



**HAL**  
open science

# A three-dimensional semi-quantitative method to monitor the evolution of polycyclic aromatic hydrocarbons from vacuum gas oil feedstocks to lighter products

Carole Reymond, Agnès Le Masle, Cyril Colas, Nadège Charon

## ► To cite this version:

Carole Reymond, Agnès Le Masle, Cyril Colas, Nadège Charon. A three-dimensional semi-quantitative method to monitor the evolution of polycyclic aromatic hydrocarbons from vacuum gas oil feedstocks to lighter products. *Fuel*, 2021, 296, pp.120175. 10.1016/j.fuel.2021.120175 . hal-03194183

**HAL Id: hal-03194183**

**<https://ifp.hal.science/hal-03194183>**

Submitted on 9 Apr 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1        **A three-dimensional semi-quantitative method to monitor the evolution of polycyclic**  
2        **aromatic hydrocarbons from vacuum gas oil feedstocks to lighter products**

3        Carole Reymond<sup>a</sup>, Agnès Le Masle<sup>a,\*</sup>, Cyril Colas<sup>b,c</sup>, Nadège Charon<sup>a</sup>

4        <sup>a</sup> IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

5        <sup>b</sup> Institut de Chimie Organique et Analytique, Université d'Orléans, CNRS UMR 7311, Rue de Chartres,  
6        45067 Orléans, France

7        <sup>c</sup> Centre de Biophysique Moléculaire, CNRS UPR 4301, Université d'Orléans, rue Charles Sadron,  
8        45071 Orléans, France

9        \*Corresponding author. E-mail address: [agnes.le-masle@ifpen.fr](mailto:agnes.le-masle@ifpen.fr) (A. Le Masle)

10       **Abstract**

11       Formation and accumulation of polycyclic aromatic hydrocarbons (PAHs) are responsible of major  
12       topical issues related to the conversion of petroleum vacuum gas oils (VGOs) in transportation fuels  
13       through hydrocracking process. To achieve an efficient management of these hydrocarbons, a  
14       detailed semi-quantitative description of PAHs contained in VGOs was provided by a three-  
15       dimensional off-line analytical approach based on centrifugal partition chromatography (CPC),  
16       supercritical fluid chromatography (SFC) and high-resolution mass spectrometry (HRMS). As a result,  
17       well-organised CPCxSFC chromatograms provided a relevant separation of PAHs according to both  
18       unsaturation level (DBE) and alkylation degree. This dedicated methodology allowed the semi-  
19       quantification of PAHs having a DBE superior to 12. For the first time, PAHs were quantified in six  
20       VGOs allowing to highlight differences in composition depending on the origin of the samples. Then,  
21       the evolution of PAH concentration was monitored during hydrotreating and hydrocracking  
22       processes. For the hydrotreated/hydrocracked (HDT/HCK) products, their sulphur and nitrogen  
23       contents were low enough to make possible semi-quantification of PAHs directly by SFC/HRMS. An  
24       accumulation of PAHs was observed when a recycle stream from the unconverted oil to HDT reactor  
25       was applied. This work demonstrates that valuable analytical data could be obtained leading a step

26 forward in the overall understanding of a process from native VGO feedstocks to the HDT/HCK  
27 products.

28 **Keywords**

29 Semi-quantification ; polycyclic aromatic hydrocarbons ; vacuum gas oil ; hydrocracking ; high-  
30 resolution mass spectrometry ; two-dimensional liquid chromatography

31

## 32 1. Introduction

33 Today many topical issues have to be addressed in the energy field and one of them is to meet the  
34 increasing worldwide demand for transportation fuels while fulfilling narrow product specifications  
35 [1]. For this purpose, efforts are continuously made to improve performances of advanced  
36 conversion technologies such as hydrocracking (HCK) dedicated to the transformation of the heavy  
37 petroleum fractions to targeted light and middle distillates [2]. Vacuum gas oils (VGOs) are high  
38 boiling point petroleum cuts (350-550°C) that are typically used as feedstocks in HCK units. They  
39 contain significant contents of sulphur and nitrogen compounds, known to act as poisons towards  
40 HCK catalysts, so a first hydrotreating step (HDT) is generally performed in order to remove these  
41 heteroelements in presence of an excess of hydrogen [3,4]. During this HDT step, olefins and many  
42 aromatic compounds may be saturated, leading to an increase of the number of hydrogen  
43 atoms/number of carbon atoms ratio (H/C). Once VGO has been hydrotreated, it is converted into  
44 lighter and valuable products by breaking the carbon-carbon bonds in a HCK reactor. There are  
45 several HCK configurations including single-stage or two-stage units, with or without recycle. In a  
46 once-through configuration, hydrotreated VGO corresponds to the unique hydrocarbons feedstock  
47 entering into the HCK reactor. In a recycle configuration, VGO goes through HDT and HCK reactors  
48 and then a part of the unconverted oil (UCO) resulting from the distillation of HCK products is used as  
49 a co-processing feedstock, mixed with the original VGO, at the inlet of either HDT or HCK reactor [5].  
50 The objective of the recycle operation mode is to increase the conversion of VGO and thus to get  
51 more light products. Thanks to this advanced technology as well as to the improvement of the  
52 catalysts performances [6], the overall conversion yields exceed 95 wt% [7]. However one great issue  
53 of hydrocracker operating with recycle of UCO is the formation and accumulation of polycyclic  
54 aromatic hydrocarbons (PAHs), and more specifically of heavy PAHs with more than eight aromatic  
55 rings. These heavy compounds are not initially present in native VGOs but come from unwanted  
56 reactions involving PAHs with 2-6 rings and their alkylated derivatives which are already contained in  
57 VGO feedstocks [8,9]. In a recycle configuration, PAHs are concentrated in UCO distillate and go back

58 to the HCK reactor, which ultimately leads to coke formation, deactivation of catalysts and clogging  
59 issues in the recycle piping.

60 In order to optimise process conditions, analytical characterisation and kinetic modelling are  
61 required. In the literature, many modelling approaches for HCK of heavy oils have already been  
62 reported [10–17]. Most of them employ lumping techniques using macroscopic properties (*e.g.*  
63 density, boiling point, elemental analysis, etc.). However, the predictive power of this kind of  
64 modelling is limited and for example cannot take into account the PAH accumulation phenomenon.  
65 At the opposite, molecular models give reliable prediction by considering the molecular composition  
66 of feedstocks and products. One major impediment of this modelling approach is the availability of  
67 detailed chemical data. Although analytical devices become more and more powerful, petroleomics  
68 is still a challenge for chemical analysis [18]. Ultra high-resolution mass spectrometry such as Fourier-  
69 transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) plays an important role in this  
70 research field by identifying several thousands of oil components and globally improving knowledge  
71 about HCK reactions [19–22]. Nevertheless, mass spectrometry alone cannot resolve the complexity  
72 of petroleum due to ionisation competition leading to qualitative data and the inability to  
73 differentiate isomeric species [23]. The use of ion mobility spectrometry-mass spectrometry (IMS-  
74 MS) can be a solution to bring additional information on the structure and differentiate isomer  
75 species [24]. However, ionisation competition cannot be solved with IMS-MS. Using chromatographic  
76 separation is a relevant way to overcome this limitation; for instance, Panda *et al.* proposed a non-  
77 aqueous reversed phase chromatography (NARP) method to quantify PAHs in a recycle UCO stream  
78 [25]. Unfortunately this method is well-adapted to streams with low sulphur contents but is not  
79 applicable to VGO feedstocks. Supercritical fluid chromatography (SFC) is used to propose a  
80 quantification of aromatic families (non aromatic, monoaromatic and polynuclear aromatic) (ASTM-  
81 D5186) or a quantification of olefin content (ASTM-D6550) in petroleum samples using a flame  
82 ionisation detector (D5186). High-temperature two-dimensional gas chromatography (HT-GC×GC) is  
83 also proposed to elute highly aromatic hydrocarbons like coronene but no molecular detailed

84 quantification is described with FID [26–28]. The hyphenation with HRMS is necessary for mixture as  
85 complex as VGO.

86 In a previous work, we have proposed an off-line comprehensive three-dimensional methodology to  
87 quantify PAHs in VGO samples [29]. This method consists in using centrifugal partition  
88 chromatography (CPC) as a first dimension and SFC as a second dimension hyphenated to FT-ICR-MS.  
89 The ionisation of PAHs was performed thanks to an atmospheric pressure photoionisation (APPI)  
90 source operating in positive mode. Since PAHs have an ionisation energy smaller than 10 eV, their  
91 direct ionisation can be performed thanks to photons from the krypton lamp [30]. Moreover, several  
92 works showed that APPI in positive mode is one the most suitable and efficient atmospheric pressure  
93 ionisation source for PAHs ionisation [31–33]. The first dimension of the three-dimensional method,  
94 CPC, allows a separation according to the alkylation stage of the hydrocarbons whereas the second  
95 one, SFC, is based on their double bond equivalent (DBE). Thanks to this specific hyphenation, it has  
96 been demonstrated that no matrix effect occurs in the ionisation source and thus PAHs in VGOs  
97 could be quantified by mass spectrometry for the first time.

