulative variance and log(eigenvalues) values.

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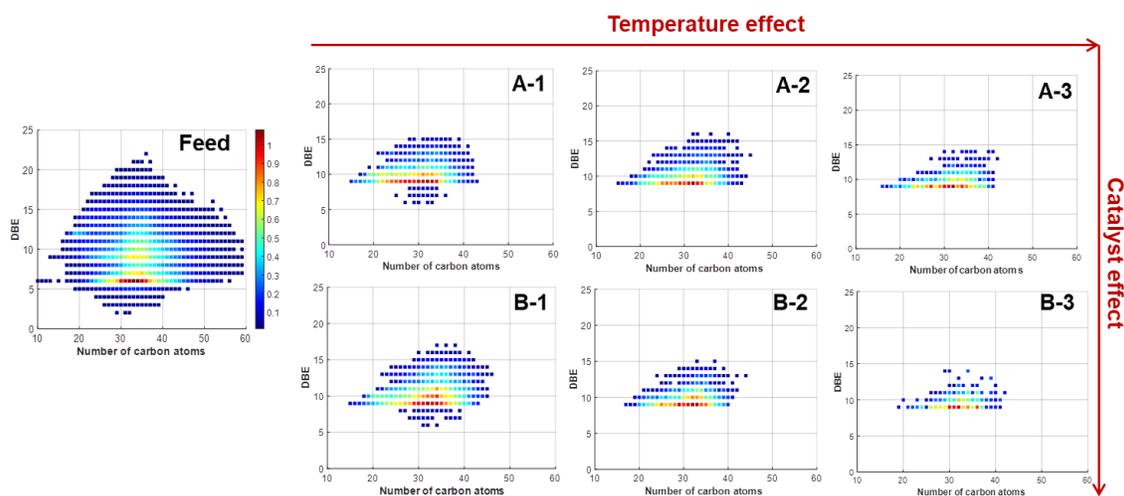
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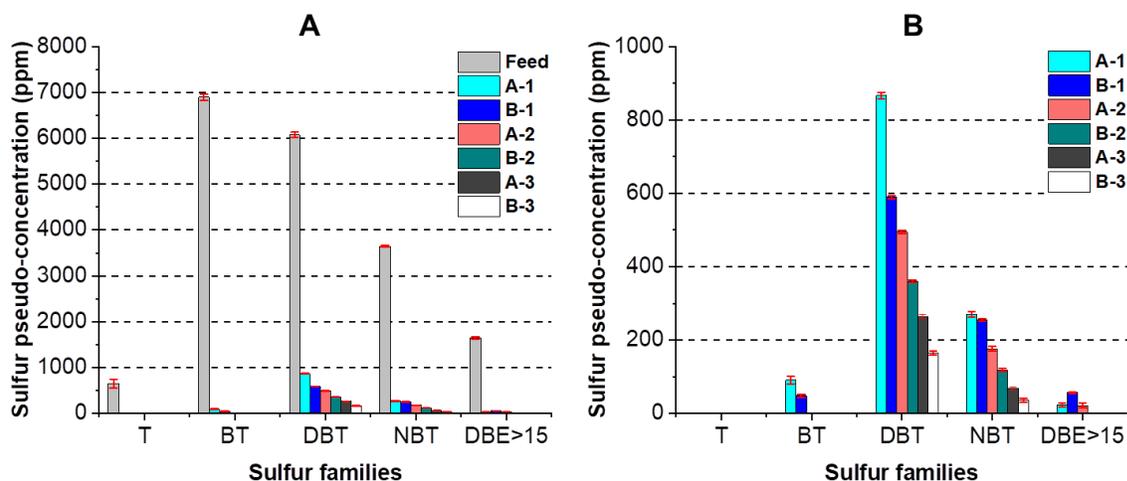
178 **3. Results and Discussion**

