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1 IMPACT OF FEEDSTOCK PROPERTIES ON THE DEACTIVATION OF A VACUUM
2 GASOIL HYDROCRACKING CATALYST
3

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9

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11 ABSTRACT

12 The aim of this study was to understand the impact of vacuum gas oil (VGO) properties on the
13 deactivation rate of a hydrocracking catalyst (a nickel-molybdenum sulfide dispersed on a carrier
14 containing USY zeolite). For that purpose, two hydrotreated feeds of different density, organic
15 nitrogen (~120-150 ppmw) and aromatic content, were hydrocracked under operating conditions
16 that favor catalyst deactivation, i.e., high temperature (T=418°C) and high space velocity (LHSV=3
17 h⁻¹). The catalyst performance was followed by measuring the VGO conversion (370°C+ petroleum
18 cut) and determining the apparent kinetic constants for the main hydrocracking reactions
19 (cracking, hydrodenitrogenation, hydrodesulfurization and aromatics hydrogenation). The
20 experiments were stopped after different times on stream (either 6 or 30 days) in order to assess
21 the evolution of the catalyst as a function of time. The spent catalysts, obtained from three different
22 reactor locations, were characterized by elemental and textural analysis and by thermogravimetry
23 to investigate the quantity and nature of the coke formed. Catalytic tests with different model
24 compounds (toluene, n-heptane) were carried out to determine the residual activity of the
25 hydrogenating and acid catalyst functions. It was found that, at the evaluated conditions, both
26 organic nitrogen and aromatics, nature and content of the feedstock, have a determinant role on

27 the deactivation rate. The organic nitrogen determines the ratio between available metal and acid
28 sites. The aromatics generate coke precursors on the available acid sites. Both factors play a
29 coupled role that promotes coke deposition on the catalyst surface, which leads to an increase in
30 the deactivation rate on top of the end boiling point of the feed.

31 1 INTRODUCTION

32 Catalyst deactivation is a physical and/or chemical process that decreases the activity of a given
33 catalyst [1]. The deactivation is a problem of great concern in the practice of industrial catalytic
34 processes. Costs for catalyst replacement and process shutdown total billions of dollars per year
35 [2]. Deactivation depends on feedstock, operating conditions and catalyst properties [3].
36 Concerning the feedstocks, it is known that in the hydrocracking of vacuum gasoils (VGO), the
37 formation of coke and quasi-irreversible poisoning by heavy nitrogen molecules are the primary
38 reasons for catalyst deactivation [4,5]. The contribution of metals to deactivation becomes evident
39 with deasphalted oil and increases as the feed becomes heavier, such as with atmospheric and
40 vacuum residues [6].

41 Carbonaceous deposits ("coke") on catalysts are gradually formed during the hydrocarbon
42 conversion reactions. Deactivation by coke is due to physical blocking of active sites or because
43 large amounts of coke can lead to pore blocking and prevent reactant molecules from reaching
44 the active sites inside the pores [1]. Coke formation depends on the type of processed feed. For
45 example, aromatic feedstocks form more coke than aliphatic ones under similar processing
46 conditions because polyaromatic structures are more easily formed from aromatics [7]. Coking is
47 more pronounced with condensed ring systems (e.g., naphthalene, anthracene) than with the
48 corresponding linked systems (biphenyl, terphenyl) [8,9]. Heterocycles produce more coke than
49 hydrocarbon analogs [10]. For alkyl-substituted aromatics, coke deposition increases with the
50 length of the side chains rather than with the number of alkyl substitutions [9]. In the case of heavy

51 oils and residues, precipitation of asphaltenes from the feed is another important source of coke
52 formation [11]. Asphaltenes are stabilized by the presence of resins. Therefore, if resins are
53 eliminated at a faster rate during hydroprocessing of asphaltenes, precipitation of the latter occurs
54 on the surface of the catalyst, leading to the possibility of greater coke formation [12]. Several
55 studies [13–17] on catalyst deactivation by coke deposits during the hydroprocessing of AR and
56 VR without considering the metals concluded that the coke formed during the early stages of the
57 operation deposited on the support rather than on active phase. However, while coke reaches
58 pseudo-steady-state equilibrium after an initial rapid buildup [18,19], the deposition of metals
59 continuously increases with time-on-stream [20,21]. To various degrees, the deactivation by coke
60 and metals occurs simultaneously.

61 Two different mechanisms have been proposed for coke formation on the metal and the acid sites
62 for bifunctional catalysts. On metal sites, it is presumed that coke results from successive
63 dehydrogenations leading to atomic carbon or partially hydrogenated intermediates that combine
64 to form graphitic coke [22,23]. On acid sites, it is accepted that coke results from polymerization
65 of dehydrogenated intermediates generated on the metal sites [24].

66 Concerning spent catalysts from VGO hydroprocessing, Sahoo et al. [25] characterized two
67 samples after a dichloromethane extraction. The soluble part was termed as “soft coke,” and its
68 structure was similar to those of the VGO heavy components. The insoluble part, named as “hard
69 coke”, was more aromatic. Coke on catalysts deactivated during the hydroprocessing of
70 atmospheric (ARs) and vacuum residues (VRs) is even “harder”. Amemiya et al. [26] took catalyst
71 samples from a VGO hydroprocessing unit after 12 months on stream. These samples were
72 extracted from different locations in the axial direction of a single fixed bed. The amount and the
73 graphitic nature of the coke increased toward the end of the bed. Koizumi et al. [27] also found an
74 amorphous coke structure at the inlet and a graphitic structure at the catalyst bed outlet.

75 Nitrogen compounds play an important role in the deactivation. The type of N-compounds and the
76 total amount of nitrogen vary from feed to feed [28]. The five and six-membered N-rings, classified
77 as non-basic “neutral” and basic N-compounds, respectively, are predominant structures [29]. The
78 less basic or neutral nitrogen derivatives are readily decomposed into ammonia [30], which acts
79 as an inhibitor of the cracking reaction. The more basic compounds are cataloged as poisons as
80 they are strongly adsorbed on the acid sites of the catalyst [31].

81 N-compounds hinder the adsorption of other reactants and slow down the hydrogen activation
82 process [32]. The availability of active surface hydrogen [33] for the other hydroprocessing
83 reactions and the coke formation is thus limited. Therefore, at least part of the coke is formed due
84 to the catalyst poisoning by N-compounds. Studies on model compounds and real feeds indicate
85 that less than 50 ppm of organic nitrogen in the feed can poison catalytic sites [4,34]. The important
86 contribution of N-compounds to catalyst deactivation during the hydroprocessing of a VGO was
87 also confirmed by Massoth et al. [35]. However, due to the slow desorption of N-compounds from
88 the acid sites [5], it is sometimes difficult to distinguish strong inhibition [36,37] (i.e. the direct
89 impact on conversion via adsorption on the active sites) from deactivation (i.e. the indirect impact
90 via favoring coke formation).

91 In our recent work [38], an accelerated deactivation procedure for hydrocracking catalysts was
92 developed using real feeds (VGO) at conditions close to typical process conditions. The aged
93 catalysts from this protocol showed comparable properties to some industrial spent catalysts.
94 Through this experimental procedure, it was found that the organic nitrogen content of the
95 feedstock is crucial since it determines the ratio between the available metal and acid sites. In
96 turn, this ratio determines the coking reactions that take place and, therefore, the type of coke
97 produced. The nature of nitrogen compounds and of aromatic coke precursors differs depending
98 on the geographical origin of the crude and the VGO type (straight-run VGO, Coker Gas Oil, Cycle
99 Oil, etc.) [39–41]. However, studies evaluating the effect on the deactivation of these compounds

100 with industrial feeds are very rare in the case of VGO. This work, therefore, aims to evaluate the
101 effect of the feedstock properties on deactivation. For this purpose, the catalyst was submitted to
102 the mentioned protocol using two different VGO's. The reactivity evolution of the main
103 hydrocracking reactions and the deactivation phenomena by coke and nitrogen compounds were
104 studied in a coupled way.

105 2 EXPERIMENTAL SECTION

106 2.1 Feedstocks

107 Two different feedstocks were used to evaluate the impact of feedstock properties on catalyst
108 deactivation. Feedstock A consisted of a hydrotreated straight-run vacuum gas oil (VGO-HDT);
109 the feedstock B was a hydrotreated blend of 71% vacuum gasoil, 16% coker gasoil and 13% light
110 cycle oil on a weight basis. The main properties of these feeds are shown in Table 1. Both
111 feedstocks have a quite different boiling range, feed A being heavier than feed B. The distillation
112 yields for each one are presented in Figure 1. Dimethyl disulfide and aniline were added to the
113 hydrotreated feeds to generate the hydrogen sulfide and ammonia partial pressures
114 representative of the mother feed containing sulfur and nitrogen contents of 1,18 wt% and 0,25
115 wt%, respectively.

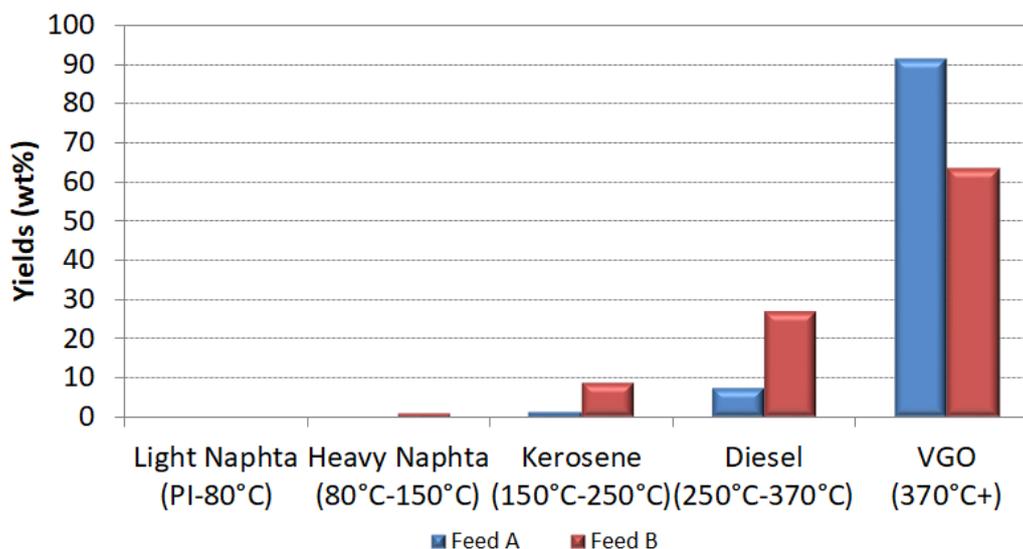
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Table 1. Feedstocks properties.

