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Abstract - In the extraction of the oil, it is mixed with water thus forming emulsions. The emulsions are found in almost all the stages of production and processing of the oil and in some cases is very difficult to be "broken". The presence of emulsifiers agents is one of the responsible factors for the stability of emulsions. Certain fractions of high point of boiling, such as the as phaltenes and resins, can be emulsifier's agents and to stabilize emulsions W/O. In some stages of refining, the oil suffers thermal treatments like the atmospheric distillation in order to separate the interest fractions. As the chemical composition of petroleum is much complex, it is interesting to evaluate the possible molecular transformations that can happen in those fractions as phaltenics. Temperature variations, pressure and chemical composition can cause some problems like the precipitation of the asphaltenes of the crude oil. In this work, the aim of is to evaluate if the effect of conditions as, for example, ambient temperature, presence of light and humidity can influence in the quantity of water and mainly in the structures of asphaltenes of two Brazilian oils, A and B, that were submitted for a period of stockage of two years in not inert atmosphere and the atmospheric pressure. Significant modifications had been observed in two oils principally in the amount of the asphaltenic fraction that can have the structural characteristics of the species contained in this fraction that can have action differentiated on emulsions water in oil.

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Modifications in Molecular Parameters of Asphaltenes of Two Brazilian Oils for Action of Stockage Time

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Abstract - In the extraction of the oil, it is mixed with water thus forming emulsions. The emulsions are found in almost all the stages of production and processing of the oil and in some cases is very difficult to be "broken". The presence of emulsifiers agents is one of the responsible factors for the stability of emulsions. Certain fractions of high point of boiling, such as the as phaltenes and resins, can be emulsifier's agents and to stabilize emulsions W/O. In some stages of refining, the oil suffers thermal treatments like the atmospheric distillation in order to separate the interest fractions. As the chemical composition of petroleum is much complex, it is interesting to evaluate the possible molecular transformations that can happen in those fractions as phaltenics. Temperature variations, pressure and chemical composition can cause some problems like the precipitation of the asphaltenes of the crude oil. In this work, the aim of is to evaluate if the effect of conditions as, for example, ambient temperature, presence of light and humidity can influence in the quantity of water and mainly in the structures of asphaltenes of two Brazilian oils, A and B, that were submitted for a period of stockage of two years in not inert atmosphere and the atmospheric pressure. Significant modifications had been observed in two oils principally in the amount of the asphaltenic fraction that can have the structural characteristics of the species contained in this fraction that can have action differentiated on emulsions water in oil.

I. INTRODUCTION

The oil can be defined as a complex mixture of natural occurrence, consisting predominantly of hydrocarbons and, in lesser amount, of sulphurates organic compounds, nitro genated, oxygenated and organometallics beyond inorganics impurities as salts and sediments. The main components of the oil are divided in four categories: saturated, aromatics, resins and as phaltenes. This classification is known for SARA that is a quantitative analysis of these fractions in the oil (Tissot and Welt, 1978; Speight, 2001; Wang et al, 2002). According to Gauthier et al (2008), as phaltenes consists of a heterogeneous mixture complex composed for condensed poliaromatics rings, aliphatic chains, naphthenic rings, heteroatom and metals as iron, nickel and vanadium. The as phaltenes are unque stionably

the fraction most complex of the oil. In variations of pressure, temperature or composition of oil, as phaltenes tend to associate and to precipitate causing some operational problems since the transport until the refining (Duda and Lira, 2006; Trejo et al, 2007). With passes of the years, it had a significant increase in studies about as phaltenes due the great discoveries of heavy oil reserves with low degree API (<20°) in Brazil (Montserrat, 2008). These oils heavy present a bigger presence of compounds as resins and as phaltenes (Merdrignac and Espinat, 2007). Another problem related with presence of as phaltenes in oil is its participation in emulsion stability. The oil is produced together with the water and it can be found in free form or emulsified form, generating a series of operational problems as blockage of separation equipment (Saudi Sunil and, 2005). In the oil are found emulsifying agents natural as as phaltenes, resins and wax. These species are accumulated in the interface oil-water forming a rigid interfacial film that prevents the coalescence and consequently stabilization of the drops in emulsion (Montserrat, 2008; Saudi Sunil and, 2005). When an emulsion ages, the stability increases due oxidation, loss of light fractions, precipitation of some components, and, mainly, greater accumulation of the natural surfactants in the interface, propitiating formation of more rigid interfacial films. With relation of all oil fractions, the molecular structure of as phaltenes is less understood (Trejo et al, 2007). Some researchers (Oak, 2003; Salazar et al, 1995; Speight, 1999) has concentrated its efforts in improving information regarding this mixture developing its knowledge on the involved chemical structures, characterizing the existing functions and establishing its behaviors front the solvents.