179 **3.1. Global vacuum gas oils analysis**

180 After hydrotreatment, only HC, N1 Ox and S1 compounds are found in the hydrotreatment
181 samples (see Figure S1 in Supporting Information) both in radicalar M^+ and protonated $[M+H]^+$
182 forms. A small proportion of disulfur compounds has been identified in the feedstock but no
183 disulfur compounds have been identified in the hydrotreated samples meaning that the disulfur
184 compounds have been removed during hydrotreatment and thus are not considered in this study.
185 The plots of DBE as a function of the carbon number for the 7 samples (Feed and hydrotreated
186 products) are very useful to get a quick overview of the effects of both catalysts and
187 temperatures. Indeed, as seen in Figure 1, the rise of temperature (Low, Middle and High
188 temperature) is directly linked to the decrease of identified S1 compounds which is in accordance
189 with expected behavior. The relative abundance of the S1 class also decreases accordingly to the
190 sulfur content in the sample, as seen in Figure S1 in Supporting Information. The specificities of
191 each catalyst are also highlighted as profiles obtained are different for a given temperature.



192
193 **Fig. 1. Comparison of obtained DBE=f(#C) diagrams for the feed and the six hydrotreated**
194 **samples (A-1 to B-3) for the class S1.**



195

196 **Fig.2. (A) Comparison of sulfur families identified for the feed and its hydrotreated**
 197 **samples. (B) Zoom over the hydrotreated samples.**

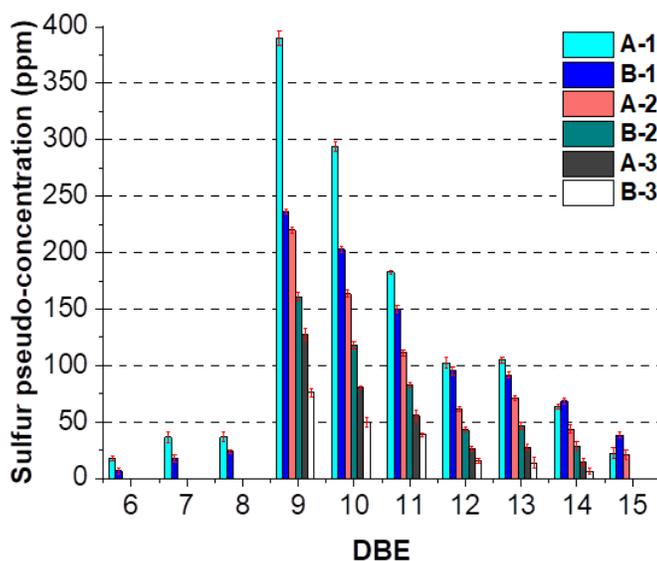
198 A large range of sulfur families is observed in Feed sample with mainly benzothiophenes (BT)
 199 and dibenzothiophenes (DBT), as shown in Figure 2A. In the hydrotreated samples, a sharp
 200 decrease is observed for most of sulfur families, visible in Figure 2B. This is obvious for BT
 201 whose concentrations are close to zero at highest HDS conversion level revealing the high
 202 reactivity of these compounds. Naphtobenzothiophenes (NBT) and especially dibenzothiophenes
 203 (DBT) are the main remaining families within the most severely hydrotreated sample (B-3)..
 204 Their refractory character is well known in the literature[1,3,4]. The reactor temperature effect is
 205 also observed with gradual decreasing of pseudo-concentrations as the temperature rises.
 206 Regarding the catalysts, catalyst B is more efficient than catalyst A in removing the BT and
 207 DBT compounds. For the HDS of NBT family, no obvious difference is observed between both
 208 catalysts indicating that for a given low temperature catalyst B is not more efficient than catalyst
 209 A to hydrogenate NBT compounds. This reversal of efficiency might could be related to a
 210 possible difference in apparent activation energy on the HDS of the NBT compounds. The
 211 activation energy might be lower for catalyst A than for catalyst B, which could be characteristic
 212 of two different reaction pathways.