Properties		Feed A	Feed B
Density @ 15°C	g/cm ³	0.8984	0.8679
Refraction Index @ 70° C		1.4751	1.4791
Sulfur content	wt%	0.068	0.016
Nitrogen content	ppmw	149	120
Aromatics content	wt%	~37	~42
Yield of 370°C+ fraction	wt%	92	64
Initial boiling point (IBP)	°C	180	131

T50 Boiling point	°C	461	397
Final boiling point (FBP)	°C	590	554

117



118

119

120

121

Figure 1. Cut yields for feedstocks A and B.

122

Considering that the main deactivation mechanisms in the deactivation of VGO hydrocracking

123

catalysts are coking deposition and poisoning by nitrogen compounds, more detailed information

124

about the aromatics type and the nitrogen compounds is given in Figure 2 and Figure 3,

125

respectively. The aromatics content was ~37 wt% and ~42 wt% for feed A and feed B, respectively.

126

Monoaromatics were the dominating family within both feeds, followed by diaromatics and

127

triaromatics; the mass fractions of these three families were slightly higher for feed B.

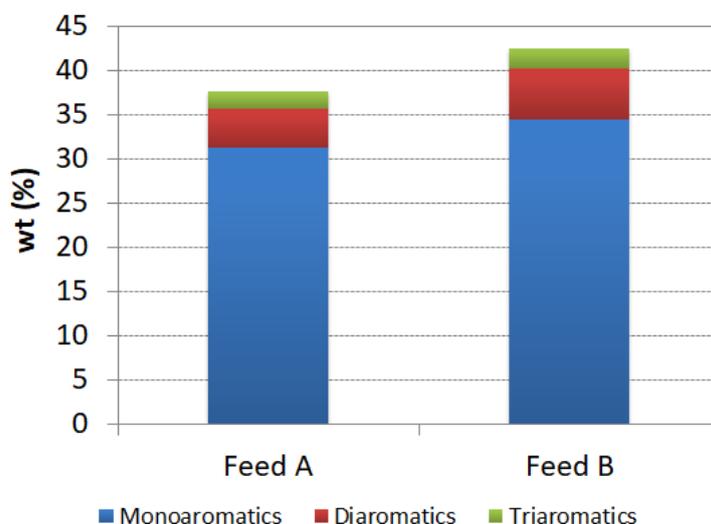
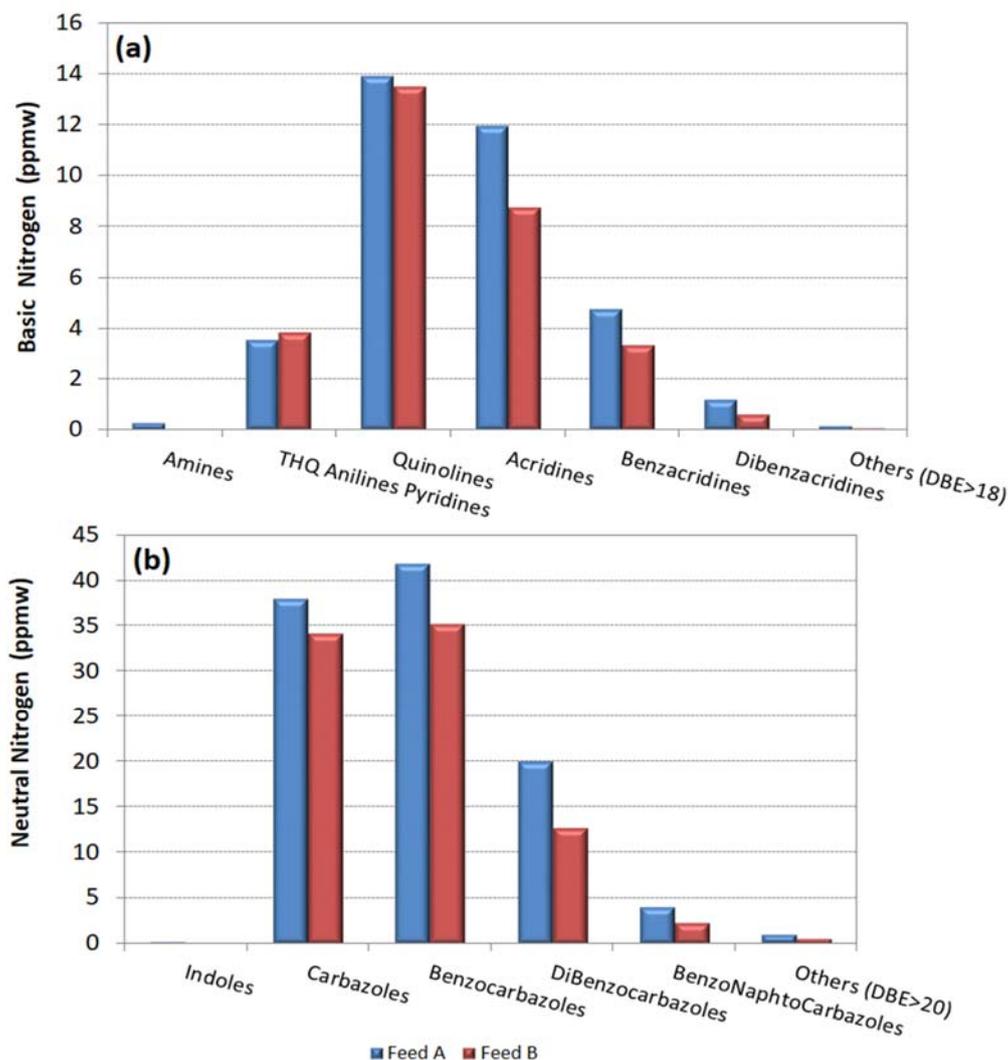


Figure 2. Aromatics type of Feeds A and B by UV spectrometry.

128
 129
 130
 131
 132 These feeds had a different organic nitrogen content: 149 ppmw (Basic Nitrogen - 36 ppmw) for
 133 feed A and 120 ppmw (~30 ppmw of basic nitrogen) for feed B. Such high nitrogen contents are
 134 untypical (usually hydrotreating is pushed to lower nitrogen concentration before entering the
 135 hydrocracking reactor) but were deliberately chosen to accelerate catalyst deactivation. To
 136 determine the distribution of the different nitrogen families, an analysis by FT-ICR/MS was carried
 137 out, as explained in section 2.6.1. The nitrogen families in both feedstocks are shown in Figure 3;
 138 these figures show the distribution of basic and neutral nitrogen families having the same range
 139 of double bond equivalence (DBE). The DBE plots as a function of the number of carbon atoms
 140 are provided in the supporting information (Figure S 1). The results show that feed A contained
 141 more acridine (basic nitrogen), carbazoles, benzocarbazoles and dibenzocarbazole (neutral
 142 nitrogen) than feed B. Carbazole compounds are usually considered as most refractory for the
 143 HDN reactions (they are left over at high HDN conversions) [42].

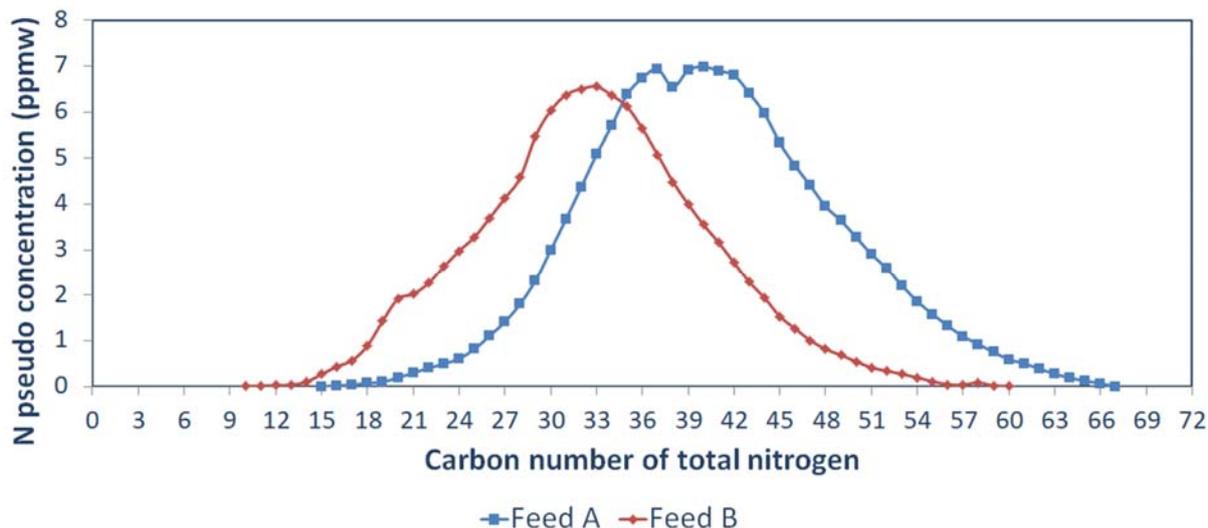


144

145 **Figure 3. Concentration of representative families by DBE in (a) basic and (b) neutral nitrogen,**
 146 **determined by FT-ICR/MS analysis for both feeds [43].**

147

148 Figure 4 presents the experimental carbon number distributions of the N-containing compounds
 149 for the two feeds. These curves are obtained from summing up the ESI (+) and ESI (-) FT-ICR/MS
 150 data. The curve for feed B shifted to a lower carbon number with respect to the curve for feed A.
 151 The carbon number for feed A is in the range of 15 to 67, whereas for feed B, the carbon number
 152 is between C10 and C60. The maximum of the carbon number distribution for feed A is around
 153 40; meanwhile, for feed B is 33. All the above indicates nitrogen molecules of higher molecular
 154 weight for feed A associated with a higher degree of alkyl substitution.



155

156 **Figure 4. Carbon number distribution curves of the total nitrogen content in the feeds by FT-**
 157 **ICR/MS analysis [43].**

158 **2.2 Catalyst**

159 The fresh catalyst consisted of an extrudate trilobe composed of nickel-molybdenum sulfide
 160 particles dispersed on a carrier containing USY zeolite. No additional information on catalyst
 161 properties is given for confidentiality reasons. The catalyst was diluted with silicon carbide particles
 162 of 1 mm diameter, and each reactor was loaded with 12.5 cm³ of catalyst diluted with 37.5 cm³ of
 163 silicon carbide.

164 **2.3 Experimental set-up**

165 The experiments were carried out in a fixed bed pilot unit with a co-current gas-liquid mixture
 166 flowing upwards. The detailed information has been reported elsewhere [38]. The pilot plant
 167 consisted of two isothermal reactors in series, which were used for the hydrocracking process. A
 168 liquid sampling system was placed between the two reactors. At the second reactor outlet, a high-
 169 pressure separator was installed to separate the gas and liquid phases. The gas effluent was
 170 transferred to a gas flowmeter and then analyzed by gas chromatography; the ratio H₂/HC was
 171 controlled at the gas outlet of the pilot plant. The liquid product was sent to a stripper and finally
 172 to a storage recipient. Liquid products were characterized by density, refraction index, nitrogen

173 and sulfur content and simulated distillation to monitor the daily performance of the catalyst. At
174 the end of the run time (6 or 30 days), liquid samples were also analyzed to measure the
175 aromatics, carbon and hydrogen contents.

