

INFLUENCE OF SULPHUR OVER THE DEVELOPMENT OF OPTICAL TEXTURES IN PETROLEUM VACUUM RESIDUALS AND THEIR FRACTIONS EXTRACTED WITH SOLVENTS

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Abstracts

The goal of this study is to observe the effect of the sulphur content and chemical composition of vacuum residual over the development of optical textures in petroleum coke from delayed coking. Three samples of vacuum residuals were characterized through elemental analysis and the C/H ratio. Subsequently, the samples were fractionated with Adsorption Chromatography assisted by Soxhlet (ACS) to collect five (5) fractions, which are defined by their solubility in selected solvents. The fractions and residuals were characterized using elemental analysis, $^1\text{H-NMR}$ and optical microscopy with heating plate (with a maximum temperature of 600°C). The microphotography attained through the latter analysis show the development of optical textures that are specific to each residual as well as to each fraction that constitute them. Such behaviour is strongly determined by the chemical reactivity of each fraction. Important differences are observed regarding the initial temperature for mesophase formation, resolidification temperature, quality of the optical texture formed: degree of development and optical texture type. $^1\text{H-NMR}$ and %S suggest that the content of S influences the condensation degree of the organic species present. In addition, it is observed that the temperature for mesophase formation decreases as the %S.

Key Words

Optical Texture, Thermal Conversion, Mesophase, Asphaltenes.

Introduction

The delayed coking is thermal process used in oil refineries to transform petroleum residues to a liquid products and gases; during the process one forms a solid by-product, rich in carbon, known as petroleum coke. Diverse realized studies (Siskin et al, 2006), (Marsh et al, 1997), (Wang and Anthony, 2003) as well as the operational practice (Ellis and Paul, 1998), (ZYDEC, 2006), they point out that the process yields are both determined by the chemical nature of the fed residual one by operation conditions of temperature and pressure. It is accepted that the asphaltenes content affects in an important way on coke yields (Wang and Anthony, 2003), and the residual aromaticity order accused influences in a determinant way the optical texture of the obtained coke (Yang et al, 2002); the compounds of sulfur tend to increase reactivity on aromatic hydrocarbons, promoting very stable heteroatomic polymers formation at high temperatures, causing a not grafitizable coke (Yang et al, 2002), (Bermejo et al, 1997). In the same sense it has been observed that the chemical reactivity of the residues components has direct incidence on the chemical process since reactivity is very high, the polymerization will be carried out in an untidy way generating structures that, on having hardened, will give place to isotropic solid, whereas if reactivity is low, the polymerization will happen in more tidy form, generating flat macromolecules that tend to be piled up forming constituted mesophase of anisotropic spheres (Menéndez et al, 1998). (Vieman, 2002) observed that conduct of liquid phase influences determinedly the superficial coke texture type bleats and type fluffs up. Stickiness affects on process allowing these spheres should come to coalescer before re-hardening. Spheres coalescence is going to give place to the formation of optical textures highly anisotropic, domains type flown in the coke (Marsh and Latham, 1986). In spite of all the studies realized up to the present, the knowledge of chemical process that it shapes the bases for simple coke formation still keeping on incomplete. There are great aspects still not known, in particular what concerns to chemical composition and synergy results of the thermodynamic and chemical aspects, which have a determinant influence on the superficial petroleum coke texture, his morphology and his optical texture. It is important to remember that on this superficial texture there is going to depend fundamentally the added value that could contribute this by-product to the process economy.

