Petroleum Asphaltenes: Experimental Determination and Characterization

Asphaltenes

SELEKOU KONSTANTINA

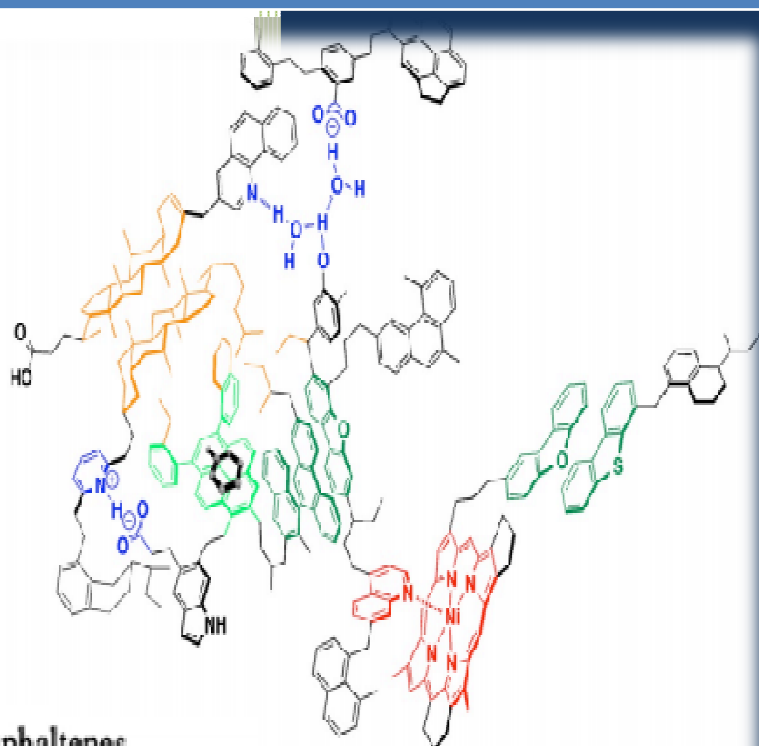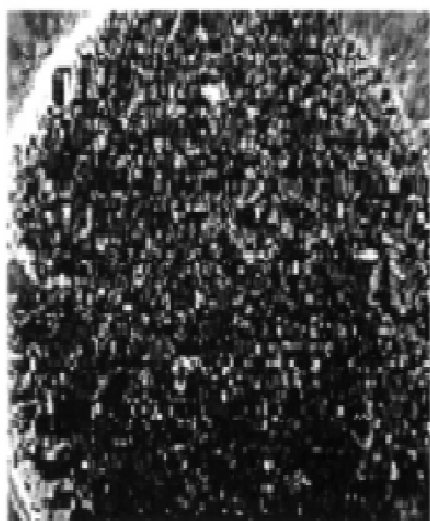**PROFESSOR: Pasadakis Nikolaos**

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MASTER THESIS

Petroleum Asphaltenes: Experimental Determination and Characterization

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Abstract

In this study information is included about the determination and the characterization of asphaltenes as it was published in the previous decades. Specifically, the purpose of the study is to collect and to give to the readers a general idea about the definition of the asphaltenes and their basic characteristics, as they have been determined by scientists from the middle '19 century until now. Firstly, basic information is given about the properties of the asphaltenes and two approaches which are associated with asphaltene physicochemical behavior (solubility and colloidal approach) are also highlighted. Furthermore, the analytical methods and techniques which are used by scientists for asphaltenes detection and characterization are mentioned. Finally, two models that can determine the asphaltenes precipitation taking into account the prevailing experimental conditions and the thermodynamical effects in asphaltene are given.

Περίληψη

Η συγκεκριμένη εργασία περιλαμβάνει πληροφορίες από δημοσιευμένα άρθρα σχετικές με τον προσδιορισμό και τον χαρακτηρισμό των ασφαλτενίων. Συγκεκριμένα, σκοπός της εργασίας είναι να δώσει στον αναγνώστη μια γενική εικόνα για το τι είναι τα ασφαλτένια καθώς και τα βασικά φυσικοχημικά χαρακτηριστικά τους, όπως αυτά προσδιορίστηκαν από τους επιστήμονες από τα μέσα του '19 αιώνα έως και σήμερα. Αρχικά, δίνονται βασικές πληροφορίες σχετικές με τις ιδιότητες των ασφαλτενίων ενώ παρατίθενται οι δύο προσεγγίσεις σχετικά με την φυσικοχημική συμπεριφορά των ασφαλτενίων (solubility και colloidal approach). Στη συνέχεια, αναφέρονται οι αναλυτικές μέθοδοι και τεχνικές που έχουν χρησιμοποιηθεί από τους επιστήμονες για την ανίχνευση και τον χαρακτηρισμό των δομών αυτών ενώ τέλος δίνονται τα μοντέλα που προσδιορίζουν το σχηματισμό των ασφαλτενίων λαμβάνοντας υπόψη τις επικρατούσες συνθήκες καθώς και τις θερμοδυναμικές διεργασίες που επικρατούν κατά τον σχηματισμό τους.

Acknowledgements

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Introduction

1.1 The origin of oil

Petroleum formation is the result a very slow process in nature, which causes the sedimentation of microorganisms, animals and plants over thousands of years. The organic matter slowly decomposed and finally petroleum is formed. According to the scientists, the oldest formations of the world's oil dates back to 500 million years ago.[1] [2]

Petroleum, which is usually mentioned as Crude oil, mainly consists of mixtures of hydrocarbons but other substances which contain   variable amounts of sulfur, nitrogen, and oxygen can be observed as well. In addition, substances contain vanadium and nickel can be also found. The presence of metals and nonmetal elements changes petroleum properties such as volatility, specific gravity, and viscosity. For instance, the presence of vanadium and nickel increases viscosity. It is also noted that because of high pressures, natural gas is also present. [2] [3]

There are several ways to classify the materials of crude oil but according to Speight (Speight, 2007) it is preferable to subdivide petroleum and other related materials into three major classes: (i) materials that are of natural origin, (ii) materials that are manufactured and (iii) materials that are integral fractions derived from natural or manufactured products, as shown in Table **1**. According to this classification asphaltenes are derived products and they can be produced by different resources such as bitumen, heavy oil or residual oil. The asphaltenes production depends on the treatment of resources, containing a low-boiling liquid hydrocarbon (i.e. hexane), and they are resulted into the separation. [2.]

Concluding this small introduction, it is observed that the field of petroleum science is too extensive and therefore, in this master thesis, a small part of it is covered, which pertains to asphaltenes structure and is further discussed in the follow chapters.

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[1] **Erika Chrisman, Viviane Lima, and Priscila Menechini.** Asphaltenes - Problems and Solutions in E&P of Brazilian Crude Oils. *Crude Oil Emulsions - Composition Stability and Characterization. Croatia: Manar El-Sayed Abdel-Raouf,* 2012, pp. 1-59.

[2] **Speight, G. J.** The Chemistry and Technology of Petroleum. 4th Edition. USA : CRC Press/Taylor & Francis, Boca Raton, FL, 2007.

[3] https://**petrowiki.spe.org**/Origin_of_petroleum

Table 4: *Subdivision and Subgroups of Petroleum (Speight 2007)*

Natural materials	Derived materials	Manufactured materials
Natural gas	Saturates	Synthetic crude oil
Petroleum	Aromatics	Distillates
Heavy oil	Resins	Lubricating oils
Bitumen[a]	Asphaltenes	Wax
Asphaltite	Carbenes[b]	Residuum
Asphaltoid	carboids[b]	Asphalt
Ozocerite(natural wax)		Coke
Kerogen		Tar
Coal		Pitch

[a] Bitumen from tar sand deposits. [b] usually thermal products from petroleum processing.

1.2 Introduction to Asphaltenes: Definition

The term "Asphaltenes" originated in 1837 when Boussingault defined them as the distillation residue of bitumen: insoluble in alcohol and soluble in turpentine (Boussingault 1837). According to several researchers the most accepted definition for asphaltenes is related to their solubility. Therefore, asphaltenes are defined as the heaviest components of petroleum fluids that are insoluble in light *n*-alkanes such as *n*-pentane (nC$_5$) or n-heptane (nC$_7$) but soluble in aromatics such as toluene (Figure **1**). [4]
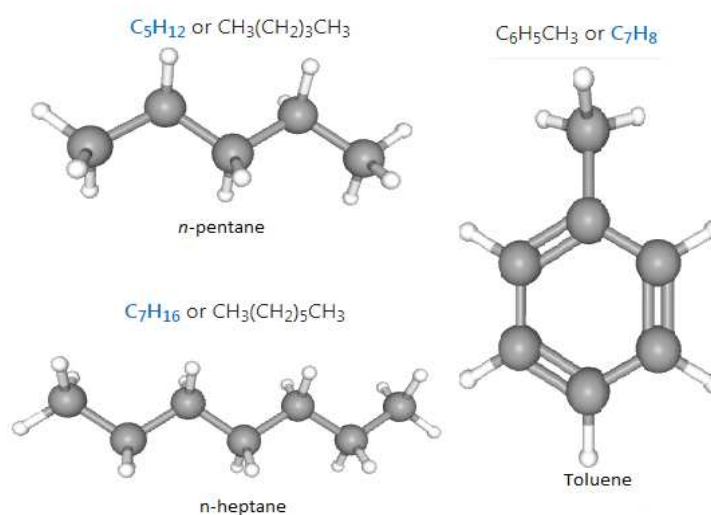
Figure 1: *Organic Solvents*

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[4] **Goual, Lamia.** Petroleum Asphaltenes. [book auth.] Manar El-Sayed Abdel-Raouf. *Crude oil Emulsions - Composition Stability and Characterization.* Croatia : s.n., 2012, pp. 27-59.

By definition, the method of asphaltenes separation is based on the use of an excess liquid hydrocarbon as solvent (hydrocarbon with low–boiling point). During the addition of the solvent into the liquid sample of petroleum, aggregates are formed and the dispersibility of the system is changed (physicochemical changes). The result of this process is the separation (precipitation) of the asphaltene fraction. As it is expected, the choice of the solvent defines the "quality" of the fraction and asphaltenes yield. [5] Studies have shown that the yields are not only function of the used solvent but they are also functions of the contact time and of the ration of oil to the diluents of the system. Furthermore, the use of heavier n-alkanes than heptane it does not change the quality and quantity of the precipitated asphaltenes. On the contrary, the use of n-heptane is actually helpful because it facilitates the formation of smaller molecules, which drop easily. [7]

Most scientists use SARA method to separate and isolate the petroleum fractions as described by the diagram of Figure **2**. SARA method proposes the use of a low-boiling point solvent such as heptane which is added to the liquid sample. The result is the separation of two kind of compounds these which are soluble to heptane and these which are insoluble. In the next step, the fractions are separated one more time and the final fractions are Saturates – Aromatics – Resins – Asphaltenes (SARA). [6] [7]
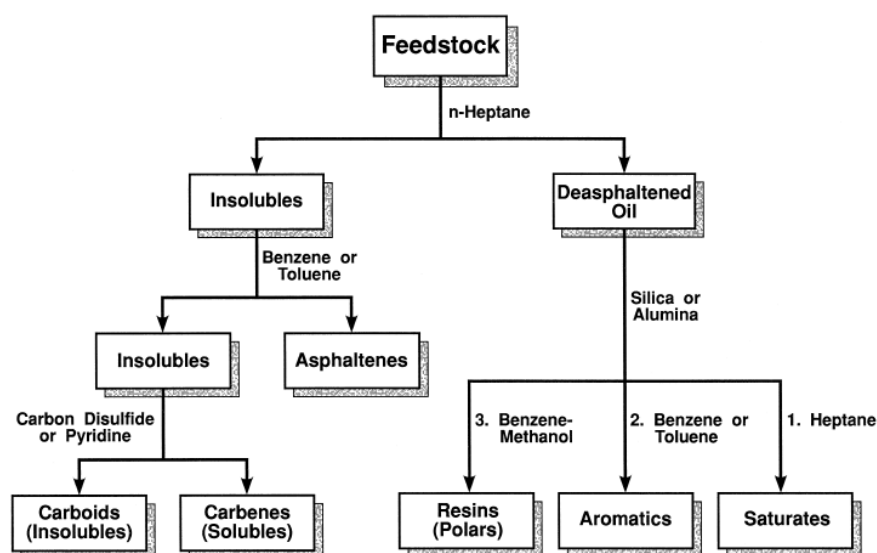
Figure 2: *The laboratory fractionation of petroleum (Speight, 1999)*

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[5] **Speight, G. J.** Asphaltenes in Crude oil and Bitumen: Structure and Dispersion. [book auth.] L Schramm and Advances in Chemistry. *Fundamentals and Applications in the Petroleum Industry.* Washington : Americal Chemical Society, 1996.

[6] **Speight J. G.** The chemical and physical structure of petroleum: effects on recovery operations. *Journal of Petroleum Science & Engineering.* 1999, Vol. 22, pp. 3-15.

[7] **Ashoori, Siavash.** *Mechanisms of Asphaltene deposition in porous media. Ph.D. Thesis* School of Engineering University of Surrey, Guildford, 2005.

In this point it is noted that resins and asphaltenes are sometimes confused because resins might be structurally similar to asphaltenes, but as opposed to asphaltenes, they are soluble to pentanes and heptanes and they also have smaller molecular weight than asphaltenes. [6] [7] Also, the color and the texture of resins differ from these of asphaltenes. Asphaltenes are black, shiny and friable solids; while resins are dark brown, shiny and gummy. Previous studies have highlighted that resins help to the dispersion of asphaltenes in the petroleum (Figure **3**). [5] [8]

By studying the published papers on asphaltene structure, it is concluded that asphaltenes are polydisperse molecules that mostly consist of polynuclear aromatics centers with different proportions of aliphatic and alicyclic moieties and small amounts of heteroatoms (oxygen, nitrogen, sulfur), and heavy metals (vanadium and nickel) as shown in Figure **4** .
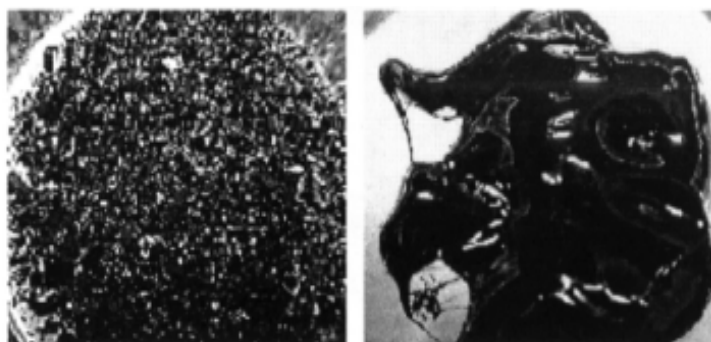
Figure 3: *Asphaltenes (left), Resins (right). (Goual L. 2012)*
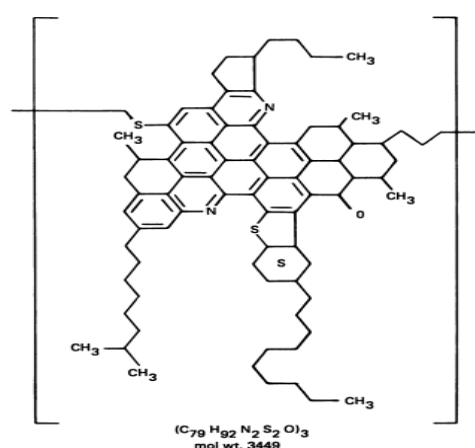
Figure 4: *Hypothetical micro-structure of a petroleum asphaltene (Speight, 1982)*

1.2.1. Asphaltenes: Constituents of Bitumen

It is known that all fractions of petroleum should be used as effectively as possible in order to cover the worldwide demand for petroleum. One of the most important fractions is bitumen which is widely used but it is rich in asphaltenes that should be isolated and removed prior to usage. [9]

According to Speight, the term *Bitumen* (also, on occasion, referred to as *native asphalt* and *extra heavy oil*) is used to characterize oil which has a color ranging from reddish brown to black, and a physical state from viscous to brittle. [2] Bitumen fractions can be produced by distillation of the crude oil followed by the de-asphalting step which is performed using the SARA method. The final asphaltene is a low value added product. [10]

In detail, a defined amount of Bitumen, as feedstock, is mixed with the requested amount of paraffin at room temperature under bar magnet stirrer conditions to improve the yield. At the end of the desired time semi-solid materials could only be separated. Produced asphaltenes are brown/dark-brown granular solids which are isolated by filtration and washed thoroughly with the paraffin until the washings are colourless. In the next step the product is dried "in vacuo" to constant weight. The same process using different conditions and solvents can be also used. The described method is the first approach of a typical process for the isolation and the collection of pure asphaltenes that is widely used. [9]

1.3 Properties of Asphaltenes

In this section physical, the chemical and thermodynamic properties of asphaltenes are studied to give a first description of their physicochemical and thermodynamic behavior. Firstly, the physical properties are analyzed as they were studied and published by various scientists all these years. Furthermore, possible chemical reactions of asphaltenes are given (chemical properties) and finally the thermodynamic behavior of asphaltenes is outlined.

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[9] **Speight, J.G., Long, R.C. and Trowbridge, T.D.** *Factors Influencing the Separation of Asphaltenes from Heavy Petroleum Feedstocks. Fuel. 1984, Vol. 63, pp. 116-120.*
[10] **Odebunmi, Ezekiel Oluyemi and Olavemu, Abimbola George.** Extraction of Chemical Constituents of Bitumen Using a Mixed Solvent System. *Open Journal of Applied Sciences.* 2015, 5, pp. 485-494.

1.3.1. Physical Properties of Asphaltenes

a. Composition of asphaltenes

As it has arisen in various studies and according to the dominant view, asphaltenes are polydispersed molecules mostly consist of polynuclear aromatics with different proportions of aliphatic and alicyclic moieties. Also, small amounts of heteroatoms (O, N, S) and metals (Va and Ni) were located. [4] It is noted that, the amount of these components and others characteristics of asphaltenes depend on the origin of the crude oil. [11] In detail, the elemental composition of asphaltenes varies having an average hydrogen-to-carbon ratio of 1.15 ±0.05%, while oxygen and sulfur contents vary from 0.3 to 4.9% (O/C) and from 0.3 to 10.3% (S/C), respectively. The ratio of nitrogen (N/C) is found in smaller proportions, ranging from 0.6 to 3.3%. [12]

b. Molecular Weight of asphaltenes

For many years, scientists were not able to determine the molecular weight of asphaltenes because of their small solubility in different solvents. Another problem which was in fact related to the molecular weight, is the absorption of resins and the dependency of asphaltenes on method and conditions of the measurement. [2][6] The first paper that mentioned the molecular weight of asphaltenes was published by Pfeiffer and Saal (Pfeiffer and Saal, 1940). In this article the molecular weight varied from 80000 to 140000Da and was determined using monolayer measurements. [13] Seventeen years later, Ray measured the molecular weight using ultracentrifuge method and suggested a molecular weight which varied from 13000 to 30000Da and he determined the particle size of molecules to be in the range of 30 to 40Å. [14] According to new studies, the molecular weight varies from 2000 ± 500 Da, and it is measured, using highly polar solvents which prevent aggregation, (Speight, 1999). [6] Until in 2009 the scientists seem to agree with this value and it is accepted that this range actually represents the real molecular weight of asphaltene. [6][7] However, according to new researches these values are declared void and the new molecular weight is calculated at 750 Da, (Mullins, 2010).

