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Studies on the evolution of asphaltene structure during hydroconversion of petroleum residues

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Abstract

The evolution of asphaltenes has been studied under hydroconversion conditions with an ebullated bed on a Buzurgan (Middle East) feedstock. A bench unit was used to produce effluents in residue conversion conditions ranging from 55 to 85 wt.%. In those conditions, asphaltene conversion ranged 62–89 wt.%. Asphaltenes from the feedstock and unconverted asphaltenes have been characterized using Size Exclusion Chromatography to evaluate asphaltene size, and ^{13}C Nuclear Magnetic Resonance to evaluate the evolution of the average molecular structure parameters of asphaltenes. Results obtained were compared to results obtained at moderate residue conversion levels in a fixed bed.

The work clearly shows that unconverted asphaltene evolution is continuous. Unit size decreases with increasing conversion while the aromaticity of the asphaltenes increases due to dealkylation. Our results suggest that the remaining asphaltenes are dissociated in smaller aggregates around 50% conversion. Below this level, asphaltene evolution may be related to dissociation mechanisms. Above 50% conversion, the chemical structure of asphaltene units still significantly evolves through dealkylation mechanisms, leading to fairly condensed structures that remain at high conversion. Based on these results, an attempt was conducted to interpret the evolution of unconverted asphaltenes as a function of residue conversion level using a simple molecular reconstruction method.

Keywords: Asphaltene; Hydroconversion; Hydrotreatment; Ebullated bed; Residue

1. Introduction

Residue conversion processes are becoming increasingly important in the world today due to a number of market and economic factors. The residual fuel oil demand continues to decline, while at the same time, there is an increasing demand for motor fuels. At the same time, crude oil production of light conventional crude oils is declining, and projected to decline further in the future. This light oil production is being replaced with heavier, non-conventional crude oils.

Residue of heavy crude oils can be upgraded through various existing processes [1,2]. One of the challenges to face while upgrading residues is to handle properly the asphaltenes contained in the feed. Asphaltenes consist of a heterogeneous mixture of highly polydispersed molecules in terms of size and chemical composition with a high content of heteroatoms [3] such as sulphur, nitrogen but also metals such as nickel and vanadium that may also be included in these complex species through various chemical structures such as porphyrines [4]. Those heavy molecules can precipitate very easily due to changes in operating conditions such as temperature or changes in the residue composition. Furthermore, asphaltenes are known to be coke precursors in acid catalysis and catalyst inhibitors.

To characterize such complex structures, several mechanisms have been proposed in the literature [5–10]. The continental configuration defines asphaltenes with large central aromatic region, whereas the archipelago model describes molecules with several smaller aromatic regions linked by bridging alkanes. Molecular associations are initiated by aromatic region stacking (by four or five) to form elementary particles, which further self-associate to form colloidal aggregates. Hydrogen and π–π bonds are the main interactions involved in such association mechanisms. The aggregate formation is however more complex with the archipelago type since intramolecular associations are possible. Numerous studies have been carried out on asphaltene analysis. Chemical and colloidal characterizations

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have to be distinguished through [11]. Several methods can be used such as elemental analyses, ^{13}C NMR, Size Exclusion Chromatography (SEC) or different coupling methods such as SEC-mass spectrometry (SEC-MS).

There are different available strategies to handle upgrading of heavy residue feedstocks containing asphaltenes: asphaltenes can either be removed from the residue feedstock or converted. Asphaltene removal is industrially carried out through Solvent Deasphalting (liquid–liquid extraction) producing asphalts on one side and deasphalted oil on the other side, or through coking processes (thermal cracking where asphaltene molecules are converted into coke). However, it is also possible to consider asphaltene conversion into valuable hydrocarbons. This requires severe operating conditions at high temperature and hydrogen partial pressure while using a hydrogenation catalyst with low-acidic support in order to avoid high-coke formation. High-asphaltene hydroconversion levels are achievable in these conditions and the yield of liquid produced by such processes is much higher than with asphaltene removal processes. When the metal content of the feedstock is low, it is possible to hydrotreat the residue at moderate residue conversion levels to reach high-asphaltene conversion levels in catalytic fixed bed reactors. It is also possible to convert more difficult feedstocks with higher conversion levels, but the high-metal content of feeds containing large amounts of asphaltenes as well as the control of reaction exothermicity then impose to operate residue hydroconversion processes with specific technologies such as ebullated bed technology [12,13]. Indeed, metals such as nickel and vanadium are concentrated in residue feeds and will progressively deposit and concentrate on the hydroconversion catalyst. Catalyst addition is then required to maintain catalyst activity during operation. Furthermore, high-conversion combined with subsequent hydrogenation generates significant reaction heat that needs to be controlled by an adequate mixing in order to avoid large thermal gradients along the reactor.

There are a few published studies in the literature to characterize the evolution of asphaltenes in hydrotreatment conditions, therefore essentially at moderate residue conversion. Buch et al. [14] studied the evolution of asphaltene structure using fluorescence depolarization techniques and Nuclear Magnetic Resonance (NMR) at moderate temperature in the range of 350–390 °C on a Middle East crude. In their conditions, it is possible to reach high-asphaltene conversion, but according to the mild reactor temperatures reported, residue conversion, although not reported, probably remained low. Ancheyta et al. [15] also studied the evolution of asphaltenes using vapour phase osmometry and NMR on Maya Isthmus feedstock with low-asphaltene conversion below 60%. They show that aromaticity increases when temperature increases. At the same time, asphaltenes molecular weight decreases. More recently, Le Lannic et al. [16] have also studied the evolution of asphaltenes in a Middle East crude during hydrotreatment at mild temperatures (380–400 °C). All the cited studies were conducted to characterize the evolution of asphaltenes in hydrotreatment conditions characterized by low-residue conversion. In these conditions, residue cracking remained limited. The overall trend reported in these studies is that asphaltene molecular weight is decreasing with increasing hydrotreatment severity, together with an increasing aromaticity of remaining asphaltenes resulting from dealkylation.

