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Heavy Organic Deposition and Plugging of Wells (Analysis of Mexico's Experience)

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ABSTRACT

The pipeline transportation of petroleum fluids can be significantly affected by flocculation, deposition, and plugging of asphaltene, paraffin/wax, and/or diamondoid in the transfer pipelines, tubulars, pumps, and other equipment. The economic implications of the problem of heavy organic depositions in such processes are tremendous.

In this report Mexico's experience with the pipeline plugging due to heavy organic deposition is reviewed and analysed based on the present state of knowledge. The modeling basis of a comprehensive estimation and prediction technique is presented. This technique is based on observed field and laboratory data, statistical mechanical theories, polydisperse polymer solution theory, continuous thermodynamics, electrokinetics and transport phenomena, colloidal solution theory, and the FRACTAL aggregation theory.

INTRODUCTION

A number of problems could arise during the production of petroleum which would drastically increase the production costs. Among these, wax deposition due to a drop in temperature, and asphaltene deposition due to a variety of causes, in the production tubing strings are the prominent problems [1-4]. Therefore, it is of great importance to understand the behavior of heavy organics under various operating conditions. An ultimate goal is to predict whether organic deposition will take place, and to be able to avoid getting to the onset of organic deposition region.

Surveys of field experiences [5-7] indicate that asphaltene deposition problem is one of the major factors that increases the production cost. Thus, being able to prevent such deposition, costs could be lowered appreciably. Mexican oil production and its heavy organic deposition problem was selected for this study because of the availability of an abundance of field and laboratory data about it. Laboratory analysis performed on asphaltenes extracted from samples of the crude oils prone to asphaltene deposition, and from the heavy organic deposits revealed that "Mexican" asphaltenes are very similar (in elemental analysis) to asphaltenes extracted from other sources, as can be seen from Table 1.

The difference would reside in the asphaltene-particle structure and charge which in the case of Mexican crude oils is negative [6,7]. The molecular nature and structure of the asphaltene fraction of crude oils has been the subject of numerous investigations. There are still serious shortcomings in consistency between such studies because of the varied assumptions that have to be made in deriving the molecular formulae.

MODELING OF HEAVY ORGANIC DEPOSITIONS FROM PETROLEUM FLUIDS

The parameters that govern precipitation of heavy organics from petroleum fluids appear to be composition of crude and injection fluid, pressure, temperature, flow characteristics, and the properties of conduit (pipeline, well, etc.) in which the reservoir fluid is flowing. With alterations in these parameters the nature of organic substances which precipitate will vary. Also, precipitation of some of the families of organic compounds (asphaltenes) is generally

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References and illustrations at end of paper followed with polymerization or flocculation of the resulting precipitate, which produces an insoluble material in the original reservoir fluid. Because of the complexity of the nature of heavy organics in petroleum fluids the phenomena of precipitation and flocculation of these substances are not well understood. Also in view of the complexity of the petroleum reservoirs, study and understanding of the *in situ* precipitation of heavy organics seems to be a challenging and timely task. Such an understanding will help to design a more profitable route for petroleum production and processing systems.

In order to model the phenomena of organic deposition from petroleum fluids under the influence of a miscible solvent, or in the process of its blending with another petroleum fluid one has to consider the following: (i) The nature of organic compounds being deposited.; (ii) The nature of the petroleum fluid as a whole.; (iii) The role of temperature, pressure composition.; (iv) The role of flow regime and the structure of the conduit (pipeline, well, etc.) through which the flow is underway.

(i) Consideration of the nature of organic compounds being deposited: The phenomenon of organic deposition is a strong function of the organic compounds being deposited. For example, wax deposition is a classical solid-liquid phase transition phenomena of polydisperse compounds which is affected mainly by variations in temperature of the system. On the other hand, asphaltene deposition can be a classical solid-liquid phase transition phenomena only at a very specific case [22]. In a general case asphaltene deposition is far from a classical solid-liquid phase transition phenomenon. It is a result of a multi-phenomena effect which includes solid-liquid phase transition, colloidal formation, growth of colloidal formations, and eventual collapse of the resulting colloids due to the limitations on the size of Brownian particles suspended in a media. When we are dealing with a petroleum fluids which contain wax, asphaltenes, resins and the other usual crude oil compounds the phenomenon of deposition could be quite complicated.

(ii) Consideration of the Nature of the Petroleum Fluid and its composition: It is generally assumed that two factors are responsible for maintaining the mutual solubility of the compounds in a complex mixture such as the petroleum crude: These are the ratio of polar to nonpolar molecules and the ratio of the high molecular weight to low molecular weight molecules in the mixture. Of course, polar and nonpolar compounds are basically immiscible, and light and heavy molecules of the same kind are partially miscible depending on the differences between their molecular weights. However, in the complex mixture of petroleum crude and the like all these compounds are probably mutually soluble so long as a certain ratio of each kind of molecule is maintained in the mixture. By introduction of a solvent into the mixture this ratio is altered. Then the heavy and/or polar molecules separate from the mixture either in the form of another liquid phase or to a solid precipitate. Hydrogen bonding and the sulfur and/or the nitrogen containing segments of the separated molecules could start to aggregate (or polymerize) and as a result produce heavy organic deposits.

(iii) Consideration of the Role of Temperature and Pressure: Temperature is the major driving force in phase transitions between condensed phases (liquid-liquid, liquid-solid, solid-solid) and separation of those phases. Such phase transitions phenomena as the appearance of freezing point, cloud point, glass transition, clathrate formation, and many phases of liquid crystals are primarily due to temperature changes in a system. In the case of petroleum fluids temperature variations could cause all, or some, of these phase transition effects. However, its role can be much more complex due to the presence of numerous variety of compounds present in the crude.

The role of severe pressure changes can have similar direct consequences in phase transitions between condensed phases as the temperature. However, the role of low and moderate pressure changes on such phase transitions could be attributed to the variations in composition of the crude and its role on phase transitions as explained above.

