

## *In Situ* Remediation of Heavy Organic Deposits Using Aromatic Solvents.

Juan H. Pacheco-Sanchez\*, & G. Ali Mansoori, SPE, U. of Illinois at Chicago.

Copyright 1997, Society of Petroleum Engineers, Inc.

This paper was prepared for presentation at the Fifth Latin American and Caribbean Petroleum Engineering Conference and Exhibition held in Rio de Janeiro, Brazil, 30 August - 3 September 1997.

This paper was selected for presentation by an SPE Program Committee following review of information contained in an abstract submitted by the author(s). Contents of the paper as presented, have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material, as presented, does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Papers presented at SPE meetings are subject to publication review by Editorial Committees of the Society of Petroleum Engineers. Electronic reproduction, distribution, or storage of any part of this paper for commercial purposes without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words. Illustrations may not be copied. The abstract must contain conspicuous acknowledgment of where and by whom the paper was presented. Write Librarian, SPE, P.O. Box 833836, Richardson, TX 75083-3836, U.S.A., fax 01-972-952-9435.

### Abstract

One of the effective and routine methods of remediation of heavy organic deposits has been the use of aromatic solvents which can dissolve the asphaltene content of the deposits and can cause the solid particles to be released from the precipitated mass. Remediation of the heavy organic deposits in the course of petroleum production has been a costly process and it has hampered the production activities in many parts of the world. In this report the authors review the *in situ* remediation of heavy organics including asphaltene, resin, paraffin / wax, etc. in oil production and transportation practices and its relation with the laboratory and theoretical simulation experiments. Asphaltene is one of the major compound responsible for various arterial blockage cases in the petroleum industry. It is demonstrated that the asphaltene interaction with other heavy organics is a major factor for arterial blockage whether depositions will occur or not. Various mechanisms of asphaltene flocculation and micelle formation are reviewed and illustrative pathways are presented for each mechanism. The current *in situ* remediation and laboratory simulation practices in the oil industry to combat the problem is reviewed and analysis are made of the cause and effect of each factor influencing them. It is demonstrated that with the development of predictive modelling of heavy organic deposition one can make alterations in the production and transportation schemes to

reduce and eliminate the deposition problem. With the development of predictive models one can also screen the candidate dispersants and solvents from the points of view of availability at the site, effectiveness and economy.

### Introduction

Arterial blockage in the petroleum industry is mostly due to the deposition of heavy organics from petroleum fluids. Heavy organics such as paraffin / wax, resin, asphaltene, diamondoid, mercaptans, and organometallic compounds may exist in crude oil in various quantities and forms. Such compounds could precipitate out of the crude oil solution due to various forces causing blockage in the oil reservoir, in the well, in the pipelines and in the oil production and processing facilities. Solid particles suspended in the crude oil may stick to the walls of the conduits and reservoirs. The toughness of the precipitate has a lot to do whether there is asphaltene present in the crude oil even in minute quantities. Asphaltene, which is a highly polar compound, could act as glue and mortar in hardening the deposits and, as a result, causing barrier to the flow of oil.

Heavy organics deposition during oil production and processing is a very serious problem in many areas throughout the world<sup>1</sup>. In the Prinos field in North Aegean Sea, there were wells that, especially at the start of production, would completely cease flowing in a matter of a few days after an initial production rate of up to 3,000 BPD. The economic implications of this problem were tremendous considering the fact that a problem well workover cost could get as high as a quarter of a million dollars. In Venezuela the formation of heavy organics (asphaltic sludges) after shutting in a well temporarily and/or after stimulation treatment by acid has resulted in partial or complete plugging of the well<sup>2</sup>. At the Hassi Messaoud field, Algeria, deposit of heavy organics in the tubing has been a very serious production problem<sup>3</sup>.

Heavy organics have played a significant role in the production history and economics of the deep horizons of the Ventura Avenue field, California<sup>4</sup>. Heavy organics deposition problems in this field ranged from deposition during early oil production and deposition resulting from well acidizing and CO<sub>2</sub> injection during enhanced oil recovery (EOR). However,

\* Permanent Address: Instituto Mexicano del Petroleo, Subdireccion de Exploracion y Produccion, Av. Eje Central Lazaro Cardenas No. 152, Col. San Bartolo Atepetluacan, Deleg. Gustavo A. Madro 07730 Mexico, D.F.

the problems were so drastic because of heavy organics (asphalt) deposition at the early history of this field that many wells were redrilled, thus affecting the economics of the project considerably. It was also reported that heavy organics deposits were found in the production tubing in the Little Creek CO<sub>2</sub> injection EOR pilot in Mississippi<sup>4</sup>. Generally heavy organics deposits could occur during primary, secondary, and enhanced oil recovery stages<sup>4</sup>. Heavy organics precipitation, in many instances, carries from the well tubing to the flow lines, production separator, pumps, strainers and other downstream equipment<sup>5</sup>. Heavy organic materials deposited into the production installations of Mexico's oil fields have caused many operational problems as it is elaborated in a report by Chavez and Lory<sup>6</sup>. For example, in the fields of Tecminoacan and Jujo depositions in many wells have caused numerous shutdowns and necessity of rather expensive aromatic washes<sup>7</sup>. A methodology to improve production through adequate stimulation treatments and control of the organic and sludge deposition existing in the south-east of Mexico was followed by Figueroa-Ortiz, et al.<sup>8</sup>. Heavy organics deposition in the North Sea and in the Gulf of Mexico oil fields in recent years have caused several under-sea pipeline plugging with substantial economic loss to the oil production operations<sup>9</sup>.

In general, solids in crude oil fall into two classes: "basic sediment" and "filterable solids". These particles have an economic impact on petroleum industry. Carried along in the oil, they can cause fouling, foaming, erosion, corrosion, etc. Depending on the case, coagulants (molecular weight < 10,000.) or flocculents (molecular weight > 10,000.), might provide an indirect aid in solids removal<sup>10</sup>. Coagulants are molecules with strong polar charge which act to disrupt charges on the surface of the oil droplet that would otherwise prevent coalescence. Flocculents, act to coalesce oil droplets, because they are very soluble in oil, but in some cases they can have drastically reduced solids removal, that is to say, solids never die, they just move around.

Depositions of the heavy organics present in oil could happen due to various causes depending on their molecular nature. For instance, by examining each heavy organic compound separately one may argue that mercaptans and organometallics cause deposition due to dissociation or solubility effects. Diamondoids and paraffin / wax may cause deposition due to lowering of the crude oil temperature and formation of crystalline solids. Resins are not known to deposit on their own, but they deposit with asphaltene as it will be elaborated later. The reasons for the asphaltene deposition can be many factors including variations of temperature, pressure, composition, flow regime, and wall and electrokinetic effect. When various heavy organic compounds are present in a petroleum fluid their interactive effects must be also considered in order to understand the mechanisms of their collective deposition or lack of it. This is specially important when one of the interacting heavy organic compounds is asphaltene. For example a regular waxy crude containing minute amounts of asphaltene will behave differently

at low temperatures (below the wax cloud point) compared with a clean waxy crude with no other heavy organics present in it, an asphaltenic crude containing some paraffin / wax, or a purely asphaltenic crude containing no paraffin / wax. Considering that the major barrier in a profitable deposition-free oil production scheme is the presence of asphaltene in the crude in what follows the *in situ* role of asphaltene in the petroleum fluids will be discussed.

### **Asphaltene Molecule, Asphaltene Steric-Collid, Asphaltene Micelle**

The investigation of the chemical constitution of petroleum heavy fractions such as resins and asphaltenes is hindered by their complex nature. The classic definition of asphaltenes is based upon the solution properties of petroleum residuum in various solvents. The word asphaltene was coined in France by J.B. Boussingault<sup>11</sup> in 1837. Boussingault described the constituents of some bitumens (asphalts) found at that time in eastern France and in Peru. He named the alcohol insoluble, essence of turpentine soluble solid obtained from the distillation residue "asphaltene", since it resembled the original asphalt.

Marcusson<sup>12</sup> classified asphaltene and resin as follows: (i) Neutral resins are defined as the insoluble fraction in alkalis and acids and it is completely miscible with petroleum oils, including light fractions; (ii) Asphaltenes are defined as insoluble fraction in light gasolines and petroleum ether. In contrast to resins, the asphaltenes are precipitated in the presence an excess ether; (iii) Asphaltogenic acid is defined as the soluble fraction in alkaline solutions and in such solvents as benzene.