Mainly coke precursors are in the feedstock processed and they are very complex materials for which, his characterization and prosecution usually turns out to be difficult. There has been proposed the residues fractioning as the first step to obtain an inventory of the families in present compounds oil inside (Carbognani et al, 1999); it is believed that a route to learn on the mechanisms associated with mesophase formation, as a precursor of the optical coke texture, can be determination of fed residue composition and evaluation of components behavior during the thermal process. First, it is possible to characterize the feedstock by means of his division in order to achieve different chemical groups separation to that shape (Carbognani et al, 1999); (Menéndez et al 1994), whereas for the second aspect, which refers specifically to the phase changes in the bosom of the liquid phase entailed by a temperature increase, it is possible to use a dynamic essay of optical

microscopy connected to a slide with warming. During this essay the sample surrenders to warming programmed in inert ambience. It turns out to be an excellent skill to evaluate the temperature influence and the speed of the warming, on mesophase formation and optical textures formed.

The present investigation developed inside the frame of pyrolysis process from residual oil, with the target to extend the knowledge that it has on the relation: Chemical composition of the feedstock - optical petroleum coke texture. For effects of the study one has proposed to characterize three typical petroleum residues by means of a skill of fractioning and study the microscopic behavior of every fraction during a controlled pyrolysis process. Fractioning there is used Chromatographic method assisted with Soxhlet, while for the pyrolysis there is used an optical microscopy method connected to slide of warming, which allows to observe in real-time the transformations that happen during warming.

Experimental

Three residues oil samples were evaluated, corresponding to RS1, RS2, and RS3 codes respectively. RS2 is a miscellany of RS1 with an additional court of the fractioning tower. To fraction the residual ones there was applied Chromatography methods assisted by Soxhlet (ACS), skill developed in a previous study. There is used a Soxhlet provided with packed dry filters with 11 g of silica gel 70-230 Mesh and with 7 g of silica impregnated with the residual one to separate (30 % p/p silica/residual); the dry packed extraction was realized by index solvents increasing polarity (IP), used in consecutive form and to his respective boiling temperatures. Chosen solvents and used sequence to carry out fractioning process were the following ones: n-hexano (IP = 0.1), benzene (IP = 2.7), methyl ketone (IP = 5.1), chloroform (IP = 4.1) and methanol (IP = 5.1). At the end of the extraction process solvent was eliminated by distillation to obtain five (5) fractions of every residual. Each of these fractions was identified by the initials F1 to F5 in accordance with the sequence of solvents mentioned, so that F1 corresponds to the fraction extracted with n-hexano, as F5 corresponds to the fraction extracted with methanol.

The residual ones, as well as his fractions, were characterized by means of $^1\text{HNMR}$ using a spectrometer JEOL model Eclipse, to 400 MHz; the elementary analysis carried out with a team mark Hermann Moritz, Model Macanal 10, which uses the skill of high combustion for C and H determination by gravimetry, and S for volumetry.

There was observed the development of the optical texture by means of a dynamic essay that is realized in a slide of warming connected to an optical reflected polarized light microscope, LEITZ, model ORTHOPLAN, provided with targets PLAN H20X/0.60 and ocular of 10X. The essays carried out at temperature up to 600°C, speed of 5 °C/min, realizing a photographic record for changes involved in optical texture of the different samples.

Results and Discussion

Fractioning Residual Applying CAES Methodology

The yields of every fraction residual show itself in Table 1. The high percentage of entire recovery for the different residual ones evaluated (superior to 97 % in all the cases) supposes an efficient fractioning methodology. On the other hand, for the three evaluated residual the fraction F1 (extracted with hexano) turned out to be the most abundant, nevertheless for the residual one RS3 emphasizes the value of the fractions F3, F4 and F5 which duplicates to that of the residual ones RS1 and RS2, which allows to infer significant differences in the composition of residual these.

$^1\text{HNMR}$ And Elementary Analysis

Table 2 summarizes results of elementary analysis and $^1\text{HNMR}$ for the residual one and his fractions. $^1\text{HNMR}$ signals demonstrate predominance of aliphatic compounds, both in the residual ones and in his fractions, in accordance with the high relative values of protons (H) methylenic β and methylenic protons (H) of alkyl chains γ . With the increase of solvent polarity used to extract each fraction, reflected in the number of the abstracted fraction, also there is observed increase on condensation levels of the features.