(iv) Consideration of the Role of Flow Regime and the Structure of the Conduit: The nature of flow regime could have a substantial role in the deposition of suspensions of a fluid in motion. It has been shown experimentally that the electrical charge of colloidal asphaltenes is a very important property and, regardless of the charge sign, it seems possible to devise colloidal asphaltene deposition preventive measures by controlling the electrical effects attributed to the charge of asphaltenes. The primary electrokinetic phenomenon in effect is the "streaming potential" generated by the movement of the electrically charged colloidal asphaltene particles due to the flow of oil. This streaming potential seems to neutralize the similar charge of the colloidal asphaltene particles and cause them to flocculate. The electric charge of colloidal asphaltenes has not been explained yet, primarily because of the complexity of the composition of asphaltic materials. The difference in charge (+or-) displayed by asphaltene particles derived from different crudes has not been explained either. One suggestion has been that the large quantities of nickel and vanadium found in asphaltene deposits may hold the key to these charges. This idea may be investigated by analyzing metal contents of asphaltene deposits that contain colloidal asphaltene particles with different electric charge.

Requirements for the Modeling: Modeling of the organic deposition problem calls for detailed analyses of reservoir fluids and development of molecular models which could describe the behavior of different families of heavy organics in hydrocarbon mixtures. From the available laboratory and field data it is proven that the heavy organics which exist in oil consist of very many particles belonging to several families of compounds (here called asphaltene, wax, and resin) having molecular weights ranging from hundreds to several hundred thousands. As a result distribution-function curves are used to report molecular weights of every family [35,36]. The wider range of molecular weight size distribution of asphaltenes (compared to the resin and wax) suggests that asphaltenes may be partly disolved and partly in colloidal state (in suspension) peptized (or stabilized) primarily by resin molecules that are adsorbed on asphaltene surface. As a result, a realistic model for asphaltene deposition should take into account both the solubility in oil of one segment and suspension characteristic of another segment of the molecular weight distribution curve of asphaltene. Generally two categories of models have emerged in describing the deposition of heavy organics from petroleum fluids: (i) Solubility models; (ii) Suspension models.

(i) Solubility Model: In order to formulate the necessary model for prediction of the onset and amount of deposition of heavy organics from reservoir fluids one can take advantage of the theories of polymer solutions [15,16,18]. Both heavy organic families and other fractions of the crude consist of mixtures of molecules with virtually continuous molecular weight distributions. In order to formulate the theory of interaction of oil and heavy organics we can utilize the concept of continuous mixture joined with the thermodynamic theory of heterogeneous polymer solutions [15,16]. *Kawanaka, et al.* have already formulated the necessary continuous mixture model for the prediction of the onset and amount of deposition of organics due to variations of temperature, pressure, and injection of miscible solvents. It should be pointed out that the cubic equation of state models are not suitable at all for dealing with asphaltene. This is because the basis of these equations of state which is the van der Waals equation of state is formulated for simple spherical molecules only.

(ii) Suspension Model: This model is based upon the concept that heavy organics exist as particles suspended in oil. Their suspension is assisted by resins (heavy and mostly aromatic molecules) adsorbed to the surface of asphaltenes and keeping them afloat because of the repulsive forces between resin molecules in the solution and the adsorbed resins on the asphaltene surface. Stability of such a suspension is considered to be a function of the concentration of resins in solution, the fraction of asphaltene surface sites occupied by resin molecules, and the equilibrium conditions between the resins in solution and on the asphaltene surface. Utilization of this model requires the following [18]: 1. Resin chemical potential calculation based on the statistical mechanical theory of polymer solutions. 2. Studies regarding resin adsorption on asphaltene particle surface and measurement of the related Langmuir constants. 3. Calculation of streaming potentials generated during flow of charged asphaltene particles. 4. Development and use of asphaltene colloidal and aggregation models for estimating the amount of asphalt which may be irreversibly aggregated and flocculated out. The amount of resins adsorbed is primarily a function of their concentration in the liquid state (the oil).

So, for a given system (i.e., fixing the type and amount of oil and asphaltenes) changing the concentration of resins in the oil will cause the amount of resins adsorbed on the surface to change accordingly. This means that we may drop the concentration of resins in the oil to a point at which the amount of resins adsorbed is not high enough to cover the entire surface of asphaltenes. This may then permit the asphaltene particles to come together (irreversible aggregation), grow in size, and flocculate.

One major question of interest is how much asphaltene will flocculate out under certain conditions. Since the system under study consists generally of a mixture of oil, aromatics, resins, and asphaltenes it may be possible to consider each of the constituents of this system as a continuous or discrete mixture (depending on the number of its components) interacting with each other as pseudo-pure-components. The theory of continuous mixtures [35,36], and the statistical mechanical theory of monomer/polymer solutions, and the theory of colloidal aggregations and solutions are utilized in our laboratory to analyze and predict the phase behavior and other properties of this system.

The Comprehensive ASPHRAC® Model: ASPHRAC is a comprehensive package of computer programs and database (developed in this laboratory) which calculates various properties of petroleum fluids containing heavy organics (asphaltene, wax, resin). This package is based on a combination of solubility model, suspension model, and the FRACTAL aggregation and growth of organics suspensions model [16]. The following principles have been used in its development: Statistical mechanical mixing rules and conformal solution equations of state, polydisperse polymer solution theories, continuous thermodynamics and various phase equilibrium algorithms, electrokinetic phenomena, transport phenomena, colloidal solution theory, and FRACTAL kinetics of aggregation theories [16,18,24,27,30-37]. This package is general enough to predict the heavy organics-oil-wall interaction problems wherever they may occur during oil production, transportation or processing. The emphasis of the package is on the prediction of the behavior of asphaltenes and their role in the production and processing of natural and synthetic hydrocarbons. This package can be utilized for: Oil recovery simulation studies and design of well completions and surface facilities; The design and performance evaluation of crude, bitumen, and asphalt related facilities and processes; The design of cost-effective anti-foulants for asphaltene fouling mitigation in various sections of plants. The kind of input data which may be used in the package are: Bottom-hole (and/or stock-tank oil) sample(s) composition data, oil aromaticity, oil resin content, characterization data for C_{7+} fraction of oil, onset of deposition and amount of asphaltene titration data, chromatography (GC, HPLC and GPC) data of oil fractions.

CHARACTERISTICS OF THE MEXICAN CRUDE OILS AND THEIR HEAVY ORGANICS

Since the beginning of the oil industry in Mexico, the crude oils produced have been described as follows:

The majority are dark brown or black, except those crude oils from the Isthmus region which have an amber or dark red color with a green bloom [9-11].

Oils from the northern section (Tampico-Tuxpan) possess a disagreeable sulphurous odor, which is also the characteristic of majority of the crude oils from the southern section, with the exception of the Isthmus type crude oils which have a pleasant and to some extent aromatic odor.