II. OBJECTIVE

The aim of this work is to evaluate if the effect of conditions as, for example, ambient temperature, presence of light and humidity can influence in the structures of as phaltenes of two Brazilian oils denominates A and B, that were submitted for a period of stockage of two years in not inert atmosphere and the atmospheric pressure.

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III. METHODOLOGY

The methodology of this work was divided in 5 parts. The first stage was quantification of water present in two oils for the method of Karl Fischer titration using a Metrohm Ltd. 831 KF. The second part involved the obtaining of atmospheric residues of two oils that were submitted to procedure of cut in 420 °C. The cut is an experiment recommended when it wants to quantify yield of as phaltenes in samples of oil with yields of light above 20% and with low yield of as phaltenes. The cut in laboratory scale is about a simple distillation, only with equipment lightly differentiated to guarantee the collect of the light fractions, to prevent losses and to allow the closing of balance of mass of the all process. The atmospheric residues were used, later, in determination of the yield of as phaltenes. A comment to be salient is that the cut was carried through to the atmospheric pressure and in duplicate. The third stage involved the extraction and quantification of as phaltenes from raw oils and of atmospheric residue following the norm based on ASTM 6560-00 standardized for the Institute of Petroleum of London. A fourth stage involved the characterization of as phaltenes, where the techniques of elementary analysis and NMR of ¹H and ¹³C were used. Finally, all the results obtained were analyzed and their molecular parameters were correlated to observe the differences promoted by the stockage time.

IV. RESULTS AND DISCUSSION

a) Water Content

Table 1 : Water Content

Year	Water Content (%)	
	Oil A	Oil B
2007	0,82 ± 0,05	12,65 ± 0,20
2009	0,39 ± 0,01	11,43 ± 0,08

Table 3 : Values of the as phaltenes obtained by ASTM 6560-00 for Oil A in 2007 and 2009

Temperature of Cut	Value of Asphaltene (%m/m) - OIL A	
	2007	2009
0 °C (raw oil)	2,85 ± 0,01	2,52 ± 0,04
420°C (residue of cut)	4,17 ± 0,25	3,08 ± 0,10

Average values of water content for crude oils A and B are shown in Table 1. Karl Fischer titrations confirm the presence of the biggest aqueous phase in oil B. For oils A and B, it is observed a decrease of water content in 2007 to 2009. For oil A, this decrease is bigger due the water to be in the free form and not emulsified as in oil B.

b) Results of Cut

With base in the results of the Table 2, it is verified that there is an increase in the value of the cut residue from 2007 to 2009 for two oils, being more accentuated in the oil A. That increase can be justified by loss of the light fraction during the time of stockage.

Table 2 : Values of Residue of cut in 420°C

Year	Residue (% m/m)	
	Oil A	Oil B
2007	59,21 ± 5,66	63,76 ± 3,15
2009	70,21 ± 2,31	70,59 ± 2,45

c) Asphaltene Quantity

The as phaltenes was extracted using ASTM 6560-00 of the raw oils and of the coming residues of the cuts gotten in 420°C. The results of as phaltenes quantity obtained starting from the oils A and B and its respective residues of cut temperature are presented in the Tables 3 and 4. Being compared the results only when it is preceded to the cut in the temperature of 420°C it is that the as phaltenes quantity suffers a significant change in both years, principally in the residue of the cut.

Table 4 : Values of the as phaltenes obtained by ASTM 6560-00 for Oil B in 2007 and 2009

Temperature of Cut	Value of Asphaltenes (%m/m) - OIL B	
	2007	2009
0 °C (raw oil)	2,19 ± 0,11	2,15 ± 0,11
420°C (residue of cut)	3,24 ± 0,01	2,42 ± 0,41

The difference between the values in 2007 to 2009 for the same type of product is not significant for the raw oils, probably by the initial homogeneity of each sample.

d) Elementary Analysis

In elementary analysis, % in m/m of C , H and N had been determined of each sample of asphaltene. The

sulphur quantity and of oxygen had been grouped and calculated as shown in the following Equation.

$$(S + O) = 100 - (C + H + N)$$

The Table 5 shows results of elementary analysis of oil A and its residue of cut obtained in the years 2007 and 2009.

