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The Influence of the Cut Temperature on Asphaltenics Fractions

Chrisman*, Erika.C.A.N.; Lima, Viviane.S.
University Federal of Rio de Janeiro, Department of Organics Processes, School of Chemistry.
Av. Horacio Macedo 2030, CT – Bloco E – sala 204 – CEP 21949-900 Rio de Janeiro, RJ, Brazil, *enunes@eq.ufrj.br

Petroleum suffers a series of processes in the refineries in order to elevate its potential of energy, since in its gross state it presents little applications. Most of these processes involve heating, as distillation that is a physical process of separation, based on the difference of the boiling points of the substances present in a mixture (Abadie, 2003). To elevate the value of the petroleum, it is necessary to obtain some fractions that grow exponentially with the temperature of cut (Leon et al, 2000). As the chemical composition of petroleum is much complex, it is interesting to evaluate the possible molecular transformations that can happen in those fractions along the separation processes. Temperature variations, pressure and chemical composition can cause some problems like the precipitation of the asphaltenes of the crude oil. The precipitation and the consequent deposition of the asphaltenes can cause problems in almost all the stages of the production, of the processing and of the transport of petroleum generating great economical impact (Leon et al, 2001). The knowledge on the molecular structure of the asphaltenes is fundamental for the development of treatments and chemical products, which are necessary to avoid its precipitation (Mullins et al, 2003). In this study, the aim was at identifying the differences observed in the structures of these asphaltenics fractions during the simulation of the atmospheric distillation in a laboratory, in 5 different temperatures. The asphaltenes were extracted from atmospheric residues of two Brazilian oils using ASTM 6560-00. Significant changes were observed in the structures of each one of the asphaltenics fractions obtained, mainly in the higher cut temperatures like 420ºC. The polarity of substance was also important in the transformations observed and in the stability of oil-water emulsion.

1. Introduction

In its gross state, the petroleum has little applications, almost serving that only as combustible oil. So that the energy potential of the petroleum is taken advantage of to the maximum, he should be submitted to a series of processes (Abadie, 2003). The

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refine is a group of processes in which the petroleum is submitted, in order to obtain several derived, indispensable to the modern man's life, among the ones which the more acquaintances are: the liquefied gas (GLP), gasoline, naphta, oil diesel. The distillation is a physical process of separation, based on the difference of the points of ebullition of the present substances in a mixture. To elevate the energy value of the petroleum, it is necessary to accomplish cut of denominated characteristic ebullition strips of fractions. The heaviest fractions, that they cannot be vaporized in the column, are removed in the fund of this, under the form of atmospheric residue (RAT) or raw reduced, and they will be further on separate in the distillation to vacuous. As those fractions grow exponentially with the cut of temperature (Leon et al, 2000), becomes interesting to evaluate the possible molecular transformations that can happen in those fractions along the separation processes. The petroleum can be defined with relationship to its chemical composition, as a complex mixture of natural occurrence, constituted predominantly of hydrocarbons and others fractions like asphaltene that causes serious precipitation problems, from its obtaining to refine it (Carvalho, 2003). The asphaltenes has many numbers of aromatic nucleus and the largest molecular mass (Leon et al, 2001), insoluble in aliphatics hydrocarbons, such as n-heptane or n-pentane and soluble in aromatic hydrocarbons as the toluene (Yasar et al, 2007; Trejo e Ancheyta, 2007; Kilpatrick et al, 2003; Speight et al, 1994). The asphaltenes are composed by rings aromatics condensed, chains aliphatics, rings naphtenics, nitrogen, oxygen and sulfur and metals like nickel and vanadium (Mullins et al, 2003; Ancheyta et al 2004; Murgich, 2002 e Sheu, 2002). Temperature variations, pressure and chemical composition can cause the precipitation of the asphaltenes of the raw oil causing extremely serious problem that affects the costs of the industry of the petroleum significantly (Duda e Lira-Galeana, 2006; Trejo et al, 2007). The need of the knowledge of the molecular structure of the asphaltenes is fundamental for the development of treatments and chemical products that are necessary to avoid its precipitation (Mullins et al, 2003). Have an enormous effort of the chemists to characterize the asphaltenes in terms of the present chemical structures in that complex mixture in order to facilitate the understanding of its properties and assistant in the development of methodologies that impede its precipitation. In this work, the main focus went verify during the process of refine of the petroleum, more specifically the atmospheric distillation, the exhibition to differentiated temperatures of court, promotes significant alterations in the composition of the asphaltenic fraction obtained of the atmospheric residues.