- The crude oils produced in the northern regions of the country are characterized as "heavy" with specific gravities usually greater than 0.950. While the ones produced in the southern section are classified as "light" (Isthmus) with specific gravities ranging from 0.792 to 0.880. The average specific gravity of the crude oils tends to become progressively lower as proceeding to a southward direction [9,10].

Mexican crude oils can be classified as mixed base type, although a distinction may be made between those crude oils from the northern regions (Tampico-Tuxpan) and those from the southern parts. Northern crudes are predominantly asphaltic, containing less than 1% of wax, while the ones produced in the south may contain up to 5% of wax in addition to asphaltene. Oils from the Isthmus fields can further be divided into waxy and non-waxy types. The so-called waxy crude oils may have a wax content ranging from 2 to 3.5%. The non-waxy crudes are those in which the wax content is less than 1%. The wax in the Isthmus crudes is frequently found to be of high melting point and amorphous [11].

At present Mexico produces mainly three types of crude oils: Maya crude (Heavy), Isthmus crude (Light), and Olmeca crude (light)[12]:

MAYA CRUDE: Classified as heavy with a hight content of metals and sulfur, The characteristics of this crude are [10,13,14]:

Gravity API @ 60°F	: 22.1
Total Sulfur content, wt%	: 2.8
Total Nitrogen, ppm	: 3778
Nickel, ppm	: 53
Vanadium, ppm	: 286
Pour test, °F	: 0.0
Viscosity, SUS, @ 70°F	: 1288
@100°F	: 709
Rvp, Psia @ 100°F	: 5.1
H2S, ppm	: 199
n-C_4 and lighter, wt%	: 1.5
n-pentane asphaltenes, wt%	: 17.1
n-heptane asphaltenes, wt%	: 10.61

ISTHMUS CRUDE: Classified as a light crude with a low content (less than 1 wt%) of metals and sulfur. The properties of this crude are as follows [10,13]:

Gravity API @ 68 °F	: 37.8
Sulfur content, wt%	: 0.9
Pour Test, °F	: -24
Viscosity, SUS., @ 60 °F	: 46.6
@70 °F	: 43.2
@77 °F	: 41.2
Rvp, Psia @ 100 °F	: 6.4
H2S, ppm	: 102
n-C_4 and lighter, wt%	: 1.2
n-pentane asphaltenes wt%:	: 1.3
saturated compounds, wt%	: 58.5
aromatics, wt%	: 32.4
resins or polars, wt%	: 8.1

Less than 1 ppm of N, Fe, Cu, Ni, V and Zn.

OLMECA CRUDE: Classified as a light crude with a low content (0.8 wt%) of metals and sulfur. The properties of this crude are as follows [12].

Gravity, °API	: 39.8
Sulfur, wt%	: 0.8
Vis., cSt @ 20 °C	: 4.1
Pour pt., °C	: -39
Con. Carbon, wt%	: 1.5
Acidity, mg KOH/g	: 0.029
V/Ni, ppm	: 0.9/0.1
C5-, vol%	: 1.0

CHARACTERISTICS OF ASPHALTENES DERIVED FROM MEXICAN CRUDE OILS

Characteristics of asphaltenes in the Maya and Isthmus crudes are reported in Tables 2-4.

From Table 2 we notice a larger amount of soluble material in the Maya-asphaltenes than in Isthmus-asphaltenes when n-heptane is used. This can be due to the larger amount of aromatic compounds in the Maya-asphaltenes. When methanol is used as solvent we notice that in Maya-asphaltenes 7.8 wt% is soluble and in the Isthmus-asphaltenes only 0.01 wt% is soluble, this indicates that the content of polar compounds is higher in the Maya-crude asphaltenes. For carbon tetrachloride and benzene similar values of solubilities are found. This is because of the nature of both solvents and asphaltenes.

Since benzene is thought to have the capacity of dissolving all organic and organometallic compounds which comprise a crude oil any value of insoluble material would correspond to inorganic compounds. From a qualitative chemical analysis by X-ray fluorescence, it was found that the inorganic elements identified are practically the same for both crude-oil-asphaltenes, with a variation in the relative amount. Table 3 shows the main and trace elements contained in the n-pentane asphaltenes for both crude oils.

From the quantitative chemical analysis (obtained by atomic absorption spectroscopy) it was found that the highest concentrations of metals are Cu, Fe, Ni and V as shown in Table 4. By analyzing Table 4 we also notice that the ratio H/C is practically the same for both asphaltenes, and if we take a look back at Table 2 we notice Maya-asphaltenes have an average molecular weight nearly twice that of Isthmus-asphaltenes. From this we conclude the main difference between these two types of asphaltenes is their heteroelemental contents.

From the study of the micro (NMR) and macro (X-ray diffraction) structures the molecular structure for both Maya-asphaltenes and Isthmus-asphaltenes were proposed [10] as depicted in Figure 1a and 1b.

An important aspect which characterizes both Maya and Isthmus crudes is their percentage of asphaltene contents (16.6 wt% in Maya and 2.2 wt% in Isthmus). If we consider the fact that Maya-asphaltenes have higher molecular weight and different content of metals, we could conclude this is the reason why these two crudes have differences in their specific gravities and viscosities. Thus, molecular structure, sulfur, and metals contents have a definite influence on the physical properties of a crude oil. From these experiments it can also be concluded that asphaltenes encountered in Mexican crude oils are similar (in elemental analysis) to those asphaltenes derived from other parts of the world.

ANALYSIS OF THE HEAVY ORGANIC DEPOSITION PROBLEM IN MEXICO

Heavy organic deposition for Mexican crude was first investigated [15] by Glazebrook, Higgins and Pannell in 1915 when analyzing the trends of viscosity increase in heavy crude oils stored undisturbed. They postulated a molecular association which resulted in the formation of new molecules which is in agreement with the recently proposed model of the growth of asphaltene aggregates [16].

Glazebrook, *et al.* rightly concluded that the formation of these new molecules accounted for the increase in viscosity due to storage. They also observed that the initial viscosity could partially be restored by violent agitation, and that it could be entirely restored by heat treatment. From these observations and from other experimental work they also rightly concluded that the phenomenon must be colloidal and thixotropical. Although the asphaltene word is never used in their report, it is obvious, according to the present state of knowledge on asphaltenes [15,16], that they in fact observed asphaltene flocculation in the storage vessels. In 1985 Del Guzman, *et al.* [17] published a paper regarding the thermogravimetric analysis of asphaltenes derived from a heavy Mexican crude oil which has led to the improvement of the already existing "DEMEX" deasphalting process. After this report, several other investigations [5,6,10] dealing with the heavy organic deposition problem in Mexico were published.

