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# Characterization of Asphaltenes from Brazilian Vacuum Residue Using Heptane–Toluene Mixtures

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Brazilian vacuum residue (VR) was separated into insoluble and soluble fractions using *n*-heptane–toluene mixtures (Heptol). Coking tests performed on the soluble fractions showed that asphaltenes vary in regard to the extent to which they form coke. VR asphaltenes were subfractionated into AS 0–10%, AS 10–20%, AS 20–30%, and AS 30–40% by stepwise extraction using Heptol. The AS 20–30% and AS 30–40% fractions had greater aromaticity and a higher proportion of quaternary aromatic carbons, as well as a larger unit size. These type II asphaltenes produced more coke than did type I asphaltenes, which consist of the AS 0–10% and AS 10–20% fractions.

## Introduction

Our increasing reliance on liquid fuels, coupled with the decrease in oil reserves, has provided the impetus for research into how alternative fuel sources, such as bitumen and petroleum residues, might be utilized. The primary means by which these sources are upgraded to distillate products are coking and catalytic hydroconversion. It is well-known that heavy oil and residues can contain significant amounts of asphaltene. Petroleum asphaltenes (AS) are the heaviest aromatic component of crude oil. They are responsible for the coke deposition that causes catalytic deactivation in the thermal and catalytic processing of petroleum residues.<sup>1–4</sup> These processes can be elucidated only through an improved understanding of asphaltene chemistry.

Asphaltenes are defined as that portion of crude oil that is insoluble in *n*-alkanes, such as *n*-heptane or *n*-pentane, but soluble in benzene or toluene. Although the literature abounds with data on asphaltenes, there is little information on the industrial process by which coke is formed from asphaltenes.

Calemma et al. observed that the thermal behavior of asphaltenes is controlled, to a large degree, by their molecular structure, particularly with respect to their reactivities and conversion yields.<sup>5</sup> For example, they found that sulfur functionalities have an important role in the thermal decomposition of asphaltenes. Conversely, Gray found that asphaltene content alone was

a poor predictor of performance in both catalytic cracking and coking; in these processes, the Conradson carbon residue (CCR) index provides a far more reliable predictor of the coke-forming tendencies.<sup>6</sup>

Rahimi and Gentzis established that the correlation between coke yield and the molecular weight of an asphaltene is far better than that of either microcarbon residues or the aromaticity of the different subcomponents.<sup>7</sup> In addition, they found that coke formation for asphaltenes derived from Cold Lake vacuum bottoms was dependent both on solvent type and on the asphaltene concentration. Both Miknis and Sato et al. studied oil shale pyrolysis and found that the aromatization reactions involved in coke formation occur not only between aromatic carbons but also with aliphatic carbons within the oil shale.<sup>8–10</sup> Wiehe postulated that the mechanism for coke formation during the thermolysis of petroleum residua involves liquid–liquid phase separation in the reacted asphaltenes to yield a phase that is poor in abstractable hydrogen.<sup>11</sup>

It is widely recognized that asphaltenes derived from different crude oil sources, or even from a single crude oil, can have vastly different properties, which, in turn, make it extremely difficult to elucidate the molecular structure of petroleum asphaltenes. One way to expedite asphaltene study is to fractionate these complex molecules into subfractions, given that the chemical characterization of asphaltenes and their subfractions is the key to understanding their nature and their properties and, hence, the processes involved in coke formation.

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Both chromatography<sup>7,12,13</sup> and differential precipitation<sup>14–22</sup> have been used for asphaltene fractionation. Rahimi separated asphaltenes into four subfractions, using a preparative silica column.<sup>7</sup> Kilpatrick et al. fractionated asphaltenes using heptane and toluene mixtures and observed that the more-polar, less-soluble fractions contributed the majority of species that were responsible for aggregation and that were most likely to cause problems, such as deposition within pipelines and in water-in-oil emulsion stabilization.<sup>15</sup> Subsequently, Kaminski et al. fractionated asphaltenes using mixtures of pentane and methylene chloride and found that the high-polarity fractions contained more metals and chlorine and had lower rates of dissolution than did the less-polar fractions.<sup>19</sup> Recently, Ostlund et al. observed that asphaltenes from different subfractions behaved differently during flocculation.<sup>22</sup> They concluded that the size, aromaticity, and molecular weight of asphaltenes are important factors in determining the tendency of asphaltenes to flocculate and that the concentration of heteroatoms was more or less the same within all asphaltene fractions.