In RS1 residue, the fraction RS1F1 contributes in high proportion to the content of methylenic protons H_β , and aromatic H_α . There is the low relative content of methylenic protons alkyl chains H_γ and in α position with regard to aromatic ring H_α , it might indicate the presence of little replaced aromatic structures and compounds of alkyl chains. In this part, the fraction RS1F2 contributes principally to the percentage of H_β methylenic protons in the residual one continued by a high contribution of H_α protons. With this information it is possible to infer that the fraction RS1F2 contains aromatic compounds highly replaced with multiple alkyl chains. The fraction RS1F3, it possesses the biggest relative content of aromatic protons, and high relative methylenic protons contained in place, indicating presence of slightly replaced aromatic compounds and

paraffins. For the fraction RS1F4, the obtained information indicates the presence of protons H_{α} , or completely replaced aromatic compounds and paraffins.

Table 1. Percentage in Weight of Recover Fractions from Residual Three Oil, Separated by Means of Adsorption Chromatography with Extraction by Soxhlet

Fraction / Extraction Solvent	% Recover fraction from residual by CAES		
	RS1	RS2	RS3
F1 / Hexane	57.4	55.5	41.8
F2 / Benzene	22.3	23,8	13.1
F3 / Methyl ketone	12.0	14.1	30.1
F4 / Chloroform	5.6	4.8	10.8
F5 / Methanol	0.4	0.5	1.4
Full Recovery	97.6	98.7	97.1

In RS2 residue and in each of his fractions also the same sequence of protons is observed brought for RS1: highest proportion of methylenic protons, followed by alkyl methylenic protons chains, protons in position alpha to the aromatic present rings and finally the aromatic protons. The fraction RS2F1 contributes in higher proportion to the content of methylenic H_{β} protons, and alkyl methylenic H_{γ} protons chains. With this it is possible to suggest that RS2F1 is shaped by it predominantly by compounds of the type parafinic and isoparafinic. The protons of RS2F2, they contribute majorly to the percentage of H_{α} protons and in high relative proportion with protons means that aromatic compounds shape this fraction with few replacements, and these replacements are of the type alkylic and aromatic. The fraction RS2F3 possesses contained relative high place of methylenic alkyl protons chains and H_{α} protons, which demonstrates the presence of aromatic compounds highly replaced with alkylic chains. In the fraction RS2F4 there was observed presence of slightly replaced aromatic compounds. Finally in the fraction RS2F5 the presence of aromatic compounds was demonstrated with multiple replacements aliphatics and ciclo-paraffins.

For the RS3 residue a high proportion of compounds were obtained with methylenic compounds, continued in percentage in weight for alkyl methylenic protons chains, protons in position alpha to the aromatic present rings and finally aromatic protons (Table 2). The fraction RS3F1 contributes in major proportion to the content of methylenic H_{β} protons, of the type of paraffinics, whereas the fraction RS3F2 has a contained high place for aromatic protons, indicating the presence of compounds with few replacements. The fraction RS3F3 possesses the biggest relative content of protons H_{γ} as well as of H_{α} and H_{α} , suggesting the presence of aromatic compounds with multiple alkylic replacements and cicloparaffins. In the fraction RS3F1 exists presence of aromatic compounds moderately replaced with lkylic chains. The information for the fraction RS3F1 indicates the presence of aromatic compounds with multiple replacements aliphatics and cicloparaffins.

In accordance with (Mochida and Korai, 1986), the relation C/H can be considered to be indicative of instauration level and condensation of the present structures, what joined the percentage protons distribution, determined for ^1H NMR, they allow to infer an increase in the number of substituyents in the aromatic structures and decrease in the proportion of cycle and isoparafins, in the isolated fractions as the solvent polarity increases used to recover the different fractions.

