DETERMINATION OF AROMATIC HYDROGENS IN ASPHALTENES AND RESINS USING FTIR AND MOLECULAR MODELLING

Roberto Rodrigues Coelho, Ian Hovell and André Lopes de Souza

[1]Núcleo de Modelagem Molecular- NMM
Centro de Tecnologia Mineral-CETEM-MCT
Av. Ipê 900, Cidade Universitária, Ilha do Fundão.21941-590 - Rio de Janeiro -RJ – Brasil
coelho@cetem.gov.br, hovell@cetem.gov.br, alopes@cetem.gov.br

Resumo - Neste trabalho é proposta uma metodologia para a determinação de hidrogênios aromáticos em moléculas médias de asfaltenos e resinas. Espectros na região do infravermelho (IV) de naftalenos metil substituidos foram estudados, no que tange aos hidrogênios aromáticos, para fins de comparação, por sua semelhança, com os asfaltenos. Para isto, considerou-se as intensidades, no espectro IV, nas regiões: 700-900cm^{-1} e 2900-3100cm^{-1}. Analisando-se os respectivos espectros experimentais, com deconvolução, e o modelamento teórico destes espectros utilizando o método ab initio HF 3-21G, testou-se a metodologia proposta com os espectros experimentais e teóricos de asfaltenos, obtendo-se bons resultados.

Palavras-Chave: asfalteno, hidrogênios aromáticos, modelagem molecular.

Abstract – In this work a methodology is proposed for the determination of aromatic hydrogen in medium molecules of asphaltenes and resins. Infrared (IR) spectrum of methyl - substituted naphthalenes were studied, with respect to the aromatic hydrogen, for comparison with Brazilian asphaltene. In order to do this, the IR intensities in the two regions, 700 - 900 cm^{-1} and 2900 - 3100 cm^{-1} were studied. The deconvoluted experimental spectra, and the respective theoretically modelled spectra using quantum mechanical ab initio methods, HF/3-21G, were compared. The proposed methodology was tested with the experimental FT IR and theoretical spectra of a Brazilian asphaltene, obtaining good results.

Keywords: asphaltene, aromatic hydrogens, molecular modelling.

1. Introduction

The asphaltenes are products originating from of the petroleum, that present complex molecular structures, that tend to form agglomerates that flocculate and precipitate according to the physiochemical conditions of the environment in which they are found (Carnahan, 2000). These agglomerates cause serious problems in the petrochemical industry, as blockages of the extraction well, pipe line transportation, deposition in the storage tanks and reduction of catalytic action in the refinery processes, with the consequent damages of economical loss and contamination of the ecosystems.

One of the difficulties in the study of asphaltenes lives in the determination of its chemical structure or even in the characterization of their functional components. A large number of analytical chemical techniques are used to this purpose such as ^{1}H NMR (Benkhedda and Landais, 1992), ^{13}C NMR (Hamaguchi and Nishizawa, 1992) and Fourier Transform Infrared spectroscopy (FTIR), Chen et. al., (1985) and Guillen et. al., (1992), among others. This group of analytical spectroscopic techniques would be employed in elucidating the average asphaltene and resin molecules under study. Faulon (1994), proposed a stochastic method, appropriate to the asphaltenic structure that resulted from the SIGNATURE program. With the increasing exploitation of heavier crude oils, studies of structural characterization of asphaltenes have been appearing in the literature, Faulon (1994), Calemma et. al. (1995), Calemma et. al. (1998), Douda et. al., (2004), Pacheco et. al. (2004)). Liang et al.(1991) and Bellamy(1957) mention the linear relationship among the relative intensities in the IR regions of 1460 and 1380cm^{-1} for the alkanes and the ratio nCH_2/mCH_3 of the respective aliphatic chains. Other regions, that show similar linear relationships, have been suggested by Gonzales et al.(2001) and Kadim et al.(1999) using the frequency regions of 2920 and 2950 cm^{-1} and 2927 and 2957 cm^{-1} respectively. The techniques, used by the mentioned authors, determined the aliphatic chain length in asphaltenes and resins, in summary, they analysed IR spectra for a series of linear and branched alkanes, focusing on the ratios of the intensities for the methylene and methyl absorption bands. In this way, with the IR intensity peak values for asphaltene from its IR spectrum, considering the same region, it is possible to locate in the graph, built for the alkanes, the ratio, nCH_2/mCH_3 respectively. Coelho et al., (2002) obtained the same type of linear relationship for alkyl substituted benzenes, calculating the molecular weight of the asphaltene and resin aliphatic chains starting from the ratio, nCH_2/mCH_3.