Snape and Ladner produced a table to assist with the chemical characterization of asphaltenes; it shows the assignment of carbon atom types among pure compounds.<sup>23</sup> Netzel developed specific quantification procedures using a combination of <sup>13</sup>C NMR and distortionless enhancement by polarization transfer (DEPT) techniques to ascertain the distribution of aliphatic CH<sub>3</sub>, CH<sub>2</sub>, and CH, and aromatic CH and C groups.<sup>24</sup> Kotlyar et al. reported the results of <sup>13</sup>C NMR and DEPT analyses that distinguished eleven classes of aliphatic carbons in the maltene fraction of an oil sand bitumen.<sup>25</sup> Gray et al. classified aromatic carbon into 5 classes, and aliphatic carbon into 10 classes.<sup>26</sup> In an attempt to derive more-precise structural analytical results, we have undertaken a detailed examination of the carbon spectral region shown in Table 1. This combines the regions analyzed by Gray et al.; however, it has been modified, following Kotlyar et al., to include the isoalkyl group, observed at 37.3–32.7 ppm.

The object of this work was to examine the conversion to coke of asphaltene subfractions separated from

**Table 1. Chemical Shifts of Proton and Carbon Regions**

area	chemical shift (ppm)	symbol	type
<sup>1</sup> H NMR			
Ha	10.7–6.2	H <sub>a</sub>	hydrogen bonded to aromatic carbons
Hp1	4.3–2	H <sub>α</sub>	hydrogen bonded to aliphatic carbons in the α-position on an aromatic ring
Hp2	2–1.09	H <sub>β</sub>	hydrogen bonded to aliphatic carbons in the β-position on an aromatic ring
Hp3	1.09–0.5	H <sub>γ</sub>	hydrogen bonded to aliphatic carbons in the γ-position or greater on an aromatic ring
<sup>13</sup> C NMR			
CA1	190–170		oxygenated
CA2	170–129		quaternary aromatic
CA3	129–126.4		aromatic CH
CA4	126.4–115.5		aromatic CH + bridged carbon shared with three aromatic rings
CA5	115.5–100		olefinic CH <sub>2</sub>
CP1	70–37.3		aliphatic CH <sub>2</sub>
			aliphatic CH
CP2	37.3–32.7		isoalkyl CH
CP3	32.7–30.8		CH <sub>2</sub> from third to terminal CH <sub>3</sub> in a long chain (C > 5)
			CH <sub>2</sub> in Et to aromatic
CP4	30.8–28.5		fourth CH <sub>2</sub> from the terminal CH <sub>3</sub> in a long chain (C > 5)
			CH <sub>2</sub> in Et to aromatic
CP5	28.5–25		naphthenic CH <sub>2</sub>
CP6	25–21.9		naphthenic CH <sub>2</sub>
			CH <sub>3</sub> next to aromatic C
			CH <sub>2</sub> next to the terminal CH <sub>3</sub> in a long chain (C > 5)
CP7	21.9–17.6		CH <sub>3</sub> next to aromatic C
CP8	17.6–14.7		terminal CH <sub>3</sub> in aromatic ethyl
CP9	14.7–12.3		terminal CH <sub>3</sub> in a long chain (C > 5)
CP10	12.3–0		terminal CH <sub>3</sub> in branched ethyl

**Table 2. Properties of Brazilian Vacuum Residue**

property	value
elemental analysis (wt %)	
C	87.2
H	10.6
N	0.69
S	0.98
O, by difference	0.53
H/C ratio	1.45
metals content (ppm)	
V	73
Ni	59
aromaticity, fa	0.29
molecular weight	935
asphaltene content (wt %)	14.2

Brazilian vacuum residue using *n*-heptane and toluene mixtures (Heptol) under normal processing conditions. The different asphaltene subfractions were characterized using elemental analysis, gel permeation chromatography (GPC), NMR, and microcarbon residue (MCR) analysis in an attempt to establish a correlation between asphaltene structure and coke formation.