[11] **Nabzar, L. and Aguilera, M. E.** The Colloidal Approach. A promising Route for Asphaltene Deposition Modeling, Oil & Gas. *Science and Technology.* 2008, Vol. 63, 1, pp. 21-35.

[12] **Speight J. G.** Petroleum Asphaltenes, Part 1. Asphaltenes, Resins and the Structure of Petroleum. *Oil & Gas Science and Technology.* 2004, Vol. 59, 5, pp. 467-477.

[13] **Pfeiffer, J.P and Saal, R.N.J.** Asphaltic Bitumens as a Colloidal System. *Journal of Physical Chemistry.* 1940, Vol. 49, pp. 139-149.

[14] **Ray, R.B, Witherspoon, P.A and Grim, R.E.** A Study of the Colloidal Characteristic of Petroleum using the Ultracentifuge. *Journal of Physical Chemistry .* 1957, Vol. 61, pp. 1296-1302.

c. Particle size of asphaltenes

The first repost about the particle size of asphaltenes was published by Katz and Beu in 1945. They were examining the behavior of asphaltic bitumens in the wellbore and under pressure drop, when they observed that the particle size of asphaltenes was less than 65Å. They used an electron microscope to measure the size of the particles. [15] Half century later, Espinat *et al.* concluded that asphaltenes are flat aggregates structures whose size and molecular weight mainly depend on solvent and temperature. As temperature increases, a decrease of molecular weight and particle size of asphaltene was noticed, while by increasing the solvent proportion the molecular weight and particle size of asphaltene were increased. The results of their study, which were measured by neutron and small angle X-ray scattering, are given in Tables **2** and **3**. [7] [16]

Table 5: *Molecular weight and particle size at different temperatures, (Espiant, 1993)*

Temperature (℃)	Molecular weight	Diameter (nm)
-27	138100	20
-10	83100	15.6
22	49700	13.3
77	21900	10

Table 6: *Molecular weight and particle size with various amounts of n-heptane, (Espiant, 1993)*

n-heptane (% w/w)	Molecular weight	Diameter (nm)
0	49700	13
30	81300	15.5
35	104700	17.7
40	136800	20

An alternative view was expressed by Rassamdanna and Sahimi who concluded that the particle size is a time-dependent quantity which evolves together with the aggregation of the asphaltene. [17]

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[15] **katz, D.L and Beu, K.E.** Nature of Asphaltic Substances. *industrilal and Engineering Chemistry .* 1945, Vol. 37, 2, pp. 195-200.

[16] **Espiant, D. and Ravey, J. C.** Colloidal Structure of Asphaltene Solutions and Heavy-Oil Fractions Studied by Small-Angle Neutron and X-Ray Scattering. *SPE International Symposium .* SPE Paper No. 25187, 1993, pp. 365-373.

[17] **Rassaamdana, H. and Sahimi, M.** Asphalt Flocculation and Deposition: II Formation and Growth of Fractal Aggregates. *AICHE Journal.* 1996, Vol. 42, 12, pp. 3318-3332.

d. Density of asphaltene solutions

It is known that asphaltenes are solids at ambient conditions and therefore, the density at the reservoir conditions or at the production conditions could be approached using a solvent (indirectly measurements of density) in order to understand the behavior of the fluid. In the most published articles the density of asphaltenes was indirectly measured using toluene as a solvent. For this purpose, the densities of a series of asphaltene solutions in toluene or another mix of solvents at different concentrations were measured. Yarranton and Marvey (1996) studied the density of asphaltene using different concentrations of toluene. They recorded the average density which varied from 1123 to 1162 kg/m³. The solvent mixture was *n*-hexane – toluene from 20vol. % to 100vol. % toluene. The measurements were taken under constant temperature at $25.7 \pm 0.05℃$ and the measurements were calculated with an accuracy of $\pm$ 0.03 kg/m³. [18] Another study that was published by Alboudwarej *et al.* (2003) mentioned the distribution of the density using samples of different geographic origin. The density of asphaltenes varied from 1181 kg/m³ to 1192 kg/m³ in 50 wt. % *n*-heptane – toluene, at 23℃. The densities were defined with an accurate of ± 0.5 kg/m³. [19] Finally, new studies assuming that asphaltenes form regular solutions when they are mixed with aromatic solvents use the following equation to calculate the density. [20]

$$\frac{1}{\rho_{mix}} = \frac{mass\ fraction\ of\ toluene}{density\ of\ toluene} + \frac{mass\ fraction\ of\ asphaltenes}{density\ of\ asphaltenes}$$

1.3.2. Chemical Properties of Asphaltenes

Literature related to reactions of asphaltenes is limited. However, asphaltenes are able to participate in reactions. Their reactions depend on the energy of the bonds with respect to the temperature, the pressure and the reaction time. In addition, the existence or the absence of functional groups and the stereochemistry of the molecule have an important role in the success of the reaction. Moreover, it has been observed that the

[18] **Marvey, Yarranton W. και Jacob, Masligah H.** Molar Mass Distribution and Solubility Modeling of Asphaltenes. *AIChe Journal.* 1996, Τόμ. 42, 12, σσ. 3533-3543.

[19] **Alboudwarej, Hussein.** Regular Solution Model for Asphaltene Precipitation from Bitumens and Solvents. *AIChe Journal.* 2003, Τόμ. 49, 11, σσ. 2948-2956.

[20] **D., Powers P., et al.** Regular solution based approach to modeling asphaltene precipitation from native and reacted oils: Part 1, molecular weight, density, and solubility parameter distributions of asphaltenes. *Fuel.* 2016, 178, pp. 218-233.

reactions of the asphaltenes are based not only on their condensed aromatic structure but also on the appending alkyl- and naphthenic- moieties. [2]

In detail, one of the basic reactions of asphaltenes is the oxidation which can be achieved using common oxidizing solutions such as acid and alkaline peroxide, acid dichromate, and alkaline permanganate. It is usually a slow process and the main products have phenolic and carboxyl groups. Another reaction is the hydrogenation which is performed either by addition of molecular hydrogen or by addition of various functional groups into the asphaltene molecules, such as sulfomethylation ($-CH_2SO_3H$ group). The products are usually resins and oils at temperatures higher than 250°C, while under much milder conditions such as in lithium – ethylenediamine or sodium – liquid ammonia the reaction produces lower molecular weight molecules. Other typical reactions of asphaltenes are the halogenation (Cl, Br, I), which leads to halo-derivatives, the metallation, the phosphorylation and the sulfur reactions. Metals can be introduced to the asphaltene molecule using elemental metals or metallo-organics substances while reactions of asphaltenes with sulfur can be achieved using elemental sulfur which is in turn converted to hydrogen sulfide. [2]

Finally, asphaltenes can be thermally decomposed at low temperature (470°C) and afford as products light oils that contain higher (to > C_{40}) paraffins and coke, (Figure **5**). Also, asphaltene pyrolysis (350°C to 800°C) produces substantial amounts of alkanes (having up to 40 carbon atoms in the molecule). However, at high temperatures aside from paraffins formation benzene and naphthalene nuclei are observed as the predominant aromatics in the light oil while the amounts of coke are increased. In conclusion, thermal decomposition of asphaltenes affords light oil that has similar composition with the heavy oil and hydrocarbon gas composed of lower paraffins, which after the removal of the by-products (water, ammonia and hydrogen sulfide) has good burning properties. [2]

$$H_2, CO, CO_2, H_2S, SO_2, H_2O$$

Asphaltenes Fraction

$$CH_4, CH_2=CH_2, CH_3CH_3, CH_3(CH_2)_n CH_3$$
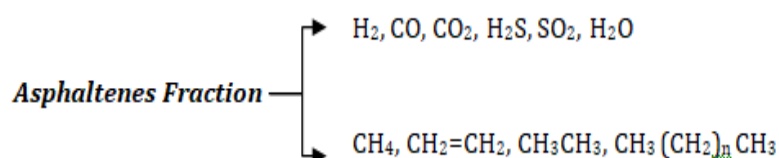
Figure 5: *Thermal decomposition of asphaltenes at 470°C (Speight, 2007)*

1.3.3. Thermodynamics of Asphaltene

Thermodynamics is a powerful tool to predict the development and the maximum precipitated amount of asphaltene which can be observed in a crude oil under specified conditions. There are two different schools of thought about the nature of asphaltenes in solution:

➢ One school of researchers suggested that, asphaltenes are dissolved and they form one liquid phase, from which they can be precipitated depending on the thermodynamic conditions applied (temperature, pressure and composition). Therefore, the asphaltene precipitation is recognized as a thermodynamically reversible process. This theory is called "Solubility Approach".[7][21]

➢ The second school of researchers considers that asphaltenes are solid particles, which are suspended colloidally in the crude oil and they are stabilized by large resin molecules. Consequently, the deposition process is irreversible. This approach is called "Colloidal Approach" and it is used to describe the phenomena of asphaltene deposition.[7][22]

a. **Solubility Approach**

According to this approach asphaltenes are molecules that are considered dissoluble in the oil while the dissoluble proportion is a function of the thermodynamic conditions of the system. The precipitation process is considered as a completely reversible process dependending on the conditions and the thermodynamic state of the system.[7] The solubility phenomenon of asphaltenes may consist of a number of different equilibria which can be generalized into three categories:

➢ Solubility or distribution between liquid and solid phase:

$$\text{Asphaltene (L)} \leftrightarrow \text{Asphaltene (S)}$$
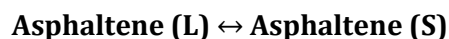
➢ Aggregation or association of asphaltene molecules:

$$A_1 + A_{i-1} \leftrightarrow A_i$$

According to Andersen and Birdi, the aggregation process of asphaltenes molecules in solution or in mixtures takes place at different stages or step-wise according to the scheme (Figure **6**). Micelles can be formed by associations of the particles through the

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[21] **G.A.Mansoori, T.S., Jiang and Kawanaka, S.** Asphaltene Deposition and its Role in Petroleum Production and Processing . *The Arabian Journal for Science and Engineering .* 1988, Vol. 13, 1.

[22] **K., Leontaritis and Mansoori, G.A.** Asphaltenes Flocculation During Oil Production and Processing: A Thermodynamic Colloidal Model. *Society of Petroleum Engineers.* 1987, SPE 16258.

hydrogen bond and afterward larger aggregates can be formed by the association of many micelles. However, the study was concluding that the particle size is less than the critical sedimentation size and the aggregation can minimal increase the solubility. [23] [24]

Monomers → (particles → micelles) → aggregates
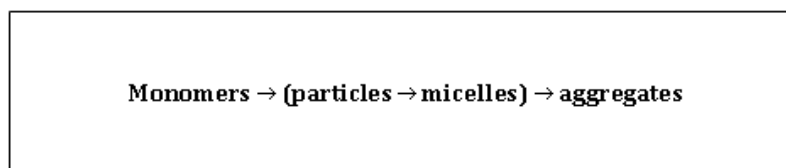
Figure 6: *Scheme of aggregation steps*

➤ Interaction with resins:

$$A + R \leftrightarrow A\!-\!R$$
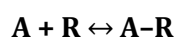
Andersen (1999) observed that the solubilization of asphaltenes depends on the amounts of resins (peptization with resins) in the solution. The decrease of the resins proportion causes a decrease in the solubility of asphaltenes. [23]

Scientists use two models to describe the solubility of asphaltenes. The first model is based on the application of the cubic equation of state (Eq. **1**) while the second is based on the use of the Hildebrand solubility parameter (δ) (or the concept of cohesion energy density), (Eq. **2**). According to Andersen the second model is enough prevalent and involves either direct calculations using the Scatchard – Hilbebrand (S–H) equation (Eq. **3**) or calculations of interactions parameters between the asphaltene constituents and the remaining constituents of the oil.

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = R\,T \tag{1}$$

where $a = 3\,p_c\,V_c^2$ and $b = \dfrac{V_c}{3}$

The solubility parameter, δ, is a measure of the cohesive energy density or as it is also called the initial pressure. This pressure is exerted by molecules in the solution. It is defined as:

[23] **Andersen, I. Simon and Speight, G. James.** Thermodynamic models for asphaltene solubilty and precipitation . *Journal of Petroleum Science and Engineering.* 1999, Vol. 22, pp. 53-66.
[24] **Andersen, I. Simon and Birdi, S. Kulbir.** Aggregation of Colloid and Interface Science. 1991, Vol. 142, 2, pp. 497-452.

$$\delta = \frac{\Delta U}{V} = \frac{\Delta H - RT}{V} \qquad (2)$$

where ΔH is the heat of vaporization of a particular liquid,

      R is the gas constant,

      T is the absolute temperature.

It is noted that the value of the solubility parameter (δ) is characteristic of one specific molecule. Therefore, when two liquids which have different molecules are mixed the molecules with the highest pressure (higher value of δ) "squeeze" the others molecules and this process causes two immiscible phases. [7] However, changes in the temperature may have an effect on the solubility parameter (δ). Also, big differences between two solubility parameters (δ) reflect the phase separation phenomenon. Another approach related to this model is the Scatchard – Hilbebrand (S–H) equation by which the solubility parameter can be calculated. However, the main assumption is the regular solution theory which should be applied to crude oil. [23]

$$\ln \alpha_a = \ln \ + \frac{M_a}{R} T \rho_a [\Phi_s^2 (\delta_s - \delta_a)^2] \qquad (3)$$

where α_a is the activity of the solute,

      X_a the solubility (mol fraction),

      M is the molecular weight,

      ρ_a is the density,

      Φ_s the volume fraction of solvent,

      δ_s, δ_a are the solubility parameters of the solute (asphaltenes) and solvent (deasphalted oil), respectively.

The other model is based on the cubic equation of state such as the Soave –Redlich – Kwong (SRK) and Peng –Robinson (PR) equations. These equations are used to calculate the equilibrium properties of the system like the temperature, the pressure and composition relationships. [23]

The following figure depicts the solubility approach as it is given by Leontaritis (Figure **7**). It can be observed that all the molecules exist at equilibrium and are soluble in the solution.
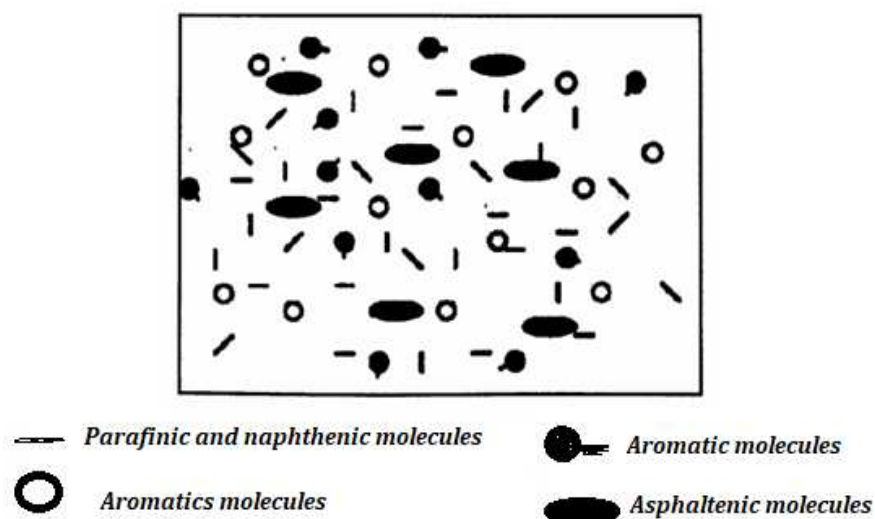
Figure 7: *Molecular – Thermodynamic model (Leontaritis, 1988)* [7]

b. Colloidal Approach

In 1988 Leontaritis proposed a thermodynamic colloidal model to describe the flocculation of asphaltenes. The model is based on statistical thermodynamics and colloidal science. The main assumption of the model is that asphaltenes "exist in the oil as solid particles in colloidal suspension" while resin particles help them to stay stable as asphaltenes are absorbed on their surface, (Figure **8**). Also, the small intermolecular repulsive forces between resin molecules prevent the flocculation of asphaltenes, (Figure **9**). [22] The principle of the model is the transfer of resins from the asphaltene phase to the oil face and vice – versa. The peptide bond between resins and asphaltenes is destroyed and the asphaltene micelles are attracted to each other, they are grown in size and the asphaltene molecules abandon the colloidal phase (formation of aggregates). [7] [22] The amount of the resins which exist in the liquid phase (oil phase) directly affects the aggregation of the asphaltenes. The decrease of the resin amount causes a reduction in the peptide bonds between resins and asphaltenes (reduction of absorbed resins), and the surface of the asphaltene molecule cannot be coved allowing the micelles to aggregate and eventually flocculate. [22]

Finally, the model uses the chemical potential in order to predict the asphaltene behavior. The basic assumption is that two phases exist which are in equilibrium. Therefore the chemical potential of the resins in liquid phase is equal to the chemical potential of the solid phase. Also, it is assumed that the behavior of the resins and the asphaltenes stays the same regardless of what the composition of liquid phase is because it is assumed that from the beginning to the end the physical state of the solid

phase is the same as the colloidal phase of asphaltenes (asphaltenes particles covered with resins). [22]
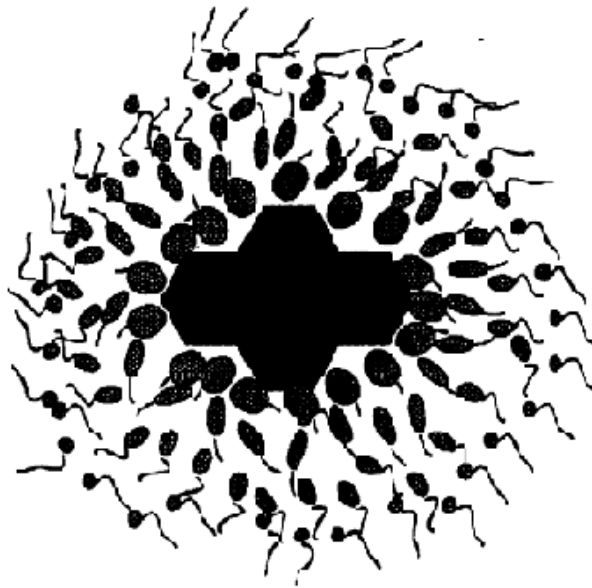
Figure 8: *Asphaltene – Resin micelle (Leondaritis, 1988)* [7]

○   Resin molecules

●   Aromatics molecules

╴╴   Molecules of different size and paraffinic nature

⬤   Asphaltenic particles of diffrent sizes and shapes
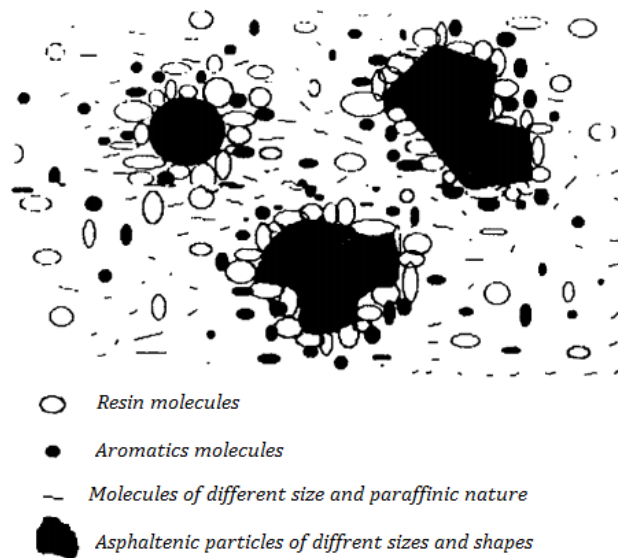
Figure 9: *Thermodynamic –Colloidal model (Leontaritis. 1988)* [22]

Possible Structure of Asphaltenes

2. Introduction

Many researchers tried to determine the structure of asphaltene by using different methods and techniques,. However, a great number of assumptions has been made in these efforts to determine the highly complex molecular structure of asphaltene. According to Speight, asphaltenes could be better described in terms of several structure types rather than a definite molecular structure. [25]

According to the published papers, spectrometric techniques are usually used to identify the asphaltenes and they give information about the carbon skeleton of the asphaltene molecules. Also, studies have demonstrated that asphaltene structure contains molecules of variable aromaticity, and different content of heteroatoms such as sulfur and nitrogen and metals (nickel and vanadium). It is noted that asphaltenes that were studied came from various petroleums and natural asphalts.