No literature has been published, regarding with the IR absorption, about the linear relationship between the number of aromatic hydrogens with symmetrical, asymmetrical stretching and out-of-plane vibrations for these hydrogens. This work, proposes a methodology, for the functional characterization of the aromatic hydrogens of asphaltenes, using two infrared regions; the first being 700-900cm^{-1} that corresponds to the out-of-plane absorption for the hydrogens in the aromatic ring, where an isolated, paired, or groups of three or four neighbouring hydrogens can be distinctly characterized, Chen et. al., (1985) and Guillen et. al., (1992). The second region, 2900-3100cm^{-1} shows the absorption due to symmetrical and asymmetrical stretching of aromatic hydrogens, Guillen et. al., (1992). Proportionality was considered to exist, as usual, between the number of hydrogens, in a given absorption, with the respective intensities. For this, the theoretical spectra, obtained by quantum mechanical calculations and deconvoluted experimental spectra, Spectra .Galactic (2004), were analysed for both regions.

Methyl substituted naphthalenes were studied for the development of this methodology, with respect to their aromatic hydrogens, for they possess a simpler structure yet at the same time are similar in structure to asphaltenes and resins. In this way, starting from an analysis of theoretical and respective experimental IR spectra for a number of methyl substituted naphthalenes, using the intensity regions in question, correlations were obtained with the spectra of the asphaltenes in study.

2. Materials and Methods

The experimental gas phase IR spectra for the substituted naphthalenes were obtained from the open on-line Spectra Galactic IR database (assessed 2004). The deconvolutions, of these spectra, were accomplished using the BOMEN GRAMS 386 IR.

The asphaltene, originating from vacuum residues (RV), of Brazilian petroleum products, were extracted using the Calema et. al. (1995) method, with modifications proposed by Monte et al. (2004) of exhaustive reflux heptane washing and control of the maltene presence using UV-visible spectroscopy. The FTIR asphaltene spectra were obtained by diffuse reflectance using a Bomem Spectrophotometer, model MB102, with a DTGS detector using ultra pure potassium bromide (KBr), obtained from Merck & Co. Inc, in such a way as to obtain a homogeneous solid mixture. This mixture contained 20mg of asphaltene with 220 mg of KBr. This solid mixture was placed in the appropriate accessory for diffuse reflectance, and each sample was swept a 1000 times at a speed of 20 sweepings per minute, for the wavelength interval of 4000 to 400 cm^{-1}, with a resolution of 4 cm^{-1}

The same ab initio Hartree-Fock (HF) method, and basis set level, 3-21G, was used for the quantum mechanical calculations of the variables considered in this study in both, HyperChem, version 7.0, of HIPERCUBE INC. and Gaussian 03W, software packages.

3. Results and Discussion

Substituted naphthtalenes were selected which had characteristics similar to the asphaltenic structures, with regard to the aromatic hydrogens being considered: one free hydrogen and 2 adjacent hydrogens, in the same way as they are usually found in asphaltenic structures, as can be seen in figure 1. In order to obtain a good comparison between the theoretical and experimental IR spectra the theoretical spectra were calculated using a quantum mechanical HF/3-21G method, which provides good resolution in the IR regions in question. The 2900-3100cm^{-1} region in the experimental IR spectra was deconvoluted to increase the peak separation. The percentages of aromatic and aliphatic hydrogens found in the experimental IR spectra, for the substituted naphthalenes, were calculated using the deconvoluted peak.