98 The objective of this study is to extend the quantification of PAHs to their alkylated derivatives and to  
99 apply the methodology to a diversified set of samples. Firstly, six VGOs coming from different process  
100 operating conditions were investigated and their PAH composition was described from a qualitative  
101 and semi-quantitative viewpoint. Secondly our analytical method was used to measure the evolution  
102 of PAH contents from a native VGO to hydrocracked UCO products in both once-through and recycle  
103 configurations.

## 104 **2. Experimental section**

### 105 **2.1. Samples**

106 Six VGO samples including four straight-run vacuum gas oils (SRVGO), one VGO coming from deep  
107 conversion (DCVGO) and one blend (SRVGO and DCVGO 50/50 v/v) were investigated in this study.

108 Details on these samples are given in Table 1. Large ranges of nitrogen and sulphur contents are  
109 covered by the selected VGO, going from 2974 to 25792 mg/kg for sulphur contents and from 982 to  
110 3510 mg/kg for nitrogen contents.

111 Process parameters during the sampling of recycle stream are detailed in Table 2.

## 112 2.2. *Chemicals*

113 All solvents were purchased from VWR (Fontenay-sous-Bois, France). Acetonitrile (ACN), heptane  
114 (HEPT), dichloromethane (DCM) and toluene were HPLC grade. Methanol (MeOH) used during SFC  
115 analyses was HPLC-MS grade. Anisole was  $\geq 99\%$  pure. Carbon dioxide SFC grade (99.97%) (B50  
116 cylinder under pressure) was purchased from Air Liquide (Paris, France).

117 Anthracene, pyrene, benz(a)anthracene, perylene, benzo(ghi)perylene and coronene were purchased  
118 from Sigma-Aldrich (Saint-Quentin-Fallavier, France). 1-methylpyrene, 4-methylpyrene,  
119 4,5-dimethylpyrene, 2,7-dimethylpyrene, 1-ethylpyrene, 1-propylpyrene, 1-butylpyrene and  
120 1-methylcoronene were purchased from BCP Instruments (Oullins, France).

## 121 2.3. *Methodology*

122 In a previous work, a three-dimensional method consisting in the off-line hyphenation of CPC and  
123 SFC/HRMS was developed [29]. The fractions collected from CPC separation were evaporated, then  
124 dissolved in 300  $\mu\text{L}$  of toluene and analysed by SFC/HRMS. For one sample, 40 base peak  
125 chromatograms (BPC) were extracted from the mass signal, corresponding to each CPC fraction.  
126 Thanks to a home-made software, 2D plot could be traced by combining the BPC. The complete  
127 methodology is presented on Figure 1.

## 128 2.4. *Centrifugal Partition Chromatography (CPC)*

129 CPC experiments were carried out with a SCPC100 associated to a Spot Prep II from Armen  
130 Instrument (Gilson Purification, USA). The system included an automatic sample injection with a 5 mL

131 loop, a quaternary pump, a diode array detector (DAD) ranging from 200 to 400 nm and a fraction  
132 collector. A 131 mL column was used. Chromatographic data were managed using the Armen Glider  
133 CPC software. Experiments were conducted at room temperature.

134 Solvent system consisted in HEPT/DCM/ACN 45/10/45 (v/v/v). Biphasic system solvent was prepared  
135 in a separatory funnel. Descendant elution mode allowed to use the heptane-enriched phase as the  
136 stationary phase and the acetonitrile-enriched phase as the mobile phase. The stationary phase ratio  
137 was measured at 60%. Samples were prepared as follows: 1 g of sample was diluted in 5 mL of  
138 stationary phase. After 10 min of equilibration with the mobile phase at 30 mL/min and 500 rpm,  
139 elution took place during the first 30 min of the run (2000 rpm, 10 mL/min of mobile phase), then the  
140 run ended with 10 min of extrusion (2000 rpm, 30 mL/min of stationary phase). One fraction was  
141 collected each minute (40 fractions in total per run). These fractions were evaporated under vacuum  
142 to dryness using a Rocket Synergy evaporator (Biopharma Technologies, France) at 40°C. The dry  
143 extracts were dissolved in 300 µL of toluene for further analyses with SFC/HRMS.

#### 144 2.5. SFC/HRMS

145 SFC experiments were carried out on an Acquity UPC<sup>2</sup> (Waters, USA). The instrument control was  
146 performed by Empower 3 software (Waters). SFC method was optimised in a previous work [29].  
147 Briefly, separations were achieved with a back pressure of 10.5 MPa at 55°C on a Torus 2-PIC column  
148 (3 × 100 mm, particle size 1.7 µm, Waters). Methanol was used as co-solvent. The mobile phase flow  
149 rate was 1.1 mL/min. The method started with an isocratic step of 5 min with 100% of CO<sub>2</sub>, then the  
150 organic co-solvent ranged from 0 to 30% in 15 min. The injection volume was 1 µL. The detection UV  
151 wavelengths ranged from 210 to 400 nm. Finally, the flow was split, one part going to the mass  
152 spectrometer and the other one to the waste via the automated back pressure regulator (ABPR).

153 The chromatographic system was hyphenated to a linear ion trap - Fourier-transform ion cyclotron  
154 resonance mass spectrometer (LTQ-FT-ICR Thermo Scientific, Germany) equipped with a 7 T magnet.  
155 Ionisation was carried out using APPI in positive mode. Anisole was employed as APPI dopant with a



156 100  $\mu\text{L}/\text{min}$  flow rate at the outlet of the diode array detector (DAD). Ionisation and transfer  
157 conditions were optimised with a design of experiments approach according to a previous work [29].  
158 Sheath, auxiliary and sweep gas flow rates were set to 10, 34 and 0 A.U. respectively. APPI vapouriser  
159 and transfer capillary temperatures were equal to 348 and 200°C respectively. Transfer capillary and  
160 tube lens voltages were set to 48 and 100 V respectively. The mass range was set as  $m/z$  98-1000. In  
161 order to have at least 10 points to correctly describe each chromatographic peak, a resolving power  
162 of 12500 at  $m/z$  400 and 2  $\mu\text{scans}$  were used. External mass calibration was performed using Calmix  
163 from Thermo Fisher Scientific. The mass accuracy was better than 2 ppm.

## 164 2.6. *MS data processing*

165 Data were processed using MZmine 2.53 software [34]. Raw data were directly imported into the  
166 software. After mass detection, ADAP chromatogram builder functionality [35] was applied. The  
167 feature lists were processed as follows: first isotopic peaks were grouped with the pseudo-molecular  
168 ion, then a smoothing was performed in order to facilitate chromatogram deconvolution. The 40  
169 feature lists coming from the CPC fractionation of one sample were aligned so that all the MS peak  
170 areas for one ion associated to its retention time are indicated on the same line. Finally, molecular  
171 formulae were assessed with the following conditions:  $\text{C}_{1-100}\text{H}_{1-100}\text{O}_{0-1}\text{S}_{0-1}\text{N}_{0-1}$  and a mass accuracy of  
172 2 ppm.  $[\text{M}]^{+\bullet}$  were the main formed ions. Based on the formulae list obtained, several properties  
173 could be calculated such as the double bound equivalent (DBE) which represents the number of rings  
174 plus the number of double bonds. DBE values are calculated by the following equation for  $\text{C}_c\text{H}_h\text{O}_o\text{S}_s\text{N}_n$   
175 compounds:

$$176 \quad \text{DBE} = \frac{2c - h + n + 2}{2}$$

177 The processed data were exported in Excel software (Microsoft, USA) for further calculation as  
178 regards PAH semi-quantification. For each fraction, concentrations were calculated thanks to an  
179 external calibration. External calibration included pyrene, benz(a)anthracen, perylene,

180 benzo(ghi)perylene and coronene. All compounds with a DBE of 12 were quantified with pyrene  
181 calibration curve. Benz(a)anthracene was used to quantify compounds with a DBE of 13 and 14;  
182 perylene for DBE of 15 and 16; benzo(ghi)perylene for DBE of 17 and 18 and coronene for DBE of 19  
183 and 20. Only fractions with a concentration greater than 5 mg/L were quantified. Two calibration  
184 ranges were prepared: the first ranging from 5 to 100 mg/L and the second up to 500 mg/L.  
185 Compounds with a concentration below 100 mg/L were quantified with the first range, while the  
186 second range was used for those with a concentration above 100 mg/L. Then, the concentrations  
187 were converted in amount of analytes in each fraction. Finally, by summing the quantities of analytes  
188 in all the fractions, the total concentrations in the VGO could be measured. Taking into account the  
189 limit of quantification of 5 mg/L in the CPC fractions and that one compound eluted in around five  
190 CPC fractions, the limit of quantification in VGOs could be estimated to 10 mg/kg.