Finally, all the researchers have concluded that the asphaltene fraction is a complex mixture of polydispersed molecules in terms of size and chemical composition. These structures cannot be represented by only one molecular model and therefore, in the literature several models have been proposed to describe asphaltene structure.

2.1. Literature Review on Asphaltene Structures

The first reference to the physical state of asphaltenes in the literature was published in **1924** by **Nellensteyn**. Nellensteyn's model of bitumens is made of micelles that are protected by absorbed resins and hydrocarbons, which are dispersed in the hydrocarbon medium. The center of the micelle is supposed to be made of elementary carbon and the difference in the composition of the absorbed molecules determines the different kind of bitumens. [26] In **1933** in the 1st World Petroleum Congress Nellensteyn

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[25] **G.James, Speight and Speros, Moschopedis E.** On the Molecular Nature of Petroleum Asphaltenes. *American Chemical Society.* 1982, Vol. 195, pp. 1-15.

[26] **Teh, Yen Fu.** Structure of Petroleum Asphaltene and its Significance. *Energy Sources.* 1974, Vol. 1, 4, pp. 447-463.

suggested that the nuclei of asphaltene micelles consist of microcrystalline graphite particles which could be observed by X-ray diffraction. [27]

Hilman and **Barnett** (Hilman and Barnett, **1937**) published an article in which resins and asphaltenes consist of polycyclic nuclei that form a chain structure and whose number varies from 3 to 6. They tried to define the resins and the asphaltenes and they concluded that they differ in the size of their nuclei. [26]

Some years later, **Pfeiffer** and **Saal** (Pfeiffer and Saal, **1940**) proposed that asphaltenes consist of high-molecular aromatic hydrocarbons. They also observed that asphaltenes had a tendency to absorb aromatic hydrocarbons of low molecular weight while their centers were being formed by the absorption of a part of the maltenes, which includ n-alkanes that are soluble to pentane or heptane, on the surface or the interiors of the asphaltene particles. Finally, they noted that the structure of micelles required the substances with the greatest molecular weight and the most pronounced aromatic nature to be arranged close to the nuclei. These structures were surrounded by lighter constituents of a lesser aromatic nature and so on, until the inter-micellar phase was formed (Figure **10**). [13]
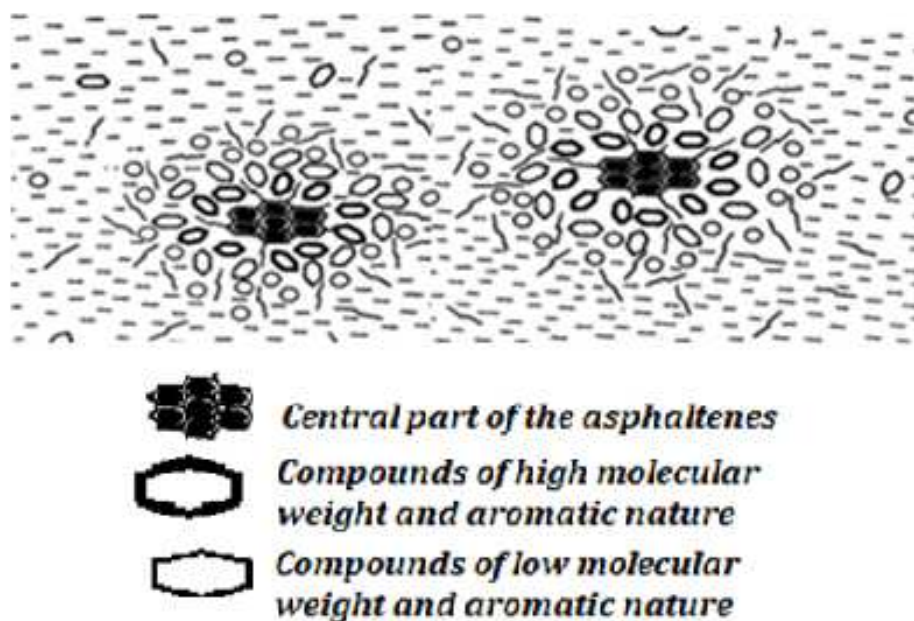
Figure 10: *Representation of peptized asphaltene micelles, (Pfeiffer and Saal, 1940).*

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[13] **Pfeiffer, J.P and Saal, R.N.J.** Asphaltic Bitumens as a Colloidal System. *Journal of Physical Chemistry.* 1940, Vol. 49, pp. 139-149.
[27] **Nellensteyn, F.J.** Theoretical Aspect of the Relation of Bitumen to Solid Matter. *1st World Petroleum Congress.* London, 1933.

Studies which were published in late '**50** suggested that aromatic and aliphatic alkyl structures exist in the asphaltene molecule but there was no evidence that naphthenic structure was present. These studies were based on spectroscopic techniques, IR, NMR and X-ray diffraction techniques. [28]

In **1961**, **Yen** published the first review which mentioned all the previous results about asphaltene structure. He summarized and supported the following: asphaltene molecules contained alkyl and aromatic structures which were determined using IR and NMR techniques, the molecular weight values varied depending on the method of the measurement while X-ray diffraction measurements showed aromaticity and crystallite parameters in the asphaltene samples. Finally, he proposed a macrostructure model of the asphaltenes as illustrated in Figure **11**. [29]
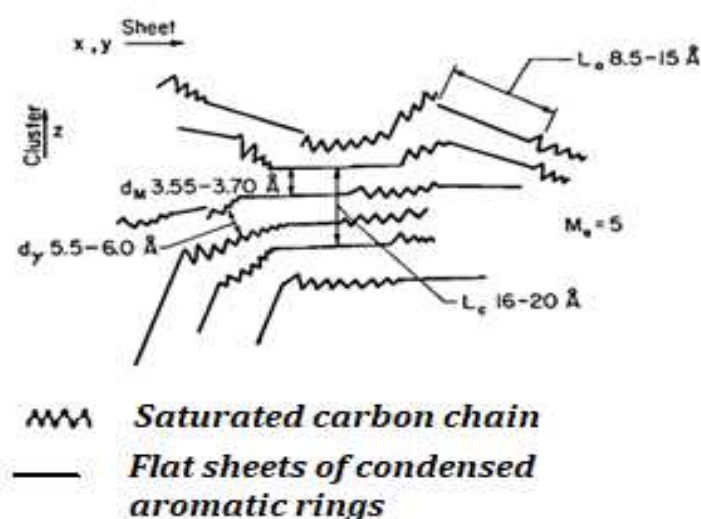
Figure 11: *Cross-sectional view of an asphaltene model based on X-ray diffraction, (Yen, 1974)*

Some years later, **Dickie** and **Yen** (Dickie and Yen, **1967**) studied seven different samples of asphaltenes for which they attempted to correlate molecular weight values with possible structures of asphaltenes. They used many techniques such as X-ray diffraction and scattering with high and low angle, mass spectroscopy, gel permeation chromatography and vapor pressure osmometry. They concluded that the asphaltene molecule was consisted of alternating sequences of n-alkyl groups and condensed aromatic disks, which were called "islands". In the same study, they tried to optimize

[28] **Otto, P. Strausz, Mojelsky, Thomas W. and Lown, Elizabeth M.** the molecular structure of asphaltene: an unfolding story. *Fuel.* 1992, Vol. 71, pp. 1355-1363.
[29] **Teh, F. Yen, Erdman, G. Gordon and Pollack, S. Sidney.** Investigation of the Structure of Petroleum Asphaltenes by X - Ray Diffraction. *Analytical Chemistry.* 1961, Vol. 33, 11, pp. 1587-1594.

and visualize the asphaltic environment shown in Figure **12**. [30] According to the authors, the above figure was the result of all the knowledge that accumulated till then and it visualized all the knowledge about asphaltenes and their environment. However, this figure depicts some of the possible combinations of unit sheets that can exist. [30]

A.	Crystallite	B.	Chain bundle
C.	Particle	D.	Micelle
E.	Weak link	F.	Gap and hole
G.	Intracluster	H.	Intercluster
I.	Resin	J.	Single layer
K.	Petroporphyrin	L.	Metal
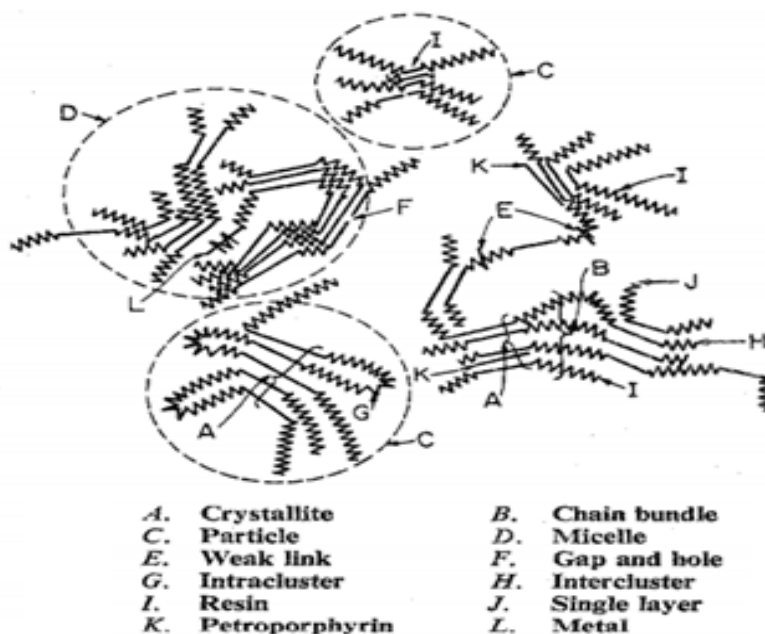
Figure 12: *Macrostructure of asphaltics, (Dickie-Yen 1967)*

In **1974**, **Yen** consulted previous studies that were published the last five decades to propose a model for the average structure of resins, asphaltenes and others bitumens. According to his model the asphaltene structure is divided in two types: a ***micro-structure*** (*fine*) and a ***macrostructure*** (*bulk*). The first type is related to structural parameters such as aromaticity, possibility of substitution, etc. (chemical methods), while the second is related to dissociation-association, change-transfer, excitation, etc. (physical approaches). [26]

a. Fine Structure (micro-structure)

Based on oxidation rate studies which had been already done, Yen noted that asphaltenes contain distinctive aromatic nuclei. Taking into account the HIeA ratio, which is an indicator of compactness in the clusters, NMR and X-ray data, he observed a peri-condensed polynuclear aromatic system and concluded that the aromatic nuclei are 50-70% substituted by other alkylchaind, the majority of which are methyls, and

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[30] **John, Dickie P. and Teh, Yen Fu.** Macrostructures of the Asphaltic Fractions by Varius Instrumental Methods. *Analytical Chemistry.* 1967, Vol. 39, 14, pp. 1847-1852.

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naphthenics. [26] Also, in the asphaltene molecules neither branched chains (secondary and tertiary carbons) nor short methylene bridges between the aromatic centers could be observed. Finally, he noted that the amount of aromatic hydrogen atoms did not exceed the value of 5%, and these were not associated with other heteroatoms such as sulfur, oxygen and nitrogen that were also detected. The concept of average structure depicted in Figure **13**, in which a proposed molecular formula for asphaltene is shown. [26]
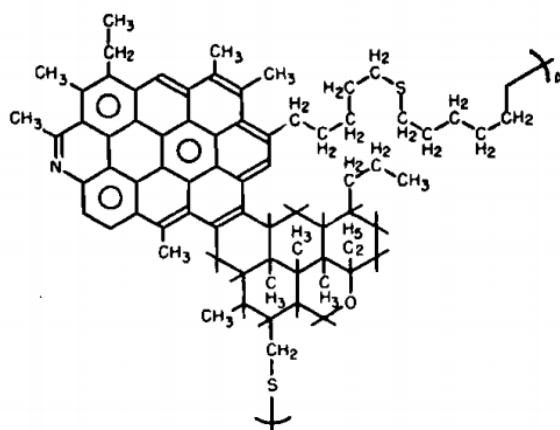
Figure 13: *Hypothetical molecular formula of an asphaltene, (Yen, 1974)*

b. Bulk Structure (macrostructure)

In this structure, Yen proposed that the π-electrons of the aromatic rings were attracted to each other forming layer structures through association. This association was based either on intermolecular or intramolecular interactions. In the case of the intramolecular association the aromatic character of the centers can occupy different locations in one molecule, also known as delocalization of π-electrons, resulting in the overlap of the π-systems, as shown in Figure **14**. He found that the packing of the asphaltene molecules in the medium consisted of approximately five layers as it has been already shown in Figure 11. In this case the conventional meaning of molecular weight could not be applied but the molecular weight of one single layer could be taken instead. However, the molecular weight of the micelles which can be formed after the aggregation may be also measured. Finally, in these layers there exist some gaps or holes which are possible sites for coordination of metals that may be associated with the asphaltic sheets. The existence of the metals is caused by the metallo porphyrins. The way of association can be either the π-π interaction or the coordination through the heteroatoms in the sheets, (Figure **15)**. It is noted that the separation of layers can be achieved by a variety of chemical means, e.g., charge-transfer process. [26]
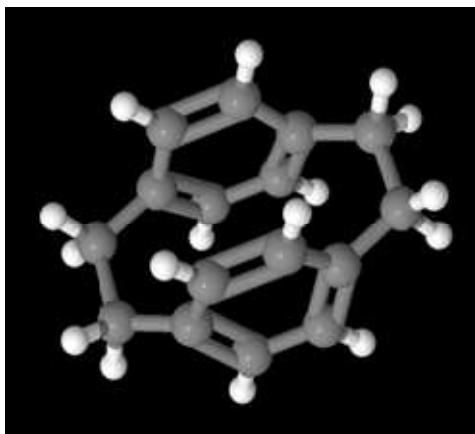
Figure 14: *Overlay of aromatic rings* [31]
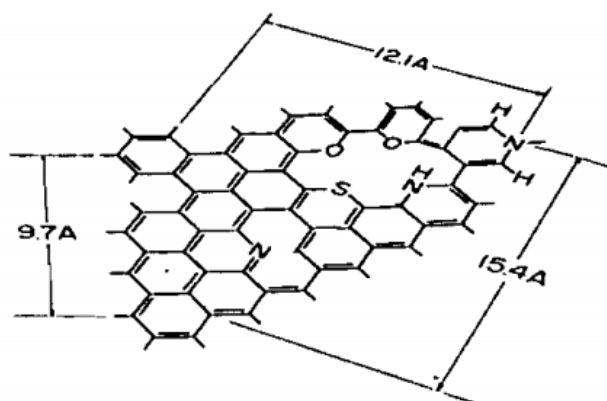
Figure 15: *An aromatic sheet of the asphaltene structure – Fisher model, (Yen, 1974)*

In the late 70s, **Strausz** *et al*. (Strausz, **1977**) based on the study of the molecular weight, tried to determine the molecular structure of asphaltenes. Strausz applied chemical methods such as electron transfer and anions using octylation or protonation and other chemical reactions using potassium, silylation and diazomethane. From the amounts of octyl groups and potassium atoms which were consumed by the reaction with the asphaltene molecule the molecular weight of a single molecule of asphaltene could be measured. Some of the reactions are shown in Figure **16**. [32]

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[26] **Teh, Yen Fu.** Structure of Petroleum Asphaltene and its Significance. *Energy Sources.* 1974, Vol. 1, 4, pp. 447-463.

[31] http://www.chemspider.com/Chemical-Structure

[32] **Ignasiak, T., Kemp-Jones, A.V. and O.P.Strausz.** The molecular structure of Athabasca Asphaltene. Cleavage of the Carbon-Sulfur Bonds by Radical Ion Electron Transfer Reactions . *Journal Organic Chemistry.* 1977, Vol. 42, 2, pp. 312-320
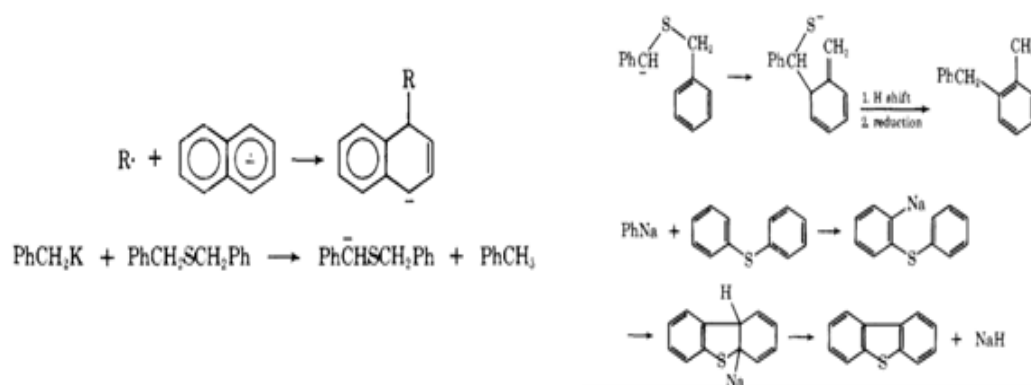
Figure 16: *Determination of molecular weight using chemical reactions, (Strausz, 1977)*

Also, by the same study was pointed out that the average value of the aromatic carbons were 42% while the aromatic hydrogen atoms were determined at 8% using NMR spectroscopy. Finally, they noted that oxygen was present in hydroxyl and carbonyl groups while the sulfur atoms formed disulfide bonds. [32] In another work, Strausz (Strausz, **1979**) studied the pyrolysis products of one asphaltene sample. The results gave high amounts of mono-, di-, tri-, and tetracyclic condensed aromatic molecules, which were substituted as presented in Figure **17**. [33] At the same time, other researchers studying the pyrolysis products of the asphaltenes measured small amounts of nitrogen and sulfur which were lost during pyrolysis (i.e. as hydrogen sulfide), and they concluded that there was a tendency for nitrogen and sulfur atoms to remain after thermal decomposition, as opposed to the easy elimination of oxygen. Therefore, the nitrogen and sulfur stability was affected by their location in ring systems. [25] [34]
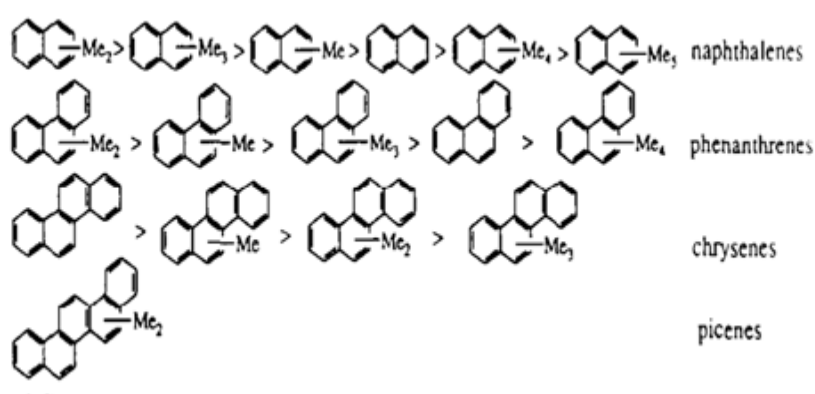
Figure 17: *Aromatic fragments using pyrolysis from an asphaltene sample, (Strausz, 1992)*

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[33] **Rubinstein, I and Strausz, C. Spyckerelle and O. P.** Pyrolysis of asphaltenes: a source of geochemical information . *Geochimica et Cosmochimica Acta.* 1979, Vol. 43, pp. 1-6.
[34] **Ritchie, R. G.S., Rodney, S. R. and W., Steedman.** Pyrolysis of Athabasca tar sands: analysis of the condensible products from asphaltenes. *Fuel.* 1979, Vol. 58, pp. 523-530.