Also a tendency was observed to the increase in sulfur content with the increase of the relation C/H in the residual one and the fractions, as it is demonstrated in the Figure 1; sulfur tends to concentrate on the extracted fractions according to highest polarity of the solvents, which allows to infer that the sulfur heteroatoms award polarity to the molecules, this factor might affect reactivity during cracking and polymerization. On the other hand, the coincidence of the increase of the percentage of sulfur with the increase in the proportion of substituyents in aromatic compounds, it might indicate sulfur heteroatoms presence on alkylic substituyents or sulfur groups connected to aromatic rings. In the literature (Gray and Mc.Caffrey, 2002), (Huhey, 1981), the linkage energies for dissociation in which the sulfur intervenes correspond to a half of the energy approximately corresponding to linkage of carbon, so the presence of this heteroatom must help to increase the reactivity of the species.

Optical Microscopy on Slide of Warming

For effects of this study it was defined (as) (Tim) as the beginning temperature for mesophase formation or beginning of the development of the optical texture. In the Figure 2 bring the temperature (Tim) observed during dynamic essay in slide of warming, both for the three evaluated residual ones and for his respective fractions; in the same Figure 2 presents to himself a micrography of the texture that develops in every essay. It be observed that every residual one as well as each of his fractions exhibits a different texture, being evident except that not in all the cases he goes so far as to form mesophase. Comparing the micrographies of the three residual ones it is observed that the residual RS2 does not develop properly a texture that could be qualified like mesofase, and this is an interesting result since it is good to remember that residual is a miscellany of the feeding of the residual one RS1 and the current of fund of a fractioning tower. Additionally, it detects to itself that the beginning of the mesophase in the residual one RS1 begins almost at 80°C before the beginning of formation of texture in RS2, this difference is significant for all that it can reflect a process of slower coquization in case of RS2.

Table 2. Elementary Analysis and Protons Percentage Determined for ¹H NMR, in Fractions from the Residual Ones.

Sample	Elemental analyses				¹ H NMR			
	%S (± 0.03)	C/H	% C (± 0.5)	%H (± 0.5)	H _a * 6.00-9.50 ppm	H _α * 2.10-3.80 ppm	H _β * 1.15-2.10 ppm	H _γ * 0.50-1.15 ppm
RS1	3.90	0.57	86.7	12.7	5.0	7.5	59.4	28.1
RS1F1	3.13	0.50	83.9	14.1	5.1	7.7	58.8	28.3
RS1F2	4.22	0.69	85.9	10.4	3.7	9.4	50.0	36.9
RS1F3	5.26	0.77	85.8	9.3	6.7	7.0	55.5	30.7
RS1F4	4.65	0.78	78.3	8.4	0.0	9.5	62.0	28.6
RS2	3.33	0.64	87.6	11.4	4.8	9.6	59.5	26.2
RS2F1	2.20	0.46	87.0	15.7	4.7	5.9	63.8	25.6
RS2F2	3.83	0.51	85.3	14.1	6.6	11.6	59.6	22.1
RS2F3	5.01	0.59	78.9	11.1	4.3	10.9	60.4	24.4
RS2F4	6.98	0.58	79.1	11.3	7.6	7.3	60.8	24.2
RS2F5					4.4	11.3	61.7	22.6
RS3	6.40	0.58	85.4	12.2	4.4	10.8	58.7	26.1
RS3F1	3.62	0.53	85.9	13.6	5.2	7.4	65.1	22.4
RS3F2	4.98	0.69	84.3	10.2	10.4	10.1	50.0	30.0
RS3F3	7.42	0.63	83.4	11.0	8.1	10.1	50.2	35.6
RS3F4	-	0.74	72.5	8.2	5.3	20.2	56.8	17.7
RS3F5					2.4	9.5	58.3	30.1

(*) H_γ: methylenic protons alkyl chains / H_β: methylenic protons / H_α: protons in α position with regard to the aromatic ring. / H_a: aromatic protons.