191 The repeatability and reproducibility of the semi-quantitative method were evaluated by repeating  
192 three times the VGO 1 analysis: two times the same day and operator, and the last time at several  
193 weeks interval with a different operator. The averages of the relative standard deviations (RSD) for  
194 all the DBE families were 8 and 11% for repeatability and reproducibility respectively. Thus, the  
195 confidence interval for PAH quantification was  $\pm 30\%$ .

### 196 **3. Results and discussion**

#### 197 **3.1. *Quantification methodology***

198 In this study, in order to apply our semi-quantitative three-dimensional method to a pool of samples,  
199 some points must be validated. The first one concerned the recovery efficiency of the off-line  
200 method as an evaporation step occurring between the CPC fractionation and the SFC analysis could  
201 lead to some losses of sample. The second one was about the quantification of alkylated PAHs. It is  
202 well known that VGOs contain hydrocarbons which could have up to 50 carbon atoms [36–38]. To  
203 quantify these more or less alkylated compounds, their response factors had to be compared to their  
204 non-alkylated homolog compounds.

205 *3.1.1. Recovery of standards during a CPC×SFC/HRMS run*

206 A solution of anthracene, pyrene, perylene, benzo(ghi)perylene and coronene was prepared at *ca.*  
207 50 mg/L for each compound using toluene as solvent. Five mL of this solution were injected into CPC.  
208 The complete analytical method was applied including the evaporation step. MS data were  
209 processed as explained in the experimental part. Concentrations of standards in the 40 fractions  
210 were calculated thanks to an external calibration. Based on these concentrations, the amounts of  
211 standards in the fractions were calculated and summed. MS quantification showed recovery yields  
212 higher than 90% for all PAH standards except for anthracene (Table 3). The recovery of this latter  
213 (82%) might be due to a loss of standard during the evaporation of CPC fractions.

214 Based on these results, only PAHs with at least 4 rings (*i.e.* pyrene) were quantified in VGOs.

215 *3.1.2. Study of alkylated PAH standards*

216 Seven alkylated pyrenes including methyl and dimethylpyrene substituted at different positions,  
217 ethyl, propyl and butylpyrene as well as methylcoronene were selected to study the impact of the  
218 alkylation on the MS response (Figure 2). One  $\mu\text{L}$  of each of them at 200 mg/L was injected in  
219 SFC/HRMS.

220 Mass spectra of pyrene and alkylated pyrenes are presented in Figure 3. Mass spectrum of pyrene  
221 shows  $[\text{M}]^{+\bullet}$  ion whereas alkylated pyrenes form additional ions coming from in-source  
222 fragmentation of  $[\text{M}]^{+\bullet}$ .

223 Indeed,  $[\text{M}]^{+\bullet}$  ions are less stable than  $[\text{M}+\text{H}]^+$  ions and will therefore fragment more easily. The  
224 tendency of compounds to form  $[\text{M}]^{+\bullet}$  or  $[\text{M}+\text{H}]^+$  ions depends on the nature of the molecule but  
225 also on the experimental conditions used and in particular the nature of the dopant in the case of  
226 APPI. The ionisation of analytes via a dopant can take place either by charge or proton transfer. To  
227 favour the proton transfer in order to form predominantly  $[\text{M}+\text{H}]^+$  ions, the dopant must have both a  
228 low ionisation energy (IE) and a low proton affinity (PA). It was demonstrated in previous works that  
229 anisole provides better sensitivity than toluene [29,39,40]. Anisole has an IE of 8.20 eV compared

230 with 8.83 eV for toluene [41]. Both dopants have a lower IE than the photon energy of the krypton  
231 lamp and higher than IE of PAHs. Thus, they can ionise our compounds of interest by charge transfer.  
232 On the other hand, PA of anisole is higher than that of toluene or acetone. Thus, the latter two  
233 dopants would be likely to promote proton transfer. However, the use of toluene as a dopant did not  
234 result in the formation of  $[M+H]^+$  ions during SFC/HRMS analysis. The very low IE of PAHs favours  
235 charge transfer and it will therefore be difficult to find conditions for  $[M+H]^+$  ion formation.  
236 Moreover, it is preferable to form only one type of ion rather than a mixture of radical and proton  
237 ions. The instability of  $[M]^{\bullet+}$  ions coming from alkylated PAHs leads to in-source fragmentation which  
238 might not be avoid. Since the desolvation conditions are relatively mild (APPI temperature  $< 350^{\circ}\text{C}$   
239 and ion transfer capillary temperature at  $200^{\circ}\text{C}$ ), modifying them would probably not completely  
240 prevent fragmentation.

241 For methyl and dimethylpyrenes, the most intense ion remain  $[M]^{\bullet+}$  while for pyrene with a longer  
242 alkyl chain (ethyl, propyl or butyl),  $m/z$  215 which corresponds to  $[M-\text{CH}_3]^+$ ,  $[M-\text{C}_2\text{H}_5]^+$  or  $[M-\text{C}_3\text{H}_7]^+$   
243 ions becomes the most intense one. This ion is also visible on the mass spectra of methylpyrenes and  
244 dimethylpyrenes as  $[M-\text{H}]^+$  and  $[M-\text{CH}_3]^+$  ions respectively, but in a smaller extend. Finally,  $[M-\text{H}]^+$   
245 ions are also formed during the ionisation of the dimethylpyrenes. All the mass spectra are different,  
246 even for two isomers, the relative intensities of each ion are different. This uniqueness is a great  
247 source of information and allows to distinguish the kind of alkylation (*i.e.* dimethylpyrene *versus*  
248 ethylpyrene). However, it leads to a more complex quantification and especially for data processing.

249 External quantification with individual standards is not possible due to the lack of available  
250 commercial standards and the fact that thousands of compounds are present in a VGO sample. Thus,  
251 in this work, we have decided to semi-quantify PAHs using one standard per DBE family. For example,  
252 pyrene family has a DBE of 12, so all compounds with the same DBE will be quantified using the  
253 calibration curve of pyrene. However, to apply this methodology, MS responses of alkylated PAHs  
254 have been evaluated and compared to the corresponding non-alkylated PAHs. As said previously,

255 alkylated PAHs showed multiple ions. Two main ways are possible to take into account all the ions.  
256 The first one (Method#1) consists in quantifying individually each ion using the pyrene calibration  
257 curve and then summing the calculated concentrations. The second way (Method#2) consists in first  
258 summing the areas of each extracted ion chromatograms (EIC) of the different ions and second  
259 calculating the global concentration of the alkylated pyrene. The two methods were applied and the  
260 results are given in Table 4. Both methods gave quantifications with errors smaller than 10% except  
261 for 2,7-dimethylpyrene. Most of the time Method#1 had better accuracy than Method#2. Finally,  
262 alkylated pyrenes were also quantified using UV detection and the UV calibration curve of pyrene  
263 (Table 5). Despite the selection of the wavelength allowing the maximum response for each  
264 compound, significant biases were observed by systematically underestimating actual  
265 concentrations.

266 In conclusion, for the rest of the study Method#1 using mass spectrometry was employed to semi-  
267 quantify PAHs in VGO samples. Moreover, the experiences conducted on commercially available  
268 alkylated PAHs showed that the response factors of alkylated PAHs and their corresponding non-  
269 alkylated PAHs were relatively closed (Table S1). Thus, the alkylated PAHs could be semi-quantified  
270 using the response factors of the corresponding non-alkylated PAHs. Then, the calibration curves of  
271 several standards showed that PAHs with the same DBE had similar response factors. Figure S1  
272 illustrated the example of chrysene and benz[a]anthracene which both have a DBE of 13. Finally,  
273 based on the hypothesis, supported by experimental data, that alkylated PAHs as well as all PAHs  
274 with the same DBE have a similar response coefficient, we proposed to semi-quantified PAHs using  
275 the response factor of one standard for each DBE family. Although this approach has its own  
276 limitations, it can allow to have access to valuable data to compare different VGOs, as well as to  
277 monitor the evolution of PAHs formation during a process. All compounds with a DBE of 12 were  
278 quantified with pyrene calibration curve. Benz(a)anthracene was used to quantified compounds with  
279 a DBE of 13 and 14; perylene for DBE of 15 and 16; benzo(ghi)perylene for DBE of 17 and 18 and  
280 coronene for DBE of 19 and 20. A possible error on the quantification of alkylated PAHs may be done.