Some years later **Speight** (Speight, **1982**) published a review in which he approached asphaltene structure from a different point of view. In this review he proposed a hypothetical structure of asphaltene based on the analytical method which was used. Therefore, two categorizes were arisen; in the first case, there exist a hypothetical micro-structure and a macrostructure of asphaltenes based on the spectroscopic data while in the second case the asphaltene structure was based on chemical analysis data. [25]

a. Determination of asphaltene structure using spectroscopic data

Based on NMR data and spectroscopic and analytical results, as well as to the different composition fractions of N/C, H/C, O/C and S/C, Speight proposed a hypothetical microstructure of asphaltene which consists of condensed polynuclear aromatic ring systems (6 to 20 aromatic rings) which have alkyl side chains (Figure **18**). However, it is difficult to recognize all the possible structures (changes in the structure) that are part of the asphaltene molecule. [25] Concerning the macrostructure of asphaltenes he kept the same structure as it was described by Yen (Yen, 1961) while he achieved to measure the dimensions of the asphaltene unit including the interlamellar distance, the layer diameter, the height of the unit, and the number of the aliphatic chains which contributed to the micelle structure (Figure **19**). [25]
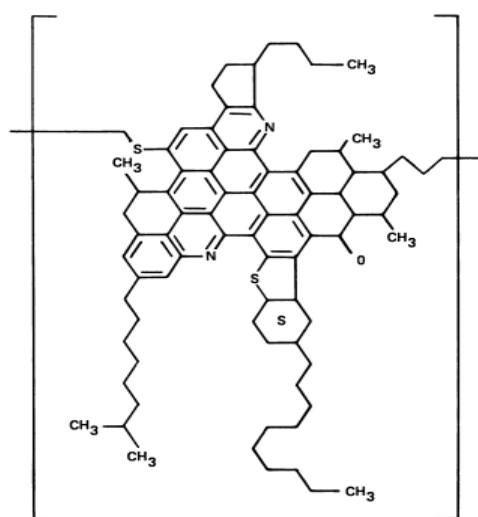
Figure 18: *Hypothetical micro-structure using spectroscopic data (Speight, 1982)*
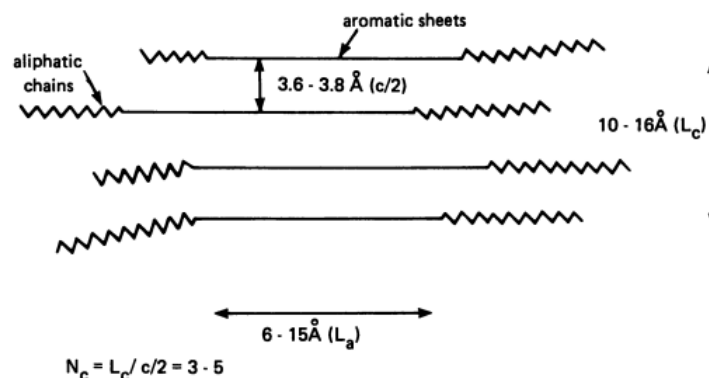
Figure 19: *Hypothetical macro-structure using X-ray data (Speight, 1982)*

b. Asphaltene structure using chemical data

Speight summarized the chemical results which arose in the reactions experiments as they were proposed by Strausz. The use of potassium naphthalide in the asphaltene sample gave sulfur polymers (Figure 20 left) and regular hydrocarbon polymers (Figure 20 right), as they had been already proposed by Strausz. According to Speight the success of the process is based on the ability of the potassium naphthalide (organometallic reagent) to break the carbon-carbon bonds in various diphenylmethanes or 1,2-diarylethanes products. Yet, further transmetallation of the products would give products of questionable composition. Finally, the last step of the identification of the reaction products was an extremely difficult process. [25] [28] [33] [35]
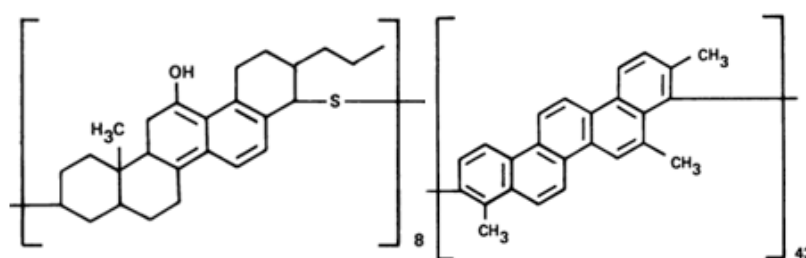
Figure 20: *Sulfur and hydrocarbon polymer using potassium naphthalide, (Speight, 1982)*

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[25] **G.James, Speight and Speros, Moschopedis E.** On the Molecular Nature of Petroleum Asphaltenes. *American Chemical Society*. 1982, Vol. 195, pp. 1-15.

[28] **Otto, P. Strausz, Mojelsky, Thomas W. and Lown, Elizabeth M.** the molecular structure of asphaltene: an unfolding story. *Fuel.* 1992, Vol. 71, pp. 1355-1363.

[33] **Rubinstein, I and Strausz, C. Spyckerelle and O. P.** Pyrolysis of asphaltenes: a source of geochemical information . *Geochimica et Cosmochimica Acta.* 1979, Vol. 43, pp. 1-6.

[35] **Payzant, J. D., Rubinstein, I and Strausz, A.M. Hogg and O. P.** Field-ionization mass spectrometry; application to Geochemical analysis. *Geochimica et Cosmochimica Acta.* 1979, Vol. 43, pp. 1187-1193.

Throughout the '80s the study of the asphaltene structure was in deadlock because of the technological limitations. So researchers resigned to chemical solutions. Strausz used specific chemical reagents to achieve specific reactions such as catalyst ruthenium-ion (RICO - react selectively), thereby succeeding in oxidizing only the aromatic carbons of the asphaltene, that led to its decomposition, while leaving the saturated carbons intact (Figure **21**). [28]
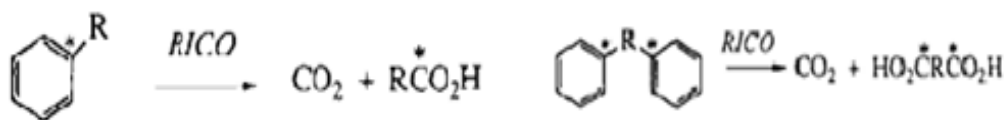
Figure 21: *Chemical reaction using RICO, (Strausz, 1992)*

Strausz and co-workers (Strausz, **1992**) continued to follow the same pattern of chemical reactions and succeeded in decomposing the asphaltene molecule and indentifying the products. The products are given in Figure **22**. Using NMR spectroscopy, they observed that the destruction of aromatic structure of asphaltene was fairly complete and these reactions were nearly quantitative. [28] Furthermore, by taking into consideration the pyrolysis results from previous studies the group tried to connect all the pieces of the "puzzle", proposing a possible structure of asphaltene molecule, as it is illustrated in Figure **23**. [28]
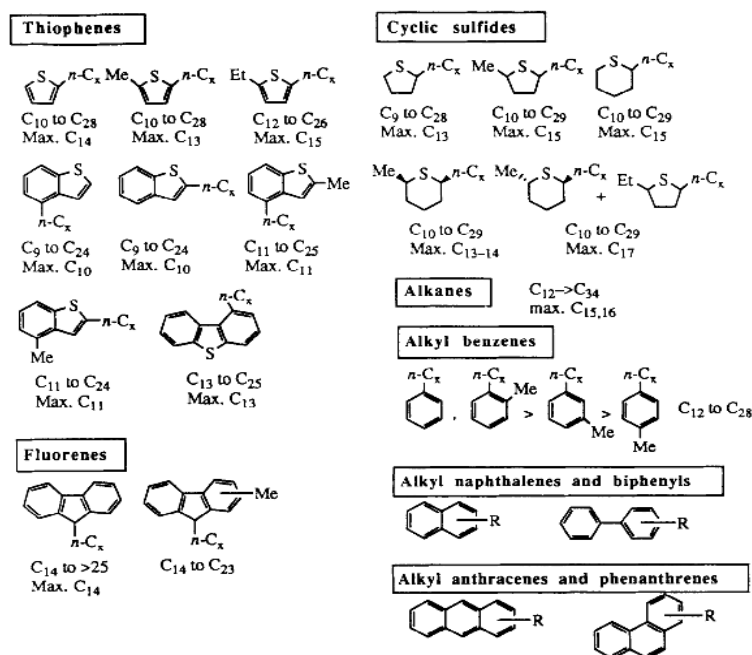
Figure 22: *Structural units indentified using pyrolysis, (Strausz, 1992)*
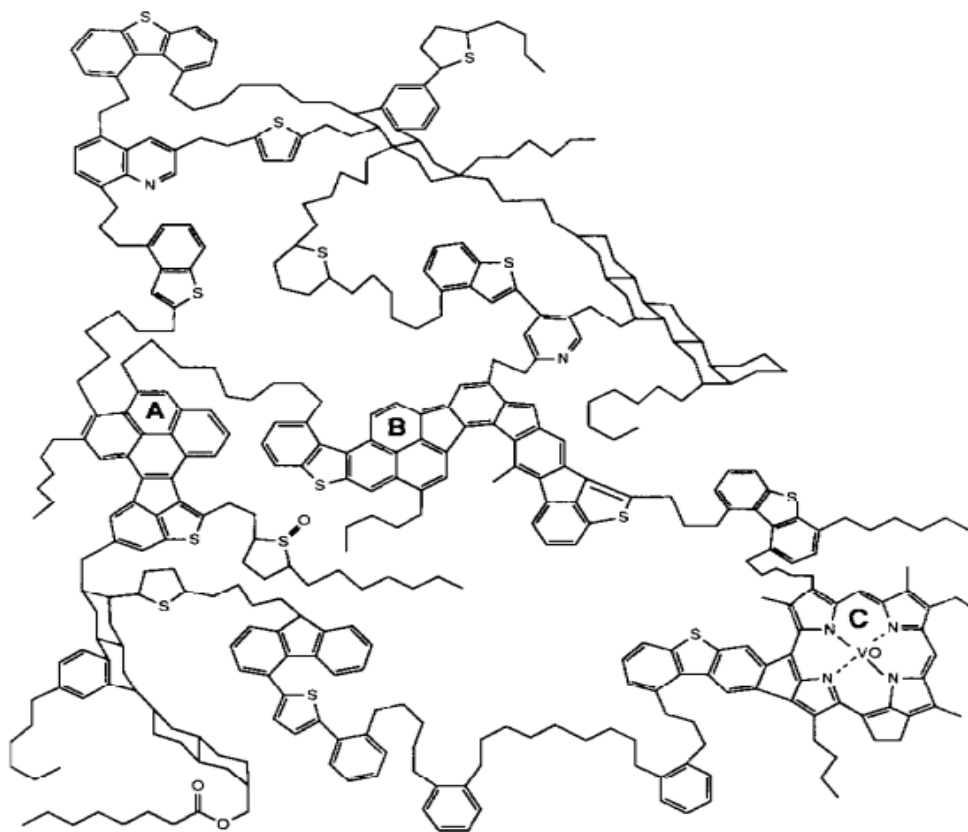
Figure 23: *A hypothetical asphaltene molecule as it is proposed by Strausz et al. A, B and C represent larger aromatic clusters, (Strausz, 1992).*

It seems that the aromatic rings in the asphaltene molecule do not form a single condensed system but rather there are sets of smaller aromatic "islands" linked by bridges, as summarized by the "archipelago model".

Murgich et al. (Murgich et al., **1996**) published an article in which the aggregated structures of asphaltenes and the creation of micelles were studied. They tried to depict the molecule into three dimensions in order to understand in which way the molecules could come close enough to form micelles. They supported that the hydrogen bonds help the systems to come closer but the acceptor sites in the molecule are affected by the stereochemistry of the molecule. Nevertheless, if the molecules of asphaltene and resin have sufficient flexibility, aggregation can occur even if some apparent discrepancy exists between the donor and acceptor sites in the molecule. They concluded that the three-dimensional shape arising from the presence of alkyl and cycloalkyls groups in asphaltenes is very complex and it prevents the formation of the micelles. The formation of micelles can be achieved when the resin molecules fit into the aromatic regions

without the disturbance of the alkyl groups. The results of their study are illustrated in Figures **24** and **25**. [36]
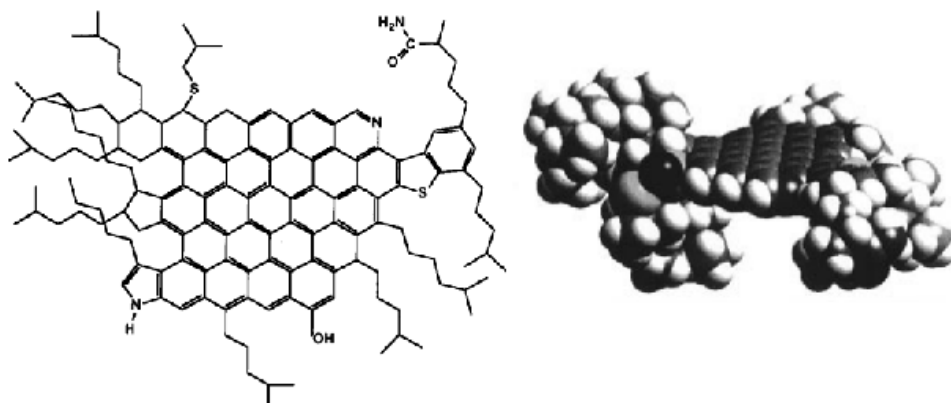
Figure 24: *2-D and 3-D model of asphaltene, (Murgich, 1996)*
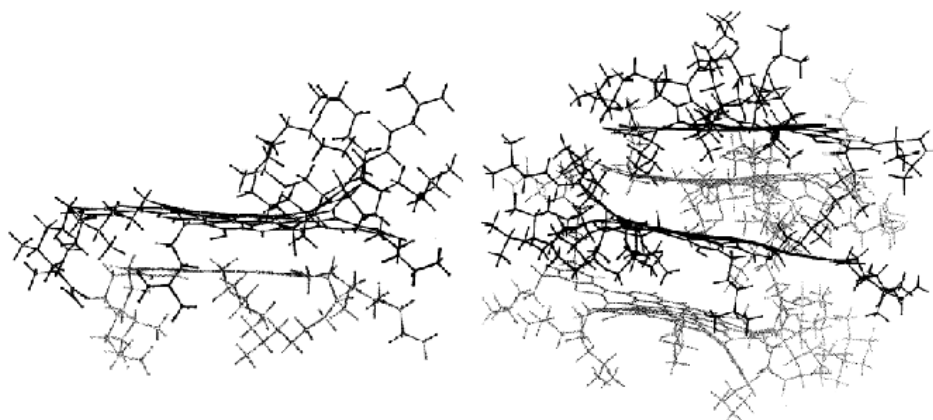
Figure 25: *2-D models of micelles, (the black structure is asphaltene and the grey is resin), (Murgich, 1996)*

In the next few years, most of the published papers were dealing with the issue of asphaltene aggregation and its relationship with resins until 2010, when Mullins proposed a new model based on the existed model of Yen. **Mullins** stated the "Modified Yen Model" (Mullins, **2010**), while trying to approach all the information which existed by then. According to the modified model, the asphaltene molecule has a "nuclei" consisting of polycyclic aromatic hydrocarbon (PAH) ring system (a single one) which can be substituted with cycloalkane, branched- and straight-chain substituents. There are often heteroatoms; nitrogen and sulfur are within the PAH structures while small amounts of oxygen appear in various groups (Figure **26**).

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[36] **Murgich, J., Rodriquez, J. and Aray, Y.** Molecular Recognition and Molecular Mechanics of Micelles of Some Model Asphaltenes and Resins. *Energy & Fuel.* 1996, Vol. 10, pp. 68-76.
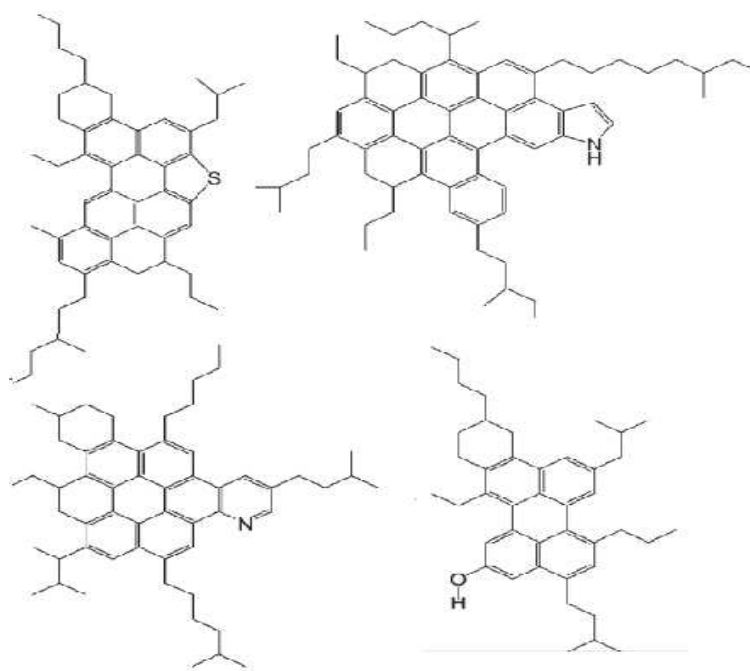
Figure 26: *Modified Yen model: Asphaltene molecular structures, (Mullins, 2010)*

Moreover, when these structures come close enough, they are able to form "nanoaggregates". The usual number of nanoaggregates is six while the exterior of a nanoaggregate consists of alkane substituents, (Figure **27** left). In the next step, these nanoaggregates can form "clusters" of nanoaggregates, (Figure **27** right). These clusters usually consist of eight nanoaggregates. [37] Among other things, Mullins pointed out that the number of distinct PAHs (not conjugated) in a single asphaltene molecule could not be determined. He also added that in the past the asphaltene structure was studied using destructive methods, while the model which was proposed, "Archipelago model", was characterized by many different isolated PAHs within a molecule, with the "islands" being the individual covalently cross-linked PAHs. However, this theory was abandoned as data from nondestructive and carefully controlled destructive methods came to light. More recent data indicate that the asphaltene molecule consist of one central PAH which is called "island" that has pendant aliphatic chains. This model is called "Island" model or "Yen-Mullins" model.[37] In the next five years, more researchers studied the asphaltene molecules and tried to find evidence for the existence of the "Island" structure of asphaltenes.