The asphaltene fraction of a petroleum crude is defined according to Nellensteyn<sup>13</sup> as the fraction insoluble in low boiling point paraffin hydrocarbons, but soluble in carbon tetrachloride and benzene. According to Pfeiffer<sup>14</sup> asphaltene is defined as the fraction insoluble in n-heptane but soluble in toluene.

Recently, asphaltene is defined by chemists as the part precipitated by addition of a low-boiling paraffin solvent such as normal-pentane and benzene soluble fraction whether it is derived from carbonaceous sources such as petroleum, coal, or oil shale. Since asphaltogenic compounds are present in petroleum in insignificant quantities, resins and asphaltenes are most important compounds of petroleum. There is a close relationship between asphaltenes, resins, and high molecular weight polycyclic hydrocarbons. In nature, asphaltenes are hypothesized to be formed as a result of oxidation of natural resins. On the contrary, the hydrogenation of asphaltic compound products containing neutral resins and asphaltene produces heavy hydrocarbon oils, i.e., neutral resins and asphaltenes are hydrogenated into polycyclic aromatic or hydroaromatic hydrocarbons. They differ, however, from polycyclic aromatic hydrocarbons by presence of oxygen and sulfur in varied amounts.

On heating above 300-400 °C, asphaltenes are not melted,

but decompose, forming carbon and volatile products. They react with sulfuric acid forming sulfonic acids, as might be expected on the basis of the polyaromatic structure of these components. The color of dissolved asphaltenes is deep red at very low concentration in benzene as 0.0003 % makes the solution distinctly yellowish. The color of crude oils and residues is due to the combined effect of neutral resins and asphaltenes. The black color of some crude oils and residues is related to the presence of asphaltenes which are not properly peptized.

Our knowledge of the asphaltenes is very limited. Asphaltenes cannot be separated into individual components or narrow fractions. Thus, the ultimate analysis is not very significant, particularly taking into consideration that the neutral resins are strongly linked by asphaltenes and probably cannot be quantitatively separated from them. Not much is known of the chemical properties of asphaltenes. Asphaltenes are lyophilic with respect to aromatics, in which they are forming highly scattered micellar solutions. Specifically, asphaltenes are lyophobic with respect to paraffins like pentane and petroleum crudes. They can be associated with the initiation of the precipitation due to the phenomenon of metastability. There have been considerable efforts by analytic chemists to characterize the asphaltenes in terms of chemical structure and elemental analysis as well as by the carbonaceous sources. A number of investigators have attempted to postulate a model structure for asphaltenes, resins, and other heavy fractions based on physical and chemical methods. Physical methods include IR, NMR, ESR, mass spectrometry, x-ray, ultracentrifugation, electron microscopy, small angle neutron scattering, small angle x-ray scattering, quasielastic light scattering spectroscopy, VPO, GPC, etc. Chemical methods involve oxidation, hydrogenation, etc.

One of representative structure for the asphaltene molecule belongs to the Maya crude<sup>15</sup> and includes carbon, hydrogen, oxygen, nitrogen, sulphur as well as polar and non-polar groups as it is shown by (Fig. 1).

Asphaltene particles can assume various forms when mixed with other molecules depending on the relative sizes and polarities of the particles present. It has been shown that asphaltene molecules span a wide range of molecular weights as it is shown in (Fig. 2). Their structure can vary from source to source as it is studied by Yen et. al.<sup>16</sup>.

Due to this polydispersivity, entropic effects are important in mixtures containing asphaltenes. In addition, they behave lyophobic and steric, and they possess electrostatic and associative forces.

Thus, asphaltene particles are believed to exist in oil partly dissolved and partly in colloidal and/or micellar form. Whether the asphaltene particles are dissolved in crude oil, in steric colloidal state or in micellar form, depends, to a large extent, on the presence of other particles (paraffins, aromatics, resins, etc.) in the crude oil. The existence of various states of asphaltenes in crude oil has been extensively discussed in numerous other publications<sup>17-20</sup>. Small asphaltene particles can be dissolved in

a petroleum fluid, whereas relatively large asphaltene particles may flocculate out of the solution and then can form steric-colloids in the presence of excess amounts of resins and paraffin hydrocarbons as it is demonstrated by (Fig. 3).

Flocculation of asphaltene in paraffinic crude oils are known to be irreversible. Due to their large size and their adsorption affinity to solid surfaces flocculated asphaltenes can cause irreversible deposition which may not wash away by current remediation techniques. Asphaltene and its flocculates are known to be surface active agents. This characteristic of asphaltene particles was utilized by Young<sup>21</sup>, to develop an experimental technique based on the measurement of oil/water interfacial tension, (Fig. 4), to detect the onset of asphaltene precipitation.

The flocculated asphaltene will precipitate out of the solution unless there is enough resin in the solution so that they can cover the surface of asphaltene particles by adsorption and form steric-colloids as it is shown by (Fig. 5)

Experimental evidence<sup>2,22</sup> suggests that for an oil mixture there is a critical concentration of resins below which the asphaltene flocculates may precipitate and above which they cannot precipitate regardless of how much the oil mixture is agitated, heated, or pressurized, sort of changing its composition. The onset of steric colloidal formation of asphaltenes in a crude oil can be accurately detected using viscometric techniques as demonstrated by Escobedo and Mansoori<sup>23</sup>. In (Fig. 6) we report the detection of the onset of steric colloid formation of flocculated asphaltene.

Various investigators have established the existence of asphaltene micelles when asphaltenes self-associate in aromatic cores for crude oil<sup>20,24-26</sup>. Several investigators have performed experimental measurements of critical micelle concentration for solutions of asphaltene in aromatic solvents<sup>27-31</sup>. Furthermore, the phenomenon of self-association in asphaltene/toluene systems has been confirmed through measurements of surface tension<sup>27,30</sup>. Sheu<sup>27</sup> has shown that at low concentrations, below the critical micelle concentration (CMC), the asphaltenes in solution are in a molecular state, whereas, above the CMC, asphaltene micelle formation occurs in a manner similar to that in surfactant systems where surfactant monomers are much uniform in their structure and less polydisperse. Rogacheva et al.<sup>30</sup> have also reported experimental data for the phase diagram of asphaltene micelle formation in asphaltene/toluene systems. Espinat and Ravey<sup>32</sup> with the use of scattering techniques have shown that the best model to describe the morphology of asphaltene micelle in solution is a disk. However, several other experimental investigations have shown that asphaltenes could be of spherical-like, cylindrical-like, or disk-like form<sup>16,31-33</sup>. All these investigations are indicative of the fact that asphaltene particles may self-associate, but not flocculate, and form micelles in the presence aromatic hydrocarbons as shown in (Fig. 7).

In some laboratory tests of purified asphaltene in contact with pure toluene, a further increase in the content of asphaltene,

after the start of the micelle formation, was shown to lead to the formation of larger micelles in the system, then of coacervate, and, finally, to the separation of asphaltene as a separate phase<sup>30</sup>. Considering that purified asphaltene and pure toluene were used in this experiment the possibility of its *in situ* happening in a reservoir fluid is quite remote.

While the mechanisms of asphaltene flocculation and steric colloid formation are well understood and modelled<sup>19</sup>, the phase behavior of asphaltene micelle formation is not well characterized and in many cases in recent years it is confused with the asphaltene steric colloids. Despite the experimental evidence on the micellization of asphaltenes, little or no theoretical and modelling research has been performed to explain and quantify this phenomenon. Nevertheless, the theories of micellar solutions of oil/surfactant/water are well known. These theory may be used to explain the micellization of asphaltenes in aromatic solvents if it is assumed that the properties of these systems are similar to those of oil/surfactant/water systems.

In the process of steric colloid formation of asphaltenes with resins they follow an irreversible process of flocculation<sup>1,34</sup>. When asphaltenes form micelles, a reversible self-association process is recognized similar to surfactant amphiphiles in which resins have no role.

### Solubility of Asphaltene in Solvents

Solubility of asphaltenes in hydrocarbon and non-hydrocarbon solvents has been studied by various investigators<sup>30,35-44</sup>.