176 2.4 Experimental procedure

177 The catalyst was activated in situ by sulfidation with an atmospheric gasoil spiked with 2% wt.
178 (%/feed) of dimethyl disulfide (DMDS) and 2% wt. aniline (%/feed) at 350°C and 14MPa. Once
179 sulfidation was completed, the deactivation conditions [38] were applied, i.e., 418°C, LHSV of 3
180 h⁻¹, H₂/HC = 1500NL/L and P = 14 MPa, with the feedstock spiked with aniline as described in
181 section 2.1 (N_{org} = 150 ppmw, and N_{total} = 2500 ppmw). Under the conditions applied, the catalyst
182 immediately enters a deactivation regime, which does not exhibit stabilization. However, in the
183 analysis of the experimental results, the values of the first two days of the test were not taken into
184 account, since at the beginning, the effects of the system stabilization and the catalyst deactivation
185 may be overlapped. The catalyst remained at the same conditions for 6 or 30 days, depending on
186 the test. At the end of the run, the unit was washed with atmospheric gasoil at 350°C.
187 Subsequently, the liquid feed flow was stopped, and the catalyst was stripped and dried with
188 hydrogen before being unloaded. Catalyst samples taken at the end of each experiment were
189 carefully collected to separate the particles from the inlet, middle and outlet of each catalytic bed.
190 More information about specific experimental procedures can be found elsewhere [38].

191 2.5 Data interpretation: kinetic laws, deactivation parameter and H₂ consumption

192 The catalyst performance was tracked by calculating the VGO conversion (370°C⁺ fraction) as
193 well as the HDN, HDA and HDS conversion (Equation 1). For calculating the HDA conversion, the
194 amount of aromatic carbon was estimated through the n-d-M method according to the standard
195 ASTM D3238. To use this method, the molecular weight was estimated by the Lee-Kesler
196 correlation. Yet, interpreting raw conversion data may be misleading, especially when conversion
197 is high, because the differential reaction rate necessarily decreases when the reactant is depleted

198 at increasing conversion. For a rigorous analysis of reaction rates, a kinetic model should be
 199 established, but for the complex VGO reaction network this requires a considerable amount of
 200 input data [44], which was not available in our case. Therefore, for the sake of simplicity, power-
 201 law models have been employed in this work. Several authors [45–47] have used this type of
 202 expression to calculate these constants for similar reaction systems. A first-order [48] kinetics was
 203 assumed for VGO conversion, HDN and HDA [30] (Equation 2). The first-order rate law does not
 204 account for inhibition effects, but allows correcting, albeit approximately, for the impact of depleting
 205 reactant concentration on the reaction rates. For HDS an apparent reaction order of 1.2 (Equation
 206 3) was used; from our experience this reaction order allows accounting for the fact that S-species
 207 converted at low conversions are more reactive than the refractory species left over at high
 208 conversions.

$$\%Conversion = \left(\frac{mass_x \text{ feed} - mass_x \text{ product}}{mass_x \text{ feed}} \right) * 100 \quad \text{Equation 1}$$

Where x is either the 370+ mass fraction, the nitrogen content, the sulfur content, or the aromatic carbon content.

$$k = LHSV * \ln(1 - \%Conversion/100) \quad \text{Equation 2}$$

$$k_i = \frac{LHSV}{n-1} \left(\frac{1}{(C_s^{out})^{n-1}} - \frac{1}{(C_s^{in})^{n-1}} \right) \quad \text{Equation 3}$$

209 Here $n=1.2$, C_s^{in} , and C_s^{out} are the feed and product concentration in percentage of sulfur.

210 Two decay models reported in the literature based on time on stream were assumed to dissociate
 211 the deactivation from the kinetic performance. An exponential decay model [46,49] with three
 212 parameters (Equation 4) and an hyperbolic model [50,51] (Equation 5). The experimental data of
 213 the evolution of the cracking kinetic constant with time was then fitted to each decay expression.

214

$$k_{\text{crack}} = A \cdot \exp(-\alpha \cdot \text{TOS}) + c \quad \text{Equation 4}$$

215 Where: $(A+c)$ corresponds to the kinetic constant of the fresh catalyst at time=0, c , corresponds
 216 to the residual activity of the spent catalyst and α corresponds to the deactivation rate (1/time).

$$k_{\text{crack}} = A \cdot [1 + (\alpha * (m - 1) * \text{TOS})]^{-\left(\frac{1}{m-1}\right)} + d \quad \text{Equation 5}$$

217 Where: $(A+d)$ corresponds to the kinetic constant of the fresh catalyst at time=0, α corresponds to
 218 the deactivation rate (1/t), m corresponds to the deactivation order and d , corresponds to the
 219 residual activity of the spent catalyst.

220 The hydrogen consumption was calculated from the experimental data by performing a global
 221 hydrogen balance [52] (Equation 6). It was based on the elemental analysis of liquid streams and
 222 gas chromatography. Hydrogen in gas compounds such as H₂S and light hydrocarbons (C₁ to C₆)
 223 was calculated from molar equivalents, assuming that all the light products are paraffins and all is
 224 present only in the gas product.

$$H_{\text{cons}} = H_{\text{Liq}}^{\text{out}} - H_{\text{Liq}}^{\text{in}} + H_{\text{Light HC}}^{\text{out}} + H_{\text{H}_2\text{S}}^{\text{out}} \quad \text{Equation 6}$$

225 Where H_{cons} is the hydrogen consumption, $H_{\text{Liq}}^{\text{out}}$ is the total amount of hydrogen contained in the
 226 hydrotreated liquid product, $H_{\text{Liq}}^{\text{in}}$ are the total amount of hydrogen contained in the hydrotreated
 227 liquid feed and the additives (dimethyl disulfide, aniline), $H_{\text{Light HC}}^{\text{out}}$ is the amount of the hydrogen
 228 contained in light hydrocarbons and $H_{\text{H}_2\text{S}}^{\text{out}}$ is the amount of hydrogen contained as H₂S in the gas
 229 phase.

230 2.6 Samples Characterization

231 2.6.1 Liquid Samples Characterization

232 Feed and daily liquid products were characterized by a densimeter for determining the density, by
 233 chemiluminescence for the nitrogen content, by X-Ray fluorescence spectrometry for the sulfur

234 content and gas chromatography for the simulated distillation. At the end of the test, the product
 235 samples were also analyzed by combustion and thermal conductivity detection to measure the
 236 carbon and hydrogen contents and by UV spectrometry to identify the different aromatic families.

237 In the case of the nitrogen compounds families, feed samples were analyzed by Fourier transform
 238 ion cyclotron resonance mass spectrometry (FT-ICR/MS). The analyses were carried out using
 239 an LTQ FT Ultra Mass Spectrometer FT-ICR/MS (ThermoFisher Scientific, Bremen Germany)
 240 equipped with a 7T magnet (Oxford Instruments), electrospray ionization (ESI) ion source in both
 241 polarities (ThermoFisher Scientific, Bremen Germany). With this ionization source, the technique
 242 can identify polar heteroelement compounds [53–55]. The ESI+ ionization mode is selective to
 243 basic nitrogen compounds, the ESI- mode to neutral nitrogen compounds. Mass range was set
 244 to m/z 98-1000. Seventy scans with 4 μ -scans were recorded with an initial resolution set to 200
 245 000. The sample preparation conditions are shown in Table 2.

246

Table 2. Samples preparation conditions for FTC-IR-MS analysis.

		ESI (+)	ESI (-)
Dilution level	(%v/v)	1 Toluene	1 Toluene
Mix of solvents	(%v/v)	75/25 (Toluene/Methanol)	75/25 (Toluene/Methanol)
Additive added	(%v/v)	1 (Acetic Acid)	1 (Ammonium Hydroxide)

247

248 2.6.2 Catalyst Characterization

249 After catalyst unloading, the spent samples were submitted to an extraction with toluene in a
 250 soxhlet extractor at 250°C for 7 h and dried under vacuum at 120°C for 12 h before being submitted
 251 to the following analyses. The catalyst surface area, total pore volume, and pore size distribution
 252 were measured by nitrogen adsorption-desorption in an ASAP 420 Micromeritics apparatus. The

253 surface area was calculated from the BET equation, the total pore volume was deduced from the
254 N₂ adsorption at the endpoint of the isotherm and the micropore volume was determined from the
255 t-plot method the Harkins-Jura formula, in the range from 0.35 to 0.50. The uncertainty of surface
256 area and volume measurements is 5% and 2.5%, respectively. The pore size distribution was
257 calculated from the desorption branch of the N₂ isotherm using the BJH model.

258 The carbon, hydrogen and nitrogen content determination was carried out on a Thermoscientific
259 FlashSmart equipment. Additionally, the catalyst was analyzed by elemental thermogravimetry on
260 a thermobalance Mettler ToledoTGA-DSC1 coupled with mass spectroscopy
261 (Thermostar/Pfeiffer). The MoS₂ sheets were visualized and analyzed by transmission electron
262 microscopy with a JEOL JEM 2100F microscope to determine the slab length and the promoter
263 segregation. The samples were prepared in three steps. In the first step, the catalyst was milled
264 to a fine powder. Then it was dispersed in ethanol in an ultrasonic bath; two drops of the solution
265 were deposited on a copper grid. Finally, the solvent was evaporated, and the sample was
266 introduced into the microscope. The TEM images were recorded in bright field mode. The average
267 dispersion of the MoS₂ particles was calculated from the slab length distribution, assuming a
268 hexagonal shape of the particles [56]. The promoter segregation was investigated by TEM-EDX
269 detection, leading to Ni/Mo ratio calculated for about 25 particles.

270 2.6.3 Catalytic tests with model molecules

271 The residual activity of the spent catalysts was assessed for both the hydrogenating and
272 isomerizing/cracking activities. To evaluate the hydrogenating function, the activity was
273 determined by quantifying the hydrogenated products during toluene hydrogenation. The
274 methodology used is described elsewhere [57]. An equivalent protocol was followed regarding the
275 acid function but using the hydroconversion of n-heptane as a model reaction. The catalytic tests
276 were carried out in a fixed bed reactor unit, in the presence of H₂S (generated by decomposition

277 of DMDS) under hydrogen pressure. Catalysts samples were sulfurized in situ at 350°C during 2
278 hours. The operating conditions for each experiment are presented in Table 3.