Heavy organic deposits have been found in wells of the Tecoaminoacan and Jujo fields and storage vessels of the Campeche marine Platform (all in Mexico) where several streams of crude oils from different wells are mixed together awaiting to be processed. Heavy organic deposition has also been observed in pipelines, in the gas-oil separators, and compression systems in the Campeche marine platform. The economic implications of this problem have been enormous since in many instances production has to be stopped to replace damaged equipment because deposits have grown enough to completely plug them.

The analysis of heavy organic deposition problem in Mexico will be split in two parts. The first is dealt with the case of the Campeche marine platform, and the second with the oilfields Tecominoacan and Jujo case. Remedial solutions are outlined for each case, and additional experimental and modeling work is suggested for a better comprehension of the problem.

HEAVY ORGANIC DEPOSITION IN THE CAMPECHE MARINE PLATFORM

According to Chavez *et al.* [5] in some of the facilities of this platform, there had been diverse problems due to deposition of heavy organic material. These deposits were detected in the handling equipment of the crudes produced. One example was the deposit found in the separator of the first stage of the Abkatun-1 production platform. Initially, the deposits were tried to be removed utilizing steam, diesel oil and heavy aromatics without satisfactory results. In 1982 it was decided to replace the separator. After an analysis of the possible origin of these undesirable deposits, it was concluded that blending of a crude oil produced in a well recently stimulated with hydrochloric acid to the stream was the cause of the problem. This was concluded because a laboratory analysis which revealed the crude oils produced in this marine zone generated large amounts of asphaltic sludges upon contact with hydrochloric acid. A different well-stimulation technique was developed not to provoke the formation of sludge, but the problem persisted and organic deposits were again detected in the separation equipment. This urged the need for a detailed analysis of the organic deposits and samples of the crude oils produced in the area. A chemical analysis performed on samples of the heavy organic material encountered in the separation equipment revealed they were comprised mainly of asphaltenes, neutral resins, asphaltogenic acids and carbenes (asphaltogenic acids and carbenes were present in small proportions). The deposits were found not having melting point, nevertheless they decomposed at high temperatures (300-400°C). This analysis suggested that somehow the blending of different crude oils resulted in asphaltene flocculation and deposition. Then each of the crude oil streams arriving at the Campeche marine platform were submitted to "electrodeposition", "deposition due to temperature drop", and "settling by centrifuge" tests.

The "electrodeposition" tests performed by Chavez, *et al.* [5]

cannot be conclusive because the experiments were carried out at only one low potential difference (230 Volts) between electrodes while asphaltene deposition could occur vigorously at much higher potential differences [18].

The "deposition due to temperature drop" carried by Chavez, *et al.* [5] on crude oils and blends to determine their tendency to form paraffinic deposits were at two different conditions: Crude temperature in the cell of 35 °C and cooling "finger" temperature of -10°C. Results from these tests revealed that all the crude oil samples deposited less than 0.2 wt% of paraffin due to temperature drop. Even this small percentage could cause serious problems if the operating temperature is below the freezing point of the paraffins.

The "settling-by-centrifuge" tests by Chavez, *et al.* [5] consisted of centrifuging the samples at high and moderate velocities to determine qualitatively the tendency of crude oil streams to form deposits when flowing through the production system. These tests were carried out at centrifuge velocities of 1200 & 2400 RPM, test temperatures of 0, 10, 20, 30, 40, 50 °C, and test durations of 10 & 30 minutes. We have plotted the results obtained from these experiments on Figures 2-5 for further analysis.

From Figures 2-5 we notice, as a general rule, a maximum in the amount of sediments in the temperature range of 20-30°C followed by its decrease with increasing temperature. According to Figures 2 & 3, it is also observed that when Abkatun-93 and Pol-73 crudes were submitted separately to the test the amount of deposits reached the lowest value at 50 °C, where the vol% of sediments is less than 0.3% at all test conditions. Although sizable amounts of sediments were observed in these experiments, the deposits cannot be thought to be comprised of asphaltenes, considering the fact that in order to separate asphaltenes from a live crude oil one needs to use ultracentrifuge with angular velocities in the range of 30,000-80,000 rpm and for a duration of about 9 days [19]. Therefore, we conclude the sediments observed are primarily due to paraffin/wax precipitation. Table 5 shows the characterization of the crude oils, and mixtures under analysis. From this table one can notice a large amount of paraffin (4.6 wt%) in Pol-73 crude with a melting point of 44°C. Although no paraffin/wax content is reported for Abkatun-93 crude it is obvious that its paraffin/wax content is higher because of the fact that a 50/50 vol% mixture of these two crude oils has a paraffin/wax content of 5.11 wt% (melting point 46°C). These conclusions also explain why at 50°C negligible amount of sediments are noticed; these sediments could be attributed to inorganic material from the reservoir, provided that at this temperature the melting point of the paraffin/wax has been overpassed and it exists in oil in true solution. From figures 2 and 3 one can notice at 40 °C the amount of sediments is sizeable. This is attributed to the fact that the melting point of the paraffin has been underpassed. As temperature drops, larger amounts of sediments are detected reaching to a maximum at 20-30 °C. Below this temperature we notice a decrease in the amount of sediments. A possible explanation for this may be the fact that paraffin/wax at temperatures close to the freezing point are soft [20]. Therefore, coalescence of particles is likely to occur resulting in an increase of the volume fraction of the paraffin deposit. As temperature continues to drop the probability of paraffin-particle coalescence becomes less because they harden more. Therefore volume fraction of the particles decreases as well. However, for Pol-73 crude we observe large amounts of sediments even at low temperatures at 2400 rpm for which no satisfactory answer could be arrived at. For the Chuc crude no deposition was observed at all test conditions which indicates it contains very little or no paraffin/wax.

Figures 4, which is for a 50/50 mixture of Abkatun-93 and Pol-73 crudes has a maximum of sedimentation at 20°C at all test conditions. It also presents an appreciable percentage of deposition at 50°C. The amounts of sediments here are higher than those of pure crudes, especially for duration times of 30 minutes for all the temperature range. An interesting thing noticed is that at 50°C the sediment from this mixture ranges from 1 to 1.2 vol% , whereas the pure crudes showed less than 0.3 vol% sediments at this temperature. This indicates that flocculation and precipitation of asphaltenes has occurred upon mixing of these two crudes resulting in a larger amount of deposits even at high temperature of 50 °C. In fact flocculated asphaltenes would have large cluster diameters which would cause its sedimentation at low angular velocities [18].