We have already shown that hydroconversion in ebullated bed is a very efficient way to convert asphaltenes [17]. Asphaltene conversions as high as 89% could be achieved during bench unit experiments on a heavy crude vacuum residue, representative of Middle East feedstocks (Buzurgan). Detailed investigations of asphaltene structure with SEC and ^{13}C NMR have shown that unconverted or remaining asphaltenes change as a function of conversion during hydroconversion in ebullated bed. SEC measurements clearly suggested that remaining asphaltenes are dissociated in smaller aggregates as soon as conversion level is around 50%.

The aim of this work is to complete previous reported work by exploring asphaltene evolution as a function of residue conversion in a wide range, in order to describe asphaltene evolution from initial state in the feedstock up to final state in highly converted effluents. Therefore, we used results, obtained with the same feedstock, in a fixed bed hydrotreater [16] where residue conversion level remained moderate between 14 and 48 wt.% and in a ebullated bed hydroconversion process where residue conversion was high in the range of 55–86 wt.% [17]. Detailed analysis of unconverted asphaltenes effluents is investigated using elementary analysis, SEC and ^{13}C NMR. A simple molecular reconstruction method developed by Sato (Structural Analysis of Aromatic Hydrocarbons or SAAH) [18] is then used to interpret the evolution of the structure of the asphaltenes.

2. Experiments

2.1. Feedstock

A Buzurgan vacuum residue feedstock resulting from crude oil vacuum distillation was used. This feedstock is representative of Middle East vacuum residues. Main properties of Buzurgan VR feed are summarized in Table 1. Asphaltene content reaches 13.2 wt.% whereas metal and hydrogen feed contents are, respectively, about 250 wt. ppm and 9.84 wt.%. Since there is no significant carbon rejection in hydrotreatment or hydroconversion processes, hydrogenation of the vacuum residue feedstock is necessary to convert products in lighter liquid species with a hydrogen content in the range of 11.5–15 wt.% depending upon boiling point.

2.2. Bench unit operation

To achieve hydroconversion in conditions representative of industrial operation and in order to produce asphaltene effluent samples, a test was conducted in a bench unit consisting of two elongated reactors of 2.2 l operating in ebullated bed mode and described elsewhere [17,19]. A Ni–Mo catalyst supported on alumina was loaded in each reactor prior to the test. The objective of the work was to study the evolution of asphaltene structure as a function of residue conversion level. Experiments were

Table 1
Detailed characterization of Buzurgan feedstock

C7 asphaltenes	wt.%	13.2
C5 asphaltenes	wt.%	21.8
Conradson Carbon	wt.%	22.9
Specific gravity	(–)	1.045
Viscosity at 150 °C	cSt	205
Viscosity at 100 °C	cSt	3500
Nitrogen	wt.%	0.387
Sulfur	wt.%	5.56
Hydrogen	wt.%	9.84
Nickel	wt. ppm	59
Vanadium	wt. ppm	192
Saturated	wt.%	9.9
Aromatics	wt.%	37.1
Resins	wt.%	35.3
Distillation		
500 °C	wt.%	10
540 °C	wt.%	20
560 °C	wt.%	26
580 °C	wt.%	32

conducted at constant temperature (427 °C) and pressure (≈160 bars) and residue conversion level was adjusted by modifying LHSV. Residue conversion ($X_{540\ ^\circ\mathrm{C}+}$) was obtained by combination of the bench unit mass balance on first and second reactor and the Simulated Distillation analyses of the effluents [17,19] Unconverted asphaltenes were sampled both in the residue effluents of first and second reactor through a method derived from the norm NF T60-115 with *n*-heptane at 80 °C with an oil/heptane ratio of 1/50, enabling the determination of asphaltene conversion [17]. Table 2 shows the main operating conditions achieved during the two bench unit tests in the ebullated bed. During these tests, no significant sediment formation was observed and stable operation was achieved. No operation problems were reported on the bench unit.

Hydrotreatment of the residue was conducted in a fixed bed at a lower temperature ranging between 380 and 400 °C at a constant LHSV of 0.5 h^{-1} [16]. It was possible to reach high-asphaltene conversion up to 80 wt.%, but the overall residue conversion remained below 50%. Indeed, thermal cracking severity is lower in the fixed bed, but the catalytic contribution is more pronounced.

In Fig. 1, we represent asphaltene conversion obtained in the ebullated bed at 427 °C and in the fixed bed at 400 °C as a function of 540 °C+ residue conversion. The higher temperature in the ebullated bed enables to reach higher residue conversions than in the fixed bed with a similar asphaltene conversion range. It is clear that asphaltene conversion is higher than residue conversion. Asphaltene reactivity is therefore higher than the overall residue conversion in our conditions. This is important and ensures that the asphaltene concentration in residue effluents is lower than the asphaltene concentration in the residue feedstock. This suggests also that asphaltene conversions higher than 80 wt.% are achievable both in fixed bed and ebullated bed.