279

Table 3. Operating conditions of the catalytic tests with model molecules.

		Toluene Hydrogenation	n-Heptane
			Hydroconversion
Concentration of reactant	wt %/feed	20*	95.15
DMDS concentration	wt %/feed	6	4.85
P	MPa	6	6
LHSV	h ⁻¹	2	4
T	°C	350	350/360/380
H ₂ /HC	NL/L	450	330

280 * in cyclohexane as solvent

281

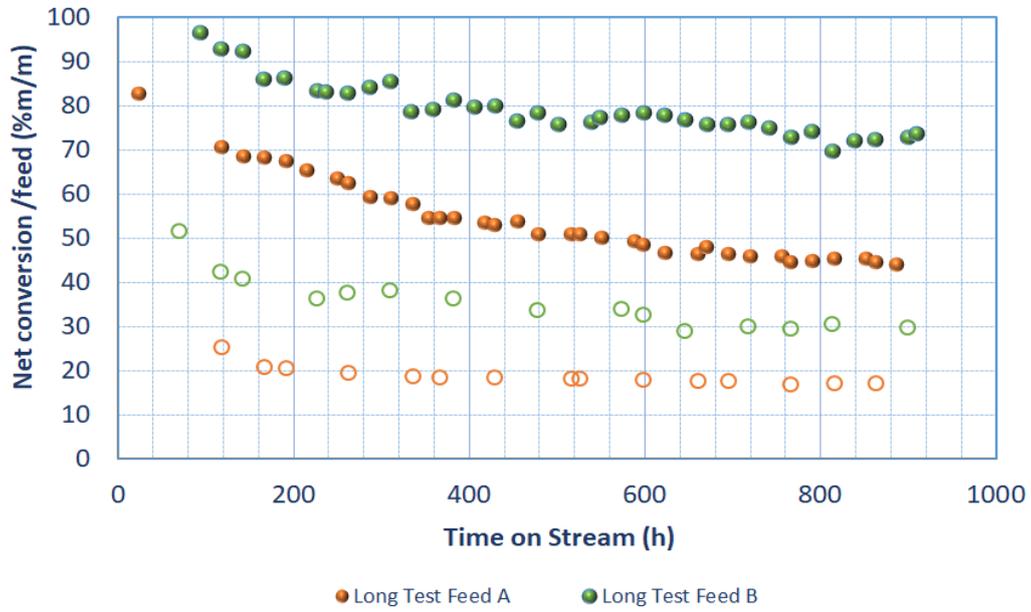
282 3 RESULTS

283 3.1 Apparent kinetic constants

284 The evolution of the global net conversion during the long-term tests for both feeds is represented
285 in Figure 5. The performance for the short-term tests was very close to the corresponding period
286 of the long test, so the related data are not shown. As expected, the curves exhibited a lower
287 conversion for feed A, which was heavier and had a higher organic nitrogen content than feed B.
288 The loss of conversion under the accelerated deactivation protocol conditions was more
289 appreciable for feed A than for feed B.

290 One can further observe that the contribution of the first reactor to overall conversion (20% for
291 feed A and 40% for feed B) was lower than that of the second reactor. The distillation curves of
292 the final effluents of the long-term experiment at the first and second reactor outlets are shown in
293 Figure 6. No significant shift with respect to the related feed was observed for the effluents from
294 the first reactor. This behavior was not observed in the case of the effluents from the second
295 reactor. It suggests that cracking reactions in the first reactor were limited; the conversion in the

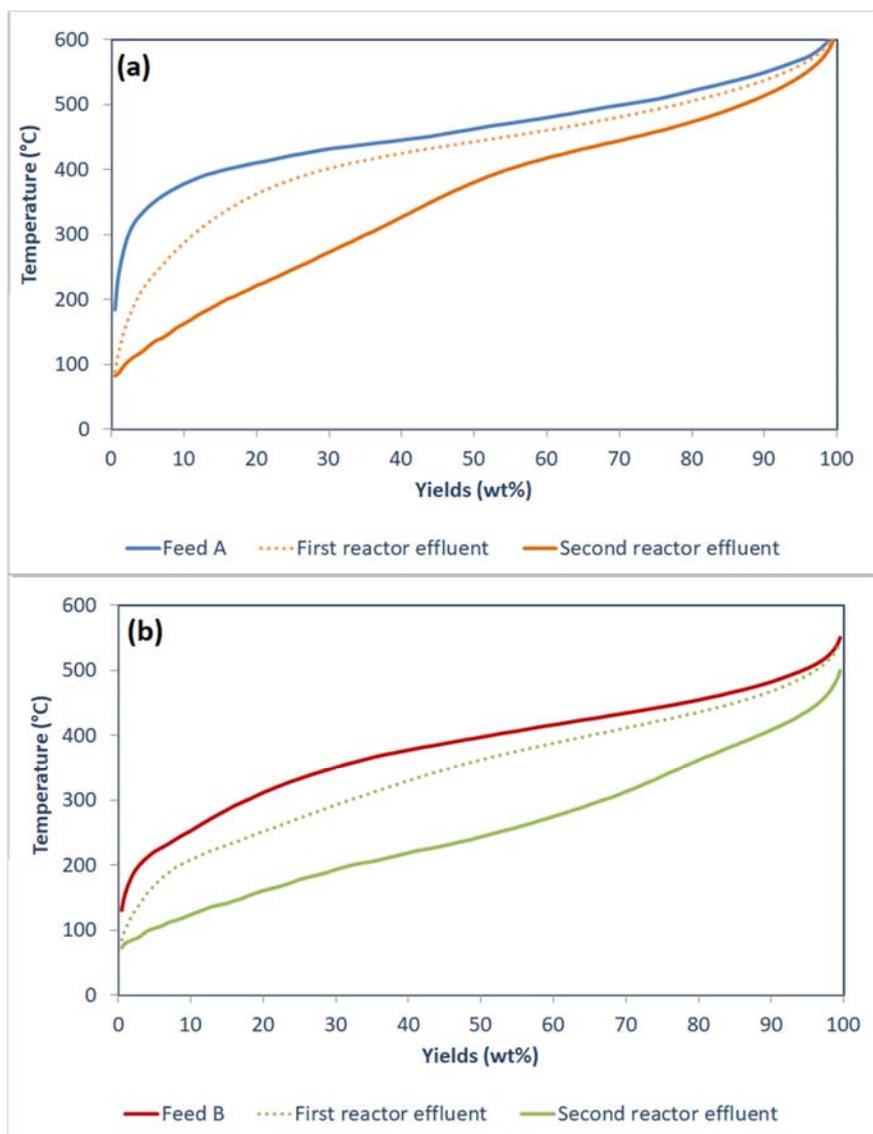
296 first reactor was mainly due to dealkylation and hydrogenation reactions carried out on the metal
297 function.



298

299 **Figure 5. Net conversion evolution with time on stream during long tests with feed A and feed B**
300 **Full symbols=Total effluent, open symbols=First reactor effluent.**

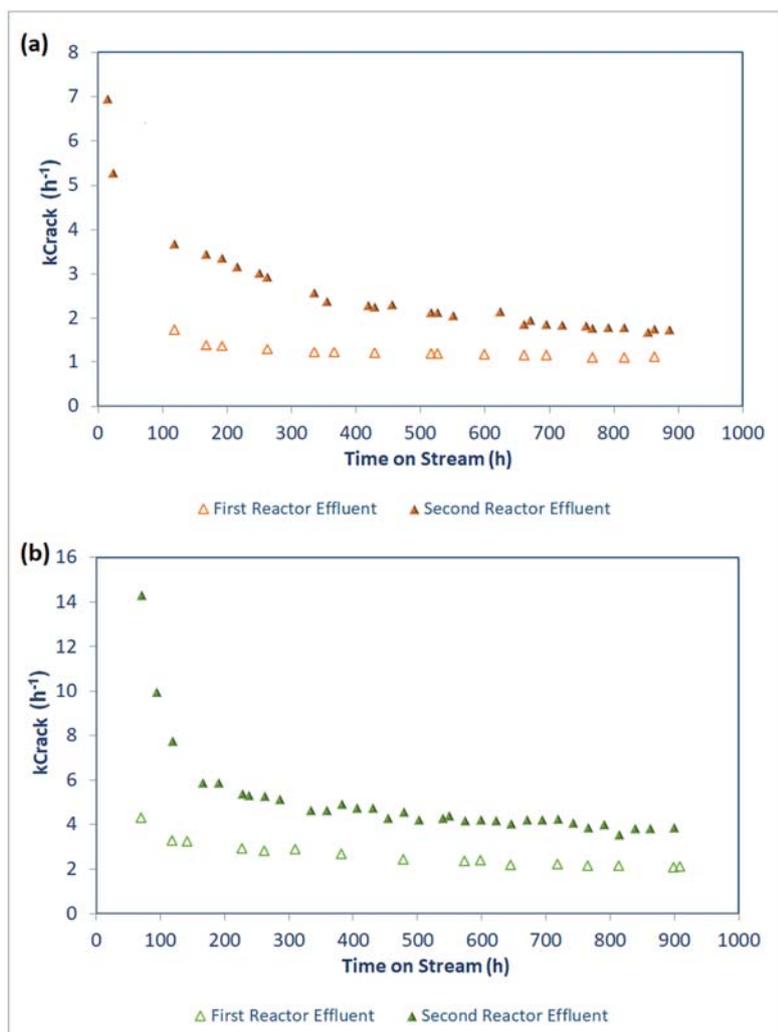
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302



303 **Figure 6. Simulated distillation curves obtained for the feed, first reactor outlet, second reactor**
 304 **outlet with a) feed A, b) feed B for the long-term tests. Dotted line=First reactor effluent,**
 305 **continuous line=Total effluent.**
 306
 307

308 The evolution of the apparent kinetic constants of the relevant chemical reactions (cracking, HDN,
 309 HDA and HDS) with time on stream (TOS) is shown in the figures below. Both the global
 310 performance of the two reactors and the one for the first reactor are presented for the two different
 311 feeds during the long-term test.

312 Regarding the global performance, the data for the cracking constants (Figure 7) showed that, as
 313 was foreseeable, feed B was more reactive than feed A. The rate coefficients of the HDN reactions
 314 (Figure 8) were also higher for feed B. This can be attributed to the lower amount of carbazole,
 315 benzocarbazole and acridine in this feed (Figure 3), identified among the most refractory
 316 compounds in the neutral and the basic nitrogen families [55,58,59]. The higher degree of alkyl
 317 substitution (Figure 4) of the nitrogen heterocycles in feed A further reduces their reactivity [43].