To determine the solubility properties of asphaltenes, Hirschberg, et al<sup>36</sup> carried out a series of titration experiments on tank oil. Furthermore, they proposed an extension of Flory-Huggins polymer solution theory to model the asphaltene solubility in petroleum fluids. They assumed that asphaltene precipitation was a reversible process, based on their experience. De Boer et al<sup>42</sup> used the same expression for solubility of asphaltenes in oil as Hirschberg et. al. Furthermore, they developed an expression for the dependence asphaltene saturation on pressure reduction, that is to say, an expression for the decrease of solubility with decreasing pressure. Their method was applied for the screening of crude with respect to the asphaltene precipitation during production. However, they said that if all asphaltenes would immediately precipitate when supersaturation is reached, many oil production operations would be impossible. Therefore, most supersaturated asphaltenes remain in solution.

In the model of Kawanaka et. al.<sup>37</sup> is presented a good agreement between their theoretical calculations and experimental results of solubilization of petroleum crude in six different n-paraffins solvents. However, it is well known that stabilization is caused by surfactants, then, there are micelle formation, Sadeghi et. al.<sup>45</sup> found surfactant vesicles formed during Tar Sand Recovery experimentally, they said that after peptization by resins, supermicelle or floc (>220 Angstroms) are formed and they precipitate or floc, when they are of the order of 2000 Angstroms or more. If it is thought that

porphyrin particles are presents inside of the asphaltene-micelle, then when this particles try to settle, resins interlocked to the micelle, cause flocculation. The fact is that, asphaltene-amphiphiles self-associate in order to form asphaltene-micelle in the presence of aromatic solvent, however, asphaltene precipitates in the presence of n-alkane solvent. Therefore the main problem, is a better study of solubilization.

In the normal alkane environment, Pan and Firoozabadi<sup>44</sup> made predictions of micellar size and growth of systems constituted by asphaltenes stabilized with resins, and they say that their results are in line with experimental observations. However, Andersen<sup>29</sup>, Rogacheva<sup>30</sup>, Sheu<sup>39</sup> and other investigators, have shown that asphaltenes self-associate in an aromatic core, and Sheu has found cavities residing near the polar sites, therefore their consideration of micellar asphaltene systems in normal alkane environment is a mistake, because actually, the asphaltene-micelle is surrounded by asphaltene-amphiphile and resins, there are not experimental evidence that resins self-associate forming micelle with an asphaltene core; the experimental evidence is that asphaltene self-associate forming micelle with an aromatic core. It has been shown that asphaltene molecules span a wide range of molecular weights and structures [Yen et. al.<sup>46</sup>, Kawanaka et al<sup>34</sup>, Sheu<sup>27</sup>] depending on their origin. Therefore asphaltenes are polydisperse. Pan and Firoozabadi<sup>44</sup> obtained titration results which seem in agreement with experimental titration data only because they made a gross approximation, while their theory of micelle formation in presence of excess amounts of paraffin hydrocarbons is not validated by any experimental data.

The results of micellization formation when asphaltene particle is in contact with toluene molecule, presented by Pacheco and Mansoori<sup>47</sup>, are indicative of nucleation and crystallization formation, because the core of asphaltene-micelle is aromatic, and the body is compound of asphaltene-amphiphile that it have a lot of paraffins, furthermore, lower CMC of asphaltene and upper CMC of asphaltene are coexisting, depending on the temperature. Afanas'ev et. al.<sup>48</sup> measured crystallization formation for temperatures from 25 to 65 °C and content of solid paraffin from 0 to 100 wt%. That is to say, aromatics in asphaltene material is like water in ice. So water is coexisting within ice, as aromatic is coexisting within asphaltene material, depending on the temperature. It is important to mention that in lake Maracaibo the asphaltene problem was controlled by simple temperature and pressure manipulations of the reservoir fluid<sup>1</sup>. Furthermore, Speight<sup>40</sup> is reporting, arbitrarily defined physical boundaries for petroleum using carbon number and boiling point, where the graph of condensed aromatics is from 0 to 800 °C and from 0 to 40 carbons; and, the graph for n-paraffins is from 0 to 800 °C and 0 to 75 carbons.

On the other hand, if the temperature of petroleum fluid were the only variable that is changing, the effect would be nucleation and crystallization for low temperatures, liquid phase for higher temperatures, and solid phase for very high

temperatures. Furthermore, if the composition of petroleum fluid is altered, the core and the body of the asphaltene-micelle are swelling, and this growing is finishing in the separation and precipitation of asphaltene-amphiphiles. An alteration in the pressure of petroleum fluid will modify both composition and temperature of the system, causing dispersion of many asphaltene-amphiphiles of a lot of sizes, and thermal equilibrium respectively.

When petroleum-crude is diluted with normal alkane (paraffin hydrocarbons), it is well known that the amount of asphaltene precipitated is depending of the number of carbons of the solvent. In the normal alkane environment asphaltene flocculates and then precipitates into a solid phase<sup>5</sup>. The solid phase, is a result of particles such as porphyrin, carbon, sulphur, etc. connected to the asphaltene. That is to say, by introducing additional alkane, the asphaltene (-micelle and -amphiphile) flocculates because they are swelling until they are breaking down, that is to say, they will grow in size and will precipitate out of the solution. In case there are resins there will be also steric colloidal formation. Resins, under the right conditions, surround the asphaltene, extending their aliphatic side chains into the aliphatic oil components. This neutralizes the polar charge thereby making the micelle more soluble (highly dispersible) in the crude oil. This is what happens, in the first place in paraffinic environment of the oil reservoir, oil well, etc. which then requires the in situ remediation using aromatic wash.

Stabilization<sup>49-52</sup> of petroleum fluids is due to the presence of surfactants. Surfactants are part of the asphaltene-amphiphile that is forming micelles in the presence of aromatic molecules. When the asphaltene-micelle is in the presence of excess amounts of paraffin molecules, their core is swelling until they are breaking down, causing precipitation of asphaltene-amphiphiles because as their core is dissolved by n-alkane, the core is losing linking with their asphaltene-amphiphiles. However, in an excess of aromatics, such asphaltene-amphiphiles recover their core, and they start to self-associate again. In this process, a lot of micelles are breaking down, and many others are growing only their size. This is in agreement with the wide range of size, or molecular weight distribution of asphaltene-micelles in petroleum fluids and with the well known fact that the solubilisation is depending of the solvent and of the quantity of such solvent. Furthermore, it is important to mention that petroleum crude is in a process of ripening (this process is indicative of creation of drops of petroleum fluids; however, annihilation of such drops becomes when volatilization and the extraction of petroleum fluids are taking place). In the process of ripening, asphaltene-micelles are growing by sintering or coalescence, what it is an irreversible process finishing on phase separation and precipitation. However, the settling process is reversible, because it is not a process of creation of particles. Settling is caused by aggregation of particles under the influence a drag force, such as the gravity force, and it is a consequence of an appreciable

difference between the continuous and disperse phase.

Oil well stimulation is very well known and practiced in the petroleum industry. Well stimulation is used to increase pressure in oil recovery<sup>50,53</sup>. However, when acids are used, foaming, erosion, corrosion, etc., are caused. For example, to prevent corrosion, acid-neutralizing additives are used; to demulsify spent acid in oil surface active agents are used; and to develop low tension acids surfactants sometimes are added to acids. Islam<sup>41</sup>, said that well stimulations in fluids, such as HCl, can cause significant damage in wells that produce asphaltic crude oil. The acid can cause precipitation of asphaltene and rigid films when it contacts the crude oil and, in turn, cause significant damage to the porous media near the wellbore.

It must be mentioned that, Figueroa et. al.<sup>8</sup> controlled organic deposits and sludge in a severe hostile environment by stimulations of HCl (hydrochloric acid) and aromatic within a good quality control. The production improved notoriously for wells in the south-east of Mexico distributed between the tertiary sands of the Cretaceous and Jurassic dolomitic limestone's, these were found in the 5,000 to 6,200 meters (m) range, with temperatures in the 125-155 °C. The reservoir was characterized by natural fractures with a 35° API sludge tendency crude containing asphaltene in the 10-15% range, paraffin in the 15-20% (High Molecular Weight) and 2-5% (Low Molecular Weight) causing routine deposition in the production equipment, tubing and formation. Figueroa et. al.<sup>8</sup> said that emulsifying the acid treatment with an aromatic (external phase) minimizes direct contact of the acid with tubular goods causing less iron contamination, they also said that emulsion stability needs to be checked with the temperature. It is important to mention that conductivity experiments for asphaltene-toluene-HCl systems are indicative of monomer packing in asphaltene micelle<sup>27</sup>. Sheu concludes that asphaltene molecules are interlocked within micelle, and, that there exist cavities within the micelle. He says: "HCl molecules exhibit stronger affinity with the polar core of asphaltene micelle than the solvated solvent. When HCl is added, they repel some solvated solvent molecules in the cavities, in order to reside near the polar sites. Due to the packing constraint, the energy required to unfold a micelle is too high. As a result, the micelles do not swell or redistribute upon HCl addition." When cavity spaces are filled, the micelles may percolate to accommodate more HCl molecules; or system will phase separate. In order to initiate self-association, several investigations have pointed toward charge interactions. Other possibilities include the dipole-dipole interactions and nucleation.