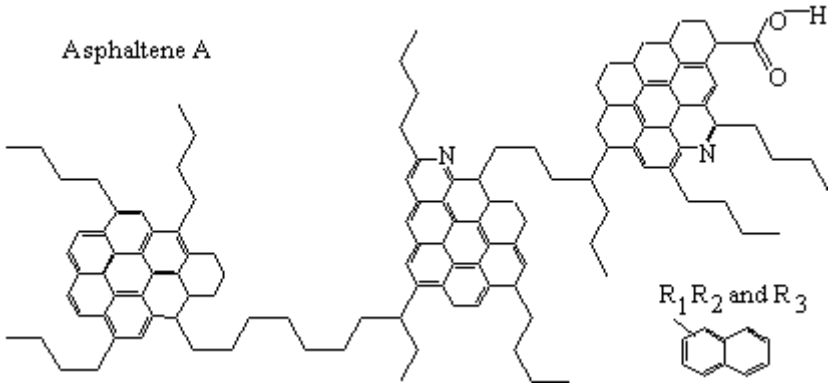


Figure 1 – R_1,R_2 and R_3 = (1,3; 1,4; 2,3; 2,6) dimethyl naphthalene; 1-bromo, 4-methyl naphthalene; 2,3,6 trimethyl naphthalene. Average molecule of asphaltene proposed in the literature (De Souza et al. 1999).

Out-of-plan vibration of the aromatic hydrogen occurs in the 700-900cm^{-1} region, summing the intensities of these absorptions in the theoretical and experimental spectra allowed the determination of the percentages of isolated aromatic hydrogens in comparison with paired aromatic hydrogens. The results are presented in table 1. For the methyl-substituted naphthalenes, the analysis of the intensities of the hydrogens, in this region, was predominantly isolated and doubly adjacent aromatic hydrogens, in the same way as they are found in asphaltene structures. The absorptions due to four aromatic hydrogens grouped together, as are present in some of the methyl substituted naphthalenes in table 1 were not included, since they were considered as not being pertinent to the analysis. However, the intensities of the four aromatic hydrogens grouped together were considered in the 2900-3100cm^{-1} region, because of the fact that all of the aromatic hydrogens, present in the methyl-naphthalenes studied, are found in this region, represented by two "packages" of intensities: one containing absorption intensities for aromatic hydrogens (3010-3090cm^{-1} region) and another containing absorption intensities of aliphatic hydrogens (2900-2985cm^{-1} region) as can be seen in figures 4 and 5. In this way, it is possible to determine, in this region, the percentages of the distribution of the hydrogens, distinguishing them as being aromatic or aliphatic.

Table 1: Region 700-900 cm-1. Hydrogens attached to the aromatic ring (out-of-plan vibration).

R_1, R_2, R_3	Single H (%)		Paired H (%)	
Naphthalene	T	E	T	E
1,3 dimethyl (A)*	40	36	-----	-----
3 methyl phenantrene(B)	2	7	60	55
1,4 dimethyl (C)**	------	------	37	38
2,6 dimethyl (D)	39	43	61	57
2,3,6 trimethyl (E)	39	33	61	67
2,3 dimethyl (F)*	41	43	-----	-----
2 methyl antracene	48	41	5	7
9 methyl antracene*	30	22	-----	-----

Structures with: *1 and 4 adjacent aromatic hydrogens and **2 and 4 adjacent aromatic hydrogens. A, B, C, D, E and F relate to the respective methyl substituted naphthalenes to their experimental IR spectra shown in figures 2 and 3.
T = theoretical, E = experimental

Table 1, shows the determination of the percentage of isolated and paired aromatic hydrogens calculated from theoretical (T) and experimental (E) IR spectra. There is a difference of around 2 to 6% for the isolated hydrogen between T and E. A difference of 1 to 6% was found between T and E spectra for the paired aromatic hydrogens. These differences were considered to be acceptable.

In the absorption region of 2900-3100cm^{-1}, the intensities are assigned as symmetrical and asymmetrical stretching absorptions of the aromatic and aliphatic hydrogens. The analysis of the theoretical and experimental spectra gave, in each case, information between the group of aromatic and aliphatic hydrogens in the substituted naphthalenes. The result of the analysis done for this region is presented in table 2.