If the micrography of every fraction is compared having the micrography of the residual one present, it is observed that every fraction has a different response opposite to the temperature. On the other hand, an interesting observation gets rid of this analysis for the three cases, fractions they all have one Tim lower than that of the residual one. It is possible that the effect of miscellany of components of different chemical structure provokes a deceleration in the formation process for mesogenes and his piling up, which precisely gives place to mesophase formation. In case of the residual one RS1 it seemed that his optical final texture is defined strongly by the fractions F2, F3 and F4, while in case of RS2, the transformations of the fractions F2 and F3 he remains darkened by the fraction F1. Although as it will be remembered RS2 it is a miscellany of

F1 and residual other. As for RS3, it is notable to observe that the optical texture of the residual one does not look alike to any of the optical textures showed by his fractions; nevertheless, it is possible that as in case of RS2, the fraction F1 wraps up the effect of other fractions. A wider discussion on this point will develop further on.

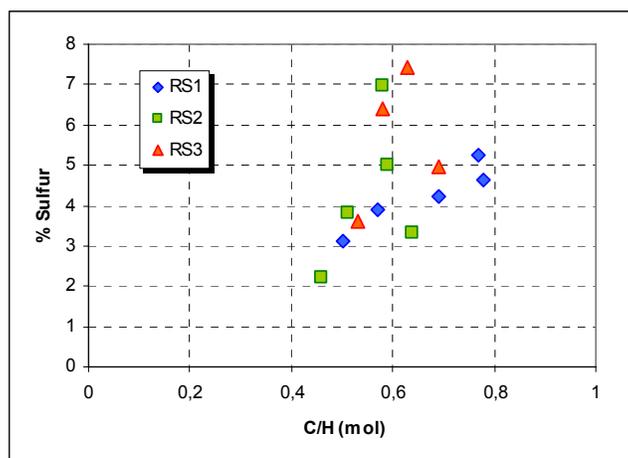


Figure 1. Change of the Sulfur Content with the Relation C/H of the Residual Ones and His Fractions

An analysis of the development of the optical textures in the fractions, taking in account the polarity of the solvent used for his extraction indicates, in the fractions of the residual ones of RS1 and RS2, a tendency to diminish temperature for mesophase formation as it increases the index of solvent polarity. For RS3, a definite tendency is not observed since mesophase formation only is observed in the residual one and in the fraction F2.

In accordance with the brought for diverse authors (Sevage, 1993), (Martín et al, 2000), (Rodríguez-Reinoso et al, 2001), (Martínez-Escandell et al, 1999), (Eser, 1991), (Rahimi et al, 1998), the initial temperatures for mesophase formation are related to the advance of polymerization reactions that lead to mesogenes, for which a mechanism is accepted for radical free, for whose beginning and spread they turn out to be of big importance the dissociation energies of the different chemical linkage present in the compounds type of every fraction. The breakage of the linkage C-C (dissociation energy 344 kJ/mol) and C-H (411, 398 and 464 kJ/mol for primary, secondary and aromatic hydrogens, respectively), thermodynamically is favored over temperatures between 410 and 550°C; a similar situation appears for the linkage S-S (226 kJ/mol), S=S (284 kJ/mol), C-S (272 kJ/gmol), C - Or (357 kJ/g) and C-N304 kJ/mol); nevertheless, for the above mentioned dissociation energies brought in the literature turn out to be approximately equal to the half of the brought ones for connect with atoms of carbon. This major reactivity suggests for the fractions with raised contents of sulfur and heteroatoms, which one have been removed by heat treatment, generates radical free that become stable for polymerization; on the other hand, the stability of the formed radical ones affects the progress of the mesogenes formation reactions. With base in these remarks three (3) proposes the reactions showed in Table 3 to explain the participation of the alkylic compounds and sulfurated in the mesogenes formation and development of coke texture. Dissociation energies of linkage (Gray and Mc.Caffrey, 2002), (Huhey, 1981) and the raised mechanisms, allow to relate the content of heteroatoms of carbonaceous materials at the beginning temperature where occurs changes in the optical texture. The general tendency observed in Figure 3, is that to major content of sulfur in each of the analyzed fractions, the temperature T_{im} diminishes. With the information obtained it is estimated the percentage of sulfur constitutes a determinant factor for the process of formation of the mesofase in the residual ones and the fractions to RS1 and RS2, it is the proportion of sulfur in the samples. For the case of the samples of RS3, it might be said that there is no sufficient information to establish a pattern of behavior, nevertheless, it is observed, in a general way that the relation is invests, to major content of compounds of minor sulfur. This might justify if it is considered that the sulfur in the RS3 could be connected in a different way in the residual ones of RS1 and RS2, for example it might be under the form of structures heteroaromáticas of major thermal stability, which would award to the samples a contained high of sulfur, without this one interferences with the temperature of beginning of the reactions of thermal cracking.