About steric stabilization of emulsions Cardenas et al.<sup>51</sup> said that in the specific case of emulsions that are stabilized with non-ionic emulsions, the stabilization is based on the interaction between the hydrophilic chains of the surfactant, that are penetrating in the aqueous phase and they are forming a protector film surrounding the dispersed drops. When for such interaction, the variation of the Gibbs free energy (DG) is negative, flocculation is produced by attraction between the

drops. However, if DG is positive, dispersion of the drops by repulsion between themselves is produced, and in this case the drops stay stabilized due to osmotic repulsion.

Experimental results for bitumen in water emulsions stabilized by non-ionic surfactant, showed that an increase in the storage temperature promote flocculation, while the presence of electrolytes opposes the effect<sup>51</sup>.

### Laboratory Simulation Tests and *In Situ* Field Remediation Methods

In petroleum production initially it is necessary to take any number of steps necessary to prevent the deposition problem. If the problem of heavy organics precipitation can be eliminated by modification of the production practices, rather than by chemical or mechanical means, the cost of production can be reduced appreciably. This can be achieved by proper laboratory tests, development of deposition prediction models, and design of the oil production and transportation systems accordingly.

Since asphaltenes are amorphous "non-crystalline" in nature and do not uniformly melt in the presence of heat the heavy organic deposits resulting from asphaltene flocculation are quite hard to deal with in petroleum production practices. Asphaltenes are also a common nucleation site for paraffin crystallization and are, therefore, often found within the same deposit. Asphaltenes and resins are responsible for adding most of the color to crude oils. "Black oils" usually contain the highest asphaltene content. As it was mentioned before asphaltene molecule is mildly polar and in purified form it is insoluble in non-polar aliphatic solvents. Asphaltenes exist in crude oils forming micelles. Resins, under the right conditions, surround the asphaltene, extending their aliphatic side chains into the aliphatic oil components. This neutralizes the polar charge thereby making the micelle more soluble (highly dispersible) in the crude oil. This structure, however, is easily disrupted by various destabilizing forces such as: pressure drops; mixing with lean crude oils; mixing with rich gases (miscible floods); pH shifts and adding incompatible polar solvents like methanol.

Heavy organics deposition due to asphaltene flocculation can be controlled through the better knowledge of the mechanisms that cause the deposition in the first place<sup>20</sup>. Processes can be altered to minimize the deposition and chemicals can be used to possibly control the deposition when process alterations are not effective.

Asphaltenes may be destabilized in any area of the oil production facility from as far back as the near wellbore area to as far down the system as the refinery feed stock. Flocculation and deposition of asphaltenes can be controlled using various production and chemical treatment techniques.

#### A. Production techniques include:

- A(i) Reduction of shear,
- A(ii) Elimination of incompatible materials from asphaltic crude oil streams,

A(iii) Minimization of pressure-drops in the production facility, and

A(iv) Minimization of mixing of lean feed stock liquids into asphaltic crude streams.

#### B. Chemical treatment techniques include:

Addition of dispersants, antifoulants, and aromatic solvents which may be used to control asphaltene deposition. Dispersants work by surrounding the asphaltene molecules similar to the natural resin materials. Aromatic solvents for asphaltene deposits need to have a high aromaticity to be effective, and antifoulants have proven effective in condensate stabilization units in gas plants. Asphaltene deposition can be controlled through better knowledge of the mechanisms that cause the deposition in the first place. Processes can be changed to minimize the deposition and chemical applications can be used effectively to control the deposition when process changes are not cost effective.

Whether asphaltenes actually precipitate depends on the degree of supersaturation created by the pressure drop during production, not on the amount that can eventually be precipitated. In order to investigate about asphaltene solubility or precipitation De Boer et. al.<sup>42</sup> tested several inhibitors. Their results, indicate that, the activity of inhibitors is not only dependent on the acidic head, but also of the aliphatic or aromatic tail of the inhibitor. Particularly, for the sulfonic acids, when the chain-length of the aliphatic group increased from 13 to 24 carbon atoms, the inhibitor activity increased 5 fold. Substitutions of the hydrocarbon within C<sub>18</sub>-sulphonic-acids by aromatics like benzene, toluene, ortho or para-xylene gave approximately the same activity.

An economical study might indicate that mechanical removal methods of cleaning is spending more resources than cleaning using solvents. However, when an asphaltenic deposit is in contact with aromatic solvents, such as AROMINA<sup>54</sup>, an interface with a viscosity of up to 1000 Poise was formed, and it was obstructing a greater penetration of the solvent. On the other hand, it was observed that the AROMINA was not able to keep the deposit in suspension when the stirring of the mixture was suspended, causing a settling of asphalt particles. However, Garcia-Hernandez et. al.<sup>54</sup> elaborated an additive dispersant of asphaltenes named IMP-DAS-301, and they observed that an increase of 100% of production, it was achieved combining the cleaning system and the stimulation with this dispersant. This additive was designed in the physical model of laboratory presented in the (Fig. 8). The disperser top used by this model is presented in the (Fig. 9).

Organic material deposited into the production installations of petroleum crude that was causing operational problems, it was detected in the study elaborated by Chavez and Lory<sup>6</sup>. They initially tried to dissolve such deposits by means of vapor, diesel and heavy aromatics, without satisfactory results. They estimated that the deposition was caused because of the blending of fluids from two oil well productions and their mixing with acids. They considered to elude the problem using a system of

specifically designed additives to stimulate the wells. Their results were then satisfactory despite of the fact that organic deposits persisted into the separation equipment. The chemicals optimally dosificated were a mixture of an inhibitor of asphaltene precipitation (IMP-SIA-301), an asphaltene dispersant (IMP-DAS-301) and an antifoaming agent (IMP-RA-11).

### Predictive and Preventive Modeling

Resolution of the heavy organic deposition problem calls for detailed analyses of heavy organic containing oils from the microscopic standpoint and development of molecular models which could describe the behavior of heavy organics in hydrocarbon mixtures. From the available laboratory, field, and refinery data it is proven that the heavy organics which exist in petroleum generally consist of very many particles having molecular weights ranging from a few hundred to several hundred thousands. As a result distribution-function curves are used to report their molecular weight distribution. Most of the heavy organics present in the oil deposit due to the first or second order phase transitions from liquid to solid state. However, this is not generally the case for asphaltene particles. The high affinity of asphaltene particles to association with one another, their tendency to adsorb resins, and their extensively wide range of size distribution suggest that asphaltenes are partly dissolved and partly in colloidal state (in suspension) in oil peptized (or stabilized) primarily by resin molecules that are adsorbed on asphaltene surface. As a result, a realistic molecular model for the interaction of asphaltene and oil should take into account both the solubility in oil of one segment and suspension characteristic (due to resins) of another segment of the molecular weight distribution curve of asphaltene.

Initially laboratory work may be necessary to quantify and characterize the various families of heavy organics present in a crude and in general shed light on the reasons for such depositions. Laboratory work joined with statistical mechanical modeling may result in the construction of heavy organics deposition envelop (HODE) such as the graph shown in (Figs. 10 and 11) which would indicate the ranges of temperature and pressure where the crude deposits out heavy organics compounds at various temperatures, pressures, compositions/blending, and electrokinetic effects and flow conditions.