Table 2
Main operating conditions and performances

	Condition 1		Condition 2	
	R1	R2	R1	R2
Catalyst age (m^3/kg)	0.19		0.36	
LHSV (hr^{-1})	0.30		0.20	
Reactor temperature (°C)	427.5	427.1	427.5	426.8
Reactor pressure (bar)	159.9	156	159.9	156.1
X540 °C+ (wt.%)	55.8	74.1	67.2	85.4
XAsC7 (wt.%)	62.7	85.8	75.1	89.0

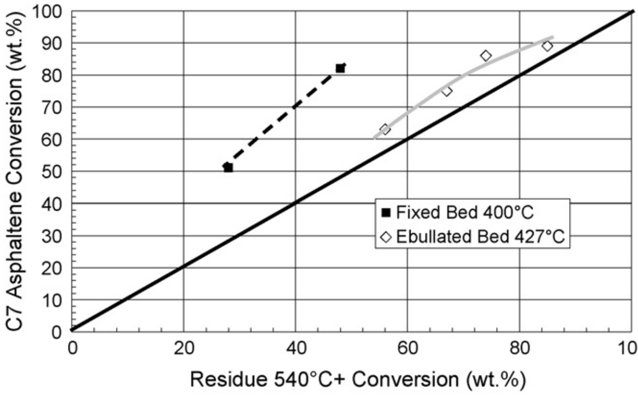


Fig. 1. Asphaltene conversion as a function of residue conversion.

2.3. Analytical characterization of asphaltenes

In order to characterize asphaltenes, samples of feedstock and bench unit effluents were sent for analysis. Precipitation of asphaltenes was performed through a derived method from the norm NF T60-115 with *n*-heptane at 80 °C with an oil/heptane ratio of 1/50.

One of the important parameters generally used to represent the colloidal state is the molecular weight (MW). However, the characterization of asphaltenes, in term of molecular weights (MW), is complex due to their high polydispersity, heterogeneity and properties to form aggregates. The association state of these molecules is known to be very sensitive to experimental conditions such as concentration, temperature and solvent [20,21]. Due to these properties, the interpretation of analytical results may be tedious. It has been shown that the molecular weight of asphaltenes measured with different technologies can vary by several orders of magnitude since the asphaltenic structures are not measured in the same state [22]. We chose in this study the SEC analysis since it can be routinely used to estimate apparent MW of oil fractions. In case of asphaltene measurements, results may however be biased due to association and non-size effects [23,24]. SEC was performed on a WATERS 150CV$^+$ using a refractive index detector. On-line SEC-MS coupling was also conducted with the mass spectrometer instrument QStar-Pulsar (Applied Biosystems) without split. More details can be found in Ref. [17].

In order to further characterize their chemical structure as a function of conversion, asphaltene samples were also analyzed using ^{13}C Nuclear Magnetic Resonance (NMR). This technique enables to quantitatively characterize the various carbon types found in asphaltenes.

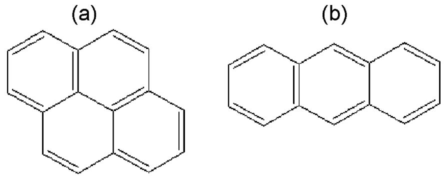


Fig. 2. Peri-condensed rings (a) and cata-condensed rings (b).

NMR experiments were performed on an Advanced 300 MHz Bruker spectrometer [17]. Based on this method, it was possible to determine the proportion of CH and quaternary C (Cq) present in aromatic part and the proportion of CH_3, CH_2, CH and quaternary C (Cq) present in the aliphatic part. Using the amount of total aromatic carbon and the detailed %CH and %Cq, it is possible to calculate the substitution index I_s [17] defined as the ratio between the substituted and the substitutable aromatic carbons and the condensation index which corresponds to the average number of condensed aromatic rings. It is also possible to compute a condensation index I_c [17], which corresponds to the average number of aromatic cycles composing the structure using two ideal aromatic cycles arrangements (peri- and cata-condensed, as shown in Fig. 2). The representation of peri- and cata-condensed rings can be illustrated by model molecules such as pyrene and naphtalene as shown in Fig. 2a and b, respectively.

3. Results

3.1. Analytical evolution of asphaltenes as a function of residue conversion

In Fig. 3, SEC chromatograms are plotted for different conversion levels. Results correspond to asphaltenes in the feedstock and asphaltenes remaining in the effluents from either the fixed bed (FB) at moderate severity or from the ebullated bed (EB) at higher severity. Clearly, the chromatogram of the feedstock exhibits a bimodal profile, typical of the asphaltene distribution between associated (high-molecular weight) and less associated state (low-molecular weight) of the asphaltenes aggregates. The low-molecular weight tailing of the trace chromatogram may come from the non-size effects, which are basically due to adsorption of species on the stationary phase of the column. The comparison between apparent molecular weight distributions from the feed and effluents shows a significant evolution with the conversion. Results show that there is a continuous evolution between feed and effluents from fixed bed and ebullated beds as a function of conversion. Residue conversion seems to be a relevant parameter to follow this evolution. To some extent, it summarizes the severity of operation. In hydrotreatment conditions with the fixed bed (lower conversion), chromatograms show a decrease of the apparent MW, but large aggregates are still remaining. In that case, it seems that asphaltene dissociation (or conversion into smaller aggregates) is less pronounced although asphaltenes conversion can be quite high and similar to some of the asphaltenes conversions encountered in hydroconversion conditions in ebullated bed. Overall, it seems that during the conversion process, asphaltenes first dissociate into smaller aggregates. In ebullated bed conditions, most of the asphaltenes remaining in converted effluents seem to be dissociated, which is not the case of unconverted asphaltenes downstream of the fixed bed reactor operating at a lower severity.