Discussion on Optical Texture and Chemical Composition for the Residues and His Fractions

Hot-stage microscopy permits observation direct of events occurring during samples pyrolysis. The most interesting micrographics are shows in the Figure 2 and the temperature of initial from mesophase are registered too. The results obtained from this study were analyzed to determine the contribution of each fraction to the formation of the mesophase in the residues, to relate the parameters of composition and chemical structure to the optical texture resultant of the process of carbonization.

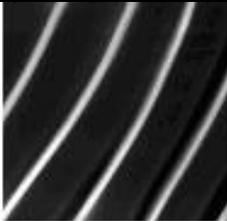
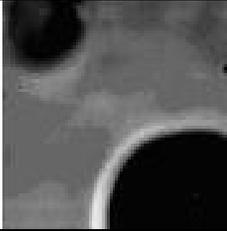
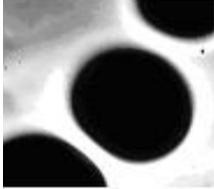
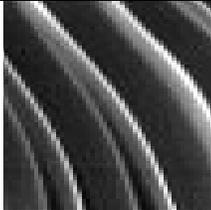
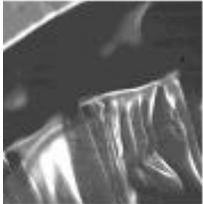
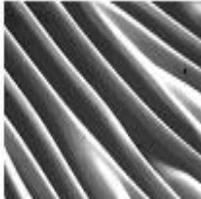
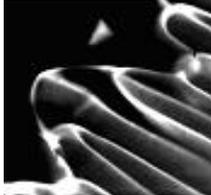
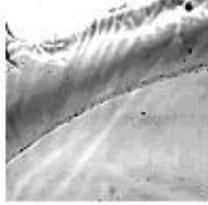
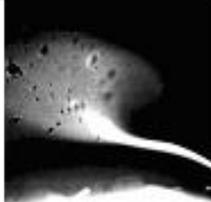
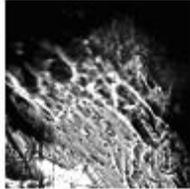
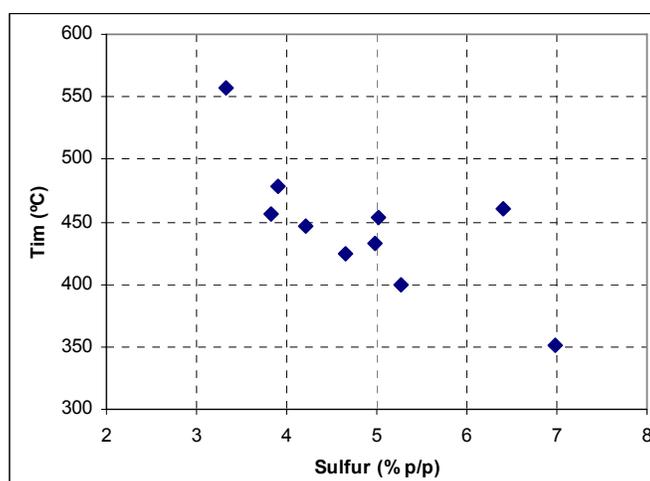
MUESTRA	RS1	RS2	RS3
Residual			
	T im = 478°C	T im = 557 °C	T im = 460°C
F1			
F2			
	T im = 447-472°C	T im = 456-500°C	T im = 433-446°C
F3			
	T im = 400 – 442 °C	T im = 453°C	T im = ---
F4			
	T im = 425°C	T im = 351°C	T im = -
F5			
T _{im} .	T im = -	T im = 277-364°C	T im = -