## Experimental Section

**Sample Preparation.** The main properties of the vacuum residue (VR) from Brazilian crude oil used in this study are shown in Table 2. Approximately 3 g of VR were dissolved in 3 mL of toluene in a 1000-mL flask. A 40-fold excess of solvent, based on the amount of VR and toluene, was added and stirred under reflux for >2 h before being allowed to stand overnight. Mixtures of *n*-heptane and toluene were used as solvents with the toluene content in the Heptol ranging from 0 vol % to 60 vol %.

After standing, the mixture was centrifuged at 15000 rpm and the cake washed with *n*-heptane before being vacuum-dried to yield the insoluble fraction. The solvent was removed

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from the Heptol-soluble portion by rotary evaporation at 60 °C, followed by vacuum-drying to give the soluble (maltene + some asphaltene) fraction. These soluble fractions were used in the coking test.

To clarify the properties of the asphaltene, the VR asphaltene was fractionated into AS 0–10%, AS 10–20%, AS 20–30%, and AS 30–40% fractions via stepwise Heptol extraction, where AS 30–40% is taken as being equivalent to AS 30–100%.

**Coking Test.** Coking experiments were undertaken in batches using 18-mL quartz tubes. They allowed the reactant, which consisted of soluble fractions in Decalin solvent at a concentration of 35 wt %, to be placed in and removed from the autoclave without loss. The tube was loaded with 3 g of reactant, placed in a 50-mL autoclave, and pressurized with nitrogen to 1 MPa. The autoclave was then heated in an oven at 430 °C for 1 h while being agitated at a rate of 30 times per minute. It was then cooled to room temperature, the reactor was vented, and the gas was analyzed using GC. The liquid product was washed with 40 parts of toluene and left standing overnight. The toluene-insoluble product (coke) was separated using a centrifuge and the cake was washed with additional toluene. The toluene-insoluble solids were vacuum-dried at 60 °C overnight and weighed to provide the coke yield. The toluene was removed from the filtrate by rotary evaporation, and then vacuum-dried at 60 °C overnight to give the oil yield.

**Structural Analysis.** The asphaltene chemical structure was calculated using the Excel spreadsheet procedure of Sato<sup>27,28</sup> and the methodology of Brown–Ladner. In this procedure, <sup>1</sup>H and <sup>13</sup>C NMR analyses are essential to assign the H and C atom locations within the heavy molecule. Hydrogens are usually classified into aromatic hydrogen (H<sub>a</sub>), hydrogens bonded to aliphatic carbons in the  $\alpha$  position of an aromatic ring (H <sub>$\alpha$</sub> ), hydrogens attached to methyl groups in long side chains (H <sub>$\gamma$</sub> ), and other aliphatic and naphthenic hydrogens (H <sub>$\beta$</sub> ).

NMR analyses were performed using a JEOL model Lambda 500 spectrometer. Samples were prepared for <sup>1</sup>H NMR by mixing 10 mg of sample with 700  $\mu$ L of deuteriochloroform (CDCl<sub>3</sub>). Samples for <sup>13</sup>C NMR were prepared by dissolving ~100 mg of sample in 700  $\mu$ L of CDCl<sub>3</sub>. Two types of pulse sequences were used with the <sup>13</sup>C NMR analysis. One was an inverse gated decoupling system (NNE, pulse width of 4.85  $\mu$ s, acquisition time of 0.967 s, pulse delay of 7 s). The resulting spectrum was the product of 9000 scans. The other pulse sequence was a DEPT pulse sequence in which the signals of quaternary carbons were suppressed to quantify protonated aromatic carbons. DEPT spectra were collected at flip angles of 135° and 45° and a pulse delay of 3 s. The other conditions were same as those for NNE.