213 To go further, differences regarding aromaticity or number of carbon atoms of the samples have
 214 been investigated.

215

216 **3.2.Aromaticity changes.**

217 The aromaticity changes within each sulfur family have also been studied by comparing the
218 pseudo-concentrations for several DBE within the same family, as shown in Figure 3. The
219 compounds remaining in the most hydrotreated samples (*i.e* A-3 and B-3) have DBE values
220 contained between 9 and 14. Again, the gradual decrease of the pseudo-concentrations is
221 observed according to the reactor temperature and the higher efficiency of the catalyst B is
222 spotted for moderate and high temperatures. The most intense aromaticity degree in the most
223 severely hydrotreated sample corresponds to a DBE equal to 9 which could correspond to the
224 classical backbone DBT molecule or to a benzothiophene core with three additional naphthenic
225 rings.

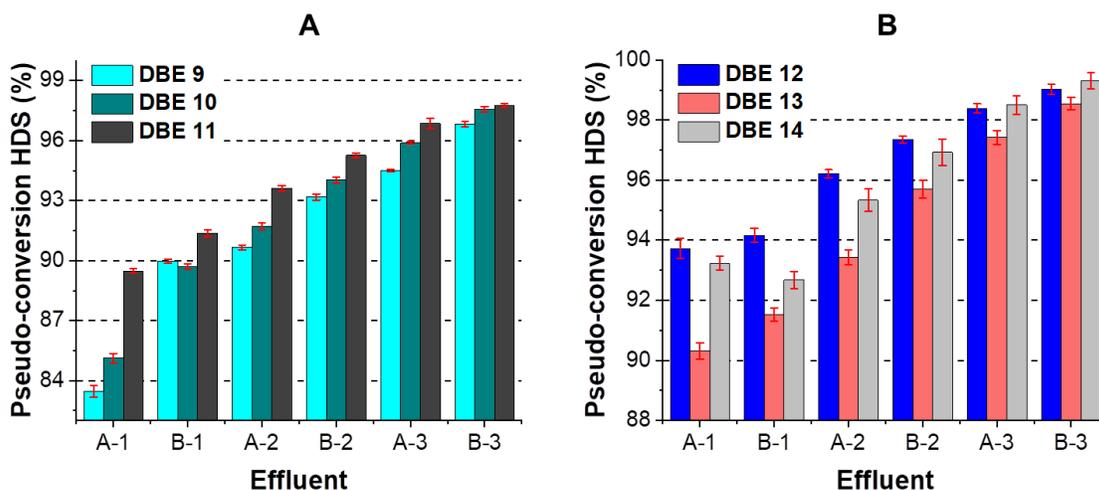


226
227 **Fig. 3. Evolutions of sulfur pseudo-concentrations as a function of aromaticity degree**
228 **(DBE) for the several hydrotreated samples.**

229 For every sulfur family considered, the HDS conversion depends on the aromaticity degree, as
230 shown in the Figure 4. The HDS conversion for each DBE were calculated based on the pseudo-
231 concentrations remaining in the hydrotreated samples compared to the pseudo-concentration
232 observed within the feed. For DBT family (Figure 4A), the HDS conversion of the compounds
233 with a DBE equal to 9 seem to be less converted than other more aromatic DBT compounds and
234 might be potentially more refractory. This result is especially interesting for DBT family as
235 previous observations reported the very refractory character of DBT with DBE equal to 9 also
236 observed for gas oil matrix as well as for vacuum gas oil matrix[21,23].

237 However, the impact of the aromaticity on the reactivity is also dependent of the catalyst. For
 238 the hydrotreated sample B-1, the DBT with DBE equal to 9 and 10 have similar reactivity, while
 239 the reactivity of these compounds in the hydrotreated sample A-1 is different. The same behavior
 240 is observed in the DBT compounds with DBE 10 and 11 for the hydrotreated samples A-3 and
 241 B-3.