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[37] **Mullins, Oliver C.** The Modified Yen Model. *Energy & Fuels.* 2010, Vol. 24, pp. 2179-2207.
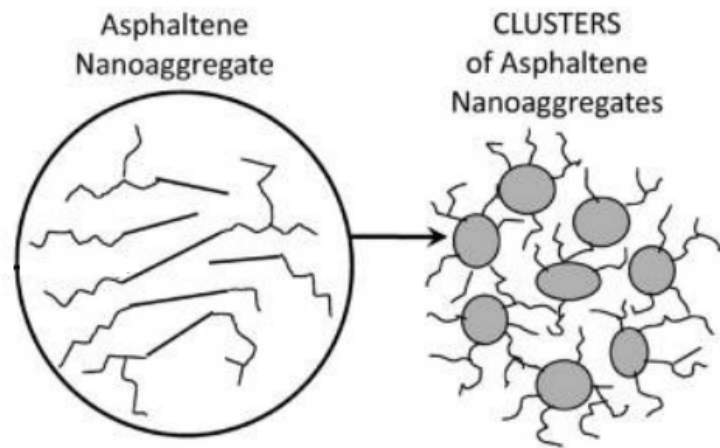
Figure 27: *Modified Yen model: Asphaltene nanoaggregates (left), Clusters of asphaltenes (right), (Mullins, 2010)*

Experimental Detection Methods

3. Introduction

According to Merdrignac (2007) the heavy products characterization can be divided into two types: the *Chemical* and the *Colloidal* characterization: [38]

- "Chemical" characterization gives information about the chemical composition and the main functional groups as well as the structural state of metals and heteroatoms in macromolecules.
- "Colloidal" characterization is based on the study of the dispersion of heavy fractions (asphaltenes) as macromolecules in a good solvent or in their natural medium (maltenes).

Therefore, the chemical characterization of asphaltenes is accomplished using the elemental analysis and the spectroscopic techniques. The results of these analytical techniques are the identification of the structure, the carbon atoms, the heteroatoms, the aromatic rings and possible bonding between them. Viscosity measurements and size-exclusion methods are two techniques which were used by scientist in order to determine the molecular weight and the particle size of the asphaltenes. It is noted that the chemical composition of asphaltenes is source dependent and this means that there exists a wide structural variety of asphaltenes molecule. Also, the aggregation measurements are a function of the experimental conditions (concentration, temperature and using solvent). Therefore, since the techniques are based on different methods and conditions, they are not equivalent. [38]

As illustrated in Figure **28,** in order for the asphaltene sample to be separated and isolated, the fractionation of the main sample should be completed. In the next step the solid sample is dissolved in a good solvent (toluene) and analyzed with the aim to study its physicochemical characteristics.

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[38]   **D., Merdrignac I. and Espinat.** Physicochemical Characterization of Petroleum Fraction; the State of the Art . *Oil & Gas Science and Technology .* 2007, Vol. 62, 1, pp. 7-32.
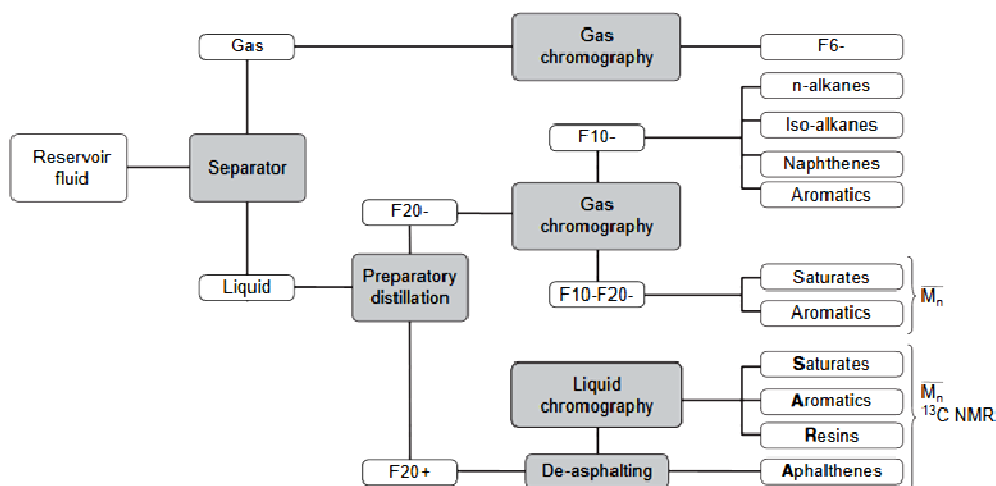
Figure 28: *Fractions of the reservoir fluid during separation process, (Pina, 2006)*

3.1. Asphaltene Isolation

The scientists used many different methods in order to achieve asphaltenes isolation, based on the fractionation of the oil and the use of solvents. In the case of the fractionation, sub-fractions with common characteristics may be isolated from oil as a function of the boiling point, while with the use of solvents, the solubility class of the sample (separation by polarity) may be defined. [38]

3.1.1. Separation Procedure

In this section the precipitation process of asphaltenes is described. To this end, several standard analytical procedures (ASTM D-893, D-3279, D-4124, D-2006, D-2007, IP 143), which mainly differ in the experimental conditions used, will be mentioned. In each one of them, asphaltene isolation is achieved using a large amount of a low-boiling point solvent such as *n*-pentane or *n*-heptane. The added amount of solvent should be higher than "30 volumes of hydrocarbon per volume of sample". After a certain time the insoluble fraction is separated and taken by filtration. The yield is reported as w/w percentage of the original sample. The use of different amounts of solvents affects the yield. [39]

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[39] **Speight, James G.** *Handbook of Petroleum Products Analysis.* New Jersey : Wiley - Interscience, 2002.

a. <u>ASTM D-893 (test method)</u>

A representative sample of oil is heated at 60±5 °C. 10g of this sample are mixed with 100ml *n*-pentane (*n*-C5) and are centrifuged. The oil solution is decanted and the precipitate washed twice with C5 and dried for 30min at 105±3°C.[40]

b. <u>ASTM D-3279 (test method)</u>

0,1mg are placed into a250ml Erlenmeyer flask and *n*-heptane (*n*-C7) is added in a ratio of 1/100 g/ml. The flask is gently heated at 38-49°C under reflux and stirring conditions on a magnetic-stirrer hot plate. The sample stays on the hot-plate for 15-20min and then it is allowed to cool down at room temperature for 1h. In the next step, a glass-fiber filter heated at 107 °C for 15minis subsequently adjusted into a Gooch-crucible, which is placed onto a suction flask. The system has been previously wetted using 5ml of *n*-heptane. The content of the Erlenmeyer flask is decanted onto the filtering crucible under vacuum. The precipitate is washed with three portions of *n*-heptane of about 10mL each and then dried for 15min at 107°C. [41]

c. <u>ASTM D-4124 (test method)</u>

The sample is warmed to become a fluid, at a maximum temperature of 110°C. 0.001g of a representative sample is placed into a 500ml Erlenmeyer flask. An air-powered stirrer is intalled into the flask and then the flask is placed in a steam bath. The flask is sealed to avoid heptane evaporation. The solution is gently stirred at a temperature close to the solvent boiling point for half hour. After that, the solution is set aside overnight at room temperature in order for the asphaltenes to be precipitated. In the next step, a Gooch-crucible and a glass-fibre filter pad are set onto a 500ml suction flask. The system is wetted with heptane and the petrolene solution is added in a controlled rate. The flask is washed using additional solvent until the filtrate becomes colorless. The crucible stays at room temperature for 10min and then it is dried in an oven at 104°C. For better evaporation, a light nitrogen sparge is used [42]

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[40] **ASTM D 893-97,** (2001)**.** *Standard Test Method for Insolubles in Used Lubricating Oils.* Philadelphia, PA, Available from http://www.astm.org

[41] **ASTM D 3279-97.** (2001). *Standard Test Method for n-Heptane Insolubles.* Philadelphia, P.A.

[42] **ASTM D 4124-01.** *Standard Test Methods for Separation of Asphalt onto Four Fractions.* Philadelphia, PA.

d. IP 143 (test method)

The sample is heated at a temperature lower than 80℃. If the sample is originated from bitumens the temperature may be lower than 120℃. In a conic flask, 0.01g of the sample is placed and *n*-heptane is added in a ratio of 30ml for each 1g when the asphaltene content is lower than 25% m/m, and 50ml for each 1g when the contents is above 25% m/m. The solution is heated for 60+5 min under reflux. In the next step the sample is removed from reflux, cools down and is stored in a dark cupboard for 90-150min. A filter paper is placed in the filter funnel and the liquid is added into it. The remaining sample in the flask is removed using successive quantities of hot heptane. The filter paper and the sample are removed from the funnel and they are placed in the reflux extractor for 60min. Thereafter another flask is placed which contains 30-60ml of toluene and the process is continued until all asphaltenes have been removed from the paper. The solvent may be removed using a water bath at temperature near to its boiling point. [43]

Another method which may be used to separate the different fractions of crude oil is ABAN Fractionation. This method separates the sample in acidic, basic and neutral fractions based on their ability to create hydrogen bonds. However, this method is long and laborious. [38]

3.1.2. Asphaltenes Fractions Isolation

In the previous section the asphaltene separation from the main sample (heavy oil, bitumens, e.t.c) was described. However, in the literature, one more step for asphaltene separation is noted, namely the separation of the sub-fractions of the sample. In this case, the asphaltene sample is dissolved into a solvent such as in mixtures of CH_2Cl_2 and *n*-C5 and sub-fractions are separated based on different polarities. As a result, it is expected that this process will give information about the molecular structure of asphaltenes. A typical process is illustrated in Figure **29**. [38] [44]

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[43] **IP 143-90.** *Deterimation of asphaltenes (heptane insolubles).* s.l. : BSi Standards, 1993.

[44] **Vaidhav Nalwaya, Veerapat Tantayakom, Pornpote Piumsomboon, and Scott Fogler.** Studies on Asphaltene through Analysis of Polar Fractions. *Ind. Eng. Chem. Res.* 1999, Vol. 38, 3, pp. 964-972.
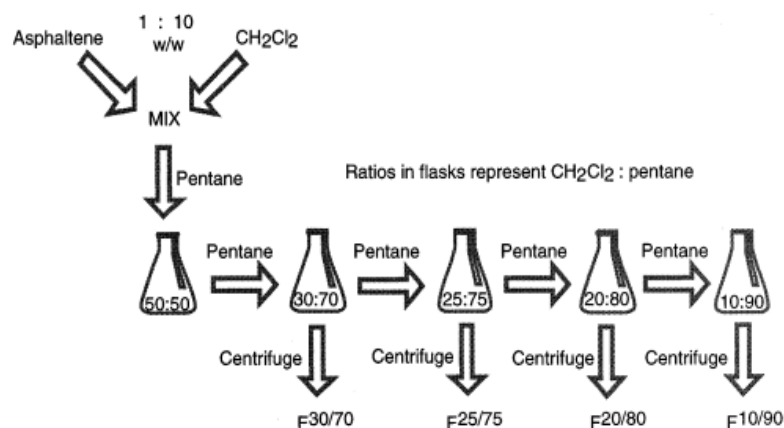
Figure 29: *Process of the asphaltene sub-fractions separation*

Finally, in the literature it is noted that when the asphaltene precipitation takes place heavy resins and waxes may be co-precipitated and this phenomenon increases the molecular weight of the asphaltenes. Also, it depends on the amount and the kind of the solvent. These compounds can identified using analytical methods. [4][45][46]

3.2. Chemical Characterization

As already mentioned, the "Chemical Characterisation" of asphaltenes includes studies about the kind and the number of the atoms which exist in the molecule as well as about their type of connection. In addition, analysis gives information about the main functional groups, the metals and the heteroatoms. Therefore, the composition analysis ultimately provides information about the quality and the possible behavior of the molecule. In order for these goals to be achieved, scientists use specific techniques such as *Inductively Coupled Plasma Atomic Emission Spectrometry* and *Mass Spectroscopy* (ICP/AES and ICP/MS), *Nuclear Magnetic Resonance* (NMR) *Spectroscopy*, X-ray *Absorption Spectroscopy* and *Chromatographic* techniques. In the last part of the twentieth century, American Society for Testing and Materials (ASTM) has published numerous instrumental elemental analysis methods which have been used for asphaltene characterization.

[45] **Strausz, Otto P., Peng, Pingan and Murgich, Juan.** About the colloidal Nature of Asphaltenes and the MW of Covalent Monomeric Units. *Energy Fuels.* 2002, Vol. 16, 4, pp. 809-822.
[46] **Martin Fossen, Johan Sjoblom, Harald Kallevik, JoakimJakobsson.** A new Procedure for Direct Precipitation and Fractionation of Asphaltenes from Crude Oil. *Journal of Dispersion Science and Technology .* 2007, Vol. 28, pp. 193-197.

a. <u>Inductively Coupled Plasma using Atomic Emission Spectrometry or Mass Spectroscopy, (ICP/AES and ICP/MS)</u>

In this technique the sample is used directly or after dilution in a solvent. ICP technique is based on the use of plasma which is an electrically conducting gaseous mixture containing cations and electrons. The most commonly used gas is argon that is ionized by a strong electric field. Plasma can achieve temperatures as high as $10.000°K$. Such a system is illustrated in Figure **30**. In the last step, the sample is carried into the hot plasma at the head of the tubes by argon. In the first case when AES is used, the intensity of wavelengths emitted from the plasma is measured to determine the quantity and quality of the elements in the sample (i,e Ni, Va). The produced wavelength of the atomic spectral line in the emission spectrum gives the identity of the element while the intensity of the emitted light is proportional to the number of atoms in the molecule. In the second case, ICP/MS technique combines the power of ICP for atomization and ionization of the sample with the sensitivity and selectivity of MS detection. MS system is able to achieve the separation of the ions based on their mass (m/z), where m is the mass of the ion and z is the number of fundamental charges that it bears, and finally the number of ions of each type is measured. The information from MS is usually presented as a plot of relative intensity or ion abundance versus m/z, as it is illustrated in Figure **31**. It should be noted that these techniques have different detections limits[47] [48]
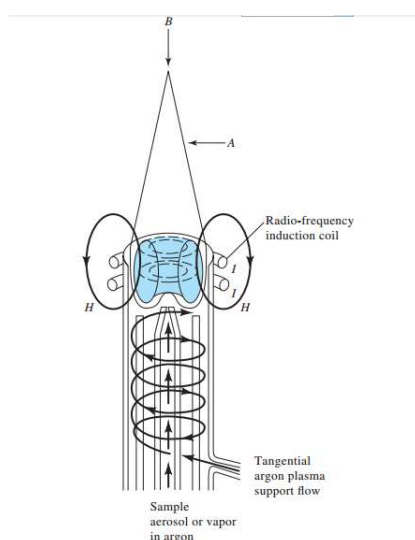
Figure 30: *A typical ICP source (Skoog, 2016)*

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[47] **Skoog, Douglas A., James, F Holler and Crouch, Stanley R.** *Principles of Instrumental Analysis .* USA, 2016. ISBN: 978-1-305-57721-3.

[48] *Analytical Advances for Hydrocarbon Research.* New York , Chang Samuel HSU, 2003, ISBN: 0-306-47476-X.
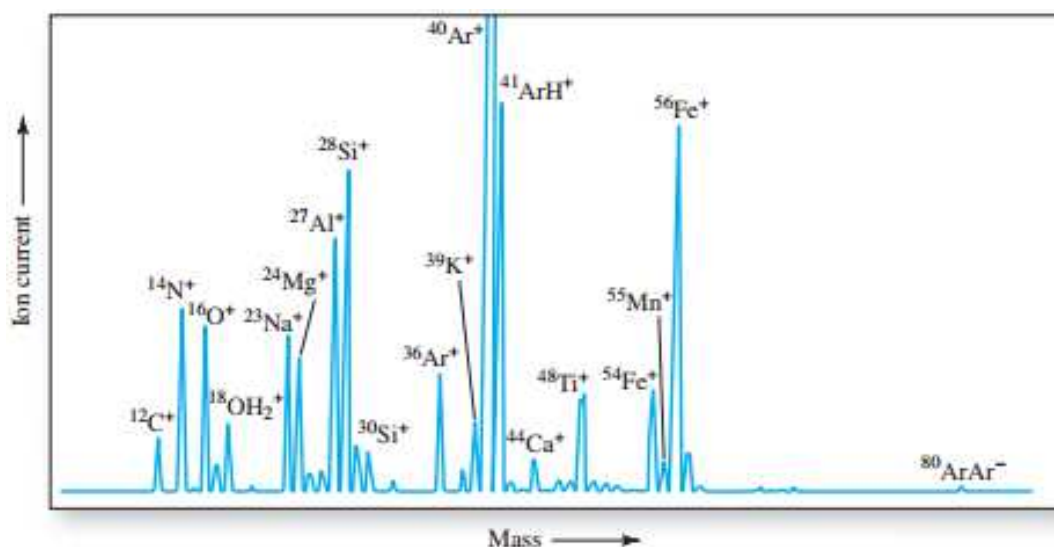
Figure 31: *The mass spectra of a sample, (Skoog, 2016)*

b. Nuclear Magnetic Resonance Spectroscopy (NMR)

Another useful technique is the nuclear magnetic resonance spectroscopy (NMR), which gives detailed structural, dynamic and chemical information of organic compounds. NMR is able to identify the structure of an organic molecule providing information about the atomic connectivity of a molecule. NMR gives the structure in the vicinity of individual nuclei, specifically hydrogen and carbons. The operation principle of the instrument is based on the electromagnetic radiation which is in the form of waves and has specific energy thus specific frequency. This energy is absorbed and causes electronic or mechanical "motion"-excitation in the molecule. These excitations are observed in an NMR spectrum, as illustrated in Figure **32**. [49]

c. X-Ray Spectroscopy

X-Ray spectroscopy can be characterized as a spectroscopic surface method which provides chemical information about the composition of a surface layer that is a few tenths of nanometers (a few angstroms) to a few manometers (tens of angstroms) thick. The X-ray source provides enough energy to excite an electron from an inner shell to an outer one. X-ray absorption spectroscopy compared to other techniques for structural analysis provides a "complete" spectrum which contains information about the geometric structure (type, distance and number of neighboring atoms) as well as about the electronic structure (the nature of the chemical bond) of the molecule. Also, it is able