Figure 2. Micrographies (200x) Of Oil Residual Samples Submitted To Pyrolysis To 5°C/Min. Up To 600°C, on Slide of Warming. T_{im} = Temperature of Beginning of Formation of Mesophase (±3°C)

Table 3. Reactions of Cracking Proposed to Give Beginning to the Formation of Mesogenes.

Beginning	$R_2-CH-CH_2-S-R' \rightleftharpoons R_2-CH-CH_2-S\cdot + R'\cdot$
Hydrogen Extraction	$R_j-S\cdot + R_2-CH_2-CH_2-S-R' \Rightarrow R_j-S\cdot-H + R_2-C-CH_2-S-R'$
β -rupture	$R_2-C-CH_2-S-R' \Rightarrow R_2-C=CH_2 R'-S$
Decompose	$R_j-S\cdot-H \Rightarrow R_j + S\cdot-H$
H ₂ S production	
Hydrogen Extraction	$R\cdot + R_2-CH-CH_2-S-H \Rightarrow H_2S + R_2-C-CH_2-S-H$
β -rupture	$R_2-C-CH_2-S-H \Rightarrow R_2-C=CH_2 + S-H$
Hydrogen Extraction	$S-H + R_2-CH-CH_2-S-R' \Rightarrow H_2S + R_2-C-CH_2-S-R'$

**Figure 3.** Relation Between Sulfur Content in the Fractions and Beginning Temperature for Mesophase Formation and Development of the Coke Texture.

In the fraction that separated with benzene (F2) of the residue of RS1, there is observed the formation of fluid and aligned structures, while in the residue of RS2, although fluid structures form, the process to line up turns out because the generation of volatile matter during the pyrolysis. The chemical families separated in the F2, they shape of aromatic compounds replaced with alkylics chain, according to the information of 1HNMR and FT - IR. These types of compounds are the principal precursors of the carbonaceous mesophase, since lining up reactions of molecular rearrangements and polymerization they can easily form mesogenes, big flat molecules constituted by aromatic condensed rings. The F2 fraction of the RS3 residue, presents certain changes in its behavior, which could be determined by the presence of aromatic compounds little replaced, suggested by the essays of characterization 1HNMR and FT - IR. The proportion of aromatic protons, reaches the highest value, between all the fractions, whereas the value of percentage of sulfur, is in an intermediate status.

For the separated fraction with metil ketone (F3) of the RS1 and RS2 residues, there form fluid and aligned structures, which in case of the RS2 are so big that they get to form anisotropics domains. As for the structural considerations of the compounds groups that are part of these fractions in RS1 and RS2 residues, it is observed that alpha diminishes the presence of compounds with protons in the alpha position, as well as it increases the presence of cycle or isoparafinas and the content of sulfur with regard to the fractions that precede it. In spite of these differences between fractions the behavior about the carbonization is similar, which seems to indicate that these changes of composition were not as sudden as so that during the carbonization, the samples present a different behavior from the observed in the previous fractions. In the F3 fraction of the RS3 residue, with the softening of the sample, this one separates in two zones. In one of the zones the transition is observed towards a liquid state, whereas the other zone remains in solid state, not being observed formation of mesophase in any of the cases. The particular differences of this fraction in the RS3 residue, reside in that this one presents a content of sulfur major

than in any other of the analyzed fractions, for which the reactions of thermal cracking might begin to such temperatures that the system has not come to his point of minimal stickiness such as the coalesce is unfavorable then any mesophase is formed.