242 As regards NBT, compounds with DBE equal to 13 are more intense than others NBT (DBE
 243 12 and DBE 14), as seen in Figure 4B. This means that the addition of a naphthenic cycle over
 244 NBT molecule could decrease the hydrodesulfurization efficiency which was not observed for
 245 DBT family. Moreover, species with higher DBE (DBE 14, 15, 16...) could also be partially
 246 hydrogenated during hydrodesulfurization and would enrich the content in DBE 13.

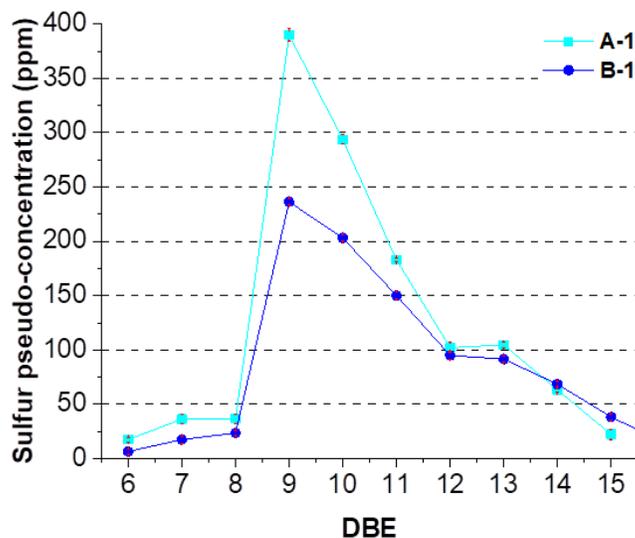


247

248 **Fig. 4. (A) Evolution of the HDS conversion percentage of the different hydrotreated**
 249 **samples as a function of DBE 9-11. (B) Evolution of the HDS conversion percentage of the**
 250 **different hydrotreated samples as a function of DBE 12-14.**

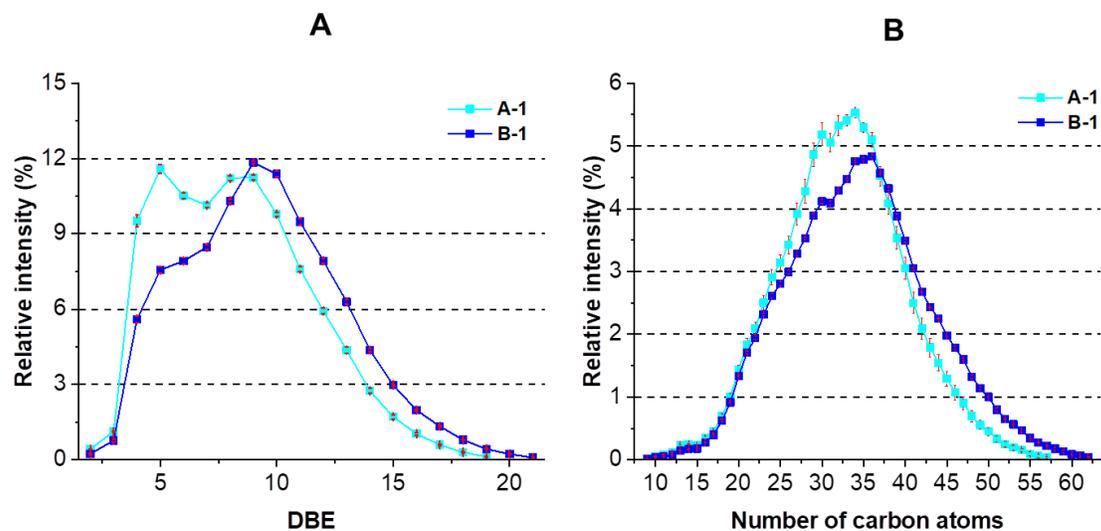
251 The samples obtained at low temperature (A1-B1) seem to have a different catalytic behavior
 252 according to sulfur families, as seen in Figure 5. The HDS of benzothiophenes compounds,
 253 (DBE between 6 and 8) is similar for both catalysts, while the catalyst B is more active (i.e more
 254 selective) than catalyst A on the HDS of the DBT compounds (DBE between 9 and 11). The
 255 activity of the catalysts become similar again between DBE 12 and 13. Finally, a selectivity
 256 inversion is observed with catalyst A being more active than catalyst B for the compounds with
 257 DBE between 14 and 16. Thus, catalyst B is globally more selective towards dibenzothiophenes