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[49] **Vollhardt, Peter and Schore, Neil.** *Organic Chemistry: Structure and Function.* 6th Edition. New York : s.n., 2011. pp. 387-427.

to give data about the orientation of molecules at the surface of a sample and the interaction of molecules with surfaces. [47] [48] [49]
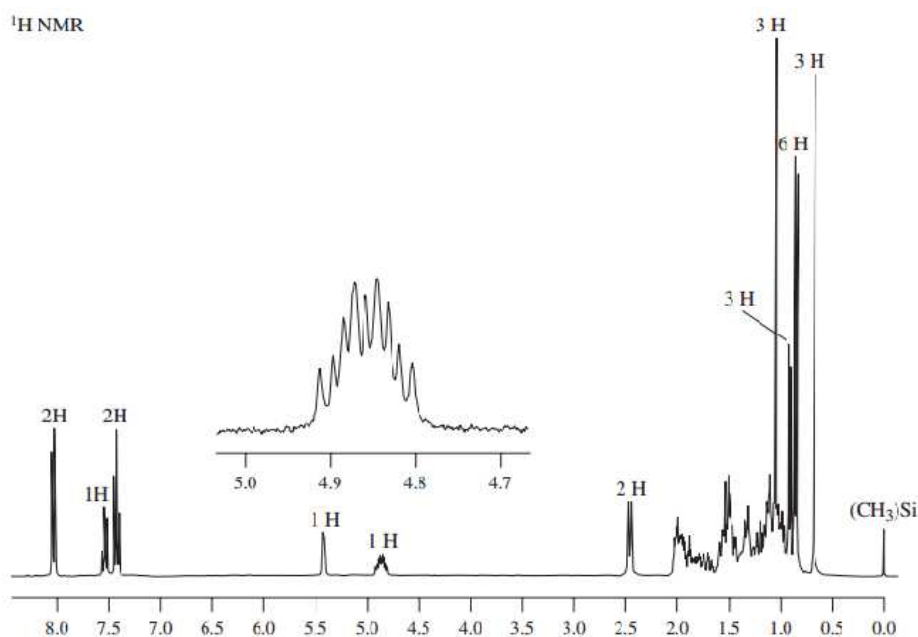
Figure 32: *3000-MHz ^{1}H NMR spectrum ppm (δ) (Vollhardt, 2011)*

3.3. Physical and Colloidal Characterization

This section is referred to the techniques which are used to determine the physical behavior (precipitation of molecules) and the colloidal dispersion of the asphaltene molecules in the sample. If the behavior of the asphaltene molecules could be understood, scientists would be able to foresee asphaltene precipitation in the operation conditions

a. <u>Viscosity Measurements</u>

If it is assumed that asphaltenes are in "colloidal suspension", viscosity measurements can be used to determine the onset of the asphaltene precipitation. The suspension-viscosity depends on the interactions between particles of the fluid with the asphaltenes molecules and the asphaltenes with other same molecules, particle size distribution, concentration of them and the percentage of the aggregation of them. It has been shown that aggregation phenomenon causes an increase of the suspension viscosity. [50] It has

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[50] **J, Escobedo and G, Mansoori.** Viscometric determination of the onset of asphaltene flocculation: a novel method. *SPE Prod Fracil.* 1995, Vol. 10, 2, pp. 115-118.

been already mentioned that the colloidal dispersion of the asphaltenes stays stable because of the resin existence around the molecules. Therefore, if the resins are removed using a low-boiling point organic solvent (*n*-C5 or *n*-C7), asphaltene molecules will form aggregations which cause increased viscosity. Thus, measurements of crude oil viscosity at different percentages of added solvent can be a method for detecting the onset of asphaltene precipitation during a titration test of stock tank oils. [50] [51] The process which is followed in this case is the preparation of enough samples of crude oil in which low-boiling point solvent is added in order for the asphaltenes to precipitate. The solvent is added at different proportions and after that the samples are left to equilibrate at environment conditions. When the thermal equilibration has been achieved, viscosity of all the samples is measured. In the next step the same samples are prepared with the same proportions of the solvent but in this case the used solvent is benzene or toluene. These solutions are considered as references with which viscosity of mixtures of crude oil and precipitant is compared. The results of this method are given in Figure **33**. [50]
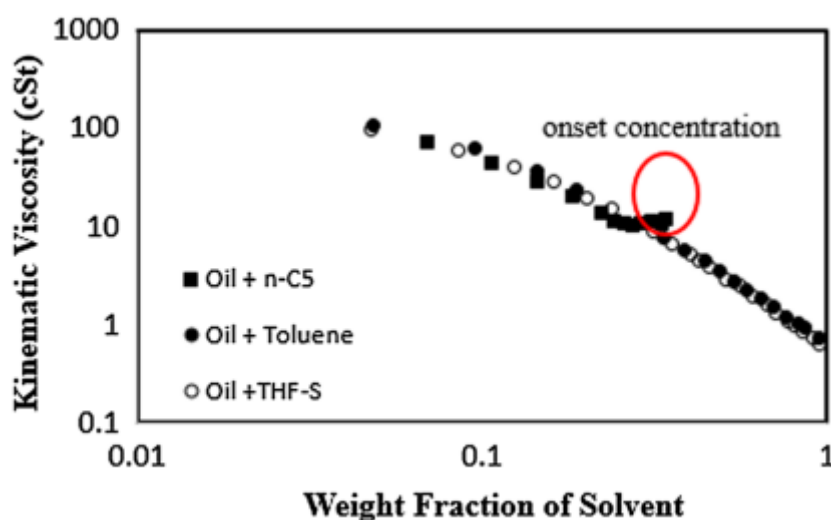
Figure 33: *Kinematic viscosity of Maya crude-solvent mixture versus weight fraction of solvent (n-C5, Toluene, THF-S), (Escobedo and Mansoori, 1995)*

b. Refractive index measurements

It is known that in the "solubility approach" the solubility parameter is used (δ) which is only for pure substances. However, the "refractive index" can be used which is an optical property of the sample and it can be easily measured. Using the "refractive index" the

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[51] **Soleymanzadeh, Aboozar, et al.** A review on methods of determining onset of asphaltene precipitation. *Journal of Petroleum Exploration and Production Technology* . 2019, Vol. 9, pp. 1375-1396.

onset of the asphaltene precipitation can be determined. The aggregation and the separation of asphaltenes are dependent on the magnitude of van der Waals forces between nonpolar molecules while the mixture refractive index can be used to quantify the ability of a crude oil to disperse its asphaltene fraction. According to Buckley the RI value of an oil sample and the RI value of the same sample after precipitation are different. Therefore, this difference is a measure of the stability of asphaltenes in their original crude oils. [52] Moreover, optical properties such as RI and microscopic properties such as polarizability of a solution can be connected using the Lorentz – Lorenz equation, (Equation, **4**):

$$f(n) = \frac{n^2 - 1}{n^2 + 2} = \frac{N_A\,\alpha\,\rho}{3\,M} \qquad\qquad (4)$$

where $f(n)$ is the refractive index function,

      n is the refractive index of crude oil,

      N_A is the Avogadro's number,

      ρ is the density,

      α is the polarizability,

      M is the molecular weight.

The effective density and the molecular weight of homogenous multicomponent mixtures are defined based on the volume fraction and the mass fraction of each component. [51] According to this equation, if the polarity of a structure is high, the polarizability (α) of it will be high and therefore the structure will have a higher RI value. Buckley concluded that the RI of a mixture represents the contributions of all components in proportion to their volume fractions. He found that asphaltenes, resins and aromtic hydrocarbons have higher RI values compared to the paraffinic compounds. However, he noted that asphaltene precipitation decreases the RI of the sample by changing solvent's properties such as polarity. Finally, when he compared solutions with the same RI value, asphaltene precipitation could be characterized as a reversible phenomenon. It should be mentioned that direct RI measurements of heavy dark oils is impossible, and for this reason a solvent should be used such as toluene. The results of the measurements are given in Figure **34,** where a jump is observed in the RI curve at the onset of asphaltene precipitation. [51] [52]

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[52] **Buckley, Jill S.** Predicting the Onset of Asphaltene Precipitation from Refractive Index Measurements. *Energy & Fuels.* 1999, Vol. 13, pp. 328-332.
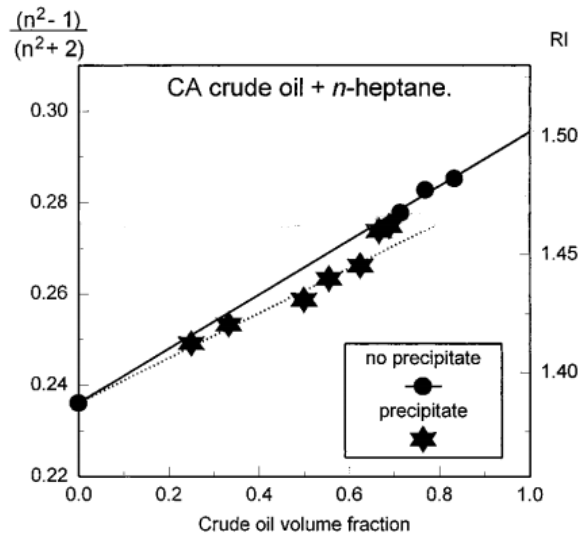
Figure 34: *RI of CA crude oil and heptane mixture versus volume fraction of heptane (Buckley, 1999)*

c. Light Scattering Technique (LST)

It is known that light-scattering techniques are used to characterize the colloidal behavior of the fluid because the light which passes through a fluid can be absorbed by the formation of either solid or gas. In the cases of dark oil samples, near infrared light (NIR) can be used because of absorbance in the visible range wavelengths in the dark oil medium. In this case the sample is placed in a visual PVT cell, and a NIR source and a detector are added (Figure **35**).[51][53] The sample stays until equilibration at the desirable conditions (pressure and temperature) and then the intersity of the NIR light is measured. With this method, the optical density is measured and plotted versus the pressure or weight fraction of the precipitant under the specific conditions. The minimum point of the graph represents the onset of asphaltene precipitation, (Figure **36**). The optical density is calculated based on Equation**5**: [54]

$$Optical\ density = \ \log\left(\frac{I_0}{I}\right) \tag{5}$$

where I_0 and I are the power of incident and transmitted light, respectively.

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[53] **A, Jamaluddin; J, Creek; Cs, Kabir; D, Mc Fadden JD D'Cruz; J, Manakalathil; N, Joshi; B, Ross.** Laboratory techniques to measure thermodynamic asphaltene instability. *Journal of Canadian Petroleum Technology.* 2002, Vol. 41, 7, pp. 44-52.

[54] **Aske, N., Kallevik, H. and Johnsen, E. E. and Sjöblom, J.** Asphaltene Aggregation from Crude Oils and Model Systems Studied by High-Pressure NIR Spectroscopy. *Energy & Fuels.* 2002, Vol. 16, 5, pp. 1287-1295.
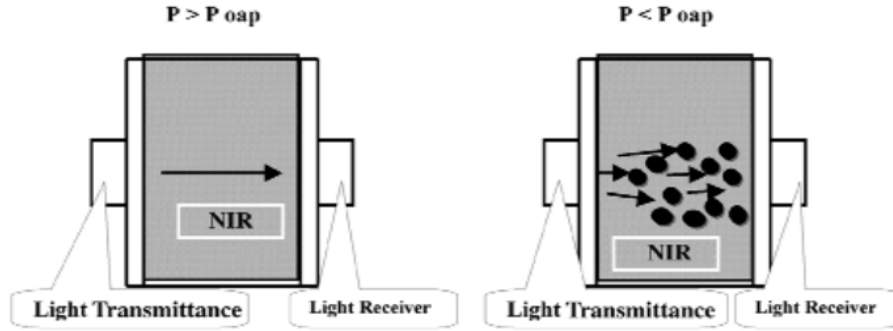
Figure 35: *Light Transmittance principle, (Jamaluddin et al. 2002)*
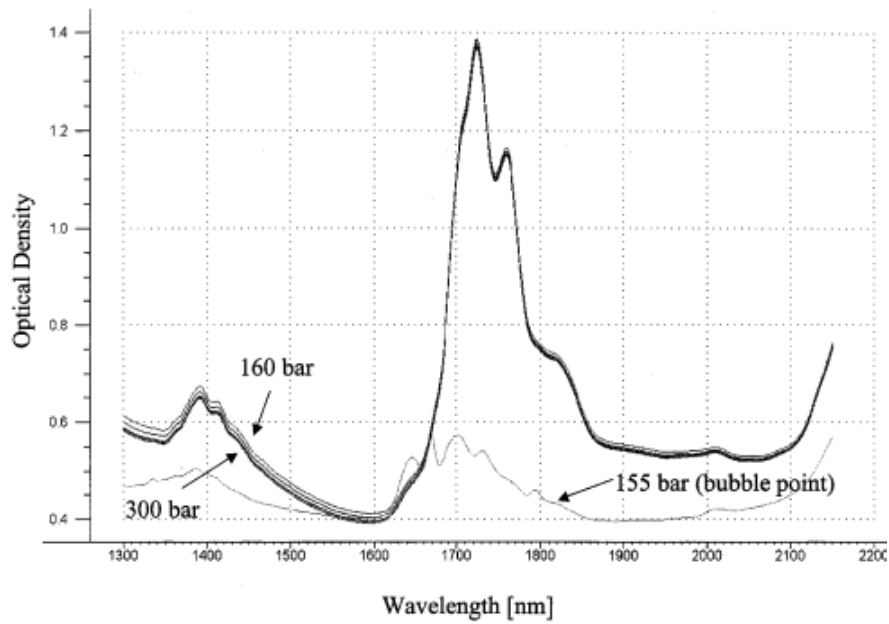
Figure 36: *NIR spectra obtained during pressure depletion from 300 to 150bar,*
(Aske et al. 2002)

As observed in the diagram, an elevation of the baseline at 1600nm is observed because of the light scattering. It means that in this area the optical density is highest for the spectra at low pressure because of the asphaltene aggregation (Figure **36)**. The aggregation is higher at low pressures. By contrast, at 1725nm a high absorption is observed which corresponds to high values of optical density. At 150bar the absorption is an effect of heavy asphaltene aggregation while at 300bar it is the result of the compressed state of the fluid. [54]
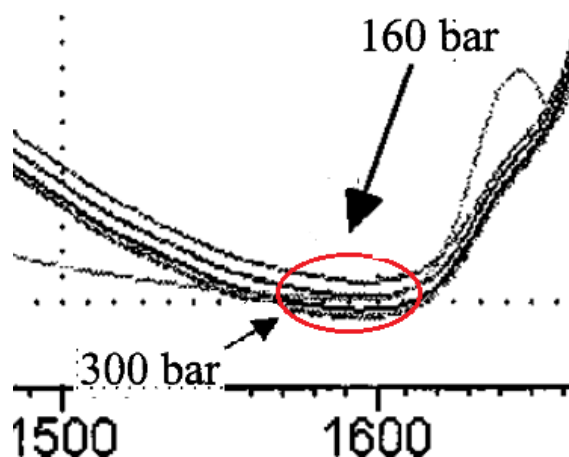
Figure 37: *NIR spectra at which the minimum optical density is depicted from 300 to 160bar, (Aske et al. 2002)*

It is noted that there exist studies in which this method is used to detect asphaltene precipitation from crude oils during titration experiments. In these cases, the absorbance of the transmitted light is measured with respect to the time instead of the power intensity and the minimum point of the graph represents the onset of asphaltene precipitation, (Figure **37**). [51] [55]
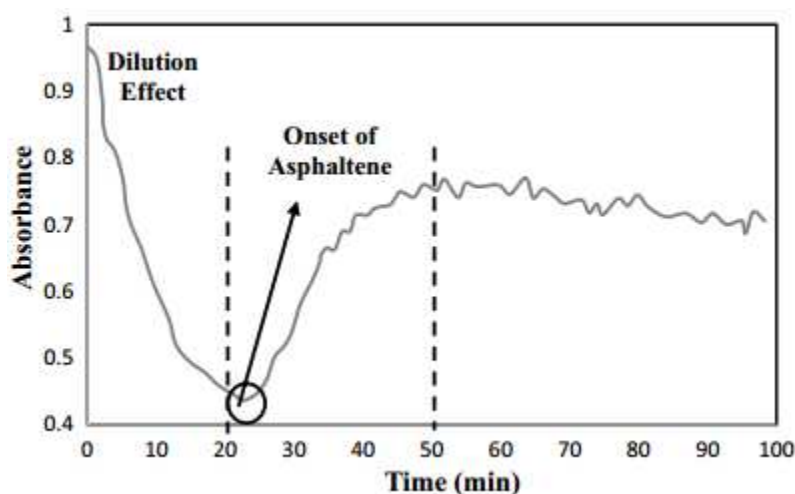
Figure 38: *Absorbance of NIR light versus time, (Fuhr et al. 1991)*

d. Interfacial Tension measurements (IFT)

This method is used to detect the onset of asphaltene precipitation. Based on the presence of heteroatoms in the asphaltene molecules (such as oxygen, nitrogen and sulfur), scientists proposed that asphaltene molecules present an interfacial tension. IFT

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[55] **B. Fuhr; C.Cathrea; Coates, L.; Kalra, H.; Majeed, A.** Properties of asphaltenes from a waxy crude. *Fuel.* 1991, Vol. 70, 11, pp. 1293-1297.

can be determined using du Noüy ring (Figure **39**) or pendant drop method. In most cases, IFT was measured between water and mixture of asphaltene - solvent or crude oil -solvent, the solvent was toluene or n-heptane. The method is based on the sudden change in the IFT values when precipitation starts. According to researchers, the precipitated polar molecules moved to the interface between the water and oil- mixture and they form a film which increases the IFT values. However, this opinion is not widely accepted. [51]

Figure 39: *Du-Nouy ring surface tensiometer (Alibaba.com)*

e. Optical Microscopy

In the previous decades many scientists used microscopic techniques to study the physical properties of asphaltenes. Karts and Beu (1945) studied the particle size of asphaltic bitumens using electron microscopy while Witherspoon and Munir (1958) using the same method determined the size and shape of asphaltic substances. [15] [56] Buckley (1996) combining two methods, the measurements of refractive index and the optical microscopy, succeeded in defining the onset of asphaltene precipitation with or without added solvents.[57] Moreover, Maqbool (2011) using optical microscopy studied the kinetics of asphaltenes precipitation. In this method an optical microscope was used during titration of the crude oil at ambient conditions. The microscope is equipped with digital camera and it is able to record the precipitation process. In this case, there are two parameters which influence the precipitation; the time and the precipitant

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[56] **Witherspoon P, Munir Z.**_Size and shape of asphaltic particles in petroleum._ s.l. : Society of Petroleum Engineers, 1958. SPE 1168.
[57] **Buckley, Jill S.** Microscopic Investigation of the onset of asphaltene precipitation . *Fuel Science and Technology International.* 1996, Vol. 14, pp. 55-74.

concentration. Maqbool used a mixture of crude oil and n-heptane and observed the precipitation process with respect to the time using the optical microscope. The time-dependent process is illustrated in Figure **39**. According to this study, the onset of asphaltene precipitation starts when the particle size is 0.5microns. It was concluded that the onset time was reduced exponentially with respect to precipitant, concentration.[58]
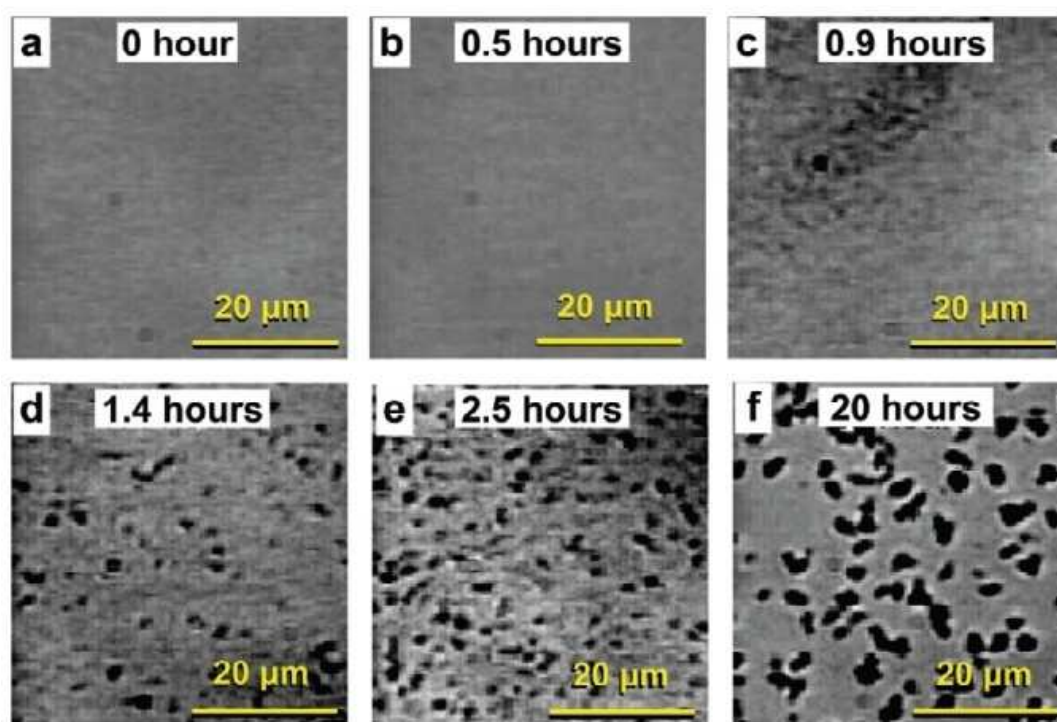
Figure 40: *Micrographs of asphaltene precipitation for a 50:50 vol% crude oil-heptane mixture with respect to the time, (Maqbool, 2011)*

Recently, scientists used a high-pressure microscope (HPM) to visualize onset of asphaltene precipitation pressure. This system is equipped with a high-pressure high-temperature cell (HPHT), with a light source in one side and with a camera on the other side, (Figure **41**). [51] In this case, the onset precipitation pressure of the sample can be determined.