### Other Requirements

The steps that appear to have the biggest effect in moderating the severity of the deposition problem are the following:

a. It is reported<sup>55</sup> that the use of standard well completion techniques when heavy organics deposition is likely has often resulted in costly workovers for deposit removal in those wells. To combat the heavy organics deposit formation the completing wells with a dual completion is necessary. This is with the purpose of: i) using the second tubing string for solvent or dispersant injection or circulation, ii) access for lowering

production testing devices, and iii) for circulating around to kill the well. Sometimes the second tubing string is used for production to meet production quotas when the main string is shut-in for maintenance or heavy organics cleaning.

b. It is suggested that all well stimulation, injection and enhanced oil recovery (EOR) fluids should be tested for static and dynamic compatibility with the reservoir fluids prior to operations, especially where asphaltenic crudes are present<sup>4</sup>. Such experimental compatibility tests may be costly if one needs to study all the possible regions of composition and pressure. However, static and dynamic compatibility modeling using the advanced statistical and fluid dynamic techniques can be quite efficient and economical for shedding light on the problem by constructing heavy organics deposition envelopes (HODE) as shown by (Figs. 10 and 11).

c. It is generally understood that there is a composition gradient of heavy organics in petroleum reservoirs with deeper zones having higher fractions of the heavy organics. The decision to produce first the top zone of the reservoir, which is generally less prone to heavy organics deposition, is always preferred. Actually most of the producing wells must be completed dual commingled. Production surveys would show from which zone most of the oil was being produced.

d. In certain circumstances mechanical removal techniques may be effective means of combating the heavy organics problems<sup>4</sup>. For example at the Hassi Messaoud field, Algeria, necessitated frequent tubing scrapings and washings to maintain production<sup>3</sup>. Cutting the deposits from the tubing by wireline methods was too time-consuming and some times impractical, so a program of washing the tubing with a solvent was established. An economical study may indicate whether mechanical removal methods of cleaning is preferred over cleaning by using solvents.

e. Solvent treatment of the oil is considered to be beneficial in some cases because it dilutes the crude oil and reduces the tendency of the heavy organics to precipitate. Solvent treatments may not be very successful largely because the solvents which can be used are limited to aromatic solvents. Xylene is generally the most common solvent selected to be used in well stimulations, workovers, and heavy organics inhibition and cleaning. In some cases xylene injection through the non-producing string actually may help to minimize the heavy organic deposition problem. In oil fields with frequent need for aromatic wash it may be necessary to design an aromatic solvent with stronger wash power and better economy for the particular deposit in mind<sup>54</sup>. Laboratory tests may be necessary to blend the most appropriate aromatic solvent and / or dispersant for a given oil field from the points of view of effectiveness, economy, and environmental friendliness. Then special formulas may be blended to achieve the goal of preventing or cleaning the heavy organics deposits which can be used by the field engineers<sup>54</sup>.

f. Circulation with hot oil may be used to avoid or reduce the heavy organics deposition problem. A combination of solvent treatment and reverse and normal circulation with hot oil have

been tried in the past in some oil wells with mixed results<sup>4</sup>.

g. Figueroa et. al.<sup>8</sup> said that the predominant factors after acidizing for precipitation of organic are iron-asphaltene sludges and emulsions stabilized by asphaltene particles. Therefore, the importance of controlling and preventing iron contamination, prior to and during treatment by:

Monitoring the quality of the acid during the different phases involved in the process: i.e. from the manufacture of the well.

Performing routine tube-cleans to the production string to minimize iron contamination during treatment.

Analysis of the tube-clean returns for iron content and designing a treatment to control for this content.

Emulsifying the acid in an aromatic external phase (e.g. xylene) to avoid direct contact of the acid with the tubular goods.

Adequate corrosion inhibitors schedules according to variations in their performance by other additives (e.g. iron control agents).

Adequate asphaltene-sludge inhibitor selection by measuring absorbance changes through UV spectrometry.

Performing all acid-oil laboratory compatibility tests at the reservoir temperature to check for the acid-aromatic emulsion stability and additional precipitation of asphaltene-sludge at high temperature.

h. Injection of dispersants or antifoulants may be effective in certain crude oils where the ratio of resin to asphaltene is not high enough to prevent asphaltene flocculation and as a result heavy organics deposition. One thing which appears to have universal acceptance is that resins in the crude act as the peptizing agents of the asphaltene particles. It is generally a good practice to analyse a crude oil for its asphaltene and resin content and ratio. In the following table such data for a number of crude oils are reported versus their API gravity.

Crude oils with higher asphaltene to resin ratios are more prone to heavy organics deposition. However, Boscan crude, which is at the top of this list, has had no such problem, while Tecoaminocan crude, which is close to the bottom of the list, is a crude with frequent deposition problems. Considering such severe exceptions to the rule one should not consider this ratio to be the only factor in evaluating the deposition potential of a crude oil. Other factors including the nature of hydrocarbons in the crude, the polydispersivities and polarities of asphaltene and resin, the presence of such compounds as paraffin / wax, organometallics and diamondoids, the nature of conduit, hydrodynamics and electrokinetics have also roles in the deposition. In order to quantify all these factors one has to develop a predictive model in which all these effects are incorporated<sup>20</sup>.

## Conclusions

Insofar as finding a rigorous universal solution to the heavy organics problem is concerned there is still a long way to go. Asphaltene deposition can be controlled through better knowledge of the mechanisms that cause the deposition in the first place. Processes can be changed to minimize the deposition and chemical applications can be used effectively to control the deposition when process changes are not cost effective.

Since heavy organics deposition takes place during primary, secondary, and tertiary oil recovery, injection of peptizing agents (i.e.: resins) in proper amounts and places may prevent or at least control the heavy organics deposition problem. Furthermore, experiments could be performed (i.e.: of the coreflood type) where peptizing agents are injected to study their effect on inhibition of heavy organics deposition or permeability reductions.

One interesting question posed by previous researchers<sup>5,9</sup> is why there was asphaltic bitumen deposited at the bottom of the well considering that no phase change or any substantial temperature or pressure changes had taken place. The conclusion was that the question could only be answered after considerable light was thrown upon the nature of the asphaltic bitumen prior to its separation from the crude oil in the well. There were a few efforts to try to determine the size and nature of asphaltene particles while they still are in the original oil<sup>5,6</sup>.

Establishing the state of the asphaltene particles in the original crude oil seems to be a basic building block in the scientific quest to find a solution to the heavy organics deposition problem. Experimental and theoretical modeling work towards this end has been performed<sup>20,57</sup>, but more is needed. More experiments need to be done to duplicate Witherspoon et. al. s'<sup>57</sup> ultracentrifuge work for different oils and possibly utilize other contemporary experimental techniques to establish the state of asphaltenes in crude oils. Meanwhile, it appears, that any modeling effort that describes the phase behavior of asphaltenes in oil should take into account the lack of positive information on the structure of asphaltenes in the original oil and their molecular characteristics. This has been the philosophy followed in our modeling activity<sup>1,19,20,38</sup> proposed for predicting the deposition behavior of heavy organics in petroleum fluids.

## Acknowledgments

This research was supported by Instituto Mexicano del Petroleo grant FIDE-PEMEX CDA-0401.

## References

1. Leontaritis, K. J. and Mansoori, G. A.: "Asphaltene Deposition: A Survey of Field Experiences and Research Approaches," *J. of Pet. Sc. and Eng.* (1988) 1, 229.
2. Lichaa, P. M.: "Asphaltene deposition problem in Venezuela crudes - usage of asphaltenes in emulsion stability," *Can. Pet. Tech. J.*, oil sands (1977) 609.
3. Haskett, C. E. and Tartera, M.: "A practical solution to the