2. Experimental Section

The first part involved the obtaining of atmospheric residues of two different Brazilian oils entitled A and B, that were submitted to 5 procedures of cut with different temperatures. The second part involved the application of the methodology ASTM 6560-00 for extraction and quantification of the asphaltenes of each one of the oils and of its different cut residues. A third stage of characterization of the asphaltenes, where the techniques of elementary analysis and RMN of ^{1}H and ^{13}C were used. Finally, all the results obtained were analyzed to establish the correlations between the cut temperatures and assistant in the proposition of some structures of medium minimum molecules possibly presents in the studied fractions.

3. Results and Discussion

3.1 Results of Cut

In the Table 01 the results of the value of each Residues of cut temperature are presented for the two oils tested.

Table 01. Values of the Results of (%mm) of the Residues of Cut obtained to leave of the oils A e B.

Temperature of Cut (ºC)	Residue (% m/m)	
	Oil A	Oil B
270	90,60 ± 1,08	84,35 ± 0,24
300	89,45 ± 0,11	83,88 ± 0,17
320	86,39 ± 0,53	83,55 ± 0,18
390	76,59 ± 1,09	72,75 ± 0,42
420	59,21 ± 5,67	63,76 ± 3,15

With base in the results of the Table 01, it is verified that there is a decrease in the value of the cut residue with the increase of the temperature. That decrease can be justified by the increase of the light fraction. It is important to observe that until the temperature of 320ºC there was not significant variation in the % of residue so much for oil A as for B. However, starting from this temperature, it is noticed a considerable decrease in the % of residue of the two oils, being more accentuated in the oil A.

3.2 Asphaltenes Quantity

The asphaltenes was extracted using ASTM 6560-00 of the raw oils and of the coming residues of the cuts, resulting in 12 asphaltenes (6 of each oil). The results of asphaltenes quantity obtained starting from the oils A and B and its respective residues of cut temperature are presented in the Table 02.

Table 02. Medium values of the asphaltenes obtained by ASTM 6560-00 for each residue of temperature of cut coming of the petroleum A and B.

Asphaltenes of the Oil A	Value of Asphaltene (%)	Asphaltenes of the Oil B	Value of Asphaltene (%)
ALOC (raw oil)	2,84 ± 0,00	ABOC (raw oil)	2,19 ± 0,11
ALRC1 (cut 270ºC)	2,98 ± 0,13	ABRC1 (cut 270ºC)	2,15 ± 0,14
ALRC2 (cut 300ºC)	3,09 ± 0,03	ABRC2 (cut 300ºC)	2,57 ± 0,01
ALRC3 (cut 320ºC)	2,09 ± 0,24	ABRC3 (cut 320ºC)	2,28 ± 0,07
ALRC4 (cut 390ºC)	2,85 ± 0,09	ABRC4 (cut 390ºC)	2,58 ± 0,12
ALRC5 (cut 420ºC)	4,17 ± 0,25	ABRC5 (cut 420ºC)	3,24 ± 0,01