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[58] **T, Maqbool.** *Understanding the kinetics of asphaltene precipitation from crude oils.*, 2011. PhD Thesis, University of Michigan.
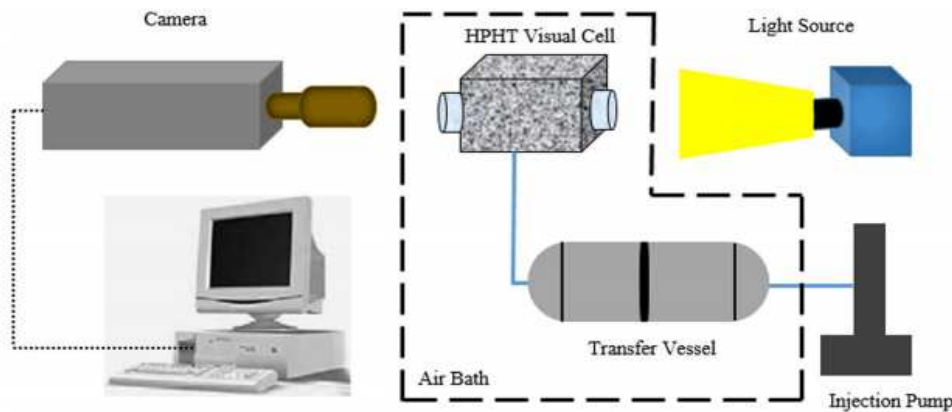
Figure 41: *Schematic of HPM method, (Aboozar, 2019)*

f. Other Techniques

Another method is the gravimetric method. In this case, the asphaltene onset pressure is defined when the sample is depressurized isothermally in a PVT cell. The conditions of the cell are the same as in the reservoir. In the next step, the pressure is reduced but stays above the bubble point. An amount of the sample is removed from the cell and it is analyzed at ambient conditions following standard methods (i.e. ASTM D-3279) in order to measure the asphaltene concentration. It is noted that the precipitation of asphaltene takes place above the bubble point because when the saturated pressure is reached the remaining oil will dissolve back in the precipitated amount, Figure **42**. The same method can be used to study the effect of different temperatures in the asphaltene precipitation, (Burke, 1990). [59]
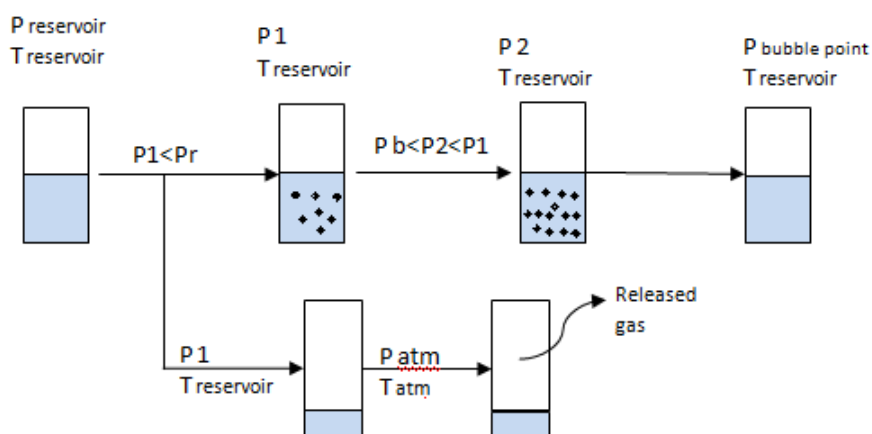
Figure 42: *Depressurized steps*

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[59] **N, Burke, R, Hobbs and S, Kashin.** Measurement and Modeling of Asphaltene Precipitation . *Journal of Petroleum Technology.* 1990, Vol. 42, 11, pp. 1440-1446.

Heat transfer has been used to detect the onset of asphaltene precipitation. The operation principle of the technique is the measurement of thermal resistance of oil sample before and after asphaltene precipitation (with and without precipitant solvent). It has been recorded by Clarke and Pruden that thermal resistance is increased during asphaltene precipitation. They succeeded in designing a cell which was able to conduct asphaltene precipitation test at conditions up to 2000psi and 400℃. The cell is illustrated in Figure **43**.
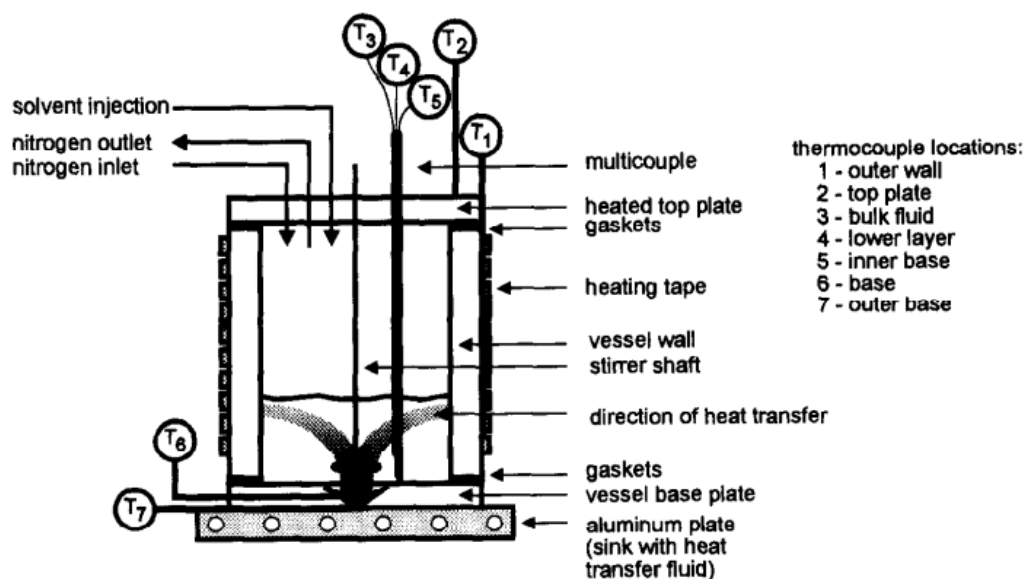
Figure 43: *Heat transfer vessel and illustration of direction of heat flow,*
(Clarke and Pruden, 1997)

The cell was designed to facilitate heat conduction through the precipitate layer which was precipitated on the base of the cell. The walls and the top of the cell were heated at constant temperature while the bottom of the cell remained cool. The sample was stirred and heated for a specific amount of time and then by using a line of the system a precipitant solvent was added. The results of the study are given in Figure **44**, where the temperature of the lower layer was depicted with respect to the solvent-bitumen ratio. It is observed that when the temperature starts to decrease the thermal resistance is increased and asphaltene particles precipitate out of the solution, thus forming a deposit layer at the bottom of the cell. [60] [61]

[60] **P, Clarke and B, Pruden.** Asphaltene precipitation: detection using heat transfer analysis, and inhitition using chemical additives . *Fuel .* 1997, Vol. 76, 7, pp. 607-614.
[61] **P Clarke, B Pruden.** The Development of an Onset-of-Precipitation Detection Technique Using Heat Transfer Analysis. *Fuel Science and Technology International.* 1996, Vol. 14, pp. 117-137.
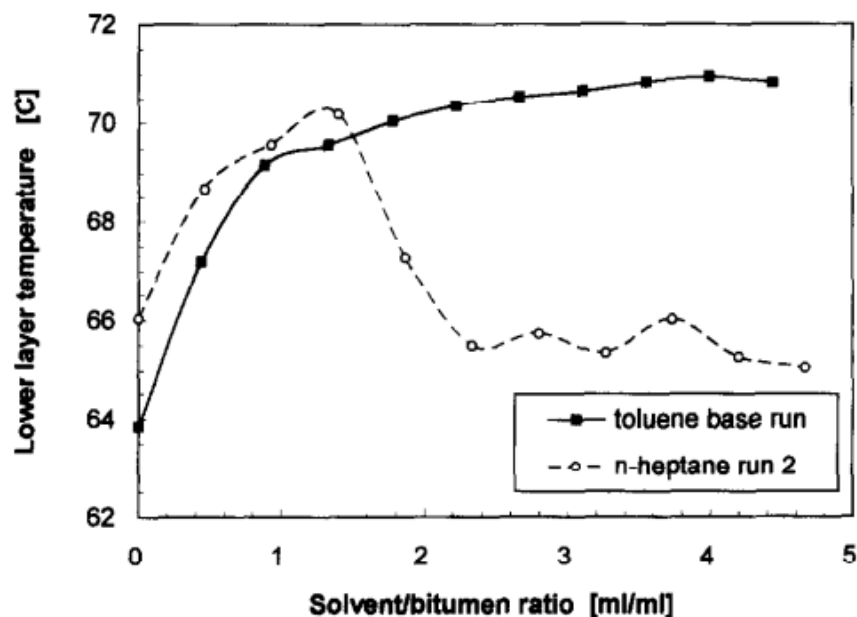
Figure 44: *Temperature of the cell bottom in the presence of toluene and n-C7, (Clarke and Pruden, 1997)*

Others scientists tried to detect the onset of asphaltene precipitation using electrical techniques. These techniques use electrodes which are placed in an oil sample in which a direct current was applied across them. Using this method the presence of heteroatoms and metals in asphaltenes molecules can be detected. Based on this theory Fotland *et al.* proposed a conductivity cell, consisted of concentric cylinders and electrodes covered with a gold layer. The conductivity and the capacitance were measured using an impedance meter. The results are given in Figure **45**.
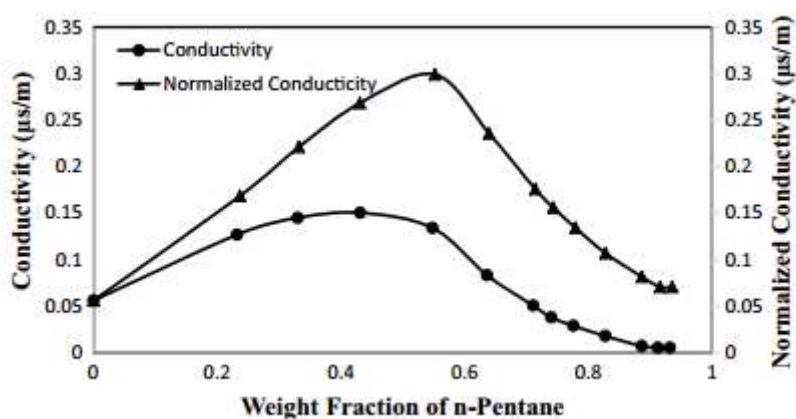
Figure 45: *Conductivity and normalized conductivity from crude oil -precipitant mixture, (Fotland et al. 1993)*

The trends from both curves at a specific amount of the added solvent are the effect of the onset of asphaltene precipitation. In the diagram authors also gave the normalized conductivity which is defined as the conductivity per mass fraction of oil in the injected solution. The lower curve represents the conductivity as a function of the added n-solvent, while the upper curve corresponds to the conductivity divided by the weight fraction of oil. The onset of asphaltene precipitation is denoted by the change of the trend in the lower curve and the maximum value in the upper curve. The cause of this change is the reduction of the viscosity of the sample as the precipitant solvent is added. The reduction of the viscosity caused mobility elevation of the molecules. This process is continued until a maximum point is reached and after this point, the curves start to have negative slope. [62]

A last technique which is recorded in the literature is the acoustic resonance (ART). The principle of the technique is the measurement of sonic wave speed in various fluid phases, (Figure **46**). It is noted that the denser the fluid is the faster the sonic wave travels. Therefore the asphaltene precipitation can be detected using the responses of fluids to acoustic waves which propagate through them. In this technique, the output is read in the form of resonance frequency with respect to the pressure, (the system HPHT cylindrical resonator is depressurized and the desired pressure is achieved). The results are given in Figure **47**.
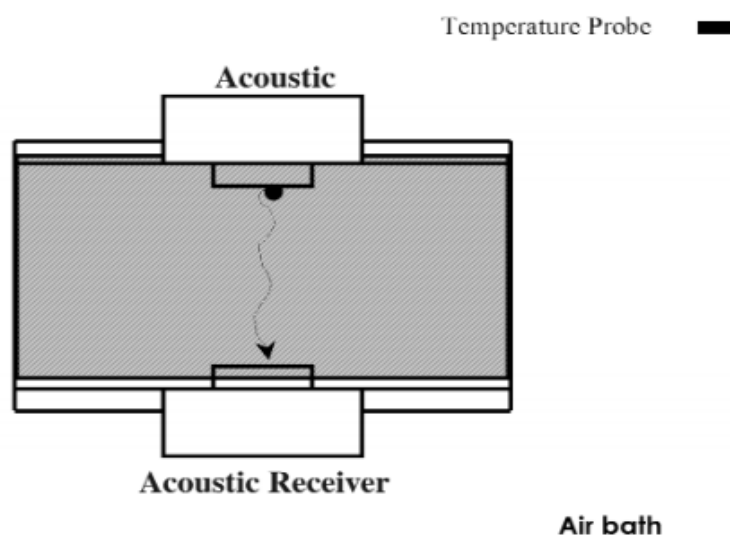
Figure 46: *Schematic diagram of acoustic resonance technology, (Jamaluddin et al. 2002)*

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[62] **P, Fotland, H, Anfindsen and F, Fadnes.** Detection of asphaltene precipitation and amounts precipitated by measurement of electrical conductivity. *Fluid Phase Equilibria.* 1993, Vol. 82, pp. 157-164.
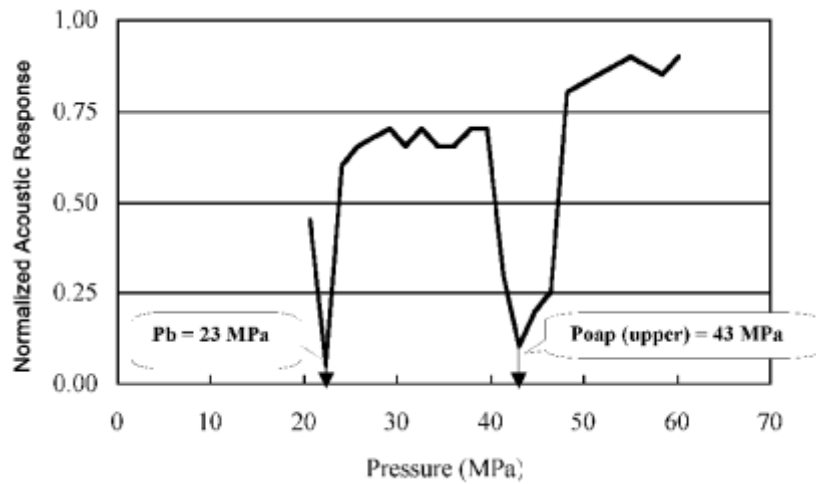
Figure 47: A typical acoustic response (isothermal depressurization at 210 ⁰F), *(Jamaluddin et al. 2002)*

According to the authors, the changes in the sonic wave speed, which is related to the phase transition, influence resonance frequency and therefore acoustic response. (Jamaluddin et al.2002). It is observed that there are two sharp changes in the acoustic responses. The first one represents the onset of asphaltene precipitation while the second one corresponds to the saturation pressure. These are related to the sudden phase changes (presence of asphaltenes and gases). As the pressure decreases the fluid density decreases and the sonic velocity is reduced. The precipitated asphaltenes increase the sonic speed. [51][53]

Precipitation Models

4. Introduction

The asphaltene precipitation is a serious problem during the oil production. According to researchers asphaltenes precipitation may occur during a pressure drop either by primary depletion or during the displacement of oil by rich gas or CO2. During primary depletion asphaltenes are precipitated when the reservoirs have three main characteristics: the fluid is characterized as light or medium oil with small asphaltene content, the initial reservoir pressure is higher than the saturation pressure and the maximum precipitation occurs around the saturation pressure. [63] It is noted that, when the heavy-oil is produced, this problem is reduced because of the bigger solubility of the asphaltenes into the heavy oil. Generally, the precipitation of asphaltenes is considered an irreversible process. However, researchers tried to match experimental data with theoretical values in order to build a model which is able to predict and describe the asphaltene precipitation and which can be used into a variety of reservoir fluids. [59]

Figure **48** gives an asphaltene envelope (ADE) and a PT saturation curve for a typical oil. Precipitation occurs above the saturation pressure (upper ADE pressure) while around the saturation pressure occurs the maximum amount of sediment. The sediment is decreased as the pressure drops further below the saturation pressure. Precipitation stops as pressure is reduced below the lower ADE pressure, (Figure 48). Above the saturation pressure the precipitation depends on the pressure while below the saturation pressure it depends on the pressure and the composition. [63]

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[63] **Nghiem, Long X and Combe, Dennis A.** Modeling Asphaltene Precipitation During Primary depletion. *Society of Petroleum Engineers SPE, Journal .* 1997, Vol. 2, 2, pp. 170-176.
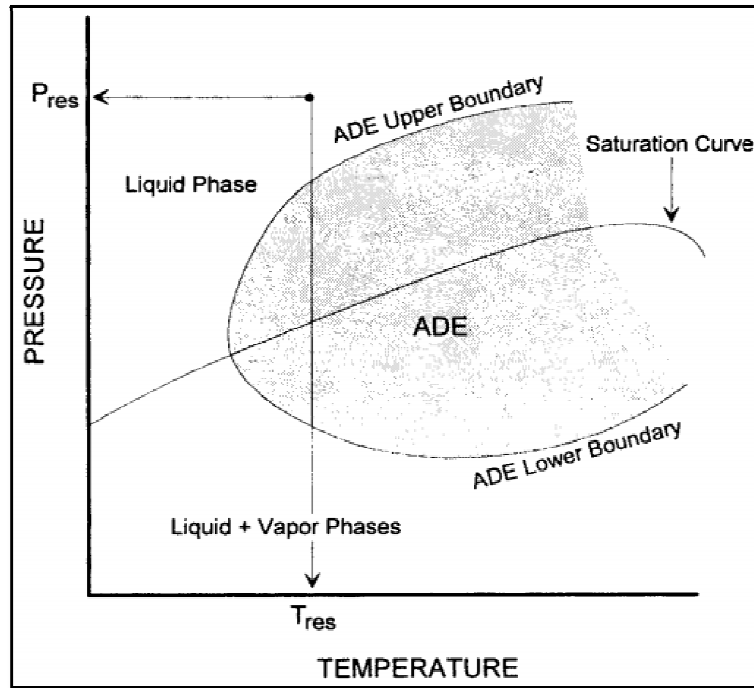
Figure 48: *P-T asphaltene deposition envelope, (Long et al. 1997)*

Studying the literature, two different models have been found which are used to predict and describe the asphaltene precipitation: the first one is the solubility model that uses the Flory – Huggins solution theory and an equation of state, and the other one is the thermodynamic model which is based on colloidal approach using an equation of state (EOS).