- problem of asphaltene deposits - Hassi Messaoud Field, Algeria.," *J. Pet. Tech.* (April 1965) 387.
4. Tuttle, R. N.: "High pour-point and asphaltic crude oils in condensates," *J. Pet. Tech.* (June 1983) 1192.
  5. Katz, D. H. and Beu, K. E.: "Nature of asphaltic substances," *Ind. Eng. Chem.* (1945) 37, 195.
  6. Chavez, J. C. and Lory, A.: "Estudio sobre la depositacion de material organico en instalaciones de produccion del area marina de Campeche," *Revista del Instituto Mexicano del Petroleo* (1991) 22 No. 1), 55.
  7. Escobedo, J. and Mansoori, G. A.: "Heavy Organic Deposition and Plugging of Wells (Analysis of Mexico's Experience)," Proceedings of the II LAPEC, paper SPE 23696, Society of Petroleum Engineers, Caracas, Venezuela, March, 1992.
  8. Figueroa-Ortiz, V., Cazares-Robles, F. and Fragachan, F. E.: "Controlling organic deposits and sludge in a severe hostile environment," paper SPE 31124, presented at the 1996 SPE Formation Damage Control Symposium held in Lafayette, Louisiana, Feb. 14-15.
  9. Adialalis, S.: "Investigation of physical and chemical criteria as related to the prevention of asphalt deposition in oil well tubings," MSc. Thesis, Petroleum Engineering Department, Imperial College of the University of London, London (1982).
  10. Schantz, S. S. and Elliot, P. L.: "Economic implications of solids in crude and their ultimate fate in the refining process," *NPRA Annual Meeting*, San Antonio, Texas, USA, March 20-22, (1994).
  11. Boussingault, M.: "Memoire sur la composition des Bitumens," *Annals de Chimie Physyque*, II, (1837) 64, 141.
  12. Sachanen, A.N.: *The chemical constituents of petroleum* Reinhold Publishing Corp., 1945
  13. Nellensteyn, F. J.: "The constitution of asphalt," *Journal of the Institute of Petroleum Technology* (1924) 10, 311.
  14. Pfeiffer, J. P., *The Properties of Asphaltic Bitumen*. Elsevier, Amsterdam, 1950.
  15. Altamirano J. J., Flores, M. A., Pic, O., Panivino, N., Arzate, C., Kapellmann, G., Lopez, M. T., Espinosa, S., Rosales, S.: "Caracterizacion fisico-quimica de asfaltenos procedentes de los crudos Maya e Itsmo," *Revista del Instituto Mexicano del Petroleo* (1986) 18 No. 2, 32.
  16. Yen, T. F.: "Multiple structural orders of asphaltenes," *Asphaltenes and asphalt, 1. Developments in Petroleum Science, 40*. Edited by Yen T. F. and Chilingarian G. V., Elsevier Science B. V., (1994).
  17. Nellensteyn, F. J.: "The colloidal structure of bitumens," *The Science of Petroleum*, Oxford Univ. Press, London, Vol. 4, (1938).
  18. Yen, T. F.: "Structure of petroleum asphaltene and its significance," *Energy Sources* (1974) 1, 447.
  19. Park, S. J. and Mansoori, G. A.: "Aggregation and deposition of heavy organics in petroleum crude," *Energy Sources* (1988) 10, 109.
  20. Mansoori, G. A.: "Asphaltene, resin, and wax depoeition from petroleum fluids," *The Arabian Journal for Science and Engineering* (1996) 21, No. 48, 707.
  21. Vuong, L. T.: "A simple and accurate experimental technique for measurement of the onset of asphaltene deposition from petroleum reservoir fluids," M.Sc. Thesis, Chemical Engineering Department, University of Illinois, 1985.
  22. Swanson, J.: "A contribution to the physical chemistry of asphalts," *J. Phys. Chem.* (1942) 46, 141.
  23. Escobedo, J. and Mansoori, G. A.: "Viscometric determination of the onset of asphaltene flocculation: A novel method," *J. SPE Prod. & Facilities* (May 1995) 115.
  24. Pfeiffer, J. P. and Saal, R. N.: "Asphaltic Bitumens as a Colloidal System," *J. Phys. Chem.* (1940) 44, 139.
  25. Dikic, J. P. and Yen, T. F.: "Macrostructures of the asphaltic fractions by various instrumental methods," *Anal. Chem.* (1967) 39, 1847.
  26. Galtsev, V. E., Ametov I. M. and Grinberg O. Y.: "Asphaltene association in crude oil as studied by ENDOR," *Fuel* (1995) 74, 670.
  27. Sheu, E. Y.: "Physics of asphaltene micelles and microemulsions-theory and experiment," *J. Phys.: Condens. Matter* (1996) 8, A125.
  28. Andersen, S. I. and Birdi, K. S.: "Aggregation of asphaltenes as determined by calorimetry," *Journal of Colloid and Interface Science* (1991) 142, 497.
  29. Andersen, S. I. and Speight, J. G.: "Observations on the critical micelle concentration of asphaltenes," *Fuel* (1993) 72, 1343.
  30. Rogacheva, O. V., Rimaev, R. N., Gubaidullin V. Z. and Khakimov, D. K.: "Investigation of the Surface Activity of the Asphaltenes of Petroleum Residues," *Colloid J. USSR* (1980) 490.
  31. Ravey, J. C., Ducouret, G. and Espinat, D.: "Asphaltene macrostructure by small angle neutron scattering," *Fuel* (1988) 67, 1560.
  32. Espinat, D. and Ravey, J. C.: "Colloidal structure of asphaltene solutions and heavy-oil fractions studied by small-angle neutron and x-ray scattering," paper SPE 25187, presented at the 1993 SPE International Symposium on Oilfield Chemistry held in New Orleans, LA, March 2-5.
  33. Storm, D. A. and Sheu, E. Y.: "Colloidal Nature of Petroleum asphaltenes," *Asphaltenes and asphalt, 1. Developments in Petroleum Science, 40*. Edited by Yen T. F. and Chilingarian G. V., Elsevier Science B. V., (1994).
  34. Kawanaka, S., Park, S. J. and Mansoori, G. A.: "The role of asphaltene deposition in EOR gas flooding: a predictive technique," paper SPE 17376, presented at the 1988 Annual Technical Conference and Exhibition, Tulsa, Oklahoma, April 17-20.
  35. Mitchell, D. G. and Speight, J. G.: "Solubility of asphaltenes in hydrocarbon solvents," *Fuel*, (1973) 52, 149.
  36. Hirschberg, A., de Jong, L. N. J., Schlijper, B. A. and Meijers, J. G.: "Influence of temperature and pressure on asphaltene flocculation" *Soc. Petrol. Eng. J.* (1984) 24, 283.
  37. Kawanaka, S., Park, S. J. and Mansoori, G. A.: "Organic deposition from reservoir: A thermodynamic predictive

- technique," *SPE Reservoir Engineering J.*, (May 1991) 185.
38. Burke, N. E., Hobbs, R. E. and Kashou, S. F.: "Measurement and Modeling of asphaltene precipitation," *JPT*, (Nov. 1990), 1440.
39. Sheu, E. Y., Storm D. A. and De Tar M. M.: "Asphaltene in polar solvents" *J. of Non-Crystalline Solids*, (1991)131-133, 341.
40. Speight, J. G.: "Chemical and Physical studies of petroleum asphaltene." *Asphaltenes and asphalt, 1. Developments in Petroleum Science, 40*. Edited by Yen T. F. and Chilingarian G. V., Elsevier Science B. V., (1994).
41. Islam, M. R.: "Role of asphaltenes on oil recovery and mathematical modeling of asphaltene properties," *Asphaltenes and asphalt, 1. Developments in Petroleum Science, 40*. Edited by Yen T. F. and Chilingarian G. V., Elsevier Science B. V., 1994
42. De Boer, R. B., Leerlooyer, Klaas, Eigner, M. R. P., van Bergen A. R. D.: "Screening of Crude Oils for Asphalt Precipitation: Theory, Practice and the Selection of Inhibitors" *SPE Production & Facilities*, (Feb. 1995) 55.
43. Victorov, A. I. and Firoozabadi, A.: "Thermodynamic micellization model of asphaltene precipitation from petroleum fluids," *AIChE Journal* (1996) 42, No. 6, 1753.
44. Pan, H. and Firoozabadi, A.: "A thermodynamic micellization model for asphaltene precipitation: Part I: Micellar size and Growth," paper SPE 36741, presented at the 1996 Annual Technical Conference and Exhibition, Denver, Colorado, Oct. 6-9.
45. Sadeghi, M. A., Sadeghi, K. M., Momeni, D. and Yen, T. F.: "Microscopic Studies of Surfactant Vesicles Formed During Tar Sand Recovery," *Oil-Field Chemistry, ACS Symposium Series 396, Oil-Field Chemistry (Enhanced Recovery and Production Stimulation)* Edited by Borchardt J. K. and Yen T. F., Washington, D. C., 1989.
46. Yen, T. F., Erdman, G. J. and S. S. Pollack: "Investigation of the structure of petroleum asphaltenes by x-ray diffraction," *Analyt. Chem.* (1961) 33, 1587.
47. Pacheco-Sanchez, J. H. and Mansoori, G. A.: "Prediction of Phase Separation in Micellar Solutions" (to be published); Pacheco-Sanchez, J. H. and Mansoori, G. A.: "Asphaltene micelle formation in the presence of aromatic hydrocarbons" (to be published).
48. Afanas'ev, A. N., Matishev, V. A., Syunyaev, Z. I. and Farafonov, V. V.: "Melting and Crystallization of Paraffins" *Chemistry and Technology of Fuels and Oils* (1993) 29, 549.
49. Borchardt, J. K.: "Chemicals used in Oil-Field Operations," *Oil-Field Chemistry, ACS Symposium Series 396, Oil-Field Chemistry (Enhanced Recovery and Production Stimulation)*. Edited by Borchardt J. K. and Yen T. F., Washington, D. C., 1989.
50. Schechter, R. S.: *Oil Well Stimulation*. Prentice Hall, 1992.
51. Cardenas, A., Rossi, S., Pazos, D. and Rivas, H.: "Estabilidad de Emulsiones de Bitumen en agua. Parte II," *Vision Tecnologica* (1996) 4, 27.
52. Smith, D. H., Covatch, G. L. and Dunn, R. O.: "Calorimetric Phase Studies of Amphiphilic Petroleum Recovery Systems" *ACS Symposium Series 396, Oil-Field Chemistry (Enhanced Recovery and Production Stimulation)*. Edited by Borchardt J. K. and Yen T. F., Washington, D. C., 1989.
53. Paris-Marcano L. C.: "Method for improving heavy crude oils by reducing the asphaltene content of crude oils and oil-containing tar sands," Patent Number 5,152,886. October 6, 1992 U.S.A.
54. Garcia-Hernandez, F.: "Estudio sobre el control de la depositacion organica en pozos del area Cretacica Chiapas-Tabasco," *Ing. Pet.* (July 1989) 39.
55. Von Albrecht, C., Salathiel, W. M. and Nierode D. E.: "Stimulation of asphaltic deep wells and shallow wells in Lake Maracaibo, Venezuela. Advances in Methods of Increasing Well Productivity and Injectivity," *Can. Pet. Technol., J.*, Oil Sands (June 1977) PD7, No. 1, 55.
56. Witherspoon, P. A.: "A study of the colloidal characteristics of petroleum using the ultracentrifuge," *J. Phys. Chem.* (1957) 61, 1296.
57. Yen T. F.: "Structural differences between asphaltenes isolated from petroleum and from coal liquid," *Advances in Chemistry Series 195, Chemistry of Asphaltenes*. Edited by Bunger J. W. and Li N. C. (Sept. 1979) 39.