The average molecular weight of the asphaltene subfractions was determined using a GPC system (JASCO) fitted with a KF403HQ Shodex column (exclusive limit: 70,000) and an evaporative laser scattering detector (ELSD). Chloroform was the elution solvent, and polystyrene was used as the calibration standard for the molecular weight.

MCR determinations were performed using ASTM Standard D-189.

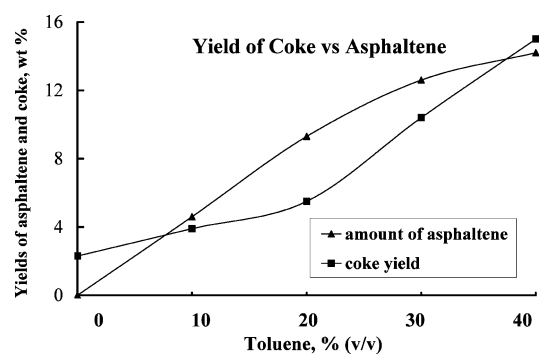
## Results and Discussion

**Coking Tests with Heptol-Soluble Fractions.** The results of the separation of the Brazilian vacuum residue (VR) into insoluble (asphaltene) and soluble (maltene + asphaltene soluble in Heptol) fractions, using Heptol extraction, are shown in Table 3. The yield of asphaltene decreased as the proportion of toluene in

**Table 3. Distribution of the Yields of Asphaltenes Obtained by Heptol Extraction**

toluene content in Heptol (vol %)	Insolubles Yield (wt %)		solubles yield (wt %)	AS content in the MA <sup>c</sup> (wt %)
	VR <sup>a</sup>	TA <sup>b</sup>		
0	14.2 (AS 0%)	100.0	85.8 (MA 0%)	0
10	10.1 (AS 10%)	71.1	90.9 (MA 10%)	4.5
20	5.4 (AS 20%)	38.0	94.6 (MA 20%)	9.3
30	1.8 (AS 30%)	12.7	98.2 (MA 30%)	12.6
40	0.1 (AS 40%)	0.70	99 (MA 40%)	14.2
60	0 (AS 60%)	0	100 (MA 60%)	14.2

<sup>a</sup> Based on vacuum residue. <sup>b</sup> Based on total asphaltenes. <sup>c</sup> MA = maltene + asphaltene.



**Figure 1.** Correlation between coke yield and asphaltene in the feed.

the Heptol increased. When the toluene proportion increased to 60 vol %, the asphaltene dissolved completely, yielding no residue. With ~40 vol % toluene in the Heptol, the insoluble portion proved to be negligible. Consequently, the fractions separated in Heptol with 0–30% toluene were used in the subsequent investigations.

The results of coking tests performed on these soluble fractions are shown in Figure 1. All experiments were performed in triplicate. The standard deviation ( $\sigma$ ) of the results was within 3%.

A high content of asphaltene in the feed has a tendency to give a high coke yield, and several investigators have reported a linear correlation between coke yield and asphaltene content.<sup>1,29,30</sup> However, our results show that an increase in the asphaltene concentration in the fractions from 0 (neat maltene), to 9.3 wt % produced an increase in coke yield of only 3.2 wt % (from 2.3 wt % to 5.5 wt %); i.e., only one-third of the asphaltene was converted to coke (see Figure 1). In the fractions soluble in Heptol with 20% toluene, the coke yield increased significantly, from 5.5 to 10.4 wt %, although the asphaltene content increased by only 3.3 wt %. In other words, the increase in coke was almost twice the increase in asphaltene. Presumably, different asphaltene fractions react differently during coke formation; the properties of asphaltenes soluble in Heptol with 0–20% toluene differ from those soluble in Heptol with 20–40% toluene.