To further illustrate the evolution of asphaltenes as a function of conversion, we plotted in Fig. 4 the average molecular weight M_p of asphaltenes as a function of the residue conversion. We defined M_p as the molecular weight observed at the top of the main SEC chromatogram peak. Molecular weights are here only indicative values since molecular weights determined by SEC are rather relative (equivalent polystyrenes) but not absolute [25]. Such a value therefore represents the evolution of asphaltenes only qualitatively, due to the response factor, which is directly correlated to the molecule nature.

The asphaltene aggregate size estimated in the feedstock is close to 10,000 g/mol and decreases to around 9000 g/mol around 30% conversion. Between 30 and 50% conversion (X540 °C+), a change in asphaltene molecular weight is noticed: the molecular weight suddenly drops to 1600 g/mol. Above 50% hydroconversion, the plot shows a predominance of low-apparent masses, which is characteristic of dissociated smaller aggregates, and tends to 440–500 g/mol at 85 wt.% residue conversion. As a function of conversion, a continuity is clearly observed. Further work including ebullated bed

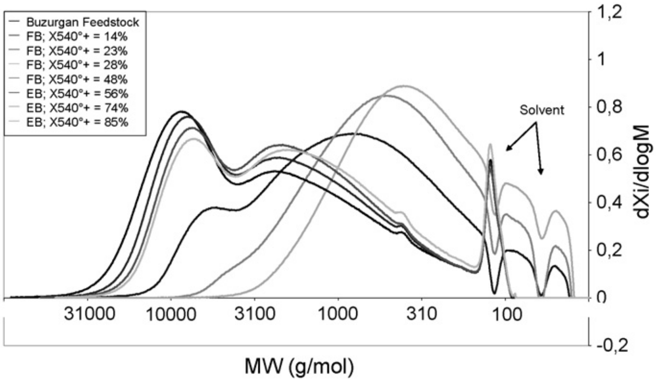


Fig. 3. SEC chromatograms of asphaltenes in the feed and hydroteated effluents with the fixed bed (FB) and hydroconverted effluents with the ebullated bed (EB).

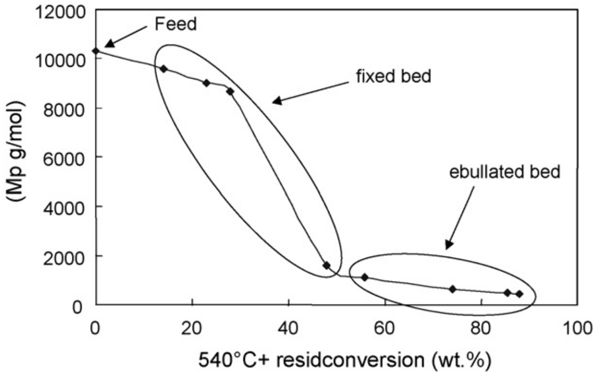


Fig. 4. Qualitative evolution of asphaltene apparent molecular weight (M_p) as a function of the residue conversion.

operation at moderate conversion shall be conducted to confirm that residue conversion is a relevant parameter to understand asphaltenes dissociation. Other parameters such as operating temperature may also have to be considered.

As already discussed, SEC is essentially qualitative and does not provide absolute estimates of average molecular weight of asphaltene species. We therefore attempted to use SEC-MS coupling [17] to analyze asphaltenes in the effluents of the ebullated bed at the highest conversion level. With this technology, the estimation of the MW is less affected by side effects that can occur in SEC chromatography where aggregation should be less promoted. The results obtained at the higher conversion in the ebullated bed, where asphaltenes in effluents are fully dissociated, were found to be very consistent with SEC results: the average molecular weight of asphaltenes unit was estimated in the range of 440 g/mol with SEC-MS while it is in the range of 490 g/mol with SEC results.

The continuous evolution of asphaltene size from the feedstock up to the highly converted effluents was confirmed when examining the detailed structure of asphaltenes using ^{13}C NMR. Fig. 5 shows the carbon repartition in asphaltenes, between aliphatic carbon ‘‘Cali’’ and aromatic carbons ‘‘Caro’’, as function of conversion for all samples analyzed. A continuity is observed as a function of residue conversion, independent of the type of conversion process, confirming the trend observed with SEC results. When conversion increases, asphaltene structure clearly becomes more aromatic. Initially, in the feedstock, carbon is almost evenly distributed between aromatic and aliphatic carbon. The amount of aromatic carbon increases in asphaltene effluents when conversion level increases. Due to asphaltene conversion, overall asphaltene content decreases but, at the same time, conversion impacts the repartition between aromatic and aliphatic carbon (Fig. 5). The higher aromatic carbon content can only be explained by a more rapid conversion of parts of asphaltenes containing aliphatic carbons. Those parts probably break more easily and disappear from the asphaltene fraction. Other mechanisms such as polycondensation into aromatic cycles and dehydrogenation of naphthenes, which could possibly explain the increasing aromaticity, are not possible here because of operating conditions: the high-hydrogen partial pressure and hydrogenation catalyst indeed promote hydrogenation and stabilize intermediate species initiated during cracking to avoid condensation of molecules.

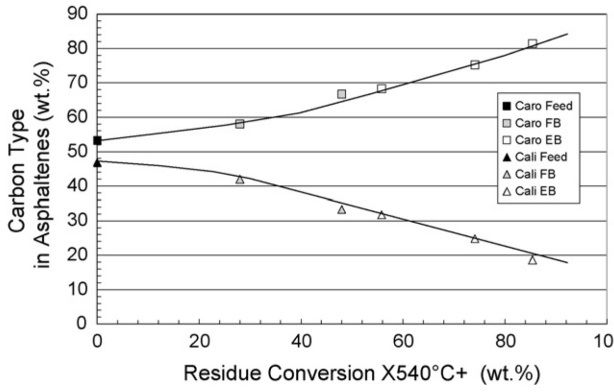


Fig. 5. Evolution of aromatic and aliphatic carbon in asphaltenes as a function of residue conversion.