258 (DBE 9-10-11) than catalyst A but surprisingly less efficient for more aromatic compounds such
259 as naphthobenzothiophenes (DBE 14-16). This behavior might be linked to a difference in
260 activation energy between both catalysts as explained in the section 3.1.



261
262 **Fig.5. Evolution of the sulfur pseudo-concentration as a function of DBE for the effluents**
263 **A-1 and B-1.**

264 Moreover, a potential hydrogenation competition between hydrocarbons and sulfur might be
265 suspected within the reactor [27] and especially within samples A-1 and B-1. To evaluate this,
266 the evolution of the DBE and number of carbon atoms of the hydrocarbons compounds (HC
267 class) in these effluents has been plotted in Figure 6. The evolution of the corresponding
268 $DBE=f(\#C)$ plots for this class from all effluents are also available in Figure S2 in Supporting
269 Information. A clear shift of the sample A-1 is spotted compared to the sample B-1 in terms of
270 aromaticity as well as number of carbon atoms. Especially, the sample A-1 should undergoes
271 more hydrogenation reactions as its relative intensities in poorly aromatic compounds (DBE < 9)
272 are higher than those observed for sample B-1. Moreover, as the alkylation range remains similar
273 between the feed and its effluents, the shift in alkylation observed for the hydrotreated samples
274 can be attributed to a reactivity difference between the “poorly” (< C40) and very alkylated
275 species (> C40). To go further, an appropriate kinetic study should be performed to fully explain
276 and understand the hydrogenation competitions between sulfur and hydrocarbons.



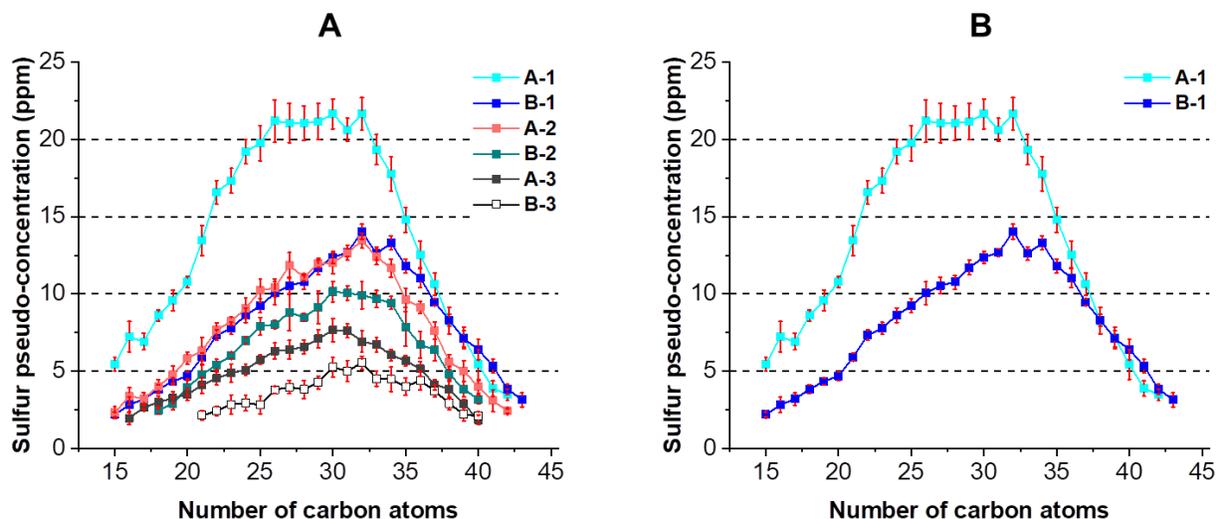
277

278 **Fig. 6. Evolution of the relative intensity as a function of (A) DBE and (B) number of**
 279 **carbon atoms for samples A-1 and B-1 for the class HC.**