Table 5 : Values of elementary analysis of oil A obtained in the years 2007 and 2009

Temperature of Cut	OIL A									
	C (%m/m)		H (%m/m)		N (%m/m)		S + O (%m/m)		Ratio of C/H	
	2007	2009	2007	2009	2007	2009	2007	2009	2007	2009
0 °C (raw oil)	87,0	86,7	7,9	7,8	1,9	1,1	3,2	4,4	0,9	0,9
420°C (residue of cut)	87,2	86,5	6,5	7,0	2,2	1,3	4,1	5,2	1,1	1,0

The ratio between amount of Carbon and Hydrogen (C/H) indicates that asphaltenes present characteristic values of heavy fractions, next to 1. Comparing results of years 2007 and 2009, it is observed a significant reduction in values of N and

consequently increase in amount (S + O). This fact can be decurrent of oxidation facilitated for the presence of heteroatom. The Table 6 shows results of elementary analysis of oil B and its residue of cut obtained in the years 2007 and 2009.

Table 6 : Values of elementary analysis of oil B obtained in the years 2007 and 2009

Temperature of Cut	OIL B									
	C (%m/m)		H (%m/m)		N (%m/m)		S + O (%m/m)		Ratio of C/H	
	2007	2009	2007	2009	2007	2009	2007	2009	2007	2009
0 °C (raw oil)	74,7	71,5	7,0	6,7	1,6	0,7	16,7	21,1	0,9	0,9
420°C (residue of cut)	66,0	70,5	5,3	5,8	1,5	0,7	27,2	23,0	1,0	1,0

Low values for % C and H are observed. An explanation for this fact is the presence in this oil, with bigger amount of water, metals and halogen, as for example, Ni, V, Sr, Ca, K, Na, Cl, among others, that are not burnt by technique of elementary analysis,

however are computed for final result given in percentage of total sample weighed. Calculating again the percentages of C and H abstaining contributions of metals and halogen, are gotten values well more coherent for as phaltenics fractions. Although these low

values, correlation C/H remains inside of indicative band for asphaltene. Also is observed a significant reduction in values of N and consequently increase in amount (S + O). This fact can be decurrent of oxidation facilitated for the presence of heteroatom.

e) *NMR*¹H

The nuclear magnetic resonance of ¹H and ¹³C was used for identification of different types of carbon

and hydrogen as basic source of information to allow the agreement of differences existing between as phaltenes of two oils submitted to thermal treatments. In Table 7, the results for molecular parameters obtained by NMR of ¹H for as phaltenes of oil A (years 2007 and 2009) are presented.

Table 7: Values of NMR ¹H of oil A obtained in the years 2007 and 2009

Molecular Parameters (%)	Oil A			
	Year 2007		Year 2009	
	0°C (Raw oil)	420°C (residue of cut)	0°C (Raw oil)	420°C (residue of cut)
Aromatic hydrogen (Har)	7,5	14,7	8,1	9,1
Saturated hydrogen (Hsat)	92,5	85,3	91,9	90,9
Alpha hydrogen (Hα)	16,5	20,1	18,6	22,0
Beta hydrogen (Hβ)	59,4	48,5	54,6	54,2
Gamma hydrogen (Hγ)	20,1	16,3	20,0	15,5

The molecular parameters change so much and inside the statistical error when are comparated the raw oil in 2007 and in 2009. Significant changes are observed when the comparison focus are the changes of the oil to residue in each time. The increase of Har of oil for residue is much more significant in 2007 that in 2009. This increase possibly that means, the aromatical part of as phaltenic fraction becomes less substituted due to loss of lateral chains or naphtenics ring opening; and/or that this aromatic part is increasing of size due to biggest ring number being formed by a possible oxidation of naphtenics rings or cyclization of lateral chains followed by oxidations. Analyzing the Hα, observes an increase in 420°C. This fact can be

explained by possible oxidation of naphtenics rings next to aromatical rings and/or cyclization to lateral chains. For the Hβ, is observed a reduction in 2007, what it can be explained by a possible loss or reduction in the length of lateral chain, arrangement differentiated of naphtenics rings next to aromatic rings, and/or cyclization of lateral chains followed oxidation of naphtenics. For the Hγ, is observed a reduction in 2007 and 2009, involving a possible cyclization of lateral chains with formation new naphtenics ring and/or elimination of aromatic part for breaking for temperature increase. In Table 8, the results for molecular parameters obtained by NMR of ¹H for as phaltenes of oil B (years 2007 and 2009) are presented.