These coke formation results are similar to those obtained by Rahimi, who found that, at high asphaltene concentrations, the yield of coke was much higher than

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**Table 4. Results of Coking Tests for Different Asphaltene Fractions**

solvent	coke (wt %)	asphaltenes (wt %)
AS 0–20%, 1 g, 430 °C, 1 h		
decalin	34.6	9.7
1-MN	36.5	7.5
quinoline	34.0	13.6
AS 20%, 1 g, 430 °C, 1 h		
decalin	49.3	7.7
1-MN	49.9	9.5
quinoline	45.8	15.5

expected.<sup>31</sup> He offered no explanation for this result, although it could result from several factors, the most important being differences between the asphaltenes in the different fractions. Kilpatrick observed that the less-soluble asphaltenes contribute most of the species responsible for aggregation,<sup>15</sup> whereas Wiehe noted that heptane-soluble maltenes inhibit coke formation by asphaltene.<sup>11</sup> When the ratio of asphaltene to maltene in the feed is small, the conversion of the asphaltene to coke is lower than that at higher ratios, because of the influence of abstractable hydrogen.

To confirm the differing responses of the different asphaltene subfractions, the original asphaltene was separated into two fractions—AS 0–20% and AS 20–40%—using Heptol with 20% toluene and the coking tests were repeated on each fraction using Decalin, 1-methylnaphthalene (1-MN), and quinoline as solvents. The results shown in Table 4 indicate that AS 0–20% yields 34.6 wt % coke and AS 20–40% yields almost 50 wt % coke, regardless of whether the solvent is Decalin or quinoline. Not only does the amount of coke produced differ, but the hardness of the product also differs. The coke derived from AS 0–20% is much softer than that from AS 20–40%. These results clearly show that the concentration of asphaltene is not the sole factor in determining the extent of coking; the subfractions of Brazilian VR asphaltene possess different properties that affect coke formation differently.

**Properties of the Subfractionated Asphaltenes.** Further subfractionation of VR asphaltene into AS 0–10%, AS 10–20%, AS 20–30%, and AS 30–40% was undertaken using stepwise Heptol extraction, to obtain more-detailed structural information on the asphaltenes. Each subfraction was analyzed and the elemental, GPC, MCR, and NMR results are given in Table 5.

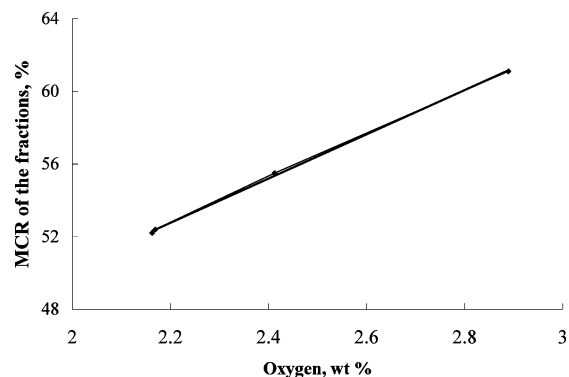
In passing from the AS 0–10% to AS 30–40% subfractions, the hydrogen content decreased, whereas the nitrogen and sulfur contents increased (i.e., the less-soluble fractions contain more heteroatoms; this is a result that is consistent with those of previous workers).

The average molecular weight (Mn) of the subfractions is in the range of 690–810 Daltons, and there is a slight increase in Mn from AS 0–10% to AS 20–30%, although other researchers have found quite different molecular weights for the different subfractions. For example, Anderson et al. used VPO to determine the molecular weight and found that it increased from 7000 to 13 000 across the subfractions.<sup>18</sup> As Gray stated, one of the more-contentious issues in the study of asphalt-