281 The error will be more in the direction of overestimation in view of the error made on 2,7-  
282 dimethylpyrene. However, these errors will be identical between the different samples since the  
283 matrix effects were limited by the CPC×SFC hyphenation. Thus, inter-sample comparisons and  
284 monitoring of PAH concentrations during a HCK process remain reliable.

### 285 3.2. *Analysis of VGOs by CPC×SFC/HRMS*

286 The six VGOs described in Table 1 were analysed using the CPC×SFC/HRMS method, providing a 2D  
287 plot specific to each sample (Figure 4). These 2D plots are fingerprints of the samples and revealed  
288 differences even for the same group of VGOs as for the four SRVGOs (from VGO 1 to 4). The use of  
289 high-resolution mass spectrometry enabled us to determine a possible molecular formula for each  
290 peak reported on the 2D plots, making it possible to distinguish PAHs and heteroelement-containing  
291 species. Nitrogen contents of the investigated samples varied from 0.10 to 0.35 wt%, corresponding  
292 to 'neutral' or 'basic' nitrogen compounds whose structures were based on respectively an acridine  
293 or a carbazole core. When a classical analytical approach is employed involving a non-structural  
294 informative detector such as flame ionisation detector for gas chromatography, nitrogen species  
295 have to be removed prior quantitative analysis because they tend to co-elute with hydrocarbons.  
296 According to CPC×SFC maps illustrated in Figure 4, nitrogen-containing compounds from VGOs were  
297 specifically eluted in the first CPC fractions as they were partitioned mainly in the CPC mobile phase  
298 enriched in acetonitrile; and in the second part of the SFC chromatograms thanks to the interaction  
299 between polar groups of the stationary phase and nitrogen atoms of analytes (red boxes in Figure 4).  
300 Using (+)APPI, between 110 for VGO 1 and 510 for VGO 5 unique molecular features could be  
301 identified as  $C_xH_yN$  without considering multiple isomers eluting at several retention times. At the  
302 opposite of nitrogen-containing compounds, PAHs were detected all along the CPC run (black boxes).  
303 Thus nitrogen compounds and hydrocarbons were directly and easily differentiated thanks to the  
304 CPC×SFC orthogonal separation conditions. Concerning sulphur-containing compounds, they are  
305 usually present in VGOs as alkyl and polybenzothiophenes. In the studied samples sulphur contents

306 covered a large range of values from 0.30 to 2.58 wt% with between 210 for VGO 1 and 570 for VGO  
307 3 identified chemical formulae. In our analysis conditions, sulphur-containing compounds were  
308 eluted all along the CPC run (*i.e.* 10-40 min) within the same chromatogram areas than the PAHs  
309 ones (black boxes). Indeed, aromatic sulphur-containing compounds have close chemical properties  
310 to aromatic compounds leading to similar retention in CPC and SFC. For example, pyrene ( $C_{16}H_{10}$ , DBE  
311 12) and dibenzothiophene ( $C_{16}H_{10}S$ , DBE 12) were both eluted between 13 and 14 min in CPC and at  
312 6.5 and 7.9 min respectively in SFC, while benzocarbazole or aminopyrene ( $C_{16}H_{11}N$ , DBE 12) were  
313 eluted between 7 and 8 min in CPC and between 13.8 and 14.6 min in SFC. So in this case, the small  
314 difference in retention time between PAHs and sulphur compounds did not allow a quantification  
315 with UV detection, but it was sufficient to distinguish them in HRMS and avoid matrix effect in the  
316 ionisation source [29]. Thus, a specific treatment of HRMS data was performed to make a distinction  
317 between sulphur-containing molecules and PAHs, resulting in 2D plots dedicated only to  
318 hydrocarbons ( $C_xH_y$  compounds) as shown in Figure 5. As hydrocarbons were eluted in SFC  
319 separation according to their unsaturation level [29], SFC retention times were used to subdivide 2D  
320 plots as a function of PAH DBE. Then it was possible to get well-organised CPCxSFC chromatograms,  
321 providing a relevant structuration of maps based on DBE values, ranging from DBE inferior to 12 up  
322 to 19 and more. Such a 2D space organisation would be undoubtedly useful to describe the chemical  
323 composition of VGOs. It should be noticed that the intensities on the 2D plots were relative, so the  
324 direct comparison of peak intensities between samples was not possible. To go further, a semi-  
325 quantification methodology previously set up was applied to the six samples and PAH contents were  
326 measured for each VGO from DBE 12. Although PAHs with a DBE lower than 12 were not quantified  
327 due to losses during the evaporation step, 2D plots in Figure 5 showed a large number of peaks in  
328 VGO 1 as well as in VGO 6, while the area dedicated to this DBE class was almost empty in VGO 5.

329 PAH contents measured for the six investigated samples from the CPCxSFC/HRMS analyses are  
330 reported in Table 6. Globally PAH contents decreased with DBE values and were scattered in a large  
331 scale depending on both the DBE value and the VGO. For instance PAH contents varied from 6296

332 (VGO 3) to 14357 mg/kg (VGO 1) when considering a DBE value equal to 12. All samples contained  
333 PAHs at significant levels for DBE comprised between 12 and 17 but fewer contained PAHs with a  
334 DBE equal to 18 (high density samples do, like VGOs 4, 5 and 6) and only one sample, VGO 5 coming  
335 from a deep conversion process, still had PAHs with a DBE of 20.

336 The three-dimensional CPCxSFC/HRMS approach used in this study offered a detailed and semi-  
337 quantitative description of PAH composition for VGOs. Thanks to the high resolution provided by the  
338 bidimensional chromatography and by mass spectrometry, it was possible to get more information  
339 about PAHs present in VGOs including data about their alkylation level. Among the set of VGOs  
340 investigated in this work, two different samples were selected as examples: a medium density  
341 straight-run vacuum gas oil (VGO 3) and a vacuum gas oil coming from a deep conversion process  
342 (VGO 5). For each sample, DBE *versus* the number of carbon atoms (nC) was plotted (Figure 6),  
343 reporting PAH contents thanks to the dot size. Such representation is classically used to describe  
344 complex products and have to be usually considered from a qualitative point of view due to matrix  
345 effects preventing quantification when the sample is introduced into HRMS analyser through direct  
346 infusion without any preliminary chromatographic separation [19]. However in our case, the use of  
347 bidimensional CPCxSFC enabled a reduction of such matrix effects [29] and provided a semi-  
348 quantification of alkyl PAHs, assuming that all alkyls had the same response factors as their non-alkyl  
349 PAH reference. Therefore dots plotted in Figure 6 represent contents of PAHs and not HRMS signal  
350 intensities, so compositions of VGOs can be directly compared with each other. For instance PAH  
351 alkylation levels notably depended on both the DBE and the kind of VGO: PAHs with low DBE and  
352 short CH<sub>2</sub> chains were mainly observed for the straight-run vacuum gas oil VGO 3 whereas PAHs were  
353 distributed over a broad range of DBE with rather long or numerous alkyl chains for deep conversion  
354 vacuum gas oil VGO 5. From the CPCxSFC/HRMS data, it was also possible to calculate a 'weighted  
355 average number of carbon atoms' (nC) by weighting the number of carbon atoms of all the alkyl PAHs  
356 belonging to the same DBE group by the content of each hydrocarbon. Plotted as dotted lines in  
357 Figure 6, these average nC took into account simultaneously the number of carbon atoms in the



358 aromatic rings and in the alkyl chains and may be considered as a gravity center dedicated to each  
359 DBE group.

360 Evolution of the weighted average nC according to DBE values for the six investigated VGOs were  
361 illustrated in Figure 7. For comparison PAHs having no alkyl substituent (*i.e.* pyrene,  
362 benz(a)anthracene, perylene, benzo(ghi)perylene and coronene) were also plotted as references in  
363 Figure 7. It appears clearly that the gap in terms of weighted average nC between the PAHs in VGOs  
364 and the non-alkyl references is higher for low DBE and tends to be alleviated for increasing DBE. For  
365 DBE 12, the non-alkyl reference, pyrene, is made of 16 carbon atoms whereas in VGO samples the  
366 weighted average nC was comprised between 22 (VGO 3) and 24 (VGO 5). Thus, compounds with a  
367 pyrene core were alkylated with on average 8 carbon atoms for VGO 5. For PAHs with a higher DBE,  
368 the alkylation level was lower with, for example, two carbon atoms in average in the alkyl chain for  
369 compounds with a DBE of 17 in VGO 6 (based on benzo(ghi)perylene as non-alkyl reference). This  
370 difference of alkylation degree between DBE could be directly observed on the 2D plots in Figure 5.  
371 Indeed, PAHs with a DBE  $\geq 17$  were eluted only in the first part of CPC while PAHs with a DBE  
372 between 12 and 14 were eluted all along the CPC run until the extrusion of the stationary phase. As  
373 already discussed from Table 6, the sample VGO 5 coming from a deep conversion process exhibited  
374 a special composition when compared to straight-run vacuum gas oils: in addition to contain heavy  
375 PAHs, VGO 5 presented a more important alkylation degree than the other VGOs. All the graphs  
376 representing the concentration as a function of nC for DBE 12 to 20 are available in Figure S2.