TABLE 1-RESIN AND ASPHALTENE CONTENT OF VARIOUS CRUDE OILS

Crude Oil	Sp. grav. ( <sup>o</sup> API)	Res- ins (wt%)	Asphal- tenes (wt%)	Asph Res (wt%)
Venezuela, Boscan	10.2	29.4	17.2	0.585
Mexico, Panuco	11.7	26.0	12.5	0.48
USA, MS, Baxterville	16.0	8.9	17.2	1.93
Russia, Kaluga	16.7	20.0	0.5	0.025
USA, TX, Hould	19.7	12.0	0.5	0.04
USA, CA, Huntington Beach	26.2	19.0	4.0	0.21
USA, LA, Brookhaven	30.6	4.6	1.65	0.36
Russia, Balachany	31.7	6.0	0.5	0.08
Russia, Bibi-Eibat	32.1	9.0	0.3	0.03
Russia, Dossor	32.6	2.5	0.0	0.00
Russia, Surachany	35.0	4.0	0.0	0.00
USA, TX, Mexia	36.0	5.0	1.3	0.26
Iraq, Kirkuk	36.1	15.5	1.3	0.08
Mexico, Tecoaminocan	36.7	8.8	1.5	0.17
Mexico, Isthmus	37.8	8.1	1.3	0.16
USA, OK, Ok. City	38.0	5.0	0.1	0.02
USA, OK, Tonkawa	40.8	2.5	0.2	0.08
USA, LA, Rodessa	43.8	3.5	0.0	0.00
USA, PA	44.3	1.5	0.0	0.00
USA, OK, Davenport	46.3	1.3	0.0	0.00

(Sachanen, 1945), (Lichaa, 1977), Garcia (1989), Altamirano, et al (1986).

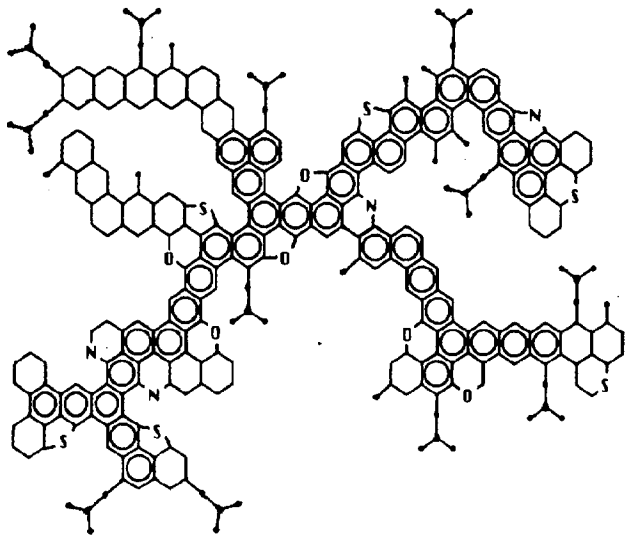


Fig. 1: Molecular structure for asphaltene derived from Maya crude, proposed by Altamirano (1986)

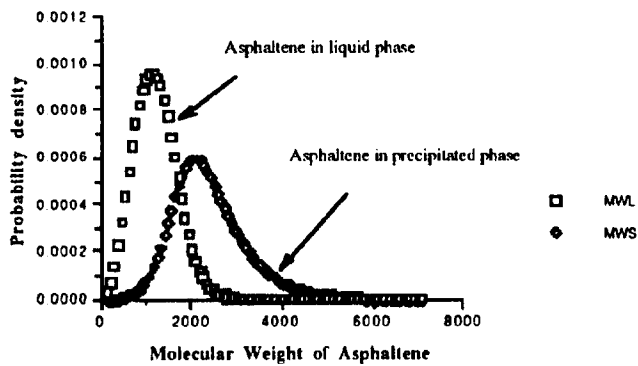


Fig. 2: Molecular size distribution of asphaltene of a California crude in solution and after precipitation by the addition of n-C5 (Courtesy of Prof. S.J. Park)

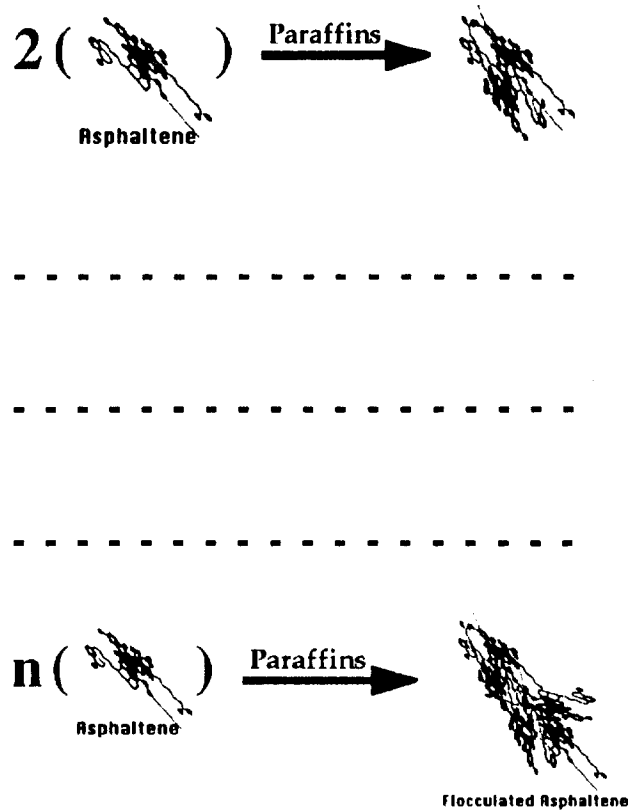


Fig. 3: Various stages of asphaltene flocculation due to excess amounts of paraffins in the solution