318

319 **Figure 7. Global and first reactor kinetic constants evolution with time on stream for cracking**
 320 **reactions. a) Feed A and b) feed B. Open symbols=First reactor effluent, Full symbols=Total**
 321 **effluent.**

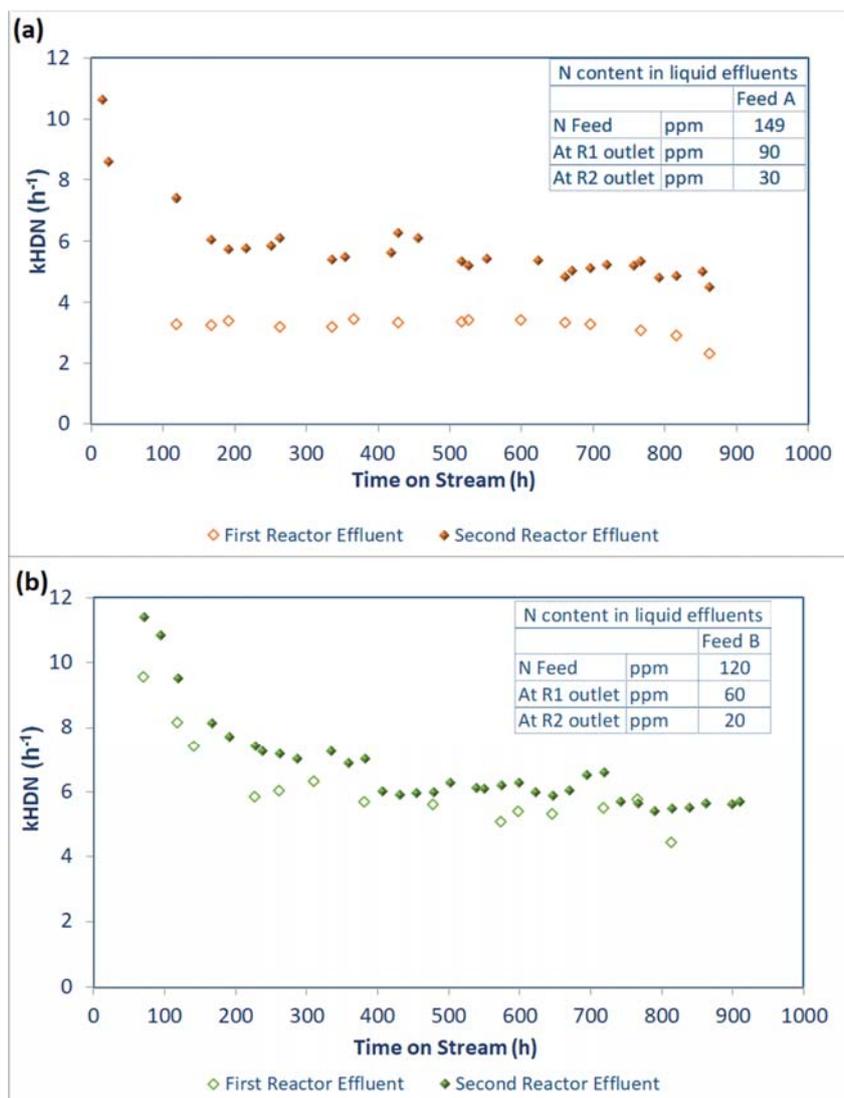
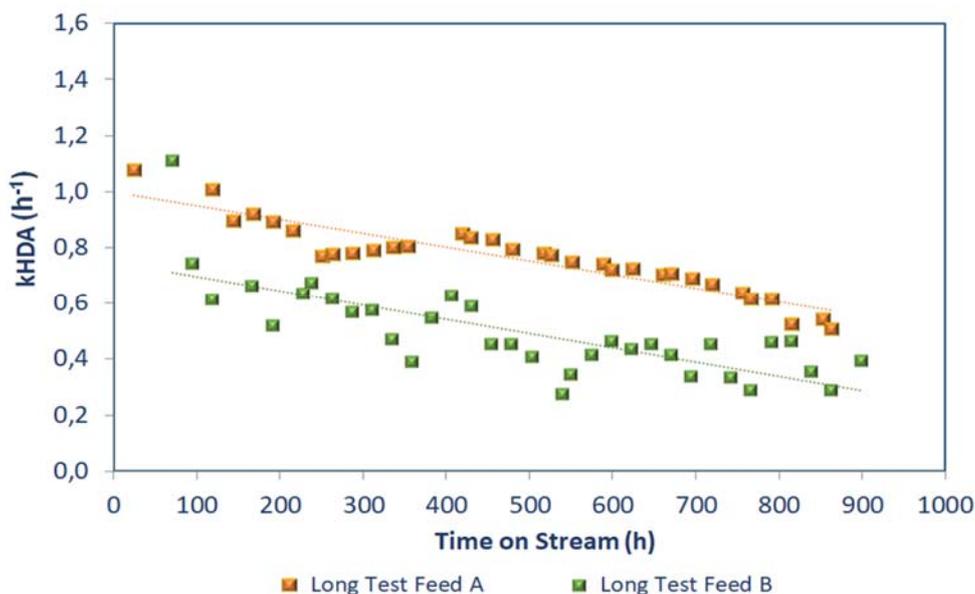


Figure 8. Global and first reactor kinetic constants evolution with time on stream for HDN reactions. a) Feed A and b) feed B. Open symbols=First reactor effluent, Full symbols=Total effluent.

322
 323
 324
 325
 326
 327
 328 Concerning the HDS kinetic coefficients, those remained nearly constant during the tests and had
 329 very similar values for both feeds (not shown). The HDA reaction rate was lower for feed B (Figure
 330 9). It is related to the origin of feed B, which is composed of streams from processes that promote
 331 the cracking reactions (LCO from fluid catalytic cracking and HCGO from delayed coking),
 332 reducing the alkyl chains, therefore, produce more condensed aromatic structures which have a
 333 refractory character to the hydrogenation.



334

335 **Figure 9. Global and first reactor kinetic constants evolution with time on stream for HDA**
 336 **reactions.**

337

338 3.2 Quantification of the deactivation rate

339 In the first reactor, all the kinetic constants were lower than in the second reactor. The nitrogen
 340 content for both feeds was so high that it provoked a strong inhibition of the hydrotreating reactions
 341 and an almost total inhibition of cracking reactions [4]. The cracking reaction rate was nearly stable
 342 for the first reactor. The inhibition of the acid function was so strong that no additional deactivation
 343 was observed.

344 With time on stream, the catalysts lost activity, the kinetic rates for cracking, HDN and HDA
 345 reactions decreased for both feeds. The loss in activity was more significant for cracking and HDN
 346 than for HDA reactions. The decrease in the kinetic rates was significantly faster at the beginning
 347 than at the end of the test. The loss in cracking activity was also reflected in a decrease of H₂
 348 consumption (see supporting information S6).

349 As it was stated, the experimental data for the cracking kinetic constant was fitted with both an
 350 exponential and a hyperbolic decay function (Supporting information, **Erreur ! Source du renvoi**

351 **introuvable., Erreur ! Source du renvoi introuvable.**) Table 4 displays the model parameter
352 values for the activity loss rate, α , for both feeds during the long-term tests. This coefficient
353 accounts for both inhibition and deactivation during the test run.

354 **Table 4. Deactivation coefficients calculated with both an exponential (exp) and a hyperbolic (hyp)**
355 **decay models.**

Case	Time on stream	α_{exp}	α_{hyp}
	days	(1/day)	(1/day)
Feed A	30	0.15	0.18
Feed B	30	0.39	0.57

356
357 Feed A was heavier than feed B and had a low reactivity for cracking and HDN reactions; it showed
358 a lower deactivation coefficient than in the case of feed B.

359 We recall that the inspection of the raw conversion data had suggested the opposite trend: the
360 conversion loss as a function of time was higher for feed A (Figure 5). However, as explained in
361 section 2, it may be misleading to look at raw conversion data. For comprehension purposes, the
362 analysis of the evolution of the apparent rate coefficients is more appropriate.

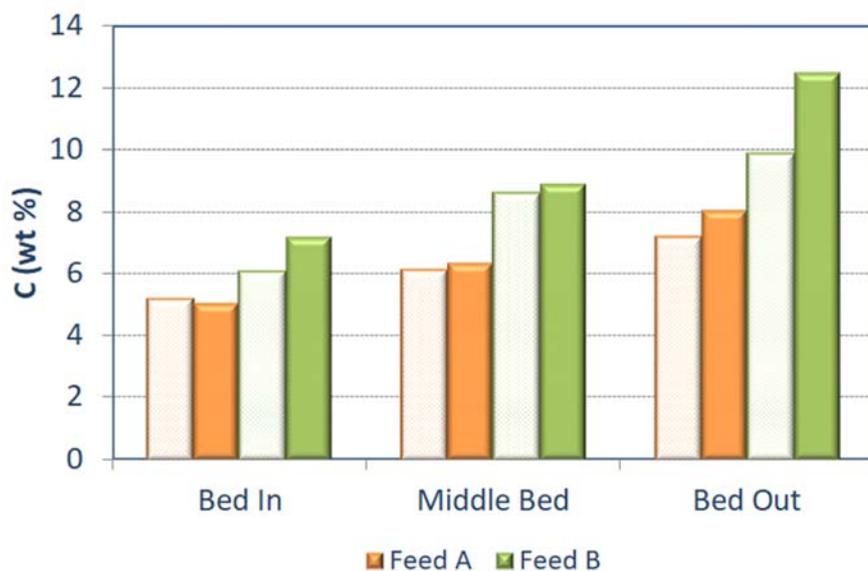
363 3.3 Spent catalysts characterization

364 Samples from the first reactor inlet (Bed In), second reactor inlet (Middle bed) and second reactor
365 outlet (Bed Out) of the catalytic bed were characterized. The samples obtained from the short-
366 term tests (6 days) and long-term tests (30 days) for both feeds were compared.