377 Finally CPC×SFC/HRMS analysis allowed a more accurate characterisation than an analysis by  
378 SFC/HRMS. As shown previously [20], a strong ionisation suppression can occur during VGO analysis  
379 by SFC/HRMS due to ionisation competition of analytes entering simultaneously in the ionisation  
380 source [29]. By calculating the weighted average nC based on the intensity of ions detected in  
381 SFC/HRMS, it appeared that the average nC for a given DBE was higher than the one calculated using  
382 data from CPC×SFC/HRMS analysis. As an example, for compounds with a DBE of 12 detected in

383 VGO 4, the average nC measured by SFC/HRMS was about 37, while this latter was only 23 by  
384 CPC×SFC/HRMS. Therefore, highly alkylated compounds seemed to be preferentially ionised over less  
385 alkylated analytes, which created a bias in the characterisation of VGOs by SFC/HRMS. The  
386 hyphenation of CPC and SFC/HRMS was therefore required to achieve a more accurate  
387 characterisation, reflecting the composition of the VGOs.

388 In addition, in the first part of this study, we have demonstrated that mass spectra of alkylated PAHs  
389 were different according to the alkyl chain type. In this way, dimethylpyrene and ethylpyrene can be  
390 differentiated for instance. As an example, mass spectra of main compounds belonging to the pyrene  
391 family (DBE 12) in VGO 6 with one, two and three carbon atoms in the alkyl chain are presented in  
392 Figure S3. For all of them,  $[M]^{+\bullet}$  were the main ion meaning that instead of an alkyl chain such as  
393 ethyl or propyl groups, carbon atoms belonged to several methyl groups. This kind of information  
394 about isomerisation of the alkyl chains should be very useful to better understand the role played by  
395 PAHs in the VGO reactivity during HDT and HCK processes.

### 396 3.3. *Evolution of PAH concentrations during hydrotreating and hydrocracking of a VGO*

397 In the previous section, PAHs were quantified in several VGOs. In this section, VGO 2 was selected  
398 and the by-products from the HDT and HCK of this feedstock were characterized in terms of PAH  
399 concentrations in order to have a global view of their evolution. Monitoring of PAH contents was  
400 performed on several products coming from single-stage HCK in a recycling stream configuration  
401 (Figure 8). HDT- $t_0$  was collected after the HDT of the feed while the unconverted oil samples (UCO- $t_i$ )  
402 were collected from the atmospheric distillation residue of HCK products with an initial boiling point  
403 temperature superior to 370°C.

404 These HCK products were collected under several process conditions: 1/ HDT- $t_0$  and UCO- $t_0$  were  
405 collected before the recycle flow was started (once-through configuration), 2/ UCO- $t_1$  to UCO- $t_5$  were  
406 sampled once UCO coming from the HCK step was recycled and introduced at the inlet of the HDT

407 reactor in co-processing with non-hydrotreated VGO 2 feedstock. Table 2 summarises the  
408 experimental conditions under which the samples were obtained.

409 The three-dimensional analytical methodology was applied to VGO 2 while SFC/HRMS could be used  
410 for semi-quantification of PAHs in HCK products as they did not contain, or in a small extend, sulphur  
411 and nitrogen compounds. Thus, the SFC and HRMS dimensions were both used for the analysis of  
412 VGO and by-products, making data comparison easier.

### 413 *3.3.1. Single-stage once-through configuration of hydrocracking*

414 A product resulting from the HDT of VGO 2 was first collected as illustrated in Figure 8 and was  
415 referred as HDT- $t_0$  sample. In a second time, it was processed in a HCK reactor to convert its heavy  
416 fraction (*i.e.* compounds having a boiling point temperature superior to 370°C) in lighter valuable  
417 distillation cuts which are naphta, kerosene and atmospheric gas oil. The vacuum residue with an  
418 initial boiling point temperature superior to 370°C, also called UCO, was obtained from the  
419 distillation of the HCK products. PAH contents were measured in the three samples: the VGO before  
420 HDT (VGO 2 sample), the liquid after HDT and prior HCK (HDT- $t_0$ ) and the vacuum residue after HCK  
421 (UCO- $t_0$ ). For comparison of the PAH contents, the distillation yield of the UCO was taken into  
422 account to calculate normalised PAH contents (referred as UCO- $t_0^*$ ) that could be directly compared  
423 to the contents in VGO 2 and HDT- $t_0$  samples.

424 Evolution of PAH contents of VGO 2, HDT- $t_0$  and UCO- $t_0^*$  samples according to DBE values are  
425 reported in Figure 9A. At first, we observed a clear drop of the contents during HDT for PAHs having a  
426 DBE comprised between 12 and 16, indicating a deep hydrogenation of these aromatic species in the  
427 investigated process conditions. For example, the concentration of compounds with a DBE of 12 was  
428 divided by 4 between VGO 2 and HDT- $t_0$  samples. Similarly, during HCK a decrease in the  
429 concentration of compounds with a DBE between 12 and 16 was observed, but in a smaller extent  
430 compared to the decrease that occurred during HDT. The concentration of compounds with a DBE of

431 12 was this time divided by a factor smaller than 3. As regards PAHs with DBE superior to 17, no  
432 significant change could be observed due to the low concentrations measured (below 10 mg/kg).

433 Moreover, evolution of the weighted average nC according to DBE values is illustrated in Figure 9B.  
434 Initially, VGO 2 contained PAHs with a decrease of the alkylation degree with the DBE value by  
435 considering the gap between the weighted average nC from PAHs in VGO 2 and the non-alkyl  
436 references. During HDT, the weighted average nC increased for DBE 12, 13 and 14 between VGO 2  
437 and HDT-t<sub>0</sub>. This observation may indicate that PAHs with a low level of alkylation were preferably  
438 hydrotreated. For DBE from 15 to 18, this observation could not be done since PAHs already present  
439 in the feed were only slightly alkylated. On the opposite, the alkylation level was rather constant in  
440 the UCO-t<sub>0</sub>\* sample whatever the DBE value was. Indeed, the gap between the weighted average nC  
441 measured for PAHs in UCO-t<sub>0</sub>\* and non-alkyl references was comprised between one and three for  
442 all DBE values. The strong decrease of the weighted average nC between HDT-t<sub>0</sub> and UCO-t<sub>0</sub>\*  
443 samples for DBE 12, 13 and 14 was the consequence of cracking reactions of highly alkylated PAHs.  
444 These semi-quantitative results obtained from three selected examples show that the content and  
445 the composition of PAHs were both specific to a kind of sample. For each DBE value, it was possible  
446 to plot the distribution of PAH contents according to nC; for instance such distributions measured for  
447 DBE equal to 12 were illustrated in Figure 9C. The number of carbon atoms for VGO 2 and HDT-t<sub>0</sub>  
448 samples was spread between 18 and 35; whereas, after HCK, nC was only distributed between 18  
449 and 23 for UCO-t<sub>0</sub>\* sample. Also, the drop of PAH content between VGO 2 and HDT-t<sub>0</sub> samples was  
450 more important for the lowest nC with for example a drop of a 13 times for PAHs with 19 carbon  
451 atoms, while the global PAH content for DBE 13 decreased with a factor of only 4. Although we  
452 observed a decrease of the concentration between HDT-t<sub>0</sub> and UCO-t<sub>0</sub>\* samples for PAHs with a DBE  
453 of 13 from Figure 9A, Figure 9C showed an increase of PAH contents with nC between 19 and 21, and  
454 a decrease for a higher nC. Cracking reactions may have transformed highly alkylated PAHs into those  
455 slightly alkylated ones.

456 Finally, during single-stage once-through hydrocracking, the HDT of the feed lead to a decrease in the  
457 PAH concentrations due to deep hydrogenation of double bonds C=C. It seemed that PAHs with a low  
458 alkylation level were preferably hydrogenated. Then, HCK allowed to convert highly alkylated PAHs  
459 into PAHs with a low level of alkylation.

### 460 *3.3.2. Single-stage with recycle configuration of hydrocracking*

461 The analytical methodology was also applied to some products collected once a part of the UCO from  
462 the HCK step and following distillation was used as co-processing feedstock together with the initial  
463 VGO 2 and was introduced into the HDT reactor (single-stage HCK configuration). In addition to UCO-  
464  $t_0$  sample collected before the start-up of the recycle stream, five UCO collected under different  
465 process conditions were investigated and referred as UCO- $t_1$ , UCO- $t_2$ , UCO- $t_3$ , UCO- $t_4$ , and UCO- $t_5$   
466 samples in relation to their increasing time on stream. As reported in Table 2, products at the outlet  
467 of HCK reactor exhibited quite similar amounts of high boiling point compounds (*ca.* 47-50 wt% of  
468 370°C+ fraction).