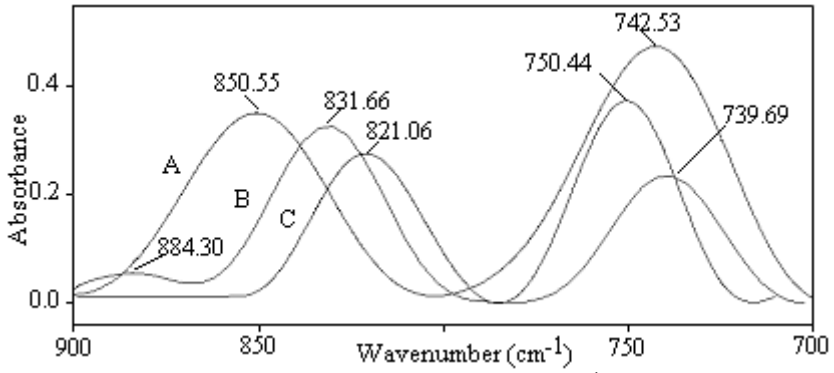


Figure 2: Experimental deconvoluted spectra in the region of 700-900 cm^{-1}. The letters A, B and C correspond to the methyl-substituted naphthalenes presented in table 1

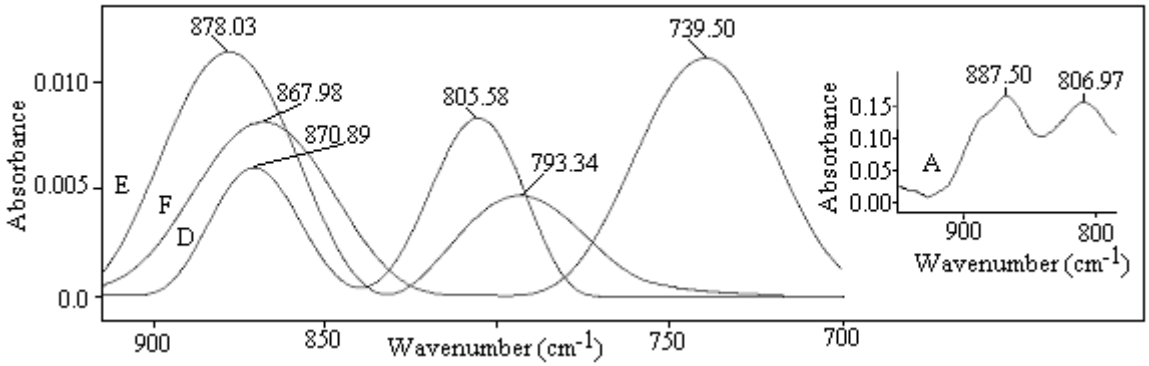


Figure 3: Experimental deconvoluted spectra, in the region of 700-900cm^{-1}. The letters D, E and F correspond to the methyl substituted naphthalenes shown in table 1. The letter A corresponds, in the smaller picture, the absorption of the asphaltene, in the same region (See Figure1)

Table 2: Region 2900-3100cm^{-1}. Aromatic and aliphatic hydrogens (symmetrical and asymmetrical stretching)

	Experimental (E)		Theoretical (T)	
R_1, R_2, R_3 Arenes	Aromatic H(%)	Aliphatic H(%)	Aromatic H(%)	Aliphatic H(%)
1,3 dimethyl	52	48	41	59
2,3 dimethyl	43	57	39	61
2,6 dimethyl	44	56	40	60
2,3,6 trimethyl	50	50	39	61
3 methyl phenanthrene	78	22	72	28
1,4 dimethyl	43	57	46	54
2 methyl anthracene	76	24	72	28
9 methyl anthracene	82	18	78	22

In the determination of the percentage of aromatic and aliphatic hydrogens there is a difference between the theoretical and experimental treatments of 3 and 11%, for the aromatic or aliphatic hydrogens, as shown in table 2, considered acceptable for the objective of this project.