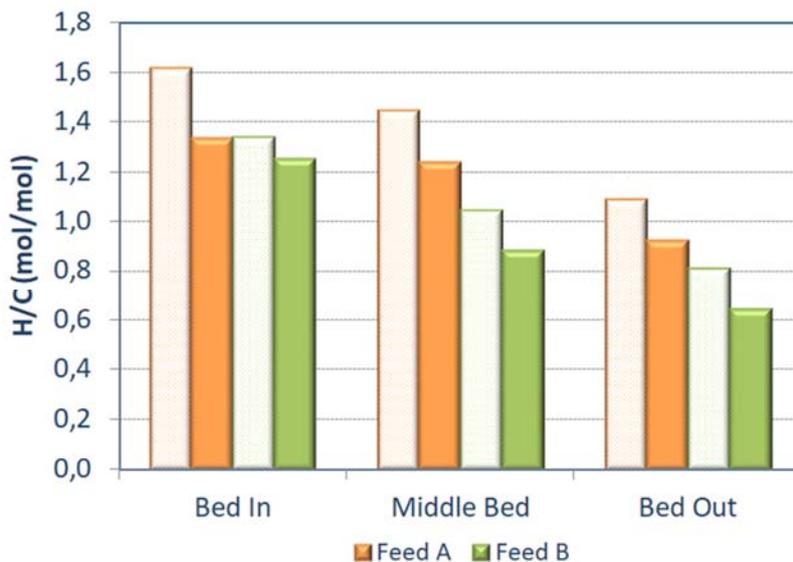
367 Results from the elemental analysis are shown in Figure 10 and Figure 11. The catalysts from
368 the tests with feed B had a higher carbon content (Figure 10) with a slightly lower H/C ratio (Figure
369 11) than the catalysts obtained from the tests with feed A. The carbon content along the reactor
370 increased from the inlet to the outlet for all the samples. Furthermore, the aromatic character
371 (inverse of H/C ratio) of coke deposits also increased in the same sense, in line with the work of
372 Koizumi et al. [27]. This tendency was confirmed by TGA. The coke gradient from bed inlet to bed

373 outlet can be explained by the inhibition of the coke formation by organic nitrogen, which
374 progressively decreases from bed inlet to bed outlet.

375 With respect to time evolution, most of the coke was formed at the start of run for both feeds
376 (Figure 10). The H/C ratio (Figure 11) diminished with time because of the dehydrogenation of the
377 carbon deposits initially formed.



378
379
380 **Figure 10. Carbon content of the spent catalysts. Full bars=30 days tests, open bars=6 days tests.**
381



382

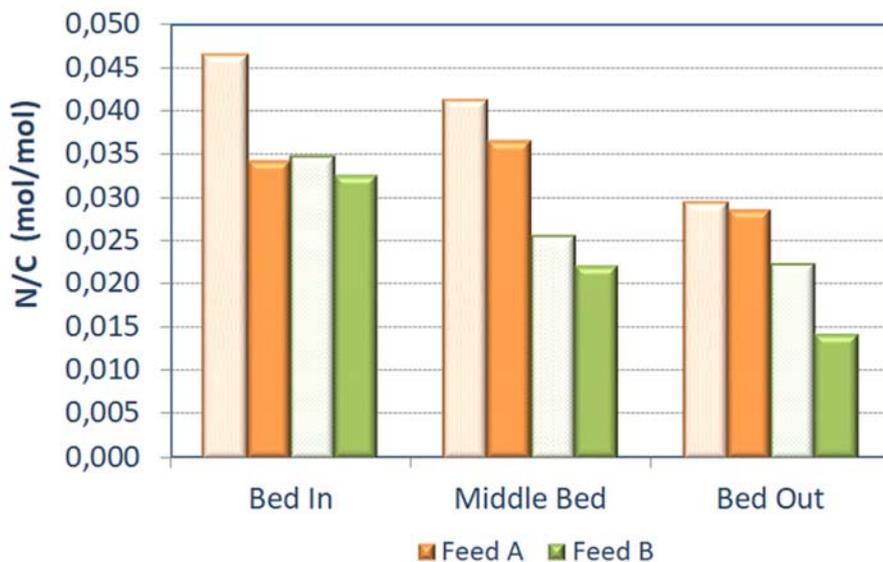
22

383 **Figure 11. Hydrogen/Carbon (H/C) ratio of the spent catalysts. Full bars=30 days tests, open bars=**
384 **6 days tests.**

385
386
387 The N/C ratios of the spent catalyst samples are displayed in Figure 12. The values were similar
388 to the ratio of typical organic nitrogen compounds in vacuum gas oils (molecules containing 20 to
389 40 carbon atoms and one nitrogen atom). The nitrogen proportion in the deposited coke was
390 higher for feed A than for feed B samples. It correlates with the higher nitrogen concentration in
391 feed A. Spent catalyst from the tests with feed B had more deposited coke with a lower N/C ratio
392 than samples from feed A. It means that the contribution of aromatics coke precursors was more
393 significant for feed B, which was related to the higher aromatics content in this feed.

394
395 The values of the N/C ratio decreased along the reactor, which agrees with the profile of nitrogen
396 concentration, which shows a maximum at bed inlet. The nitrogen compounds are strongly
397 adsorbed in the acid sites and formed coke because its desorption rate is slow compared to the
398 coke reactions rate. With time on stream, the N/C ratio (Figure 12) decreased.

399



400

401 **Figure 12. N/C ratio of the spent catalysts. Full bars=30 days tests, open bars= 6 days tests.**

402

403
 404 The coke deposit influenced the catalyst textural properties since it reduced the available pore
 405 volume and the surface area. Table 5 shows the losses in surface area (S) and pore volume (V)
 406 for the spent samples compared to the fresh catalyst. The samples from the tests with feed B, with
 407 the higher carbon contents, also exhibited the highest losses of surface area and pore volume. In
 408 the same sense, for both feeds, the loss in textural properties was more pronounced for the
 409 samples obtained from the second reactor, where the carbon deposition was also enhanced.
 410 Surface area and pore volume slightly decreased with time on stream (except for the first reactor
 411 with feed A because the coke deposition was controlled by the nitrogen inhibition). The losses of
 412 surface and pore volume were proportional to the amount of deposited coke (see supporting
 413 information **Erreur ! Source du renvoi introuvable.** and **Erreur ! Source du renvoi**
 414 **introuvable.**).

415 **Table 5. Characterization of spent catalysts: Surface area (S), total pore volume (V) and micropore**
 416 **volume (μV) of the spent catalyst relative to the fresh catalyst.**

Sample	Time on stream days	S/S _{fresh}		V/V _{fresh}		$\mu V/\mu V_{fresh}$	
		Bed Inlet (%)	Bed Outlet (%)	Bed Inlet (%)	Bed Outlet (%)	Bed Inlet (%)	Bed Outlet (%)
Feed A	6	86	82	80	75	71	71
Feed A	27	86	78	81	71	71	65
Feed B	6	85	75	81	70	67	65
Feed B	27	82	71	78	69	61	65

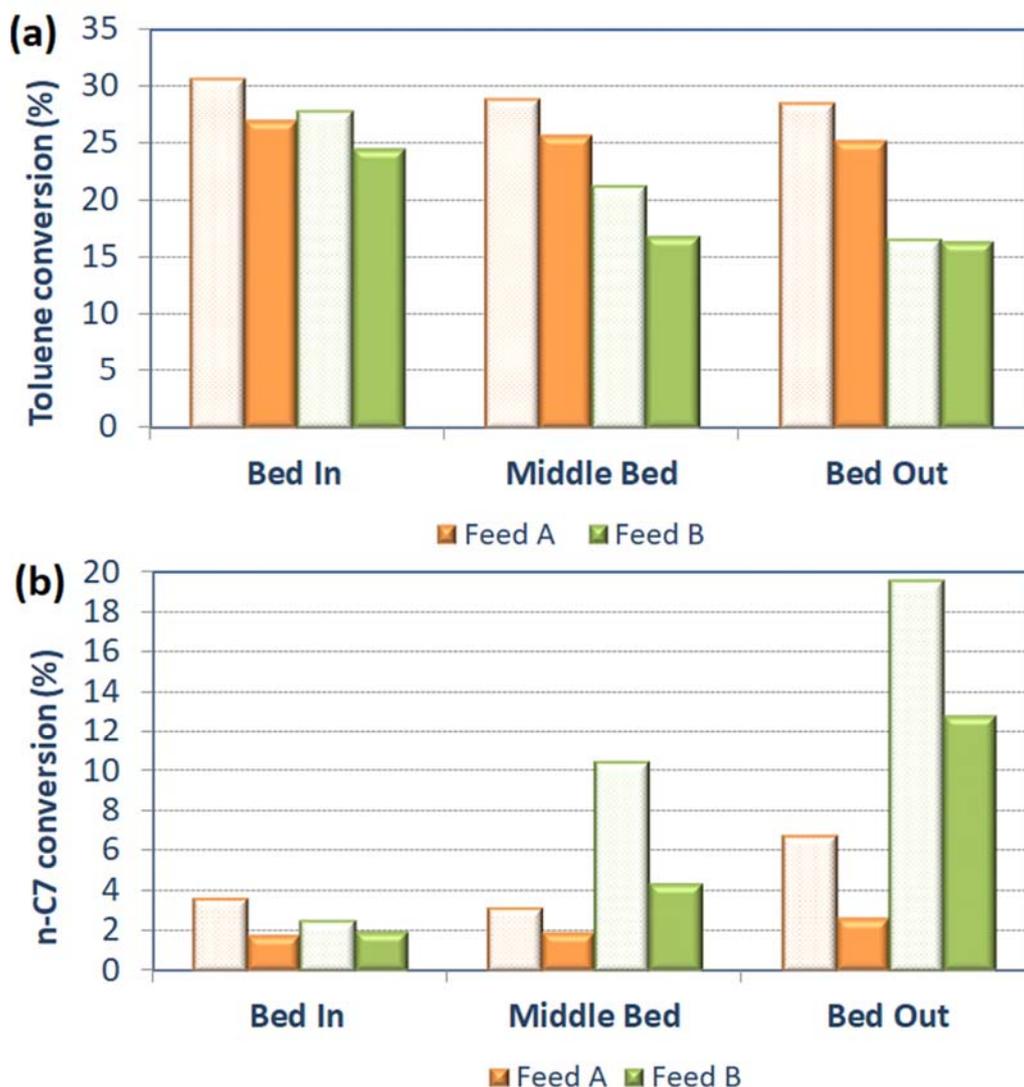
417
 418
 419 TEM/EDX analysis was performed on the spent catalysts to evaluate the morphology of the MoS₂
 420 slabs and their Ni/Mo ratio (see supporting information Table S2). As expected, slab length,
 421 average dispersion and Ni/Mo ratio in the slabs did not significantly depend on the type of feed
 422 used. There were also no remarkable evolutions as a function of time on stream or as a function
 423 of the location in the reactor. However, a slight sintering of the MoS₂ slabs and a significant nickel

424 depromotion have been observed in our previous study [38]; these results mean that sintering and
425 depromotion took place in the initial stages and then the slab morphology reached a steady state.

426
427 Catalytic assays evaluated the residual catalytic activity of the spent samples with model
428 molecules, toluene hydrogenation for the (de)hydrogenating function and heptane
429 hydroconversion for the acid function. The fresh catalyst presented a toluene conversion of 70%
430 and a n-heptane conversion of 95%. The obtained results are illustrated in Figure 13. It is clear
431 that there was an activity loss of both functions, compared to fresh catalyst, even more
432 pronounced for the acid function. The solids from the tests with Feed A exhibited a higher residual
433 hydrogenation activity but a lower cracking/isomerization activity than the solids from the tests with
434 feed B.