469 Contents of the PAHs contained in the HCK vacuum residues were measured using the SFC/HRMS  
470 approach and normalised taking into account the yield of the 370°C+ cut (see Table 2 for the yields).  
471 These contents were referred as UCO- $t_i^*$  and were expressed as mg/kg of feed, considering both  
472 VGO 2 and the recycle stream as feedstocks in the present co-processing configuration. Evolutions of  
473 the PAH contents for VGO 2 and UCO- $t_i^*$  samples are represented as a function of DBE values in  
474 Figure 10. For DBE inferior to 16, PAH contents of HCK products were all lower than the ones  
475 measured for VGO 2 whatever was the UCO recycle flow rate: these PAH contents first drastically  
476 dropped from the VGO 2 feedstock to the first HCK product (UCO- $t_0^*$ ) due to the hydrogenation of  
477 the aromatic rings; then they increased progressively with time on stream, indicating an  
478 accumulation of PAHs in the HCK reactor. For compounds with DBE  $\geq 17$  (*i.e.* PAHs with six aromatic  
479 rings at minimum), their contents became higher than in the VGO once UCO recycle stream had been  
480 started. This accumulation of PAHs tend to increase from UCO- $t_0^*$  to UCO- $t_5^*$ .

481 Evolution of the weighted average nC according to DBE values for VGO 2 and HCK products are  
482 illustrated in Figure 11A. As discussed previously, VGO 2 contained PAHs with an alkylation degree  
483 which decreases with the DBE value. On the opposite to VGO 2, HCK products were made of PAHs  
484 with a rather low and constant alkylation degree whatever the DBE value was. Moreover, the  
485 weighted averages nC were similar for all the HCK products and were particularly lower than the  
486 ones measured for PAHs in VGO 2 when considering DBE values inferior to 15. These results show  
487 that, under our conditions, PAHs with a low DBE were significantly affected by hydrogenation at the  
488 first stage of HCK and the alkyl structures still remained the same even when PAH contents strongly  
489 increased with time on stream, so the same kind of PAHs were accumulated with time in the HCK  
490 reactor as illustrated in Figure 11B for compounds with a DBE of 13.

491 Although the aim of this study was not to clearly identify the impact of each process parameter on  
492 PAH concentrations, evolution of PAHs according to R2 temperature was plotted in Figure 12.  
493 Absolute values of R2 temperatures could not be given due to confidential nature. Figure 12  
494 highlighted the impact of R2 temperature on the PAH concentration. Indeed, R2 temperature is  
495 usually increased in order to compensate the catalyst deactivation and keep a constant conversion.  
496 However, it seemed that this increase in temperature also leads to an increase of PAH concentration.  
497 For PAHs with 4 and 5 rings (DBE between 12 and 16), the concentrations range from 1581 mg/kg at  
498  $T_0$  to 7717 mg/kg at  $T_{+30^\circ\text{C}}$  which represents an increase of 390%. For PAHs with at least 6 rings (DBE  
499  $\geq 17$ ), this increase was even more important by going from 88 to 1216 mg/kg or an increase of more  
500 than 1000%.

#### 501 **4. Conclusion**

502 In this study we have successfully managed to semi-quantify PAHs in vacuum gas oils using a three-  
503 dimensional off-line CPCxSFC/HRMS approach while chemical compositions of several HDT/HCK  
504 products coming from once-through or recycle HCK configurations were described by SFC/HRMS. As  
505 regards analysis of VGOs, the use of an orthogonal CPCxSFC configuration with an enhanced

506 resolution capacity enabled a clear separation of hydrocarbons and nitrogen-containing compounds.  
507 Moreover a specific treatment of high-resolution mass spectrometric data was performed to  
508 differentiate PAHs from sulphur-containing compounds prior to their quantification. As a result, well-  
509 organised CPCxSFC chromatograms provided a relevant separation of PAHs according to both  
510 unsaturation level (DBE) and alkylation degree. This dedicated methodology allowed the semi-  
511 quantification of PAHs having DBE superior to 12. Concerning the HDT/HCK products, their sulphur  
512 and nitrogen contents were low enough to make possible semi-quantification of PAHs directly by  
513 SFC/HRMS. PAH contents tend to decrease during the HDT of VGO, PAHs with a low alkylation level  
514 being preferably hydrogenated. Then HCK reaction allowed to cut alkyl chains and convert highly  
515 alkylated PAHs into PAHs with a low level of alkylation. An accumulation of PAHs and especially of  
516 PAHs with more than six aromatic rings occurred when an UCO recycle stream was applied.  
517 Furthermore our results have shown that the temperature of HCK unit was correlated with the PAH  
518 concentration. As a conclusion, this work has demonstrated that reliable and relevant semi-  
519 quantitative data about PAH compositions in VGOs and their HDT/HCK products can be achieved  
520 thanks to our CPCxSFC/HRMS methodology. Such useful data will be crucial for a better  
521 understanding of PAH formation and a further powerful modelling.

## 522 **5. Acknowledgments**

523 Authors would like to greatly thank Luc Davy and Benoit Celse from IFP Energies Nouvelles for the  
524 precious discussions about processes and samples. Authors also thank Alexandra Berlioz-Barbier for  
525 her advices on MS data treatment.

## 526 **6. References**

527 [1] A. Demirbas, A. Bafail, A.-S. Nizami, Heavy oil upgrading: Unlocking the future fuel supply,  
528 Petroleum Science and Technology 34 (2016) 303–308.  
529 <https://doi.org/10.1080/10916466.2015.1136949>.

- 530 [2] J. Ancheyta, M.S. Rana, E. Furimsky, Hydroprocessing of heavy petroleum feeds: Tutorial,  
531 Catalysis Today 109 (2005) 3–15. <https://doi.org/10.1016/j.cattod.2005.08.025>.
- 532 [3] G. Valavarasu, M. Bhaskar, K.S. Balaraman, Mild Hydrocracking—A Review of the Process,  
533 Catalysts, Reactions, Kinetics, and Advantages, Petroleum Science and Technology 21 (2003)  
534 1185–1205. <https://doi.org/10.1081/LFT-120017883>.
- 535 [4] M. Sau, K. Basak, U. Manna, M. Santra, R.P. Verma, Effects of organic nitrogen compounds on  
536 hydrotreating and hydrocracking reactions, Catalysis Today 109 (2005) 112–119.  
537 <https://doi.org/10.1016/j.cattod.2005.08.007>.
- 538 [5] C. Peng, Z. Cao, Y. Du, R. Zeng, R. Guo, X. Duan, X. Fang, Optimization of a Pilot Hydrocracking  
539 Unit To Improve the Yield and Quality of Jet Fuel Together with Heavy Naphtha and Tail Oil, Ind.  
540 Eng. Chem. Res. 57 (2018) 2068–2074. <https://doi.org/10.1021/acs.iecr.7b04981>.
- 541 [6] O.V. Klimov, K.A. Nadeina, P.P. Dik, G.I. Koryakina, V. Pereyma, M.O. Kazakov, S.V. Budukva, E.  
542 Gerasimov, I.P. Prosvirin, D.I. Kochubey, A.S. Noskov, CoNiMo/Al<sub>2</sub>O<sub>3</sub> catalysts for deep  
543 hydrotreatment of vacuum gasoil, Catalysis Today 271 (2016) 56–63.  
544 <https://doi.org/10.1016/j.cattod.2015.11.004>.
- 545 [7] C.S. Hsu, P.R. Robinson, Practical Advances in Petroleum Processing: Volume 1, Springer, New  
546 York, 2009.
- 547 [8] R.F. Sullivan, M.M. Boduszynski, J.C. Fetzer, Molecular transformations in hydrotreating and  
548 hydrocracking, Energy Fuels 3 (1989) 603–612. <https://doi.org/10.1021/ef00017a013>.
- 549 [9] J.C. Fetzer, THE CHEMISTRY AND ANALYSIS OF LARGE PAHs, Polycyclic Aromatic Compounds 27  
550 (2007) 143–162. <https://doi.org/10.1080/10406630701268255>.
- 551 [10] K. Basak, M. Sau, U. Manna, R.P. Verma, Industrial hydrocracker model based on novel  
552 continuum lumping approach for optimization in petroleum refinery, Catalysis Today 98 (2004)  
553 253–264. <https://doi.org/10.1016/j.cattod.2004.07.056>.