In order to validate the results obtained, the correlation between the theoretical and experimental intensities of the absorptions of the aromatic hydrogens found for both regions (700-900cm^{-1} and 2900-3100cm^{-1}) was investigated and is shown in graphs 1 and 2, which show the equivalence between the sum of the absorption intensities of the aromatic hydrogens that occur in the 700-900cm^{-1} to the 2900-3100cm^{-1} region. The calculated correlations of $R^2 = 0.84$ for the theoretical treatment and $R^2 = 0.95$ for the experimental absorptions were considered appropriate in showing a reasonable correlation.

With the objective of testing the developed method, an average asphaltenic molecule was selected, asphaltene A, De Souza (1999). The vibrational intensities were summed, inorder to calculate the proportion of hydrogens attached to aromatic rings to aliphatic hydrogens present, in the theoretical and experimental IR spectra for both regions. The results for the determination of the percentage of aromatic hydrogen in the asphaltenic structure, for both infrared regions studied, are shown in table 3.

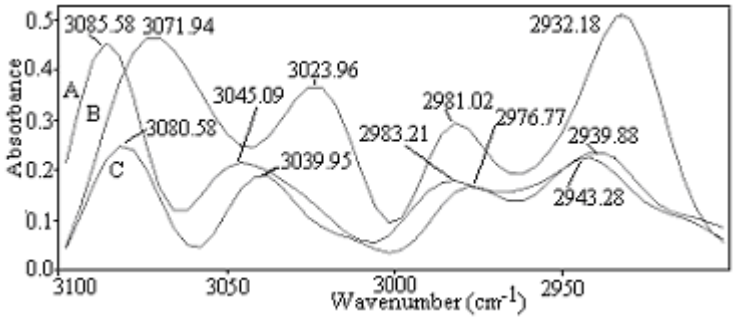


Figure 4: Deconvoluted experimental spectra, in the 2900-3100cm^{-1} region. (A, (1,3 dimethyl), B, (1 -bromo, 4 - methyl), and C (1,4 dimethyl) naphthalene.)

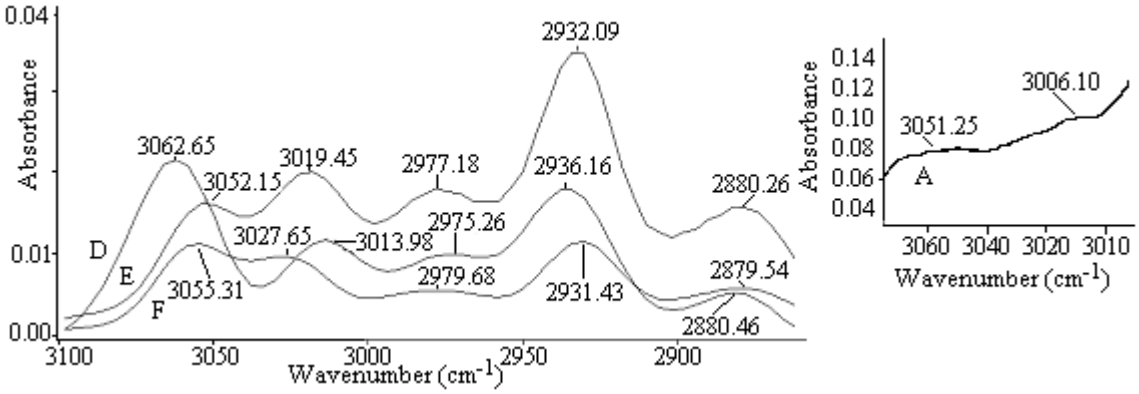
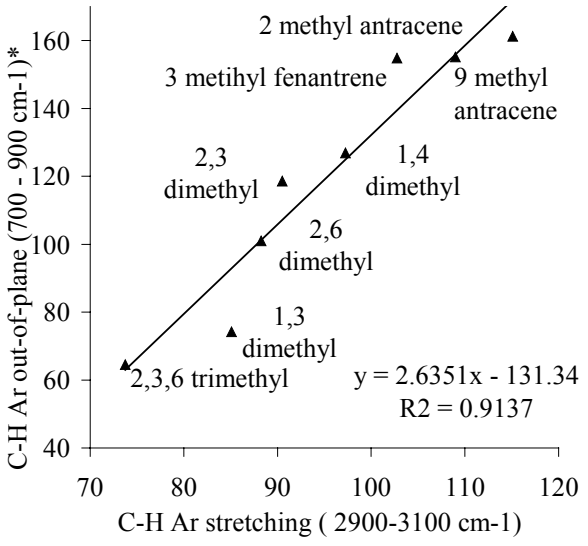
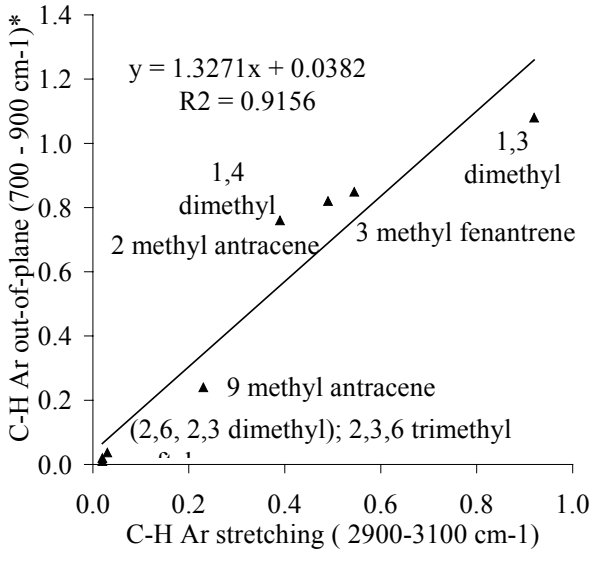