In Figure 5 the ratio Light (Chuc)/heavy (Abkatun-93) crude has been increased from 1 (50/50 vol% mixture in Figure 4) to nearly 5 (63,20,17 vol% mixture in Figure 5) and the amount of light fractions contained in the light oils has been increased as well. According to this figure large amounts of deposition occurs at lower temperatures which can be attributed to asphaltene flocculation. Also the lowest amount of sediments is observed at 50 °C. The small amount of sediments observed at 50 °C can be explained by the fact that at this temperature the paraffin/wax contents of the crude oil is being used up for asphaltene-particles peptization [22]. This observations suggest that the mixing of large volumes of light crude oils with heavier ones provokes the flocculation and precipitation of asphaltenes.

Results obtained in these experiments indicate that mixing of a light crude oil with an intermediate one will lead to flocculation and/or precipitation of asphaltenes. For example the Abkatun-93 crude (API gravity=26.38, specific gravity= 0.8933) presents sedimentation of only 0.1 vol% at 50°C and a velocity of 1200 RPM in 30 minutes. At the same conditions the Pol-73 crude (API gravity=31.65 , specific gravity= 0.8644) has a sedimentation of only 0.05 vol%. However, when a mixture 50/50 vol% of these two crude oils was subjected to the same test, the percentage of sedimentation increased to 1.0 vol%. This suggests that the light fractions contained in the Pol-73 crude are sufficient to break the intermolecular balance in which the asphaltene particles remained dissolved (or suspended) in the Abkatun-93 crude as it is reported in the literature [38]: "Low molecular weight hydrocarbons with surface tensions below 24 dynes/cm at 25°C will cause precipitation of asphaltenes." A similar situation occurs when mixing Pol-73, Chuc, and Abkatun-93. When these crudes were tested separately they showed only traces of sediments under all test conditions. However, for the mixture (63% Pol-73; 23% Chuc; and 17% Abkatun-93) the percentage of sedimentation was 0.4 of the sample (for a temperature of 50°C and a centrifuge velocity of 1200 rpm). As an example, for every 100,000 barrels of crude processed per day with 0.4 vol% sedimentation 64 m^3/day of organic deposits would be observed which is large enough to cause serious problems in the facilities.

From the above analysis, one can conclude that temperature drop could be an important factor in the deposition problem especially if the operating temperature is below the freezing point (~50°C) of the paraffin fraction of the crude. The experiments analysed here indicate that the mixing of light and heavy crudes could lead to a large amount of sediments resulting from asphaltene flocculation. This seems to be the main factor one has to focus on when trying to find a solution to the asphaltene deposition problem in the Campeche marine platform. In order to prevent the asphaltene deposition in mixing of large amounts of light crude oils with heavier ones it is necessary to study the phenomena from the fundamental principles in order to develop predicting techniques [31-36]. It is also necessary to study and predict the optimum conditions at which light and heavy crudes can be mixed together without getting to the onset of asphaltene flocculation. Being able to predict the conditions at the onset of deposition and the optimum mixing ratios would alleviate the problem greatly. This will also help to develop better inhibitors and/or peptizing agents.

ASPHALTENE DEPOSITION IN WELLS OF THE TECOAMINOACAN AND JUJO FIELDS

The Tecominoacan and Jujo oilfields are formed by two lithological zones, the first is the lower cretaceous sandstone (calcareous) and the second is the lower cretaceous and upper jurassic sandstones. Their reservoir is comprised of structural traps, primarily anticlines represented by deformation layers and faults in the structure located at a depth of 6500 m with a pay zone varying from 60 to 200 m. The initial reservoir pressure was 702 kg/cm^2 and the bubble point of crude varies from 265 to 380 kg/cm^2. The initial GOR varied from 102 to 225 depending on the geographic location of the well within the fields. The crude produced in these fields is considered to be undersaturated with an average API gravity of 37.8. Its average sulfur content is usually less than 1 wt%, and its n-pentane-asphaltene content varies from 1 to 5 wt%. The production completion tubing size is 3.5 inches in diameter. There is another tubing of 1.25 inches in diameter utilized for circulating chemicals inside the well (i.e. inhibitors for asphaltene deposition and/or chemicals for cleaning purposes) [6,8].

Recently [8] a severe reduction in light-oil production from the Tecominoacan and Jujo oilfields in Chiapas-Tabasco area was experienced which was found to be due to heavy organic matter depositing onto the walls of the production tubing. This led to a reduction in the flow area of the well and in some cases it resulted in complete plugging of the production tubing. A well workover had to be performed to re-initiate production operations, the economic implication of which were severe. It was suggested that chemical and/or mechanical removal of the organic deposits was the fastest way to remedy the problem [8]. A blended solvent, named "IMP-System", capable of dissolving the major fraction of organic deposits of the Tecominoacan and Jujo oilfields was made by trial and error using a laboratory-scale extraction unit simulating the well conditions [8]. Physicochemical analysis of deposit samples, (Table 6), in the well tubing revealed that they were mainly asphaltic material comprised of asphaltenes, neutral resins, paraffins, asphaltogenic acids and insoluble material from the formation. It was also found that the crudes produced in this zone, (Table 6), were of the paraffinic type, with an asphaltene content varying from 1 to 5 wt%.

According to Table 6 in which characterization data of crudes and deposits from Tecoaminoacan Field are reported we notice that organic deposition has occurred during the production of a light crude with a relatively small asphaltene content. The difference in the metal contents of crudes and deposits reported in Table 6 indicates that while asphaltic compounds precipitate they carry with them the metal content of the crude.

Production of the Maya crude in Mexico with an asphaltene content of 16-18 wt%, and a large content of neutral resins (more than 23 wt%) does not present any asphaltene deposition problem [14] Similarly, in Venezuela, production of Boscan crude with an asphaltene content of 17.2 wt% and a resin concentration of 29.4 wt% does not present any deposition problem during production [2]. It has been found [23] that asphaltene content of a crude may be less important than the resin concentration in the flocculation process. In other words, we may find a crude with a high content of asphaltene and no deposition problem if the amount of resins (peptizing agents) is large enough to keep the asphaltene particles suspended in the solution. Considering that resin concentrations in the crudes of Table 6 are relatively high (8-9 wt%) compared to asphaltenes concentration (1-1.5 wt%) makes one deduce that asphaltene deposition should not have occurred. Nevertheless, according to Table 6 asphaltene deposition is observed causing severe problems.