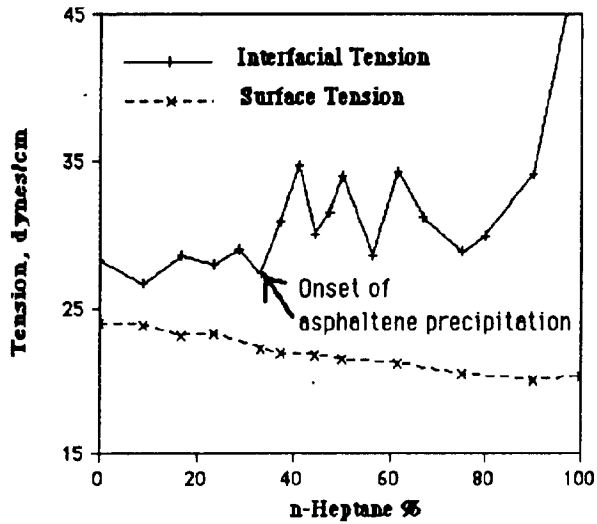


Fig. 4. Variation of surface and interfacial tensions due to the addition of n-heptane to Ranglely crude and detection of the onset of asphaltene precipitation [Kim, et. al. 1990]

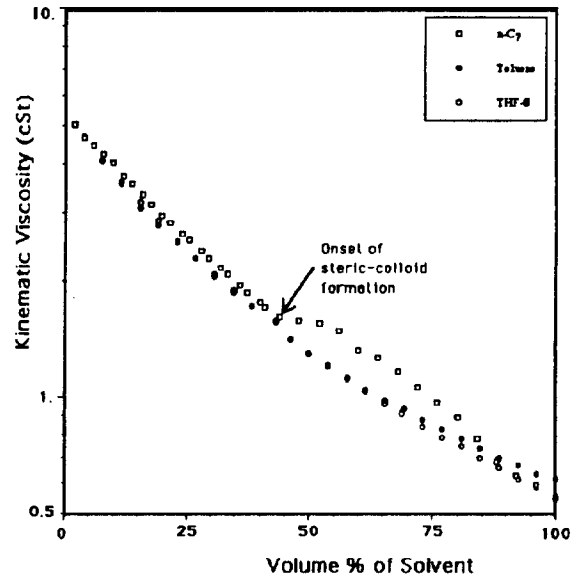


Fig. 6. Variation of viscosity of Isthmus crude due to the addition of various solvents and the detection of the onset of steric-colloid formation of asphaltene (Escobedo and Mansoori, 1995).

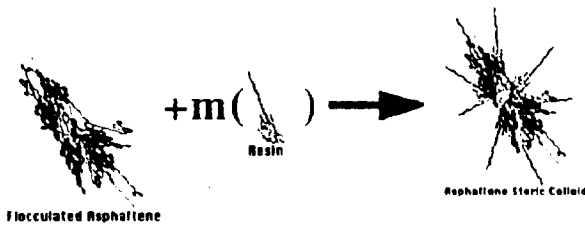


Fig. 5-Steric-colloid formation of flocculated asphaltenes with resins

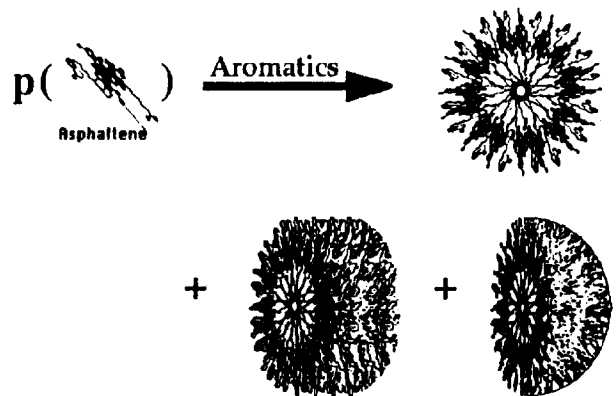


Fig. 7: Formation of asphaltene micelles in the presence of aromatic solvents

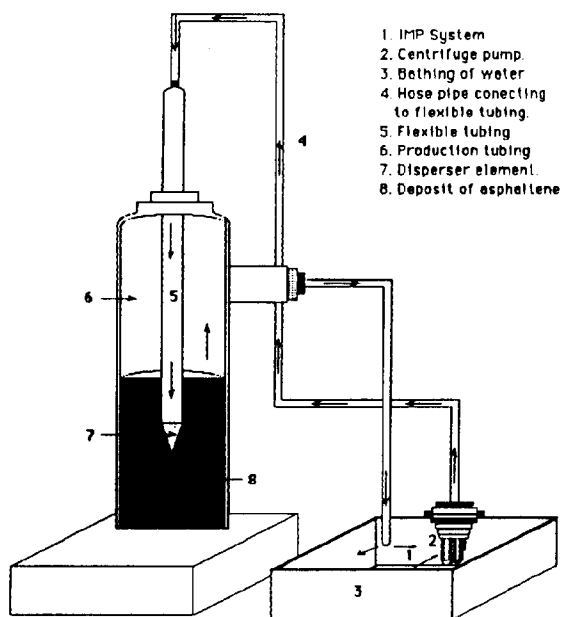


Fig. 8. A Laboratory model to simulate the remediation operations of the asphaltene deposits [Garcia-Hernandez (1989)]

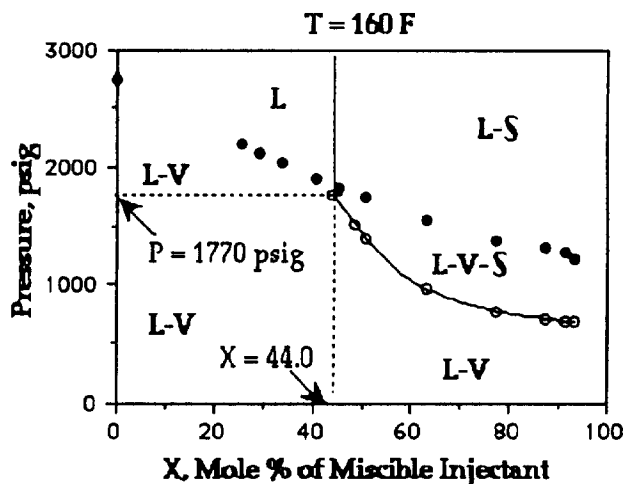


Fig. 10: Static (PX) heavy organics deposition envelope (HODE) of a crude oil mixed with a miscible injectant (MI) at 60 °F but at various proportions and pressures. In this figure L stands for liquid phase, L-V is the liquid-vapor two-phase region, L-S is the liquid-solid two-phase region, and L-V-S is the liquid-vapor-solid three-phase region [Mansoori, 1996].

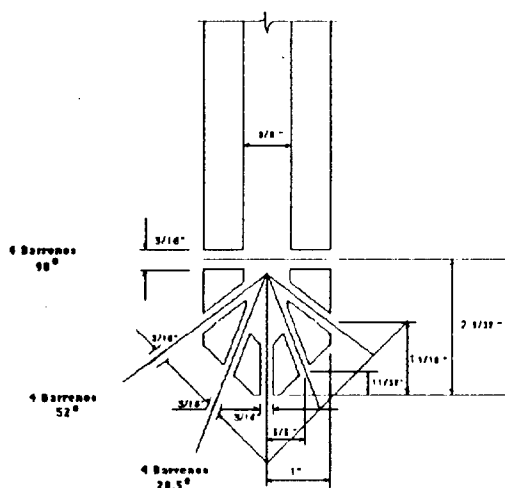


Fig. 9. Diagram of the disperser top of the laboratory unit shown by Fig. 8 [Garcia-Hernandez (1989)]

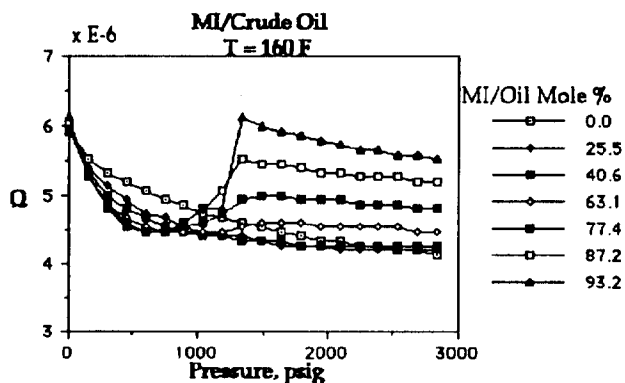


Fig. 11: Dynamic (QX) heavy organics deposition envelope (HODE) of a crude oil mixed with a miscible injectant (MI) at 60 °F but at various proportions and pressures. In this figure  $Q = U_{avg}^{1.75} d^{0.75} / k$  where  $U_{avg}$  stands for crude average velocity in a cylindrical conduit,  $d$  is the conduit diameter and  $k$  is the crude electrical conductivity. The area above each curve represents the deposition region and under the curve is the flow region with no deposition [Mansoori, 1996].