280

281 **3.3. Number of carbon atoms changes**

282 The evolutions of the pseudo-concentrations as a function of the number of carbon atoms of
 283 the samples give complementary information. The specific distribution of carbon atoms for DBT
 284 with a DBE equal to 9 has been plotted only for hydrotreated samples in Figure 7A. The number
 285 of carbon atoms range within refractory compounds have been identified is comprised between
 286 15 and 46.



287

288 **Fig. 7. (A) Evolutions of sulfur pseudo-concentrations as a function of number of carbon**
 289 **atoms of the molecules for DBT molecules with a DBE equal to 9 for the hydrotreated**
 290 **samples A-1 to B-3. (B) Zoomed for A-1 and B-1.**

291 When increasing hydrotreatment conditions, the carbon number distribution has a smaller
 292 range and starts from C21 for the most hydrotreated sample (i.e, B-3). This shows that using
 293 such catalytic conditions enables the hydrotreatment of less alkylated DBT when moderate
 294 conditions do not. Globally, the refractory compounds are most intense around C30 to C35
 295 which is a relatively high degree of alkylation.

296 The distribution of DBE 9 for the less hydrotreated sample A-1 is shifted to a smaller number
 297 of carbon atoms compared to the distribution of sample B-1, as seen in Figure 6B. Thus,
 298 dibenzothiophenes in A-1 are less alkylated than dibenzothiophenes analyzed in B-1. As
 299 mentioned before, two different desulfurization mechanisms are suspected according to the
 300 catalyst considered for low reactor temperature. At low temperature, the catalyst A is more
 301 efficient to remove very alkylated compounds while the catalyst B is more efficient towards less
 302 alkylated compounds. This trend disappears when increasing the operating temperature hence
 303 homogenizing the catalysts efficiency.

304 It can be mentioned that according to the distribution of the other hydrotreated samples (i.e A-
 305 2, B-2, A-3 and B-3), only dehydrodesulfurization may take place with both catalysts at
 306 moderate or high reactor temperature.