435 The deactivation of the metal function increased along the catalytic bed; this behavior was more
436 pronounced with feed B samples. However, this loss of activity did not strongly depend on time
437 on stream. Since the depromotion for all the samples under the deactivation conditions was
438 similar, the observed differences between the solids from the tests with both feeds can be related
439 to the carbon deposition on the catalysts (Figure 15a). For the acid function, the performance was
440 the opposite. The number of available acid sites in the second reactor was higher than in the first
441 one, despite a higher carbon content. This tendency was more marked with feed B. This will be
442 discussed in section 4.

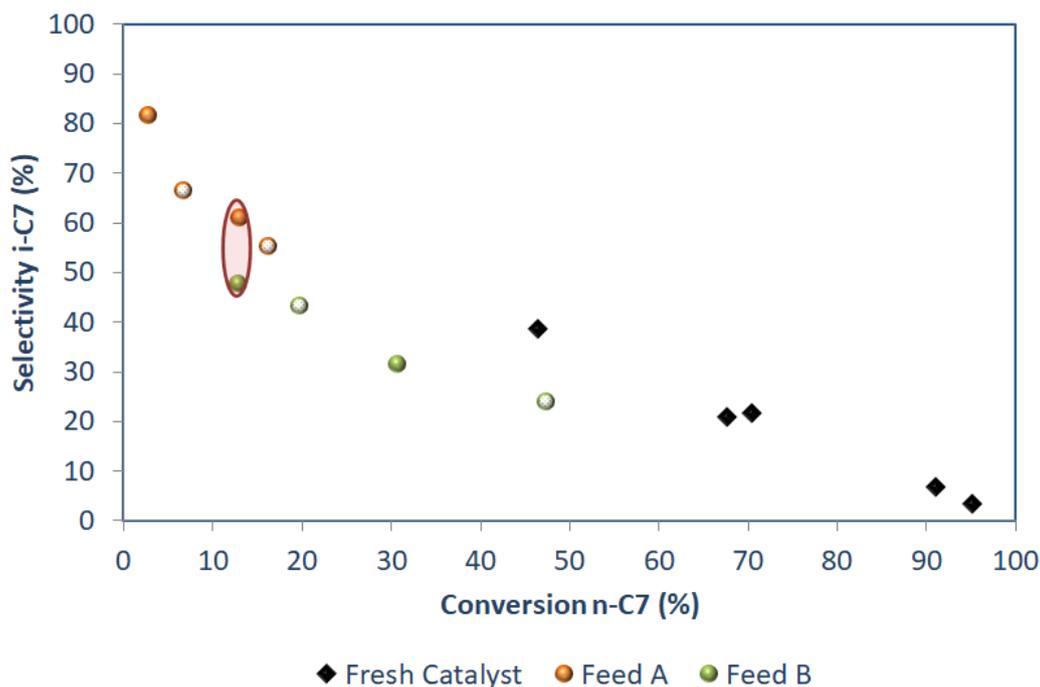
443



444
 445 **Figure 13. Residual catalytic activity evaluated by model molecules catalytic tests a)**
 446 **Hydrogenation of toluene, b) Isomerization/cracking of n-heptane at 360°C. Full bars=30 days**
 447 **tests, open bars= 6 days tests.**
 448

449
 450 The selectivity towards i-heptane formation (the primary product) in the n-heptane
 451 hydroconversion can be considered as an indicator of the metal/acid balance (as compared at the
 452 same conversion level) [60,61]. The higher the selectivity, the higher the hydrogenation activity
 453 of the metal sites compared to the activity of the acid sites. In contrast, a low i-heptane selectivity
 454 means that the acid sites are not well balanced by the hydrogenation sites. Figure 14 represents
 455 the selectivity performance for the samples obtained during the processing of both feeds. Spent

456 samples from tests with feed A showed higher i-heptane selectivity than the ones from feed B. It
457 is in line with the fact that those samples presented the highest hydrogenation activity and the
458 lowest cracking activity. It reinforces the balance of metal/acid sites and, in this way, the selectivity
459 to i-heptane.



460
461 **Figure 14. Test n-heptane Selectivity to i-C7 Vs. conversion n-C7 at 350, 360 and 380°C. Open**
462 **symbols= 6 days tests, full symbols=30 days tests. Bed outlet samples.**
463

464 4 DISCUSSION

465 4.1 Evolution with time

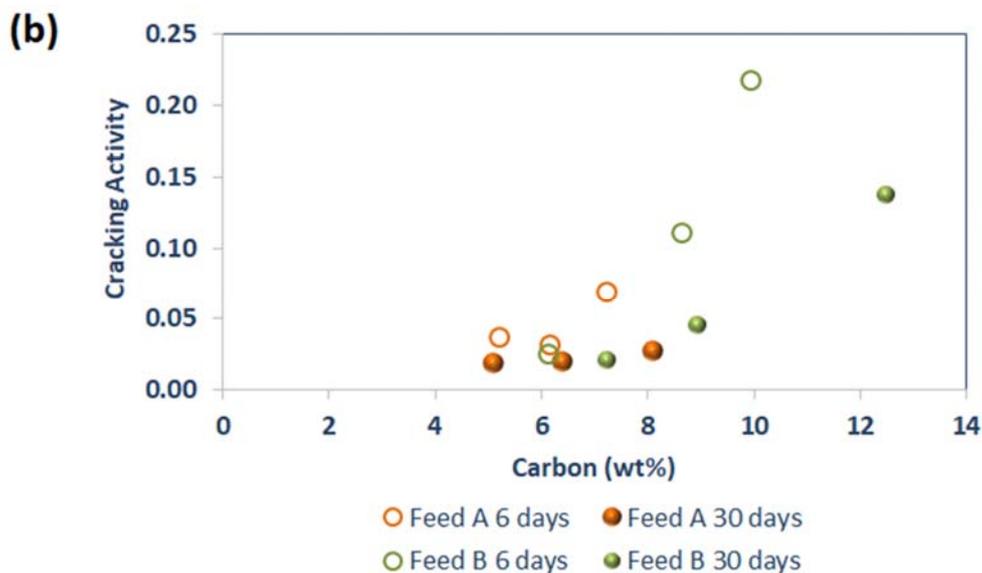
466 During time on stream, the catalysts presented a loss in activity; the kinetic rates for cracking
467 (Figure 7), HDN (Figure 8) and HDA (Figure 9) reactions decreased for both feeds. The
468 deactivation of cracking and HDN activity was very pronounced in the first 150 h, followed by
469 slower, more gradual decay. These results agree with different works [33,62,63] that reported a
470 faster activity decay at the beginning of the run.

471 Regarding the carbon content evolution with time, the data (Figure 10) indicated that the major
472 part of the coke was formed at the beginning of the tests for both feeds. During the first 6 days on-
473 stream after performance stabilization, between 90 and 95% of total final coke was deposited for
474 feed A and between 80 and 85% for feed B. It is consistent with the literature [62,64,65] that
475 claims that coke deposition initially increases rapidly before a pseudo-stable state is reached. For
476 reforming catalysts, Querini [66] et Absi-Halabi [64] found that coke equivalent to 25% of the
477 weight of the original catalyst is deposited within the first few hours of operation. The increase of
478 the coke deposition with time was smaller for feed A than for feed B due to the higher inhibition of
479 the coke reactions by nitrogen compounds. The H/C ratio (Figure 11) also decreased with time
480 because as condensation and polymerization reactions to form coke progress, dehydrogenation
481 occurs [26,27,33,67]. This evolution of the coke deposition correlates with the observed
482 performance for the deactivation rate. As was expected, textural properties followed the same
483 behavior as coke deposition. Thus, there was no meaningful change in the first reactor for feed A
484 with time on stream because the coke deposition was controlled by the nitrogen inhibition, which
485 was more important than in the second reactor.

486 The amount of N which was deposited on the catalyst also did not evolve much any longer after
487 150 h on stream. On the other hand, the N/C ratio (Figure 12) continued to decrease with time, in
488 agreement with previous works [68], which state that as the catalysts ages, N/C ratios decrease.
489 This may be related to the preferential adsorption of the nitrogen compounds on the acid sites
490 [35,64]. These adsorbed compounds in the early stages form coke precursors with moderate
491 aromaticity (relatively high H/C ratio). Subsequent accumulation of coke results from the
492 condensation/polymerization reactions of the unsaturated intermediates formed preferentially from
493 aromatic structures, which provokes a reduction in the N/C and H/C ratio.

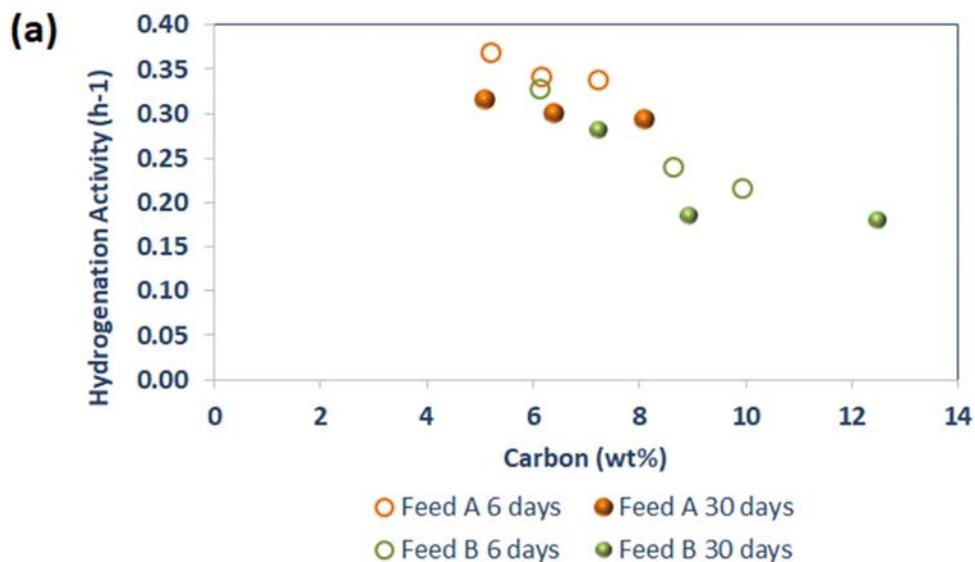
494 The model molecule tests (Figure 13) allow evaluating the effect of coke formation on the
495 hydrogenation and cracking functions. The hydrogenation activity of the spent catalysts is rather

496 well correlated with the amount of deposited coke (Figure 15a). The residual hydrocracking
497 activity, however, is totally anticorrelated with the amount of coke (Figure 15