Figure 5: Deconvoluted experimental spectra, in the 2900-3100cm^{-1} region. (D, (2,3,6 trimethyl), E, (2,3 dimethyl), and F (2,6 dimethyl) naphthalene) The inset shows the absorption of the asphaltene in the same region



Graph 1 Correlation of the Theoretical Intensities of the Absorptions of Substituted Naphthalenes in the: 700-900cm^{-1} and 2900-3100cm^{-1} regions.



Graph 2 Correlation of the Experimental Intensities of the Absorptions of Substituted Naphthalenes in the: 700-900cm^{-1} and 2900-3100cm^{-1} regions.

Table 3: Methodology test using an average asphaltene molecule (Asphaltene A, Figure.1)

Regions cm^{-1}	700-900		2900-3100	
H function (%)	2 adjacent	Single	Aromatic	Aliphatic
Average molecule	43	57	40	60
Experimental	48	52	34	66
Theoretical	47	53	38	62

Table 3 represents the results of the application of the methodology proposed in the determination of the percentage of the aromatic hydrogens in a selected average asphaltenic molecule. For asphaltene A, the maximum percentile difference between the experimental and the average molecule proposed in the literature De Souza (1999) is of the order of 5%, in the region between 700-900cm^{-1} and 4% in the 2900-3100cm^{-1} region. These values were considered compatible and appropriate.

In table 3 in the region between 2900-3100 cm-1, besides the presence of the absorption intensities for the aromatic hydrogens, there is also vibrational activity of the naphthenic hydrogens present in asphaltenes, these contribute, to the increase of the intensities attributed to the aromatic hydrogens. Consequently, the difference among the theoretical and experimental analysis type for this region is larger.

4. Conclusion.

The methodology proposed for the determination of the aromatic hydrogens, considering the absorption intensities, in two different infrared regions, between 700-900cm^{-1} and 2900-3100cm^{-1} for the theoretical and deconvoluted experimental spectra, of the substituted naphthalenes, was shown to be efficient for the calculation of percentage of hydrogen attached to aromatic rings for average structures of asphaltenes and resins, as it was shown in the application of the proposed method for the selected asphaltenic structure.