An explanation of this peculiarity can be made by comparison of the resin/asphaltene ratio in the T-127 crude (ratio = 5.87), and the (ratio = 0.24) of the deposit sample collected from the same crude in Table 6. This suggests that in the deposition process asphaltene particles are probably depeptized to a certain extent but not completely. A possible explanation for this could be that the streaming potential generated by the flow of charged asphaltenes is large enough to break the stability of the micelles. This would then result in desorption of resins from the asphaltene particle surface [24] leaving empty sites. If two asphaltene particles collide with one another on their empty sites aggregation is imminent, a process which is irreversible [24] and particle aggregation itself could lead to deposition.

The streaming potential generated during production of the crude oil under study is estimated following the model proposed by Leontaritis and Mansoori [18] and with the well data of Silva, et al. [6] with the following result:

Production rate (m^3/day)	Uavg (m/s)	Potential E (Volts)
200	0.51	13.1
443 (field data)	1.132	52.7864
600	1.532	88.6889
800	2.044	146.883
1000	2.555	216.847

According to this table streaming potential is rather high which would enhance the asphaltene deposition and increases with increasing production rate. It should be pointed out that the "electrodeposition" tests performed by Garcia [6] on these crudes did not indicate appreciable amount of deposition because the experiments were carried out at only one low potential difference (230 Volts) between electrodes while the streaming potentials estimated in the above table are three orders of magnitude higher than this.

Silva and Garcia [25] also examined the role of acids and inhibitors normally used in reservoir stimulation processes on asphaltene deposition and concluded that these could not be considered as effective factors on this matter.

ANALYSIS OF FIELD DATA

From field experiences [1-7], we know that in primary recovery the most important factors that greatly enhance the deposition problem are:

- Reservoir acid stimulation practices, since this could generate asphaltic sludges which may result in asphaltene particles deposition onto the walls of the well tubing [26].
- Streaming potential generated when charged asphaltene particles flow through the well tubing. This potential is thought to be responsible for asphaltene deposition, since it neutralizes the asphaltene-particle charge [18].
- Changes in temperature and pressure. It is well known that as crude oil flows through the well tubing, pressure drops gradually. When the bubble pressure of the crude oil is reached, the light fractions of the crude oil are released. This is thought to prevent the asphaltene deposition, since the concentration of the light hydrocarbons disolved in the crude decreases gradually as it moves through the two-phase envelope region [1].

We suggest more experimentation and modeling of the phenomena using molecular thermodynamics of continuous mixtures, polydisperse polymer solution techniques, colloidal suspension principles, and FRACTAL aggregation theories applied to the oil-asphaltene-resin asymmetric mixture [15, 16] to find the influence of these various parameters on the amount of asphaltene deposition. The production rate, bubble point depth (depth at which the bubble point is encountered) data, and organic deposition depth data of thirteen different wells in the Tecoaminoacan and Jujo fields are reported by Garcia et al. [6]. According to this data for majority of the wells deposition occurs after the bubble point depth is reached. There exists no fundamental theory at the present time by which one would be able to correlate the organic deposition depth to the bubble point, bubble point depth, or other production data of a certain well. However, we have taken the liberty of plotting the bubble point depth data versus the organic-deposition depth data, Figure 6, for the thirteen wells in the Tecoaminoacan and Jujo fields as reported by Garcia et al., [6].

According to this figure the best fit to the data is a straight line expressed by the following equation

$$\mathrm{ODD\,(m)} = \{-217.21 + 0.92502\,\mathrm{BPD\,(m)}\} \pm 445$$

where ODD stands for the organic-deposits depth and BPD is the bubble-point depth. According to this equation the depositions in the wells of this oil field occur after the bubble point depth is reached. Presently we are studying the scientific basis for this graph to see whether we could use it as a tool for predicting the organic deposition depths for new wells in this field. A predictive technique for the organic deposition depth can be quite useful in prevention and/or removal of organic deposits in early stages of its formation.

MODELING OF THE EFFECT OF STREAMING POTENTIAL ON THE ONSET OF ASPHALTENE FLOCCULATION

The following expression can be used for estimating the generated streaming potential due to flow of asphaltene particles[29].

$$E = 2.64\times10^{-2}\left[R_p(C_R)\right]^3 \frac{k\,\rho_u N_0}{\langle M_A(C_R)\rangle}\left(\frac{d^{0.75}L\rho^{0.75}}{\mu^{0.25}k}\right)u_{avg}^{1.75} \qquad (1)$$

where (μ) is viscosity of oil; (r) is density of oil; (A) is the cross sectional area of flow channel; (N_0) is number of asphaltene particles; (u_{avg}) is average velocity of oil; (L) is length of flow channel; (k) is overall conductivity of oil and pipe (or well); (d) is diameter of pipe; (k) is a constant; (r_u) is uniform charge density; $R_p(C_R)$ is radius of asphaltene particle at a given resin concentration (C_R); and <MA(C_R)> is average molecular weight of asphaltene particles at a given resin concentration (C_R).

For calculation of density, average molecular weight of asphaltene, and growing size of asphaltene, the ASPHRAC database and computer package can be applied to the flowing oil mixture. By calculating the density, viscosity, average molecular weight of asphaltene particles, and growing size of asphaltene particles, we are able to examine the effect of streaming potential on the onset of asphaltene flocculation for a reservoir fluid at different conditions of temperature, pressure and compositions. The effect of the generated streaming potential on the onset of asphaltene flocculation can be examined for different values of U_{avg}, d, and k. By defining Q;

$$Q = U_{avg}^{1.75} d^{0.75}/k \qquad (2)$$

diagrams like Figures 7-9 could be plotted [37], in order to study the variation of Q in different deposition regions of asphaltene flocculation for different compositions, temperatures and pressures. Figures 7-9 present that the asphaltene flocculation is possible in the regions above the plotted line at specified concentration of miscible injectants (MI). Pressure-composition (P-x) points at the onset of asphaltene flocculation for mixtures of crude oil and miscible injectants are also shown in Figures 7 through 9. The predicted onset mole fraction (or MI/oil weight ratio) of miscible injectant fluid is more sensitive with decreasing temperature. However, the variation of U_{avg}, d, and k is very important for the estimation of the magnitude of the generated streaming potential due to flow of asphaltene particles.