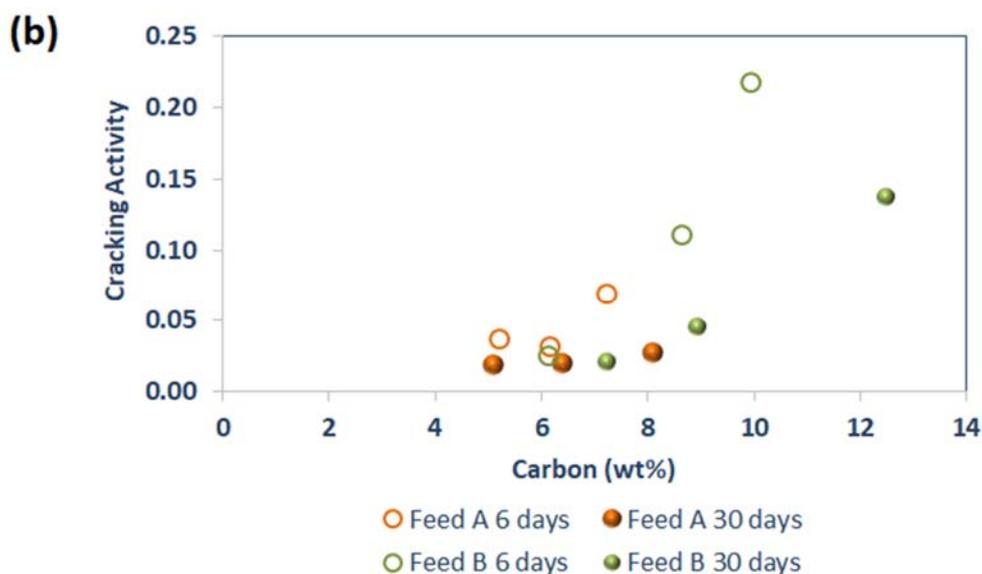
498
499 b). It drops drastically in the initial stage and continues to decay gradually (even when the total
500 coke content remains almost constant). The bed outlet always maintains a higher residual cracking
501 activity than the bed inlet, despite the lower carbon content of the latter. The concentration of
502 organic nitrogen compounds in the reactor follows the opposite trend: it decreases from reactor
503 inlet to reactor outlet and increases with time due to the deactivation of HDN. We therefore
504 suppose that the acid sites undergo a very specific deactivation due to nitrogen compounds, which
505 is uncorrelated from the global coke build-up.

506



507

508



509

510 **Figure 15. Relation between the a) hydrogenation activity and b) n-C7 cracking activity of the**
 511 **catalyst and the amount of coke.**

512 4.2 Impact of the feed

513 The effect of the type of feedstock on catalyst deactivation was studied with a hydrotreated VGO,
 514 Feed A, and a lighter mixture, Feed B. These feeds had a different organic nitrogen content: 149
 515 ppmw for feed A and 120 ppmw for feed B. The nitrogen families in both feedstocks were similar.

516 However, the distribution of the compounds was different; essentially, feed A contained slightly
517 more acridine (basic nitrogen), carbazoles, benzocarbazoles and dibenzocarbazoles (neutral
518 nitrogen) than feed B. These compounds are the most refractory for the HDN reactions.
519 Additionally, nitrogen compounds of feed A showed higher molecular weight associated with a
520 higher degree of alkyl substitution what decreases the hydrogenation reactivity of these
521 compounds. The aromatics content was ~37 wt% and ~42 wt% for feed A and B, respectively.
522 Monoaromatics were the dominating family within both feeds, followed by diaromatics and
523 triaromatics; the mass fractions of these three families were slightly higher for feed B. This feed is
524 composed of streams from processes that promote the cracking, fluid catalytic cracking (LCO),
525 and delayed coking (HCGO), reducing the alkyl chains, therefore producing more condensed
526 aromatic structures have a refractory character to the hydrogenation.

527 Both feeds were submitted to the same deactivation conditions during the same time. Results
528 based on the exponential decay function (Table 4) and textural properties of the catalyst (Table 5)
529 showed a lower deactivation rate for feed A. It is consistent with the lower coke deposition on the
530 spent catalysts from the feed A tests (Figure 10). This was unexpected considering the higher
531 molecular weight of feed A and also its higher nitrogen content. The obtained results indicate that
532 these are not the determinant factors of the observed catalyst deactivation. It is rather the nature
533 of the coke precursor molecules, i.e., aromatics and nitrogen compounds. As already mentioned,
534 this nature is dictated by the origin of the feedstocks.

535 As it was mentioned, feed A had a higher nitrogen concentration and more refractory compounds
536 than feed B. Also, a lower HDN rate was observed during the tests with feed A (Figure 7). Thus,
537 the nitrogen content was higher for feed A than for feed B at the same reactor location. The organic
538 nitrogen compounds are rapidly adsorbed on the acid sites of the catalyst due to their basic
539 character [2,3,37,69]. This adsorption leads first to the inhibition of these sites by neutralization
540 and then to irreversible deactivation by coke deposits since the adsorbed nitrogen compounds

541 react to form coke before being desorbed. Both mechanisms result in the loss of cracking activity
542 [34] and low coke deposition from aromatics [29]. These effects were less significant for feed B
543 because its nitrogen compounds were more reactive and in a lower proportion than feed A. The
544 model molecules tests (Figure 13) pointed out the bigger loss of cracking activity for the catalyst
545 samples obtained from the tests with feed A compared to feed B, except at the first reactor inlet,
546 where the activities were similar and substantially low. However, feed A leads to a lower
547 deactivation rate. As the acid function determines cracking activity, it is concluded that the solids
548 from the tests with feed B had more acid sites available than those from feed A. These sites are
549 poorly balanced by the metal sites as observed in the selectivity results.

550
551 In contrast, the toluene hydrogenation test showed a higher activity loss for all the spent catalysts
552 from the experiments with feed B than with feed A, which was attributed to a higher coke build-up
553 with feed B. As a matter of fact, the TEM/EDX analysis shows no significant differences in terms
554 of MoS₂ slab morphology and Ni/Mo ratio related to the spent catalysts in contact with both feeds.
555 The higher hydrogenating activity for feed A might be related to the higher inhibition of the
556 (de)/hydrogenation reactions by the nitrogen compounds, which also inhibit the coke deposition
557 on the metal surface.

558
559 In summary, spent catalysts from tests with feed A had a higher hydrogenation activity and a lower
560 cracking activity than catalysts from the tests with feed B. Accordingly, the balance between metal
561 sites and acid sites (M/A) of the spent catalysts was different for both feeds. The i-heptane
562 selectivity can assess this balance; results were presented in Figure 14. A high selectivity indicates
563 a high number of active metal sites with respect to acid sites. A low selectivity means that there is
564 an imbalance between the acid sites and hydrogenation sites. Hence the (M/A) ratio was lower in
565 spent catalyst obtained with feed B than with feed A. As a consequence of the different ratio, both
566 quantity and type of deposited coke were also different. Actually, during the test with feed B, since

567 there were more available acid sites, many free radicals and carbocations were formed that
568 undergo polymerization reactions before finding a metal site for being hydrogenated. Therefore
569 there was an increase in the amount of coke with a lower H/C ratio, indicating a more aromatic
570 character from the tests with feed B (Figure 11). So, after all, although feed A leads to a more
571 substantial deactivation of acid sites, this is not the main parameter explaining deactivation. The
572 metal/acid balance explains the extent of coke formation and the ranking of the deactivation rates.

573 The formed coke could originate from the organic nitrogen compounds or other coke precursors
574 like aromatic compounds. To estimate the contribution of each one of them, the N/C ratio values
575 of the spent catalyst were measured (Figure 12). Despite the higher quantity of deposited carbon
576 on the catalysts from the tests with feed B, the values of the N/C ratio were lower. The former
577 suggests that feed B might have an important contribution from aromatic compounds that may
578 condense and form coke deposits reducing the global activity. It is consistent with the higher
579 amount of aromatics.

580 Summing up the higher catalyst deactivation obtained with the lighter feed (feed B) results from
581 two joint facts: more aromatics with low reactivity and a lower nitrogen content with a less basic
582 character and more reactivity, all of this compared to feed A. Herein constituted a strong synergy
583 that leads to a poor balance in the M/A ratio because the fewer nitrogen leads to more available
584 acid sites where the aromatics can form intermediates that undergo condensation/polymerization
585 reactions rather than saturation due to a hydrogenation function also weakened for the low
586 inhibition of the coke formation by nitrogen.

587 5 CONCLUSIONS

- 588 • Combining a feedstock with higher aromatics and a lower nitrogen content creates an
589 imbalance in the ratio M/A, with a low number of metal sites in relation to the acid sites.
590 Consequently, there is poor hydrogenation of the unsaturated coke precursors species

591 produced in the acid sites, which undergo polymerization and condensation reactions forming
592 the coke deposits on the catalyst surface and promoting its deactivation. This combination
593 has an effect that outweighs the effect of differences in molecular weight and boiling range.

594

595 • For a similar type of feed with a similar final boiling point, the total nitrogen and aromatics
596 content significantly impacted the resulting catalyst deactivation. Actually, the key parameters
597 are both the content but mostly the type of nitrogen compounds because they are at the origin
598 of the inhibition of hydrogenation and cracking activities, but even more important, they
599 determine the number of acid sites available for the reactions.

600

601 • Independent of the feed properties, the catalyst was strongly deactivated during the first days
602 on-stream. Then, the kinetic rates reached almost constant values. This behavior follows the
603 evolution of coke deposition, which is mainly deposited at the beginning of the test runs. These
604 coke deposits are preferentially formed on the acid sites because of the rapid and strong
605 chemisorption of nitrogen on these sites on one side, and due to condensation and
606 polymerization of aromatics carried out on these sites, on the other side.

607

608 • The balance in the metal/acid site ratio determines the amount and type of formed coke. The
609 lower the ratio, the lower the hydrogenation of olefins produced in acid sites, and
610 consequently, the formed coke increases, and its hydrogen content decrease producing a
611 more aromatic (less reactive) coke.

612

613 • For the lighter VGO/LCO/HCGO blend cracking, HDS and HDN kinetic constants were higher
614 than for the pure VGO feed. However, the kinetic constant for HDA was lower for the
615 VGO/LCO/HCGO feed. This difference is related to the more condensed aromatic structures
616 of this feed have a refractory character to the hydrogenation because it was composed of

617 streams from processes (fluid catalytic cracking and delayed coking) that promote side-chain
618 cracking.

619 **Funding sources:** This work was supported by IFPEN Energies Nouvelles and ECOPETROL.

620 **Supporting Information:**

621 The supporting information is available free of charge on the ACS publication website: FT-ICR/MS
622 data, ESI (+) and ESI (-) modes focusing on the N1[H] class; exponential decay model; correlation
623 between textural properties and carbon content of spent catalysts; H₂ consumption data; TEM
624 results.

625

626

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