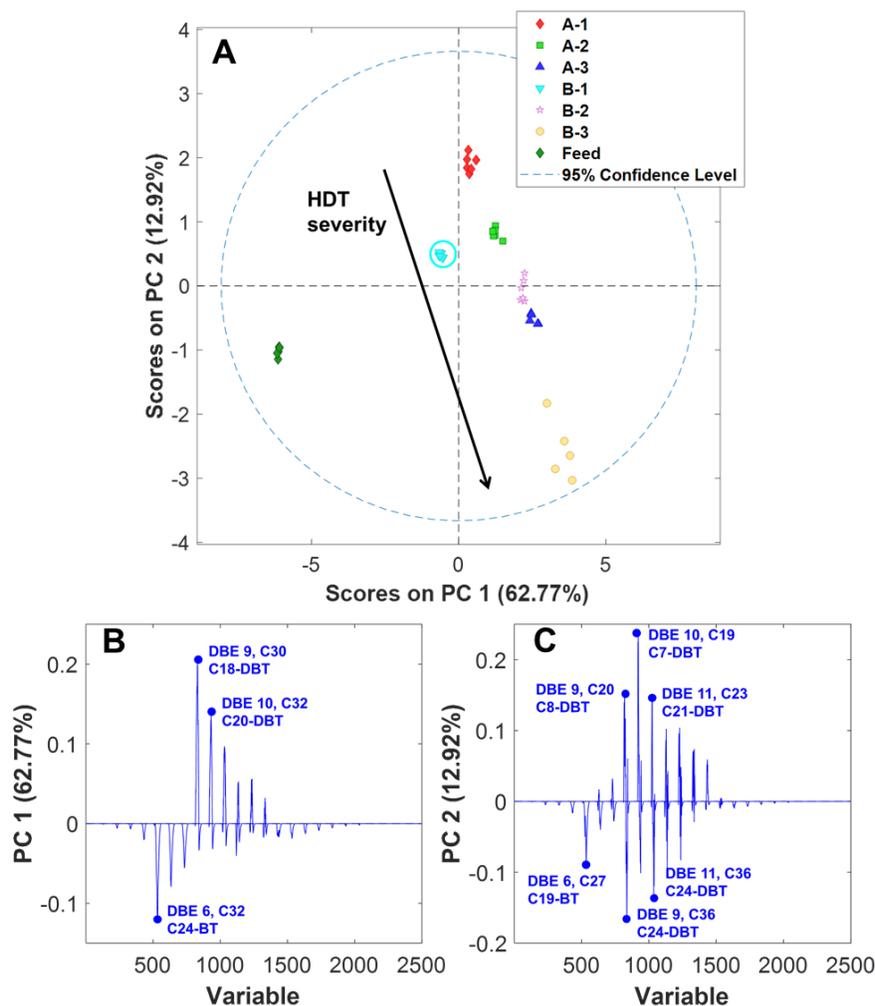
307 In summary, sulfur compounds with DBE equal to 9 and carbon atoms number starting from
308 C21 to C42 seem to be the most refractory compounds found for the most severe hydrotreatment
309 operating conditions. To go further, Principal Component Analysis (PCA) was applied on this
310 spectral dataset to extract more information on these samples.

311 **3.4. Principal Component Analysis**

312 PCA was applied on this spectral dataset, also considering only sulfur compounds (S1 class).
313 Moreover, a second statistical analysis has been performed including not only the S1 compounds
314 but also the HC compounds. This analysis showed that the sulfur compounds explain most of the
315 variance between samples and that the hydrocarbons composition does not allow discriminating
316 the different samples whereas it is the most abundant class, hence highlighting the interest of
317 studying the S1 compounds. This second analysis is available in Figure S3 in Supporting
318 Information. Considering the relatively small amount of samples available, only the sample A-3
319 (corresponding to six replicates) has been used as a validation set and all other samples have
320 been used for calibration. 2 Principal Components (PCs) have been considered in the model
321 leading to a total explained variance of 76%. One replicate from B-3 has been excluded from the
322 model because the relatively high analytical variance between the six replicates distorted the
323 statistical analysis. The score plot obtained over PC1 and PC2 is shown in Figure 7A.

324 Globally, the different replicates are close to each other for a given sample, except for B-3 for
325 which replicates are a little bit more far away from each other. This can be explained by a
326 decreased analysis sensitivity towards very hydrotreated samples. Validation sample (i.e, A-3) is
327 logically projected between B-2 and B-3 which are the closest samples to A-3 in terms of
328 hydrotreatment severity. A separation between the feed and the different effluents is observed
329 along PC1. It is interesting to note that the increase of HDT severity is visible towards a negative
330 translation over PC2. Moreover, sample B-1 is shifted from the translation over PC1 compared to
331 all other samples, indicated in cyan circle. As seen previously, sample B-1 is the only sample for
332 which a catalyst selectivity inversion is observed for a given reactor temperature. The projection
333 of this sample over PC1 and PC2 confirms its unique behavior.

334



335

336 **Fig.7.** (A) Score plot obtained over PC1 and PC2 for the feed and its hydrotreated samples. (B)
 337 Loadings plot obtained for PC1. (C) Loadings plot obtained for PC2.