- 554 [11] P.J. Becker, B. Celse, D. Guillaume, H. Dulot, V. Costa, Hydrotreatment modeling for a variety of  
555 VGO feedstocks: A continuous lumping approach, *Fuel* 139 (2015) 133–143.  
556 <https://doi.org/10.1016/j.fuel.2014.08.032>.
- 557 [12] C. Fan, J. Long, Effect of Feed Properties on Product Distribution from the Modeling of an  
558 Industrial Hydrocracking Process, *Pet. Chem.* 60 (2020) 174–180.  
559 <https://doi.org/10.1134/S0965544120020024>.
- 560 [13] H.M. Lababidi, D. Chedadeh, M.R. Riazi, A. Al-Qattan, H.A. Al-Adwani, Prediction of product  
561 quality for catalytic hydrocracking of vacuum gas oil, *Fuel* 90 (2011) 719–727.  
562 <https://doi.org/10.1016/j.fuel.2010.09.046>.
- 563 [14] H. Puron, P. Arcelus-Arrillaga, K.K. Chin, J.L. Pinilla, B. Fidalgo, M. Millan, Kinetic analysis of  
564 vacuum residue hydrocracking in early reaction stages, *Fuel* 117 (2014) 408–414.  
565 <https://doi.org/10.1016/j.fuel.2013.09.053>.
- 566 [15] H. Zhou, J. Lu, Z. Cao, J. Shi, M. Pan, W. Li, Q. Jiang, Modeling and optimization of an industrial  
567 hydrocracking unit to improve the yield of diesel or kerosene, *Fuel* 90 (2011) 3521–3530.  
568 <https://doi.org/10.1016/j.fuel.2011.02.043>.
- 569 [16] A. Pyhälähti, J. Kanervo, S. Kuitunen, Comprehensive Residual Oil Hydrocracking Reaction  
570 Kinetic Modeling Combined with Effective Phase Equilibrium Calculation, *Ind. Eng. Chem. Res.*  
571 57 (2018) 11271–11279. <https://doi.org/10.1021/acs.iecr.8b01834>.
- 572 [17] P.J. Becker, B. Celse, D. Guillaume, V. Costa, L. Bertier, E. Guillon, G. Pirngruber, A continuous  
573 lumping model for hydrocracking on a zeolite catalysts: Model development and parameter  
574 identification, *Fuel* 164 (2016) 73–82. <https://doi.org/10.1016/j.fuel.2015.09.057>.
- 575 [18] A.G. Marshall, R.P. Rodgers, Petroleomics: The next grand challenge for chemical analysis, *Acc.*  
576 *Chem. Res.* 37 (2004) 53–59. <https://doi.org/10.1021/ar020177t>.
- 577 [19] A.G. Marshall, R.P. Rodgers, Petroleomics: Chemistry of the underworld, *PNAS* 105 (2008)  
578 18090–18095.

- 579 [20] H. Muller, N.A. Alawani, F.M. Adam, Innate Sulfur Compounds as an Internal Standard for  
580 Determining Vacuum Gas Oil Compositions by APPI FT-ICR MS, *Energy Fuels* 34 (2020) 8260–  
581 8273. <https://doi.org/10.1021/acs.energyfuels.0c01365>.
- 582 [21] T.M. Schaub, R.P. Rodgers, A.G. Marshall, K. Qian, L.A. Green, W.N. Olmstead, Speciation of  
583 Aromatic Compounds in Petroleum Refinery Streams by Continuous Flow Field Desorption  
584 Ionization FT-ICR Mass Spectrometry, *Energy Fuels* 19 (2005) 1566–1573.  
585 <https://doi.org/10.1021/ef049734d>.
- 586 [22] J.M. Purcell, I. Merdrignac, R.P. Rodgers, A.G. Marshall, T. Gauthier, I. Guibard, Stepwise  
587 Structural Characterization of Asphaltenes during Deep Hydroconversion Processes Determined  
588 by Atmospheric Pressure Photoionization (APPI) Fourier Transform Ion Cyclotron Resonance (FT-  
589 ICR) Mass Spectrometry †, *Energy Fuels* 24 (2010) 2257–2265.  
590 <https://doi.org/10.1021/ef900897a>.
- 591 [23] R.P. Rodgers, M.M. Mapolelo, W.K. Robbins, M.L. Chacón-Patiño, J.C. Putman, S.F. Niles, S.M.  
592 Rowland, A.G. Marshall, Combating selective ionization in the high resolution mass spectral  
593 characterization of complex mixtures, *Faraday Discuss.* 218 (2019) 29–51.  
594 <https://doi.org/10.1039/c9fd00005d>.
- 595 [24] P.M. Lalli, J.M. Jarvis, A.G. Marshall, R.P. Rodgers, Functional Isomers in Petroleum Emulsion  
596 Interfacial Material Revealed by Ion Mobility Mass Spectrometry and Collision-Induced  
597 Dissociation, *Energy Fuels* 31 (2017) 311–318.  
598 <https://doi.org/10.1021/acs.energyfuels.6b02411>.
- 599 [25] S.K. Panda, H. Muller, T.A. Al-Qunaysi, O.R. Koseoglu, Determination of heavy polycyclic  
600 aromatic hydrocarbons by non-aqueous reversed phase liquid chromatography: Application and  
601 limitation in refining streams, *Journal of Chromatography A* 1533 (2018) 30–37.  
602 <https://doi.org/10.1016/j.chroma.2017.11.061>.

- 603 [26] M. Piparo, L. Flamant, G. Jousset, P. Cardinael, P. Giusti, Careful Investigations of PTV Injection  
604 Parameters for the Analysis of Vacuum Gas Oil by High-Temperature Comprehensive GC × GC,  
605 Energy Fuels 34 (2020) 12010–12017. <https://doi.org/10.1021/acs.energyfuels.0c01314>.
- 606 [27] T. Dutriez, M. Courtiade, D. Thiébaud, H. Dulot, F. Bertoncini, J. Vial, M.-C. Hennion, High-  
607 temperature two-dimensional gas chromatography of hydrocarbons up to nC60 for analysis of  
608 vacuum gas oils, J. Chromatogr. A 1216 (2009) 2905–2912.  
609 <https://doi.org/10.1016/j.chroma.2008.11.065>.
- 610 [28] L. Mahé, M. Courtiade, C. Dartiguelongue, J. Ponthus, V. Souchon, D. Thiébaud, Overcoming the  
611 high-temperature two-dimensional gas chromatography limits to elute heavy compounds, J.  
612 Chromatogr. A 1229 (2012) 298–301. <https://doi.org/10.1016/j.chroma.2012.01.030>.
- 613 [29] C. Reymond, A. Le Masle, C. Colas, N. Charon, Input of an Off-Line, Comprehensive, Three-  
614 Dimensional Method (CPC×SFC/HRMS) to Quantify Polycyclic Aromatic Hydrocarbons in Vacuum  
615 Gas Oils, Anal. Chem. 92 (2020) 6684–6692. <https://doi.org/10.1021/acs.analchem.0c00605>.
- 616 [30] N. Itoh, Y. Aoyagi, T. Yarita, Optimization of the dopant for the trace determination of polycyclic  
617 aromatic hydrocarbons by liquid chromatography/dopant-assisted atmospheric-pressure  
618 photoionization/mass spectrometry, Journal of Chromatography A 1131 (2006) 285–288.  
619 <https://doi.org/10.1016/j.chroma.2006.08.091>.
- 620 [31] T. Ghislain, P. Faure, R. Michels, Detection and monitoring of PAH and oxy-PAHs by high  
621 resolution mass spectrometry: comparison of ESI, APCI and APPI source detection, J Am Soc  
622 Mass Spectrom 23 (2012) 530–536. <https://doi.org/10.1007/s13361-011-0304-8>.
- 623 [32] A.K. Huba, K. Huba, P.R. Gardinali, Understanding the atmospheric pressure ionization of  
624 petroleum components: The effects of size, structure, and presence of heteroatoms, Sci. Total  
625 Environ. 568 (2016) 1018–1025. <https://doi.org/10.1016/j.scitotenv.2016.06.044>.
- 626 [33] J. Santos, M. Pudenzi, A. Wisniewski Jr., M. Breitkreitz, M. Eberlin, Optimization of Atmospheric  
627 Pressure Photoionization for the Crude Oil Analysis Using Ultra-High Resolution Mass  
628 Spectrometry, J. Braz. Chem. Soc. (2018). <https://doi.org/10.21577/0103-5053.20180214>.

629 [34] T. Pluskal, S. Castillo, A. Villar-Briones, M. Orešič, MZmine 2: Modular framework for processing,  
630 visualizing, and analyzing mass spectrometrybased molecular profile data, BMC Bioinformatics  
631 (2010).

632 [35] O.D. Myers, S.J. Sumner, S. Li, S. Barnes, X. Du, One Step Forward for Reducing False Positive  
633 and False Negative Compound Identifications from Mass Spectrometry Metabolomics Data:  
634 New Algorithms for Constructing Extracted Ion Chromatograms and Detecting Chromatographic  
635 Peaks, Anal. Chem. 89 (2017) 8696–8703. <https://doi.org/10.1021/acs.analchem.7b00947>.