Table 8: Values of NMR ¹H of oil A obtained in the years 2007 and 2009

Molecular Parameters (%)	Oil B			
	Year 2007		Year 2009	
	0°C (Raw oil)	420°C (residue of cut)	0°C (Raw oil)	420°C (residue of cut)
Aromatic hydrogen (Har)	9,4	11,9	7,4	10,6
Saturated hydrogen (Hsat)	90,6	82,7	92,6	89,4
Alpha hydrogen (Hα)	19,4	20,9	20,6	22,2
Beta hydrogen (Hβ)	55,4	47,2	56,2	51,9
Gamma hydrogen (Hγ)	19,8	14,6	17,4	19,2

For this oil B, the changes are also observed in the raw oil and the residue. The principal parameter is the aromatic hydrogen. The others molecular parameters changes like in the oil A. A reduction of Hsat from oil to residue most significant in 2007 is observed,

indicating bigger substitution of aromatic part. The increase of Har can be explained by sequence of cyclization lateral chain, resulting in new naphtenics rings and/or for an increase or break of length or ramification in lateral chains and naphtenics ring

oxidation with formation aromatic ring. For the H β , only observes a more significant reduction in 2007, that it can be explained by the same reasons cited in the case of oil A. For the H γ , is observed a reduction in 2007 but in 2009, this value increase. In this case, possible occur the increase of ramifications and lateral chains.

f) *RMN of ^{13}C*

The molecular parameters gotten by NMR ^{13}C for oils A and the B are presented in Tables 9 and 10.

Table 9 : Values of NMR ^{13}C of oil A obtained in the years 2007 and 2009

Molecular Parameters (%)	Oil A			
	Year 2007		Year 2009	
	0°C (Raw oil)	420°C (Residue of Cut)	0°C (Raw oil)	420°C (Residue of Cut)
Total Aromatical carbons (Car)	50,2	69,0	49,7	57,3
Saturated carbons Total (Csat)	49,8	31,0	50,3	42,7
Carbons Opening				
Aromatical carbon s linke d a lkil chains or heteroatom (Car-R/Het)	12,4	19,8	10,7	9,2
Aromatical carbons linked hydrogen (Car-H)	11,3	19,2	12,2	12,9
Aromatical carbons in ring junction (Car-J)	26,5	30,0	26,8	34,6
Substituted Aromatical carbons (Car-H+ Car-R/Het)	23,7	39,0	22,9	22,7

The raw oil changes so much when compared 2007 and 2009. The changes occur in the raw oil to residue in each case. An increase of Car is observed and reduction of Csat throughout of increase of temperature cut more significant in 2007, these data Confirm the results of Har and Hsat gotten in the NMR 1H . The value of quantity of Car-J suffers a more significant increase in 420°C in 2009 possible by the

formation of the increase of aromatic rings in the continental basic structure. This can be also confirmed by the results of Car-R/Het and Car-H+Car-R/Het that increase in 420°C, in 2007, what it can be decurrent of the same type of characteristic above, as well as for formation new naphtenics ring decurrent of cyclization of lateral chains but in 2009 is observed a significative reduction by possibly lost of lateral chains.

Table 10 : Values of NMR ^{13}C of oil B obtained in the years 2007 and 2009

Molecular Parameters (%)	Oil B			
	Year 2007		Year 2009	
	0°C (Raw oil)	420°C (Residue of Cut)	0°C (Raw oil)	420°C (Residue of Cut)
Total Aromatical carbons (Car)	50,5	60,7	48,7	59,6
Saturated carbons Total (Csat)	49,5	39,3	51,3	40,4
Carbons Opening				
Aromatical carbon s linke d a lkil chains or heteroatom (Car-R/Het)	13,9	13,9	8,3	10,7
Aromatical carbons linked hydrogen (Car-H)	14,0	16,6	11,2	14,9
Aromatical carbons in ring junction (Car-J)	22,6	30,2	29,2	34,0 ³
Substituted Aromatical carbons (Car-H+ Car-R/Het)	27,9	30,5	19,5	25,6

This result is the most important because more expressive changes are observed in the raw oils in 2007 to 2009. In all parameters the changes are significantly. An increase of Car is observed and reduction of Csat throughout of increase of temperature cut in two years, these data confirm the results of Har and Hsat gotten in the NMR ^1H . The value of quantity of Car-J suffers a more significant increase in 420°C in 2009. The values of Car-R/Het and Car-H+Car-R/Het decrease in 2009, what it can be possibly decurrent of oxidation and loss of lateral chains. In all cases the structures changes in the residue so significantly in comparison to the changes in the raw oil from the time.

V. CONCLUSION

With base in the results of cut, was verified that there is an increase in the value of the cut residue that can be justified by lost of the light fraction. The analysis of the quantity of as phaltene showed, for the first time, a surprise results, but with the analysis of molecular parameters in these fractions, we concluded that is very important this chemical focus to explain what happening. The oxidation and the changes in as phaltene structure is confirmed by the NMR and reforced the importance of the stock age type and time.

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