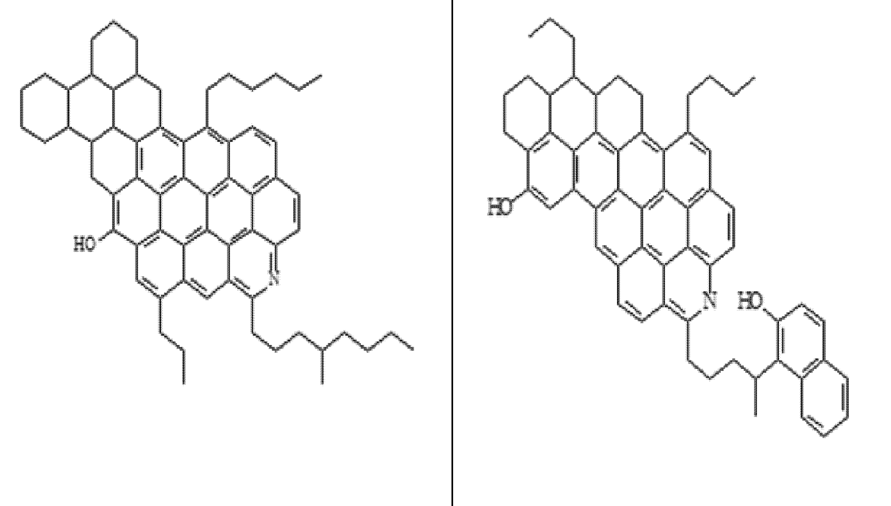
Being compared the results only when it is proceeded to the cut in the temperature of 420ºC it is that the asphaltenes quantity suffers a significant change in both oils. This considerable increase should be due to modifications in molecules of the asphaltene .

4. Proposition of Medium Minimum Structures

The proposition of structures involves the obtaining of a representative structure of a mixture, with base in the results obtained of value of asphaltenes and with the aid of used characterization techniques (RMN of ^{1}H e ^{13}C, elementary analysis). They are represented structure for the raw oil and for temperatures of cut of 420ºC for each petroleum.

4.1 Examples of Structures Minimum Averages of Asphaltenes for the Petroleum A and its RTC's.

In the Figure 01 are represented examples than it can have been happening along these processes and the changes by the increase of temperature.

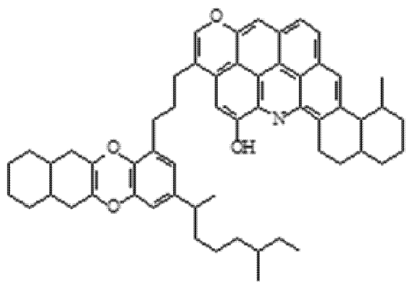


ALOC (Raw oil) **ALRC5 (420°C)**

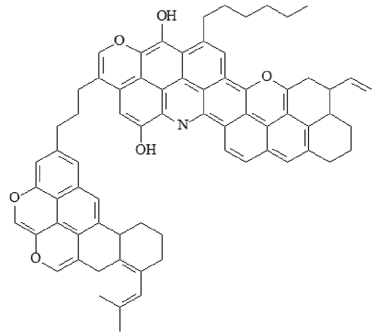
Figure 01. Structures of the asphaltenes ALOC (raw oil) and ALRC5 (420°C).

4.2 Examples of Structures Minimum Averages of Asphaltenes for the Petroleum B and its RTC´s.

For the asphaltenes of the petroleum B was observed significant changes in the structures in compared of petroleum A. The first important thing to observe is that the asphaltene of the oil B seems to have a primary structure very different from the oil A in spite of the similar numbers of total aromatic carbons. A quite significant difference is observed involving a smaller number of aromatic carbons in ring junction, what induces proposition of structure of the type archipelago (island) for the asphaltene of the petroleum B differently that the one of the petroleum A with continental structure. That difference can also explain other interesting plenty characteristics observed in the oils, as the retention of water and of metals for the petroleum B that it can be justified by the form of its structure, as that a " shell " that facilitates that the metals and water are walled for the structure proposal.



ABOC (Raw oil)



ABRC5 (420°C)

Figure 02. Structures of the asphaltenes ABOC (raw oil) and ABRC5 (420ºC) .

The modifications suggested for the asphaltene ABOC passing for the structure ABRC5 are also quite plausible and they involve the ciclization of lateral chains and the aromatization of naphtenics rings.

5. Conclusions

Both asphaltenes of the oil A and B showed significant variations in the value of asphaltene after cutting at 420ºC. It was observed that their aromatic structures were different. The asphaltene of oil A showing the aromatic structure in the continental form and the asphaltenes of the petroleum B in the archipelago form. The asphaltene B still has another very interesting feature. It features a larger amount of heteroatoms, fewer rings combined with lower linearity of them, hampering aggregation between its molecules. This may explain the difficulty encountered in the fall of the emulsion observed between petroleum B and water. Thus, we believe that this approach can be of great value to understanding the properties of this complex fraction.

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