**Table 5. Properties of Brazilian Vacuum Residue Asphaltenes**

property	Value				
	total AS	AS 0–10%	AS 10–20%	AS 20–30%	AS 30–40%
recovery (wt %)	14.2	4.1	4.7	3.6	1.8
elemental analysis (wt %)					
C	87.5	87.0	87.1	86.8	86.6
H	8.29	8.38	8.22	8.07	7.91
N	1.31	1.27	1.30	1.34	1.35
S	1.26	1.21	1.24	1.33	1.26
O	1.67	2.16	2.17	2.41	2.89
H/C	1.13	1.15	1.13	1.11	1.09
Mn (GPC)	691	743	748	806	758
microcarbon residue, MCR (wt %)	52.5	52.2	52.4	55.5	61.1
NMR analysis (%)					
<sup>1</sup> H NMR					
H <sub>a</sub>	10.5	10.5	10.5	10.7	9.9
H <sub>α</sub>	16.7	17.4	18.5	17.7	19.9
H <sub>β</sub>	51.6	53.9	54.0	52.8	53.4
H <sub>γ</sub>	21.2	18.2	17.0	18.9	16.8
<sup>13</sup> C NMR					
aromaticity, fa	49	46	47	50	52
outer QAC <sup>a</sup>	25	22	22	25	25
total QAC <sup>a</sup>	37	37	39	40	42
distribution of non-aromatic carbons					
CH	10	10	9	7	7
CH <sub>2</sub>	31	34	33	32	31
CH <sub>3</sub>	9	10	11	11	10

<sup>a</sup> QAC = quaternary aromatic carbon.

**Figure 2.** Correlation between microcarbon residue (MCR) and oxygen contents of asphaltene subfractions.

enes is the determination of their true molecular weight.<sup>6</sup>

The microcarbon residues (MCRs) of the different asphaltene fractions increased from 52.2 wt % for AS 0–10% to 61.1 wt % for AS 30–40%, i.e., MCR increases among asphaltene fractions as their solubility in Heptol decreases. There was a good correlation between the MCR and oxygen contents among the subfractions (Figure 2). Although MCR has been proposed as a useful predictor of the coke-forming tendency of an asphaltene,<sup>6</sup> there was no significant difference in the MCR values among our subfractions that could be related to their ability to yield coke. The amount of coke produced during an MCR test is significantly larger than that in coking tests. This presumably occurs because (i) the reaction temperature of the MCR test is significantly higher than that used in the coking test and (ii) solvents are present in the coking test but absent in the MCR test.

Table 5 also shows the proton distributions of the subfractions. Of the subfractions, the aromatic proton

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Table 6. Structural Parameters of Brazilian Vacuum Residue Asphaltenes

sample name	AS 0–10%		AS 10–20%		AS 10–20%	AS 30–40%
	molecule	unit	molecule	unit	molecule	molecule
number of fused ring units	1.2	1	1.1	1	1	1
total carbons	54.8	45	55.3	50	59	56
total hydrogens	62.7	52	62.0	56	66	60
aromatic carbons	27.2	22	28.5	26	32	30
terminal CH <sub>3</sub>	0.9	1	1.0	1	1	1
branched CH <sub>3</sub>	2.8	2	2.5	2	3	3
$\beta$ -CH <sub>3</sub>	0.7	1	0.7	1	1	1
$\alpha$ -CH <sub>3</sub>	0.7	1	1.3	1	1	1
number of internal aromatic carbons	12.8	10	14.3	12	18	16
number of parafinic chains on Ra	2.8	2	3.1	3	4	3
number of parafinic chains	5.2	4	5.2	5	5	5
number of ring carbons in fused ring unit	36.0	32	37.9	33	35	38
total number of rings (Rn)	10.9	9	11.1	10	11	12
number of aromatic rings (Ra)	7.6	6	8.3	7	10	9
number of naphthenic rings (Rn)	3.3	3	2.8	3	1	3
number of naphthenic rings attached to the Ra ring	3.0	3	2.6	3	1	3
number of peripheral aromatic carbons	14.4	12	14.2	14	14	14
number of aromatic tertiary carbons	7.0	6	6.8	7	8	7
number of quaternary aromatic carbons	19.8	16	21.1	19	24	23

content (H<sub>a</sub>) is ~10%, H<sub>α</sub> = 16–20 wt %, H<sub>β</sub> = 51–54 wt %, and H<sub>γ</sub> = 18.2–16.8 wt %. There was no regular pattern in the differences among these data.

The aromaticity (fa) of the asphaltene subfractions increased as the asphaltene solubility decreased, i.e., AS 20–30% and AS 30–40% have a higher aromaticity (fa = 0.50–0.52) than the other fractions (fa = 0.46–0.49). These results are similar to those of the Pendant–Core model,<sup>32</sup> which predicted that molecules with high fa values or high MCR contents produce greater amounts of coke.