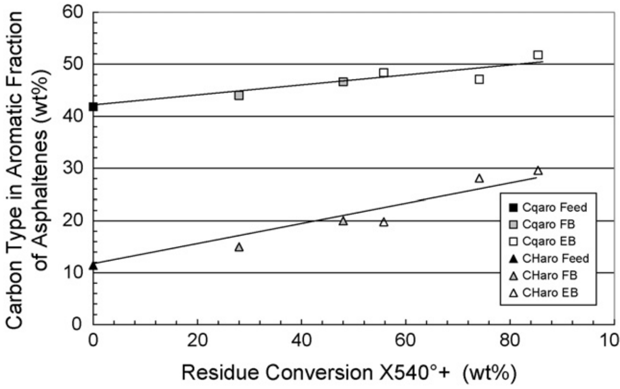


Fig. 6. Evolution of CH/Cq repartition in asphaltene aromatic carbon as a function of residue conversion.

Fig. 6 shows the evolution of the CH/Cq repartition in asphaltene aromatic carbon based on ^{13}C NMR analysis. CH aromatic carbon corresponds to unsubstituted carbons while Cq represents the proportion of quaternary carbons, either condensed or substituted. Clearly, there is a slight increase of the proportion of unsubstituted carbon when conversion increases, which could be explained by dealkylation (a), cracking of adjacent aromatic structures (b) or removal of naphthenic part of naphtheno-aromatic molecules (c), as represented in Fig. 7. Again, a continuity is observed as a function of residue conversion, independent of the conversion process.

To further investigate the aromatic carbon evolution, we studied the evolution of the substitution index I_s [17]. Fig. 8 shows that I_s decreases when process severity is increased. Once again, a continuity is observed as a function of residue conversion, but independent of the type of conversion process. ^{13}C NMR experiments show that the proportion of substituted carbon atoms decreases. This seems consistent with the mechanisms proposed above considering cracking of adjacent aromatic structures and naphtheno-aromatic structures and also a decrease of aliphatic chain bonds.

^{13}C NMR also gives the possibility to characterize the repartition of aliphatic carbon atoms between C, CH, CH_2 and CH_3. The amounts of C and CH species were found very low both in the feedstock and the effluents. Their evolution is therefore not discussed here. In Fig. 9, we represented the evolution of CH_3 and CH_2 aliphatic carbons in asphaltenes as a function of residue conversion. The increasing severity through the processes leads to a reduction of the length of carbon chains.

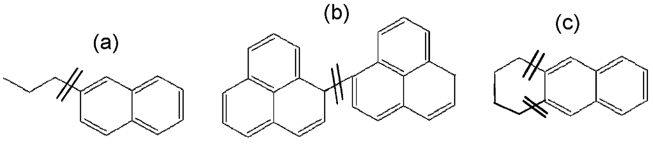


Fig. 7. Some cracking reaction mechanisms explaining the evolution of CH/Cq in asphaltene molecular evolution.

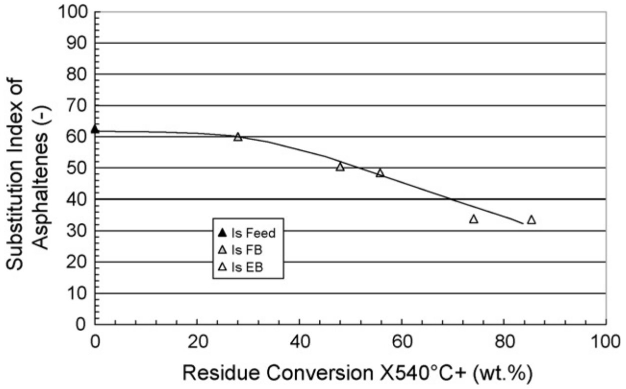


Fig. 8. Substitution index as a function of residue conversion as a function of residue conversion.

Indeed, the ratio CH_2/CH_3 decreases. Results obtained around 30% residue conversion were not considered as reliable since the low-CH_3 fraction observed here was suspicious. Overall, the decreasing trend of CH_2, CH_3 and CH_2/CH_3 ratio is in good agreement with the dealkylation mechanism of aromatic rings. Dealkylation generates an increase of the number of aromatic carbons remaining in the asphaltenes, while cracked aliphatic carbon goes into lighter fractions and disappears from the asphaltenes.

To summarize, ^{13}C NMR asphaltene characterization clearly shows that the structure of unconverted asphaltenes continuously changes during hydroconversion. Progressively, asphaltenes become more aromatic and this is probably mainly due to dealkylation mechanisms as suggested by detailed characterization. No aromatic condensation occurs despite the increase of process condition severity. The evolution of the structure of the remaining asphaltenes is found to be progressive and continuous when residue conversion level, representing the operating severity, increases. It seems however to be independent upon the type of residue conversion process.

3.2. Average molecular structure reconstruction

Based on the asphaltene characterizations conducted, we attempted to describe the evolution of average asphaltene molecules along the hydroconversion process. Several attempts are reported in the literature to represent asphaltene structures. For instance, Artok et al. [26] and Ali et al. [27] proposed a possible representation of average asphaltene molecular structure from Arabian crude mixture, based on analytical results obtained through several characterization methods. Among them, they use ^{1}H NMR, ^{13}C NMR and SEC. The problem faced in the reconstruction of large molecules is related to the number of possible molecules which increases significantly when their molecular weight increases. For asphaltenes in the unconverted fractions, limited analytical information leads to a large number of possible molecules that can be built.