For the oil-miscible injectant system of Figures 7-9, the following observations can be summarized:

(i) Below the bubble point pressure of mixtures, the magnitude of generated streaming potential decreases with increasing temperature. Above the bubble point pressure of mixtures of crude oil and miscible injectant, the magnitude of generated streaming potential increases with increasing temperature.

(ii) The magnitude of generated streaming potential decreases as the composition of methane in miscible injectant fluid increases.

(iii) Below the bubble point pressure of mixtures of crude oil and miscible injectant, the magnitude of generated streaming potential increases with increasing composition of miscible injectant of the mixture. Above the bubble point pressure of mixtures of crude oil and miscible injectant, the magnitude of generated streaming potential decreases with increasing composition of miscible injectant of the mixture.

Similar analysis can be performed for Mexican crude after appropriate data is collected regarding the conduits (wells and pipelines) under consideration.

CONCLUSIONS AND RECOMMENDATIONS

In this report the phenomena of organic deposition and plugging of wells experienced in Mexico are analysed based on our present state of knowledge. According to this analysis there exist a wide range of problems to be addressed before one can make a definite recommendation about the preventive steps that must be taken in order to avoid deposition and plugging. In order to perform a systematic analysis of the problem and come up with a long lasting solution to it the following stages of work are necessary to be completed:

(i) Collection and compilation of data: This involves collection and analysis of the available data in the literature about a particular crude oil, their contents, their behavior, and other fluids present in the reservoir. It is also necessary to compile and analyze all the available field data for production, transportation, and processing of that crude so long as the organic deposition is concerned.

(ii) Laboratory characterization of crude: In order to understand the conditions under which heavy organics will deposit from a crude it is necessary to perform a thorough characterization of that crude coming out of different oil reservoirs. This will include gas chromatography (GC), liquid chromatography (HPLC), gel permeation chromatography (GPC), onset of deposition titration, molecular weight measurements, C_{7+}- fraction characterization, and other analytical measurements.

(iii) Analysis of the collected and measured data: The data compiled in part (i) above and the data produced in the laboratory in part (ii) above must be compared and analyzed from the point of view of consistency and completeness. This will establish the possibility of the existence of gaps in the data compiled and it will suggest possible new measurements of the data.

(iv) Simulation and modelling of heavy organics deposition: Results of the above three parts will give us the necessary tools and information for simulation modelling of organic deposition from a crude oil at different cases. This will include simulation and modeling required for well and reservoir stimulation, gas injection and re-injection into the reservoir, pipeline transport of crude and its blending with other crudes or solvents, processing of crude oil in the refinery and upgrading of the heavy ends, and characterization of heavy organics and solid deposits produced in the refinery.

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Table 1. Elemental Composition of Asphaltene Fractions Precipitated by Addition of N-Pentane as the Solvent

SOURCE	COMPOSITION (wt%)					ATOMIC RATIOS			
	C	H	N	O	S	H/C	N/C	O/C	S/C
Canada	79.5	8.0	1.2	3.8	7.5	1.21	.013	.036	.035
Iran	83.8	7.5	1.4	2.3	5.0	1.07	.014	.021	.022
Iraq	81.7	7.9	0.8	1.1	8.5	1.16	.008	.010	.039
Kuwait	82.4	7.9	0.9	1.4	7.4	1.14	.009	.014	.034
Mexico*	83.0	7.7	1.5	2.0	5.2	1.13	.015	.018	.023

This table is reproduced from Speight (1981). * Data from Altamirano, et al. (1986).

Table 2. Physical Properties of Asphaltenes in Maya and Isthmus Crudes

Property		Maya Crude	Isthmus Crude
Brookfield	200 °C	15,800 cps	na
Viscosity	250	5,400	na
	300	1,600	na
	350	600	na
Ignition Point °C		310	na
Melting Point °C		153	na
Solubility in N-Heptane wt%		34.4	21.0
Solubility in Benzene Wt%		100	100
Solubility in CCl_4 Wt%		97.3	99.53
Solubility in Methanol Wt%		7.8	0.01
Average Molecular Weight		4,271.5	2,211.5
Specific Gravity		0.1005	0.0273
N-Pentane Asphaltenes, Wt%		16.6	2.2

na ~ not available; The specific gravities reported here do not seem to agree with the widely accepted value of about 1.2 for asphaltene.

TABLE 3. Elements Identified in Asphaltene by X-Ray Fluorescence

	MAYA	ISTHMUS
Main Elements (In Decreasing Concentrations)	Sulfur Vanadium Iron Nickel Chlorine Copper	Sulfur Iron Chlorine Vanadium Nickel Copper
Trace Elements	Calcium Manganesum Zinc Silica Phosphorous	Calcium Zinc Silica Phosphorous

TABLE 4. Quantitative Analysis of Elements Contained in Asphaltenes

		MAYA	ISTHMUS
Carbon	wt%	83.0	84.0
Hydrogen	"	7.7	7.8
Nitrogen	"	1.5	1.0
Sulfur	"	5.2	3.6
Oxygen	"	2.0	1.9
Copper	ppm	18.0	6.0
Iron	"	113.0	88.0
Nickel	"	343.0	95.0
Vanadium	"	2,518.0	994.0
Ratio			
H/C		1.113	1.114
O/C		0.018	0.016
S/C		0.023	0.016
N/C		0.015	0.010

TABLE 5. Characterization of Crude Oils Pol-73, Abkatun-93, Chuc, and their Mixtures [Chavez, et al., 1991]

	ABK.-93	CHUC	POL-73	MIXT.A*	MIXT. B**
Spec. Gravity 20/4 °C	0.8933	0.847	0.8694	0.8736	0.8644
API Gravity	26.38	35.1	31.65	29.94	31.6
Pour Point °C	-33	-33	-39	-33	na
Paraffin, wt%	na	na	4.62	5.11	na
Cloud Point, °C	45	na	44	46	na
n-C_7 asphaltenes, wt%	5.02	0.5	0.85	2.29	1.1

(*) Mixture A: 50 vol% of Pol-73 and 50 vol% of Abkatun-73; (**) Mixture B: 63 vol% of Pol-73, 20 vol% of Chuc, and 17 vol% of Abkatun-93; (na) ~ not available

TABLE 6. Characterization of Crudes and Deposits from Tecoaminoacan field [Garcia, 1989].