5. Acknowledgments

The authors gratefully acknowledge CNPq/CT-PETRO for their financial support

6. Bibliography.

BELLAMY,L.J." The Infra-red Spectra of Complex Molecules", John Wiley & Sons,Inc. 18-20, 1957

BENKHEDDA, Z. and LANDAIS, P.; Spectroscopic Analyses of Aromatic Hydrocarbons Extracted from Naturally and Artificially Matured Coals.; Energy & Fuels (6), 166-172, 1992

CALEMMA, V.IWANSKI, P. NALI, M.SCOTT, R. and MOTANARI, L.; Structural Characterization of Asphaltenes of Different Origins., Energy & Fuels, 9, 225-230, 1995

CALEMMA, V. RAUSA, R. D'ANTONNA, P. and MONTANARI, L.; Characterization of Asphaltenes Molecular Structure. ; Energy & Fuels, 12, 422-428, 1998

CARNAHAN, N.F.; Precipitation of Asphaltenes in Heavy Oil and Tar Sands; Chapter 12, Asphaltene and Asphalt. 2 edited by YEN, T.F. and CHILINGARIAN G.V., Elsevier, N. York, EUA, 2000

CHEN, P.; YANG, P.W.J. and GRIFFITHS, P. R.; Effect of Preheating on Chemical Structure and Infrared Spectra of Yanzhou Coal. Fuel, 64, 307-312, 1985

COELHO, R. R., MONTE, M., MIDDEA, A.; Characterization of Aliphatic Chains in Vacuum Residues of Asphaltenes Using Molecular Modeling and FTIR Techniques In: 2002 International Conference on Heavy Organics Depositions (HOD 2002), 2002, Puerto Jalarta, 2002 Proceedings- Edited - Carlos Lira - Galeana. - Mexico

DE SOUZA, W. F.; KONDO, T.; SATO, S.; MATSUMURA, A.; SAITO, I.; MD-MM Investigation on the Affinity between Solvents and Asphaltenes; Third International Symposium on Colloid Chemistry in Oil Production Asphaltene & Wax Deposition, ISCOP' 99, 1999, November, Mexico.

DOUDA, J.; LLANOS, M.E.; ALVAREZ, R. And BOLAÑOS, J.N.; Structure of Maya Asphaltene- Resin Complexes through the Analysis of Soxhlet Extracted Fractions; Energy & Fuels, 18, 736-742, 2004

FAULON, J-L.; Stochastic Generator of Chemical Structure. 1 Application to the Structure Elucidation of Large Molecules; J. Chem. Inf. Comput. Sci. , 14, 1204-1218, 1994

GONZALEZ, E. B.; GROENZIN, H.; GALEANA, C. L. and. MULLINS, O. C.; The Overriding Chemical Principles that Define Asphaltenes; Energy & Fuels; 15, 972-978, 2001

GUILLEN, M.D.; IGLESIAS, M.J.; DOMINGUEZ, A. and BLANCO, C.G. Semi quantitative FTIR Analysis of a Coal Tar Pitch and its Extracts and Residues in Several Organic Solvents.; Energy & Fuels 6, 518-525, 1992

HAMAGUCHI, M. and NISHIZAWA, T.; Quantitative Analysis of Aromatic Carbon types in Pitch by Fused-state 13C NMR Spectroscopy. Fuel, 71, 747- 750, 1992

Http://spectra.galactic.com/spectraOnline, (accessed 2004)

KHADIM, M. A. and SARBAR, M. A.; Role of Asphaltene and Resin in Oil Field Emulsions; J. of Petroleum Science and Engineering; 23, 213-221, 1999

LIANG, W.; QUE,G. and CHEN, Y.; The Chemical Composition and Characteristics of Residues of Chinese Crude Oil.; Energy Sources, 13, 251-265, 1991

MONTE, M. B.; COELHO, R. R; MIDDEA, A. Investigation of Molecular Weight and Aggregation of Asphaltenes in Organic Solvents using Surface Tension Measurements.; Petroleum Science and Technology, 8, 22, 7&8, 719-1097, 2004.

PACHECO- SANCHEZ, J.H.; ALVAREZ- RAMIREZ, F. and MARTINEZ-MAGADAN, J. M.; Morphology of Aggregated Asphaltene Structural Models.; Energy & Fuels, 18, 1676-1688, 2004