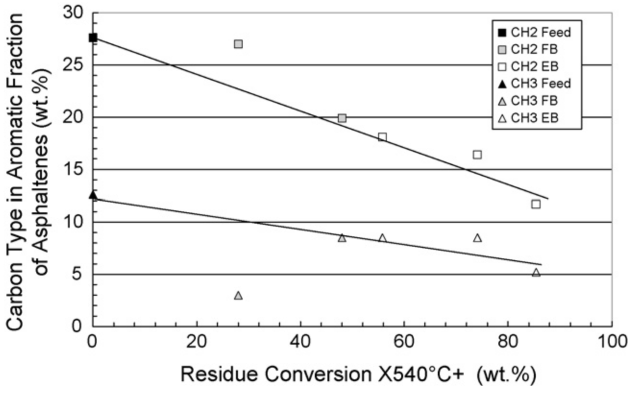


Fig. 9. Evolution of CH_3 and CH_2 (wt.%) in asphaltenes as a function of residue conversion.

Analytical results provide average characteristics of several different molecules, but the description of asphaltene with a single average molecular structure is a tremendous simplification of the reality of hydrocarbon mixtures. Systematic approaches have been already proposed to represent hydrocarbon cuts with a polydisperse molecular set. These methods consist of numerical generation of a large set of possible molecules in a mixture matching the experimental analytical characterization in average. They have already been successfully applied to light hydrocarbon feedstocks such as gasolines and middle distillates [28–30] and to vacuum distillates [31,32], and first attempts have been made to apply them to residues [28]. The complexity of these polydisperse molecular reconstruction methods is increasing exponentially however when the molecule weight increases, due to the growing number of possibilities and to the increasing difficulty to estimate individual and mixture properties for large molecules.

Our study provides additional information related to the chemical evolution of asphaltenes as a function of conversion. The fully dissociated asphaltenes observed at high-residue conversion are rather small compared to asphaltenes in the feedstock and may therefore be easier to represent based on the limited number of structures that can be built based on analytical characterization. By obviously postulating that the remaining structures at high conversion are part of the remaining asphaltenes found at lower conversion and in the feed, it is possible to include more information during the reconstruction process. We therefore attempted to describe average asphaltene molecules as a function of conversion, by starting the reconstruction based on the information collected at the highest conversion. Then, using the structure obtained at higher conversion as a basis, we reconstructed average molecular structures at lower conversion.

In order to reconstruct average asphaltene molecules based on analytical information, we used the SAAH reconstruction method proposed by Sato [18]. This method is based on information that can be obtained through SEC (molecular weight), elementary analysis and ^{13}C NMR. ^{1}H NMR can also be used but does not provide significant additional information. This leads to the calculation of four main characteristics of an average molecule:

- M is the number of structures containing condensed aromatic cycles.

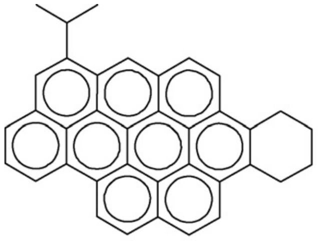
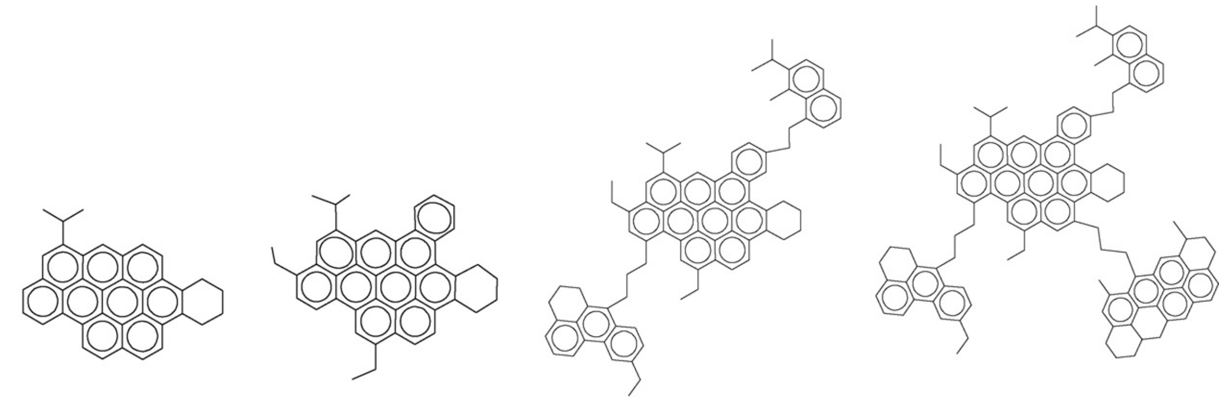


Fig. 10. Possible asphaltene molecular structures at the residue conversion level of 85 wt.%.