338 The loadings plots correspond to the visualization of the distribution of the variables over
 339 several principal components. Those obtained from the first and second principal components are
 340 shown in Figures 7B and 7C. When considering PC1, three variables are mainly expressed: C4+-
 341 BT (corresponding to a benzothiophene core with 24 additional carbon atoms with a DBE equal
 342 to 6) and two C4+-DBT (dibenzothiophenes cores with respectively 18 and 20 additional carbon
 343 atoms and DBE equal to 9 and 10). The C4+-BT variable is negatively expressed over PC1 when
 344 both C4+-DBT variables are positively expressed. Thus, the negative projection of the feed along
 345 PC1 is due to its relative intensity of benzothiophenes which is lower than the ones observed for
 346 the different effluents except for the sample A-1 which also explains its atypical character. This
 347 is in agreement with the previous observations stating that the benzothiophenes are totally

348 removed in effluents obtained at moderate or high reactor temperatures (i.e, A-2, B-2, A-3 and
349 B-3) as they are easily converted when performing hydrodesulfurization[4]. On the opposite, the
350 positive projection of the hydrotreated samples is mainly due to the major presence of
351 dibenzothiophenes with several aromaticity levels (DBE 9 and DBE 10). Again, this is consistent
352 with previous observations putting forward the very refractory character of these compounds. As
353 regards PC2, very alkylated variables are negatively expressed with DBE equal to 6, 9 and 11
354 when less alkylated variables are positively expressed with DBE equal to 9, 10 and 11. The
355 expression of C₄₊-BT is due to the negative projection of the feed along PC2. It is worth noticing
356 that for DBE 9 and 11 the distributions of the number of carbon atoms are splitted into both
357 positive and negative contributions, showing the subtle discriminative power of PCA. Thus, the
358 increase of HDS severity goes with a raise of alkylation levels for given DBEs meaning that very
359 poly-alkylated dibenzothiophenes are more refractory than lower alkylated ones. This also
360 confirms the difference of selectivity for DBE 9 observed for catalysts A and B at low
361 temperature which is actually due to alkylation degree shifts with catalyst A leading to less
362 alkylated products and catalyst B leading to more alkylated products. As the other principal
363 components (PC3, PC4, PC5...) did not allow extracting more information, they are not
364 discussed here.

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377 **4. Conclusion**

378 The relevance of FT-ICR MS as a pseudo-quantitative tool for the hydrotreatment monitoring
379 of vacuum gas oils has been assessed in this paper by comparing the pseudo-concentrations
380 obtained for one feed and its six hydrotreated samples. A comprehensive study of the effect of
381 temperature and catalyst over hydrotreatment process has been done. This helped us to highlight
382 some refractory compounds in vacuum gas oil hydrotreatment and it can be mentioned that these
383 compounds have already been found to be problematic for gas oil hydrotreatment. This indicates
384 that no matter the fact that much more aromatic and alkylated compounds can be found in VGO,
385 dibenzothiophenes and their derivatives with low aromatic content are most likely to be the most
386 problematic compounds in HDT, followed by naphthobenzothiophenes and their derivatives.
387 Especially, the study of aromaticity and alkylation levels gave some clues on the most refractory
388 aromatic levels that are DBE 9 for the dibenzothiophenes family and DBE 12 for the
389 naphthobenzothiophenes family. The number of carbon atoms of these refractory molecules has
390 also been described, coming from C21 to C42 which relates to very alkylated molecules as the
391 DBT aromatic core molecule only contains 12 carbon atoms. The application of chemometric
392 tool such as PCA confirmed all the previous observations and helped in the identification of key
393 variables explaining some selectivity differences between both catalysts at low temperature. In
394 summary, dibenzothiophenes with high number of carbon atoms and DBE equal to 9 are
395 revealed to be the main remaining species in VGO hydrotreatment process. Thus, specific
396 catalysts could be designed to target these molecules and improve HDT efficiency. Moreover,
397 other techniques could be applied such as ion mobility to identify the most refractory isomers in
398 more severely hydrotreated samples and also to identify the nature of the carbon substituents on
399 these molecules.

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495 **6. Tables and Figures**

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