Subfractions AS 20–30% and AS 30%–40% also possess the highest percentage of quaternary aromatic carbon (QAC), ~40–42 wt %, with AS 0–10% and AS 10–20% having 37–39 wt % QAC. The distribution of nonaromatic carbons shows that the numbers of CH and CH<sub>2</sub> groups decreased slightly from AS 0–10% to AS 30–40%, whereas the CH<sub>3</sub> content was similar in all the subfractions.

The elemental analytical results, along with those of the coking tests, NMR, and GPC, indicate that the main difference in coking behavior between the subfractions mainly results from differences in the fa value and QACs present in the subfractions.

**Structural Analysis.** The structural parameters calculated using the spreadsheet program are shown in Table 6. These show that AS 0–10% and AS 10–20% have 6–7 fused aromatic rings per unit, whereas AS 20–30% and AS 30–40% have 9–10 fused aromatic rings per unit. All the subfractions have three naphthenic rings, except for AS 20–30%, which has just one naphthenic ring. Although both AS 20–30% and AS 30–40% have the same aromaticity, the latter has larger molecules, which form stronger aggregates, because of the greater opportunities to form C–C bonds during pyrolysis than those with smaller aromatic-ring systems. Therefore, MCR or coke formation differs between subfractions with same aromaticity or elemental distributions. A greater understanding of this situation may be obtained from molecular dynamics simulations.

The properties of the separated asphaltene subfractions can be summarized as follows:

molecular weight: AS 0–10%  $\approx$  AS 10–20%  $\approx$   
AS 20–30%  $\approx$  AS 30–40%

unit weight: AS 0–10%  $\leq$  AS 10–20%  $<$  AS 20–  
30%  $\approx$  AS 30–40%

fa: AS 0–10%  $\approx$  AS 10–20%  $<$  AS 20–30%  $\leq$   
AS 30–40%

Rn/unit: AS 0–10%  $\leq$  AS 10–20%  $\leq$  AS 20–30%  $\leq$   
AS 30–40%

Ra/unit: AS 0–10%  $\leq$  AS 10–20%  $<$  AS 20–30%  $\geq$   
AS 30–40%

MCR: AS 0–10%  $\approx$  AS 10–20%  $<$  AS 20–30%  $<$   
AS 30–40%

Clearly, the properties of the AS 0–10% and AS 10–20% fractions differ from those of AS 20–30% and AS 30–40%. To this end, we classified AS 0–10% and AS 10–20% as type I asphaltenes and AS 20–30% and AS 30% as type II asphaltenes.

Type I asphaltenes produce less coke than type II asphaltenes. The difference between the two types mainly results from differences in unit size, such as the number of aromatic rings (Ra), the number of aromatic carbons present (particularly, internal aromatic carbons), and the number of QACs per unit.

### Summary

Brazilian vacuum residue (VR) was separated into insoluble and soluble fractions, using *n*-heptane–toluene mixtures (Heptol). Coking tests using the separated soluble fractions showed that the yield of the coke increased by 3.2 wt % (from 2.3 wt % to 5.5 wt %) as the asphaltene concentration increased from 0 (neat maltene) to 9.3 wt %; i.e., one-third of the asphaltene was converted to the coke. In the fraction that was soluble in Heptol with 20% toluene, the coke yield increased significantly, from 5.5 wt % to 10.4 wt %, although the asphaltene content increased by just 3.3 wt %; i.e., the increase in coke was almost twice the increase in asphaltene. These data show that the

asphaltene fractions have different reactivities for coke formation.

AS 20–30% and AS 30–40% have a higher aromaticity, more quaternary aromatic carbons, and a bigger unit size, as well as produce more coke than do AS 0–10% and AS 10–20%. AS 0–10% and AS 10–20% are defined as type I asphaltenes and AS 20–30% and AS 30–40% are defined as type II asphaltenes.

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