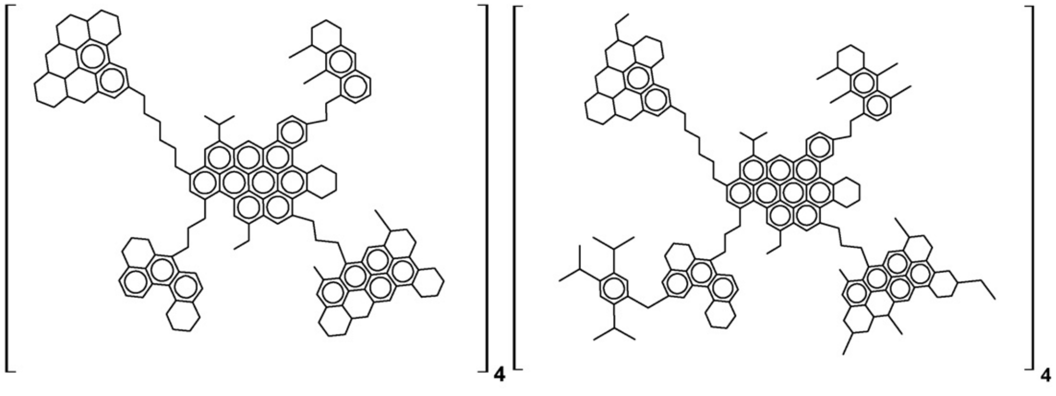
- C_{tr} is the number of cyclic (aromatic and naphthenic) carbons in those structures.
- C_{ai} is the number of internal aromatic carbons in those structures.
- P is the number of aliphatic chains branched on aromatic cycles.

Based on molecular weight information combined with elementary analysis and NMR results, the method gives a range of possibilities for those four main characteristics that facilitate further reconstruction [18]. It is then necessary to compare the detailed characteristics of the molecules obtained to elementary analysis and ^{13}C NMR results in order to select the most appropriate ones. In average, the number of heteroatoms per asphaltene unit at high conversion is far less than one. In order to simplify the reconstruction procedure, we therefore focused our effort on the overall hydrocarbon (C and H) structure of asphaltenes, without including heteroelements such as N, S, O, Ni and V.

The SAAH method was applied to the results obtained on asphaltene samples at residue conversion levels of 85, 74 and 56 wt.% in ebullated bed effluents and 48 wt.% in the fixed bed effluent. For asphaltene samples at lower conversion and in the feedstock, we simply imagined similar but larger molecules aggregates to account for the dissociation mechanism suggested by SEC results (see Fig. 4), while minimizing the number of similar molecules. The first important information provided by the SAAH method is that for the two highest conversion levels, the number of structures containing condensed aromatic cycles has to be equal to one in order to respect elementary analysis and ^{13}C NMR. Therefore, the number of molecules that match well with analytical results is limited. In Fig. 10, we represent the two types of hydrocarbon molecules that were found to reasonably match the analytical results. The two structures are very similar. We then chose one of them to reconstruct molecules at lower conversion. When conversion decreases, the aggregate size of asphaltenes increases and the number of possible molecules increases. We did not attempt to consider all possibilities (asphaltenes are too much polydispersed), but we focused our effort on



(a) X540°C^{+}=85 wt.% (b) X540°C^{+}=74 wt.% (c) X540°C^{+}=56 wt.% (d) X540°C^{+}=48 wt.%



(e) X540°C^{+}=28 wt.% (f) X540°C^{+}=0 wt.%

Fig. 11. Possible average molecular evolution of asphaltenes as a function of residue conversion X540 °C+.

molecules that could logically evolve with hydroconversion severity while respecting the main analytical results.

In order to assess the consistency of the results at high conversion, we checked the boiling point temperature of the reconstructed molecules at 85 wt.% conversion. In order to determine these temperatures, it has been necessary to use a group contribution method that was extrapolated towards larger polycyclic numbers [28,33]. Boiling point temperatures has been found in the range of 600–800 °C. This confirmed that those molecules can be found in the vacuum residue fraction.

The average molecules that may correspond to all conversion levels are shown in Fig. 11. Results of analytical work performed on all asphaltene samples as well as the characteristics of the average molecular structures obtained by reconstruction are reported in Table 3. Average molecular weights of reconstructed molecules are systematically lower than average analytical molecular weights, because we have not accounted for heteroatoms in the molecular reconstruction.

The molecular structure of unconverted asphaltenes obtained at the highest residue conversion level of 85 wt.% is highly polycondensed as shown in Figs. 10 and 11a. As discussed before, the reconstructed molecule consists of one structure containing nine condensed aromatic cycles linked to one naphthenic cycle and one paraffinic branch. When residue conversion decreases to 74 wt.%, it is necessary to add one aromatic cycle to the polycondensed structure and two short paraffinic branches, as shown in Fig. 11b.

At lower conversion, the SAAH method enables to get several polycondensed structures. Therefore, the number of possible molecules increases and the representations provided are then to be considered as examples among several possibilities. Based on the structure obtained at a conversion of 74 wt.%, we could match the analytical description of asphaltenes at 56 wt.% by adding two polycondensed structure of, respectively, two and three aromatic cycles on the main polycondensed structure (Fig. 11c). At a lower conversion of 48 wt.%, another polycondensed cycle of five aromatic cycles