4.1. Solubility Model

In this model, the F-H model of polymer solubility is used in order to determine the solubility parameter. The main assumption in the model is that asphaltenes are solvated in crude oil and that these asphaltenes are precipitated if the oil solubility drops below a certain value, which is represented by the solubility parameter. In addition, it is noted that the asphaltene precipitation occurs during the addition of a precipitant such as n-heptane, and this affects the parameters of the model which are functions of the amount of the precipitant added.

In detail, in this model it is assumed that the components of the oil are the solvent in which the asphaltenes are dissolved or suspended, (two pseudo-components).This model depends on two types of equilibrium, the vapor/liquid equilibrium (VLE) of the total fluid and the liquid/liquid equilibrium between the liquid oil and the asphaltene

phase (LLE). [59] [64] The first step is the estimation of the solubility parameter using the Flory-Huggins equation. According to this theory the changes of Gibbs free energy can be evaluated using the following equation (Equation **6**) which characterizes the asphaltene mixture with crude oil at a constant pressure. [64]

$$\Delta G_{mix} = RT \left[n_m \ln \Phi_m + n_a \ln \Phi_a + n_m \Phi_a \frac{V_m}{RT} (\delta_a - \delta_m)^2 \right] \quad (6)$$

where R is the universal gas constant and T is the absolute temperature,

n is the number of moles,

Φ is the volume fraction of solvent,

V_m is the molar volume,

δ_a, δ_m are the solubility parameters of the solute (asphaltenes) and solvent (maltenes), respectively.

The first two terms represent the Gibbs free energy change with respect to the entropy change of mixture while the third term is an effect of the enthalpy change upon mixing. Using this mode,l the compositional ranges over which asphaltene phase is stable, metastable or unstable to phase separation can be estimated. The molar volume and the solubility parameters are functions of the amount of the precipitant added and they can be calculated using the Equations **7** and **8**. [64]

$$\mathbf{V_m} = \frac{\Phi_p + \Phi_s}{\Phi_p/v_p + \Phi_s/v_s} \quad (7)$$

$$\mathbf{\delta_m} = \frac{\Phi_p \delta_p + \Phi_s \delta_s}{\Phi_p + \Phi_s} \quad (8)$$

with $\Phi_m = \Phi_p + \Phi_s$ and $\Phi_m + \Phi_a = 1$ and where subscripts p and s represent precipitant and solvent, respectively.

The chemical potential is the partial molar Gibbs free energy at constant temperature and pressure and it is known that at phase equilibrium the chemical potentials of the phases are equal (Equations **9a** and **b**). Therefore,

$$\Delta \mu_m^L = \Delta \mu_m^H, \quad \Delta \mu_a^L = \Delta \mu_a^H \quad (9a,b)$$

where L is the liquid phase and H is the heavier phase.

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[64] **Wang, J. X. and S.Buckley, J.** A two-Component Solubility model of the onset of asphaltene floculation in crude oils. *Energy & Fuels.* 2001, Vol. 15, pp. 1004-1012.

The combination of the three equations (Equation **6**, **9a** and **9b**) produces a nonlinear equation which can be solved for given volumes of precipitant (Φ_p) in order to give the asphaltene volume fractions in the two phases (liquid and heavy phase), (Equations **10** and **11**). [64]

$$\ln(1 - \Phi_a^L) + \left(1 - \frac{V_m}{V_a}\right)\Phi_a^L + x(\Phi_a^L)^2 = \ln(1 - \Phi_a^H) + \left(1 - \frac{V_m}{V_a}\right)\Phi_a^H + x(\Phi_a^H)^2$$

(10)

$$\ln\Phi_a^L + (1 - \Phi_a^L)\left(1 - \frac{V_a}{V_m}\right) + (1 - \Phi_a^L)^2 \frac{V_a}{V_m} x =$$

$$\ln\Phi_a^H + (1 - \Phi_a^H)\left(1 - \frac{V_a}{V_m}\right) + (1 - \Phi_a^H)^2 \frac{V_a}{V_m} x \quad (11)$$

Flory – Huggins interaction parameter (*x)* is defined as, (Equation 12):

$$x = \frac{V_m}{R\,T}(\delta_a - \delta_m)^2$$

(12)

It is noted that the amount of asphaltene that exists into each phase can be calculated based on the concentration of mass ρ_i (or γ_i), (Equation **13**).

$$\rho_i = \frac{m_i}{V}$$

(13)

where V is the volume of the mixture and m_i is the mass of a constituent.

Finally, this model can be simplified if it is assumed that the heavy phase is pure asphaltene, ($\Delta\mu_a^H = 0$). Taking into account this assumption the equation 11 is simplified and gives the Equation **14** and by assuming $\Phi_a^L \ll 1$ the Equation **15** is produced:

$$\ln\Phi_a^L + (1 - \Phi_a^L)\left(1 - \frac{V_a}{V_m}\right) + (1 - \Phi_a^L)^2 \frac{V_a}{RT}(\delta_a - \delta_m)^2 = 0 \qquad (14)$$

$$\Phi_a^L = exp\left[-1 + \frac{V_a}{V_m} - \frac{V_a}{RT}(\delta_a - \delta_m)^2\right] \qquad (15)$$

The input data in these equations are the solubility parameters and the molar volumes of each of the two pseudo-components, (δ_a, δ_m, V_a and V_m). An average value of molar volume of the meltenes mixture can be calculated using the measurements of density and molecular weight estimations. On the other hand the estimations of solubility parameters are based on the relationship between refractive index F_{RI} (Equation **16**) and the solubility parameter. Thus, V_m and δ_m are determined in measurements while V_a and δ_a are the only unknown parameters in the model. The results of the model are illustrated in Figure **49**, which depicts a diagram of the asphaltene solubility parameter with respect to the molar volume. [64]
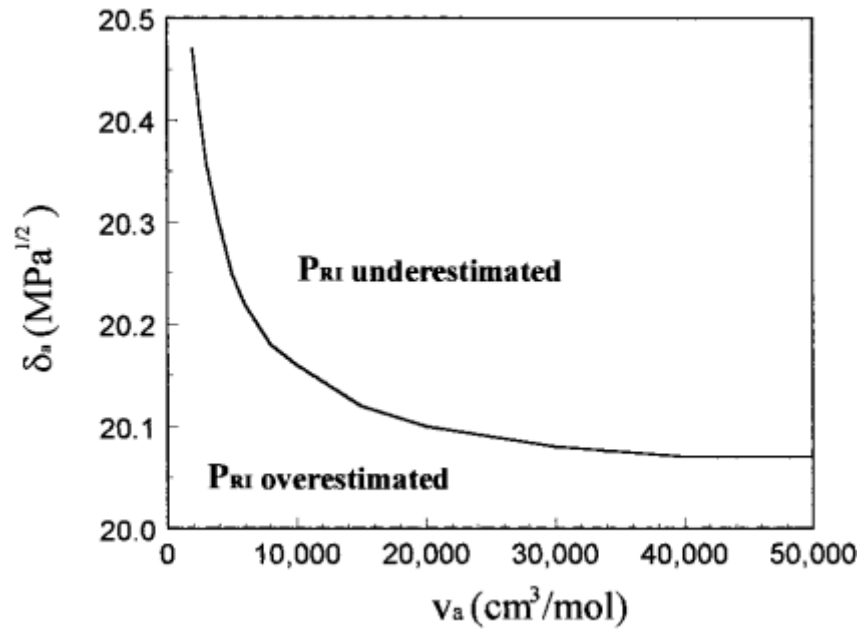
$$F_{RI} = [(RI)^2 - 1]/[(RI)^2 + 2] \qquad (16)$$

Figure 49: *Pairs of adjustable parameters V_a and δ_a, (Wang and Buckley, 2001)*

4.2. Equations of State (EOS)

On the other hand, some scientists support the colloidal behavior of the asphaltenes. In this case the thermodynamic model which can characterize this state is an EOS model. The cubic equation of state such as the Peng – Robinson (PR) and Soave – Redlich – Kwong (SRK) is used in order to calculate the temperature, the pressure and the composition values at the equilibrium of liquid -liquid phase or vapor-liquid phases. The input data which are required by the model are the critical properties of the asphaltene phase and other heavy fractions of the crude oil, (critical pressure, critical temperature and acentric factor). Also, it is assumed that the asphaltene phase is pure solid with a fixed molecular weight and the solid –liquid equilibrium can be affected by changes in the composition of the liquid phase. [23]

According to the literature, this model can be applied either during primary depletion, above the saturation pressure or during precipitant addition. In the first case, the asphaltene molecules are precipitated during the pressure drop, and the precipitant solvent is not used and the model should take into account both the pressure effect (above and below of saturation pressure) and the compositional effect (below the saturation pressure). [63] The calculations also involve a correlation of solid phase

fugacities which are defined as it is given in Equation **17**. It is noted that all the models are validated using experimental data.

$$\ln f_s = \ln f_s^* + \frac{V_s(P-P^*)}{RT} \tag{17}$$

where R is the universal gas constant and T is the temperature,

V_s is the molar volume of pure solid asphaltene,

f_s, f_s^* are the fugacities of solid at pressures P and P*, respectively.

Concerning the vapor and liquid phases the cubic equation is used to model the phase equilibrium, (i.e. PK-equation). In addition, there is a thermodynamic equilibrium at which the three phases coexist and at this point the following thermodynamic equilibrium equations should be satisfied, (Equation **18** and **19**):

$$\ln f_{i\,vapor} = \ln f_{i\,liquid} \tag{18}$$

$$\ln f_{n_c\,vapor} = \ln f_{n_c\,liquid} = \ln f_s \tag{19}$$

where i=1, ...n_c is a components of the mixture and asphaltene is the n_c-th component of the mixture.

Another approach is the use of Statistical Associating Fluid Theory (SAFT) equation of state which is similar to the group contribution theories in which the fluid of interest is considered to be a mixture of independent segments. The model predicts the changes in residual Helmholtz free energy when the segments of molecules change as shown in Figure **50**. [65] It is noted in this approach the molecules are considered as chains of spherical segments and the fluid's free energy is equal to the sum of the independent segment free energy and the change in the free energy due to chain formation and association, (Figure 50). SAFT equation related to the residual Helmholtz free energy (A[res]) of a mixture of non-associating fluid as, (Equation **20**):

$$\frac{A^{res}}{RT} = \frac{A^{seg}}{RT} + \frac{A^{chain}}{RT} = m\left(\frac{A_o^{hs}}{RT} + \frac{A_0^{disp}}{RT}\right) + \frac{A^{chain}}{RT} \tag{20}$$

where R is the universal gas constant and T is the temperature,

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[65] **Ting, P. David, Hirasaki, George J. and Chapman, Walter G.** Modeling of Asphaltene Phase Behavior with the SAFT Equation of State. *Petroleum Science and Technology.* 2003, Vol. 21, pp. 647-661.

$A^{seg}, A^{chain}, A_o^{hs}, A_0^{disp}$ are the segment, chain, segment hard sphere and segment dispersion contribution to the mixture Helmholtz free energy, respectively

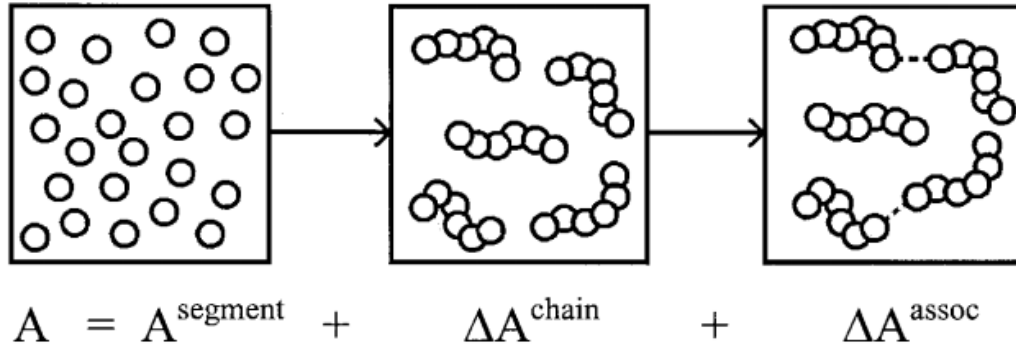m is an average of the pure species segment number weighted by their composition.

$$A = A^{segment} + \Delta A^{chain} + \Delta A^{assoc}$$

Figure 50: *States of molecules as they taken into account by SAFT theory.* [65]

4.3. Model of asphaltene precipitation in porous media

They have been already mentioned two models which give information about asphaltenes precipitation taken into account experimental data at ambient conditions. However, there exists a model which simulates the asphaltenes deposition in porous media when the experimental data is not available. The same model can be also use when the experimental data is available.

In this model, the material balance equations (Figure **51& 52**) are applied on the precipitated asphaltenes. It is assumed that the reservoir is composed of porous and permeable rocks (reservoir rocks). Therefore, there are two main parameters, the permeability (k) and the porosity (φ) of the rocks, and the average values of them (considering that the values are not the same in whole area of the reservoir). Also, the mixture of oil and the precipitated amount of asphaltenes is characterized as a Newtonian fluid for any concentration, so Darcy's law can be used in order to calculate the permeability of the system. It is noted that the porous media are full of fluid. Finally, the model are based on the existence of two sections, one with damage and a second one undamaged, while the length of damage zone increases with flow rate. [66]

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[66] **Ashoori, Siavash.** *Mechanisms of Asphaltene deposition in porous media. Ph.D. Thesis* School of Engineering University of Surrey, Guildford, 2005.
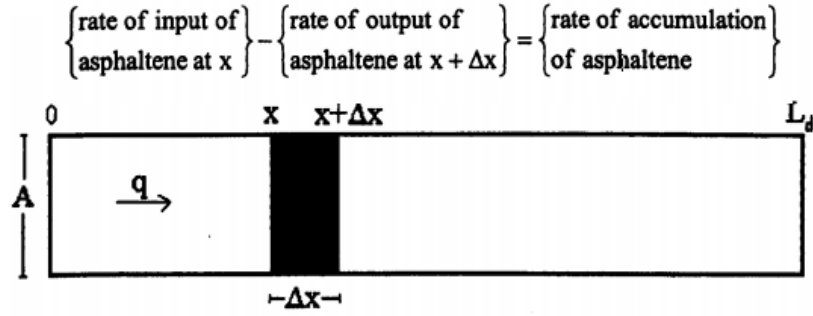
Figure 51: *Schematic diagram of the porous medium element, (Ashoori Siavash, 2005).*

Figure 52: *Material balance equations, where A is the cross-sectional area of the porous medium, C_a: the precipitated asphaltene concentration in the oil, D: the diffusion coefficient of asphaltene in oil (m^2/s), q: the flow rate, t: the time x: space variable along the flow direction, φ: instantaneous porosity and ρ_a: density of solid asphaltene, (Ashoori Siavash, 2005).*

Taking into account the mathematical analysis (Equations **21**, **22**, **23** & **24**) of the model it is known that permeability is dependent on asphaltene precipitation in the mixture, the injection flow rate and the temperature of the system. If the percentage of the asphaltenes increases and the pressure of the system stays stable, the permeability will be reduced. Moreover, low temperatures can affect the solubility of the asphaltenes and therefore the permeability of the system. Finally, considering both composition and temperature as variable parameters the study concluded that the precipitation phenomenon is completely reversible.[66]

$$\gamma_f(C_i, q) = 1 - \frac{1282.6\ C_i}{1 + 1085.4\ C_i} - 0.00059 \tag{21}$$

$$L_d(C_i, q) = 1.16 - 202.2\ C_i + 7.5\ 10^{-5}q^2 - 2.3\ 10^{-3}q \tag{22}$$

$$\lambda = \frac{4.6}{L_d} \tag{23}$$

$$\frac{k_d}{k_i} = \gamma_f \left(1 - \frac{C_i V_t [1 - e^{-\lambda x}]}{A \, x \, \varphi_i} \right)^4 \tag{24}$$

where q is the flow rate, and C_i is the inlet concentration of asphaltenes,

λ is the filtration coefficient,

A is the cross-sectional area of the porous medium,

x is the space variable along the flow direction,

φ_i is the initial porosity,

L_d is the damage length,

γ_f is the floe efficiency factor and

V_t is the cumulative volume of fluid injected.

Chapter 5

Recommendations for future work

Studying the literature plenty of articles have been found related to the physical, chemical and thermodynamic properties of the asphaltenes, to the analytical techniques and to the models which explain the behavior of these products.

However, technological improvements lead to developing new methods and techniques which may give better results. So, in the future we may have the ability to detail visualize precipitated asphaltenes or to take a clear picture of their 3D-structure.

Also, a comparison between samples from different geographic areas and from different kinds of crude oil (heavy oil, bituments) can give information about the molecular weight and the asphaltene structure with respect to these two parameters.

Finally, the study of asphaltenes with respect to the resins concentration would help to understand the precipitation phenomena in view of the fact that, when the concentration of resins decreases the asphaltenes are not anymore soluble to the initial fluid.

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