636 [36] S.K. Panda, N.A. Alawani, A.R. Lajami, T.A. Al-Qunaysi, H. Muller, Characterization of aromatic  
637 hydrocarbons and sulfur heterocycles in Saudi Arabian heavy crude oil by gel permeation  
638 chromatography and ultrahigh resolution mass spectrometry, Fuel 235 (2019) 1420–1426.

639 [37] E. Niyonsaba, J.M. Manheim, R. Yerabolu, H.I. Kenttämä, Recent Advances in Petroleum  
640 Analysis by Mass Spectrometry, Anal. Chem. 91 (2019) 156–177.  
641 <https://doi.org/10.1021/acs.analchem.8b05258>.

642 [38] W. Wang, Y. Liu, Z. Liu, S. Tian, Detailed Chemical Composition of Straight-Run Vacuum Gas Oil  
643 and Its Distillates as a Function of the Atmospheric Equivalent Boiling Point, Energy Fuels (2016).  
644 <https://doi.org/10.1021/acs.energyfuels.5b02803>.

645 [39] D.R. Smith, D.B. Robb, M.W. Blades, Comparison of dopants for charge exchange ionization of  
646 nonpolar polycyclic aromatic hydrocarbons with reversed-phase LC-APPI-MS, J Am Soc Mass  
647 Spectrom 20 (2009) 73–79. <https://doi.org/10.1016/j.jasms.2008.09.012>.

648 [40] S.S.M. Amad, Z.A. Al-Talla, Multicomponent mixed dopant optimization for rapid screening of  
649 polycyclic aromatic hydrocarbons using ultra high performance liquid chromatography coupled  
650 to atmospheric pressure photoionization high-resolution mass spectrometry, Rapid Commun.  
651 Mass Spectrom. 26 (2012) 1488–1496. <https://doi.org/10.1002/rcm.6250>.

652 [41] P. ARPINO, Couplages chromatographiques avec la spectrométrie de masse. III, 2009 (accessed  
653 26 October 2017).

654

655 **Figure captions**

656 **Figure 1:** Scheme of the CPC×SFC/HRMS methodology

657 **Figure 2:** Alkylated PAHs investigated for the study of MS response factors

658 **Figure 3:** Mass spectra of pyrene and alkylated pyrenes

659 **Figure 4:** CPC×SFC/HRMS BPC plots of six VGO samples. PAHs and sulphur-containing compounds are  
660 included in the black boxes and nitrogen-containing compounds in the red boxes

661 **Figure 5:** CPC×SFC/HRMS BPC plots specific to hydrocarbons in six VGO samples. Colour boxes  
662 correspond to DBE (refer to plot F)

663 **Figure 6:** DBE as a function of nC for (A) VGO 3 and (B) VGO 5; dotted lines correspond to the  
664 weighted average nC.

665 **Figure 7:** Weighted average number of carbon atoms for each DBE

666 **Figure 8:** Scheme of single-stage HCK in a recycling configuration

667 **Figure 9:** Evolution of (A) PAH contents for each DBE, (B) weighted average number of carbon atoms  
668 for each DBE and (C) PAH contents according to the number of carbon atoms for DBE 13 for VGO 2,  
669 HDT-t<sub>0</sub> and UCO-t<sub>0</sub>\* samples

670 **Figure 10:** Evolution of PAH contents for each DBE for VGO 2 and HCK products UCO-t<sub>0</sub>\* to UCO-t<sub>5</sub>\*

671 **Figure 11:** (A) Evolution of weighted average number of carbon atoms for each DBE and (B) PAH  
672 contents according to the number of carbon atoms for DBE 13 for VGO 2 and HCK products UCO-t<sub>0</sub>\*  
673 to UCO-t<sub>5</sub>\*

674 **Figure 12:** R2 temperature according to PAH concentrations in UCO-t<sub>i</sub>\* samples

675

676 **Tables**

677 **Table 1:** Physical and chemical properties of petroleum samples investigated in this work

Samples	Type	Specific gravity at 15°C (g/cm <sup>3</sup> )	Boiling points at 5 and 95% distilled (°C)	Sulfur content (mg/kg)	Nitrogen content (mg/kg)
		ASTM D4052	ASTM D2887	ASTM D2622	ASTM D4629
VGO 1	SRVGO	0.9208	265 – 509	2974	1160
VGO 2	SRVGO	0.9211	342 – 561	15351	1404
VGO 3	SRVGO	0.9244	352 – 544	25792	982
VGO 4	SRVGO	0.9284	394 – 581	18921	1395
VGO 5	DCVGO	0.9306	390 – 567	6702	3510
VGO 6	SRVGO + DCVGO (50/50 v/v)	0.9314	346 – 551	10777	2610

678

679 **Table 2:** Process parameters during UCO-t<sub>i</sub> sampling

Samples	Time on stream (h)	R1 temperature (°C)	R2 temperature (°C)	Yield in 370°C+ cut (wt% )
HDT-t <sub>0</sub>	0	T <sub>0</sub>	T <sub>0</sub>	49.7
UCO-t <sub>0</sub>				
UCO-t <sub>1</sub>	583	T <sub>0</sub> +3°C	T <sub>0</sub> +10°C	49.6
UCO-t <sub>2</sub>	847	T <sub>0</sub> +3°C	T <sub>0</sub> +22°C	45.4
UCO-t <sub>3</sub>	1015	T <sub>0</sub> +7°C	T <sub>0</sub> +25°C	48.7
UCO-t <sub>4</sub>	1135	T <sub>0</sub> +7°C	T <sub>0</sub> +29°C	45.8
UCO-t <sub>5</sub>	1207	T <sub>0</sub> +7°C	T <sub>0</sub> +31°C	47.2

680

681 **Table 3:** Recovery yields of PAH standards analysed with the overall off-line CPCxSFC/HRMS method

	Amount of standard injected into CPC (mg)	Total amount measured by SFC/HRMS (mg)	Recovery yield (%)
Anthracene	0.231	0.189	82
Pyrene	0.224	0.219	98
Perylene	0.233	0.210	90
Benzo(ghi)perylene	0.238	0.220	93
Coronene	0.231	0.224	97

682

683 **Table 4:** Semi-quantification of alkylated PAHs thanks to the calibration curve of non-alkylated PAHs  
 684 with two different methods

	Method#1					Method#2	
	Concentration (mg/L) of			Total concentration (mg/L)	Error with method#1 (%)	Concentration calculated with $\Sigma$ EIC areas (mg/L)	Error with method#2 (%)
	[M] <sup>+</sup> •	[M-H] <sup>+</sup>	[M-CH <sub>3</sub> ] <sup>+</sup> or [M-C <sub>2</sub> H <sub>5</sub> ] <sup>+</sup> or [M-C <sub>3</sub> H <sub>7</sub> ] <sup>+</sup>				
1-methylpyrene	142	54	0	195	-2	211	5
4-methylpyrene	179	25	0	203	2	212	6
4,5-dimethylpyrene	138	9	33	180	-10	193	-4
2,7-dimethylpyrene	231	23	9	263	31	278	39
1-ethylpyrene	50	0	152	201	1	216	8
1-propylpyrene	27	0	169	196	-1	205	3
1-butylpyrene	40	0	148	187	-6	199	-1
1-methylcoronene	216	0	0	216	8	216	8

685

686 **Table 5:** UV quantification of alkylated pyrenes

	UV maximum (nm)	Concentration calculated with UV detection (mg/L)	Error (%)
1-methylpyrene	336.6	153	-24
4-methylpyrene	330.7	157	-22
4,5-dimethylpyrene	334.2	103	-48
2,7-dimethylpyrene	331.9	168	-16
1-ethylpyrene	335.4	147	-27
1-propylpyrene	336.6	140	-30
1-butylpyrene	336.6	138	-31

687

688 **Table 6:** Contents (mg/kg) of PAHs  $\pm$  30% in six VGO samples according to their DBE (ND: non-  
 689 detected)

DBE	VGO 1 SRVGO	VGO 2 SRVGO	VGO 3 SRVGO	VGO 4 SRVGO	VGO 5 DCVGO	VGO 6 Blend
12	14357	10090	6296	8240	11905	13315
13	6215	4732	2382	4521	8748	7517
14	2909	1808	800	2098	6753	3418
15	952	1085	980	1749	3022	1616
16	13	85	91	234	1933	501
17	107	95	89	135	1916	767

<b>18</b>	ND	< 10	< 10	34	614	54
<b>19</b>	ND	ND	ND	ND	65	24
<b>20</b>	ND	ND	ND	ND	41	< 10
<b>Total</b>	24554	17902	10642	17010	34998	27214

690