Table 3
Analytical results and average molecular reconstruction characteristics

X540 °C+ (wt.%)	85		74		56		48		28		0	
	Exp	Model	Exp	Model	Exp	Model	Exp	Model	Exp	Model	Exp	Model
Molecular weight (SEC)												
Mw (g/mol)	492	470	617	576	1135	1072	1574	1498	8645	7944	10,325	9280
Elementary Analysis												
C (wt.%)	90.48		89.18		86.14		87.65		85.00		82.06	
H (wt.%)	5.30		5.68		6.39		6.50		6.91		7.12	
N (wt.%)	1.18		1.28		1.31		1.21		1.12		1.08	
O (wt.%)	0.97		0.99		0.88		0.91		0.74		1.03	
S (wt.%)	1.38		2.45		5.50		3.22		5.90		8.12	
C (Nb atoms/molecule)	37.1	37	45.9	45	81.5	83	115.0	116	612.4	612.0	706.1	708
H (Nb atoms/molecule)	26.1	26	35.0	36	72.5	76	102.3	106	597.4	600.0	735.1	784
N (Nb atoms/molecule)	0.4		0.6		1.1		1.4		6.9		8.0	
O (Nb atoms/molecule)	0.3		0.4		0.6		0.9		4.0		6.6	
S (Nb atoms/molecule)	0.2		0.5		1.9		1.6		15.9		26.1	
^{13}C NMR												
C ali total (wt.%)	18.6		24.8		31.7		33.3		42		46.8	
CH$_3$ (wt.%)	5.2		8.5		8.5		8.5		3		12.6	
CH$_2$ (wt.%)	11.7		16.4		18.1		19.9		27		27.6	
CH (wt.%)	1.7		0		5.1		4.9		11		6.6	
Cq (wt.%)	0		0		0		0		0		0	
C aro total (wt.%)	81.4		75.2		68.3		66.7		58		53.2	
CH (wt.%)	29.6		28.1		19.8		20		15		11.4	
Cq (wt.%)	51.8		47.1		48.4		46.6		44		41.8	
Cq sub (wt.%)	15		14.4		18.6		20.4		21		19	
Cq cond (wt.%)	36.8		32.7		29.9		26.2		23		22.8	
C ali total (Nb C/molecule)	6.9	7	11.4	11	25.8	25	38.3	38	257.2	260	330.4	332
CH$_3$ (Nb C/molecule)	1.9	2	3.9	4	6.9	8	9.8	10	18.4	28	89.0	76
CH$_2$ (Nb C/molecule)	4.3	4	7.5	6	14.7	15	22.9	24	165.3	192	194.9	192
CH (Nb C/molecule)	0.6	1	0.0	1	4.2	2	5.6	4	67.4	36	46.6	64
Cq (Nb C/molecule)	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0
C aro total (Nb C/molecule)	30.2	30	34.5	34	55.6	58	76.7	78	355.2	352	375.6	376
CH (Nb C/molecule)	11.0	11	12.9	11	16.1	20	23.0	24	91.9	88	80.5	84
Cq (Nb C/molecule)	19.2	19	21.6	23	39.4	38	53.6	54	269.4	264	295.1	292
Cq sub (Nb C/molecule)	5.6	3	6.6	5	15.2	14	23.5	22	128.6	128	134.2	156
Cq cond (Nb C/molecule)	13.7	16	15.0	18	24.4	24	30.1	32	140.8	136	161.0	136

was further added to the main polycondensed structure (Fig. 11d).

When residue conversion further decreases, it is important to note that there is a very large increase of apparent asphaltene molecular weight. As discussed before, this may be explained by an association mechanism. We therefore propose to keep the structure obtained at 48 wt.% conversion, assuming that at lower residue conversion (28 wt.%) asphaltenes may be a combination of several of the molecules found at 48 wt.% conversion (Fig. 11e). We found that it is then reasonable to consider an association of four molecular units very similar to the hypothetic asphaltene species, if another polycondensed cycle consisting of two aromatic cycles and five naphthenic cycles is added to the base asphaltene structure. Very little change is then required to adjust the molecular structure of the asphaltenes in the unconverted feedstock (Fig. 11f).

We have to keep in mind that the number of possible molecules drastically increases with molecular weight, that the average molecular structure is supposed to describe a mixture of thousands of molecules and that heteroelements are not included in the present analysis. Furthermore, the molecular weight considered for the reconstruction method is only an estimate. Therefore, our objective is only to suggest a possible scheme of asphaltene conversion mechanism consistent with our observations.

The proposed evolution of asphaltenes as a function of conversion may therefore suggest that asphaltenes may be composed of an assembly of several average molecular units. To simplify reconstruction, we proposed similar reconstruction units. Each of these structures is composed of a main polyaromatic structure and several smaller polyaromatic structures. The conversion mechanism enables in the early stage mainly the dissociation of molecular unit aggregates, with limited cracking of adjacent smaller polyaromatic structures. Then at intermediate severity, in the range of 50 wt.% residue conversion, cracking of adjacent polyaromatic structures may govern the evolution of remaining asphaltene molecules. At higher conversion level, asphaltene evolution is more limited. Further dealkylation of aliphatic chains can explain the evolution toward more polycondensed aromatic cycles.

The asphaltene structures obtained are rather consistent with already published information [5–9]. The main polyaromatic structure is promoting molecular associations to form elementary particles, which further self-associate into colloidal aggregates governed by Van der Waals, Coulomb and repulsive interactions. This core asphaltene structure remains even at the highest residue conversion level, which explains stability issues of effluents in conversion processes. Smaller structures are found around the large central aromatic region, which will progressively crack from the main central region and move to the distillate fractions.

4. Conclusion

Asphaltene samples resulting from hydroconversion conducted in moderate conditions in a fixed bed process or in severe conditions in a ebullated bed process exhibit a continuous evolution with respect to the residue conversion that expresses the overall cracking severity. Based on the analytical characterization and SAAH reconstruction method, results suggest that asphaltene structures may change with increasing severity. Asphaltene species would first evolve through dissociation of molecular units, then through the cracking of small polycondensed structure to end up with dealkylation of aliphatic chains. Remaining asphaltene molecules at high conversion would mainly consist of a large polycondensed structure of several aromatic cycles.

To confirm these results, further investigations are needed. To obtain a high degree of structural information, experiments on a Fourier Transform Ion Cyclotron resonance mass spectrometer will be performed. With this very powerful technique of extremely high resolution, asphaltene structures may be resolved enabling assignment of chemical formulas [34,35].

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