The F4 fraction tends to develop fluid textures little aligned (RS1 and RS2) or extensive isotropics domains (RS3) possibly as result of an elevated level of stickiness in the middle of the reaction that obstructs the formation of mesophase. Between the peculiarities of these fractions as for the chemical structures that shape them, there are an increase of the relations C/H and proportion of sulfur with regard to the previous fractions. This suggests the presence of functional groups with heteroátomos that intervene in the process of carbonization, it is possible that the biggest reactivity of the molecules that contain sulfur increases the speed of reaction and makes difficult the formation of condensed structures that give place to the mesophase. In the F4 fraction of the RS3 residue, the generation of volatile material during the warming, has caused the formation of a structure with internal and external pores, specie of internally hollow sphere and with hollows in his surface, but without generation of mesophase. In this fraction they increase with regard to the previous one, the relation C/H and the proportion of protons in the alpha position to the aromatic rings. As it was indicated previously, this type of behaviour during the carbonization also can be attributed to the very rapid evolution of the volatile matter, which generates internal porosity and in the surface of the formed structures.

In the F5 fraction, extracted with methanol of the RS1 residue, mesophase was not generated. In the F5 fraction of the RS2 residues, there was formation of the mesophase generating fluid structures but little faced in the whole sample. In the F5 fraction of the RS3 residue, generation of volatile matter was observed forming pores in the sample once he surrendered to pirólisis. These fractions present compounds with functional groups-OH and-NH, with low relative content of aromatic compounds, which was determined by the proportions of alpha protons and aromatic protons in the samples, which indicates that, on having diminished the presence of nuclei of aromatic compounds, the reactions of ciclization, condensation, isomerization and polymerization, do not take place and it is unfavorable for the formation of optical fluid and aligned textures.

On having observed the micrographics of the residues by hot-stage microscopy, it is had that in all the cases formation of mesophase happened with generation of structures, which in case of RS1 and RS3 residues, are faced and aligned, whereas for the RS2 residue, few alignment is observed in the fluid formed structures. These differences can be explained in terms of the development of the process of formation, growth and coalescence of the mesophase, for which there have been proposed models of general character in which it assumes preponderant role to the stickiness of the mesophase and of the way (Martínez-Escandell et al, 1999), (Sima et al, 2003), (Santamaría-Ramírez et al 1999), (Rahimi et al 1998). This relation stickiness / quality of the mesophase has direct bearing to the evolution of volatile matter during the growth and the coalescence, modifying the formation of fluid and aligned structures (Martín et al 2000), (Santamaría-Ramírez et al 1999). As for the parameters of characterization of each one of residues, associated to the quality of the mesophase, it had that more fluid and faced structures are formed, when the temperature of beginning of the mesophase is relatively low, minor proportions of aromatic protons and relation C/H, that is to say, little condensed structures and with aromatic nuclei replaced with alkylics groups, as well as also, minor proportions of the fractions 1 and 2 separated from the residues with hexano and benzene, respectively.

Conclusions

The microphotography attained through the latter analysis show the development of optical textures that are specific to each residual as well as to each fraction that constitute them. Such behaviour is strongly determined by the chemical reactivity of each fraction. Important differences are observed regarding the initial temperature for mesophase formation, resolidification temperature, quality of the optical texture formed: degree of development and optical texture type. ¹HNMR and %S suggest that the content of S influences the condensation degree of the organic species present. In addition, it's observed that the temperature for mesophase formation decreases as the %S.

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