ELEMENTAL ANALYSIS	CRUDE AT-127	CRUDE AT-145	ORG. DEPOSITS	
			DT-127	DT-448
Carbon wt%	86.1	86.0	84.5	78.5
Hydrogen wt%	12.5	12.5	8.6	6.7
Nitrogen wt%	0.4	0.3	0.4	1.1
Iron ppm	< 1	< 1	267.0	< 1
Copper ppm	< 1	< 1	3.0	65.0
Nickel ppm	< 1	< 1	20.0	23.0
Vanadium ppm	1	1	171.0	250.0
Zinc ppm	< 1	< 1	6.0	41.0
Spec. gravity (20/4 C)	0.837	0.839	------	------
API Gravity	36.7	37.2		
Viscosity sus., @ 60 F	45.2	46.6		
@ 70 F	42.2	43.2		
@ 77 F	41.0	41.2		
Pour Point C	-30	-24		
Sulfur wt%	0.9	0.9	2.9	3.9
n-C_5 Asphaltenes	1.5	1.0	42.0	73.8
Solubles wt%	89.7	90.9	48.0	19.8
Saturated wt%	52.3	58.5	42.1	10.9
Aromatics wt%	37.4	32.4	5.1	8.9
Resins or Polars wt%	8.8	8.1	10.0	6.4

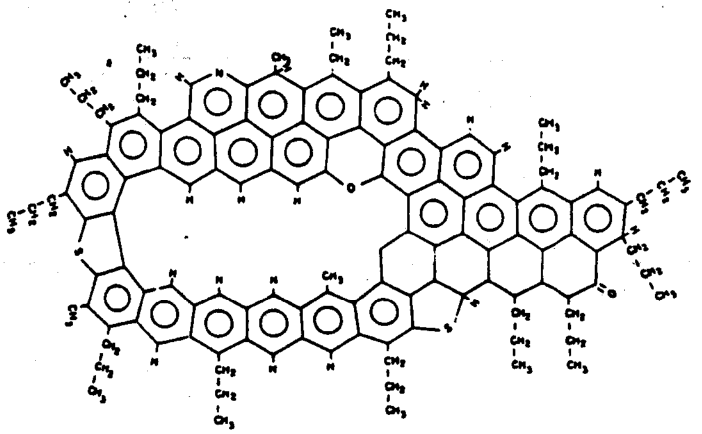


Figure 1b. Molecular structure for asphaltenes derived from Isthmus crude oil, proposed by Altamirano, 1986.

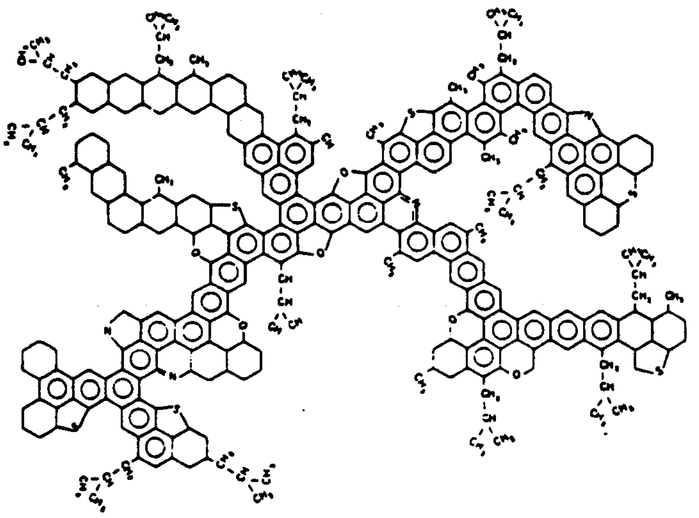


Figure 1a. Molecular structure for asphaltenes derived from Maya crude, proposed by Altamirano, 1986.

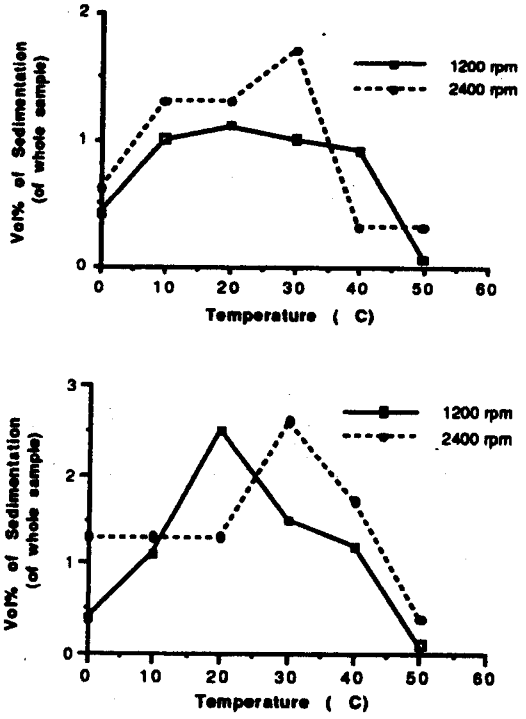
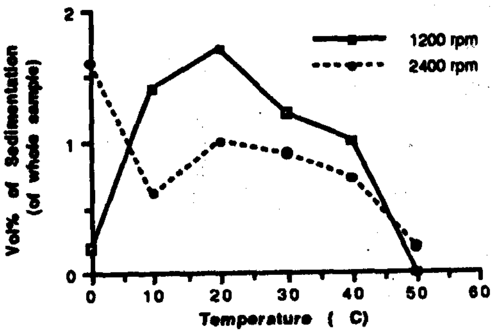


Figure 2. Volume percentage of sedimentation from Abkatun-93 crude versus temperature for centrifugal angular velocities of 1200 & 2400 rpm's and for durations of 10 and 30 min's [Data of Chavez, et al., 1991].



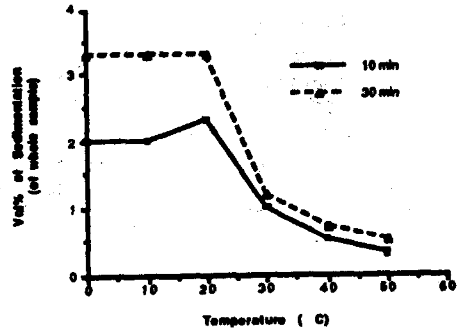


Figure 5. The same as in Figure 2 but for a 63/20/17 mixture (by volume) of Pol-73/Chuc/Abkatun-93, crudes at 1200 rpm.

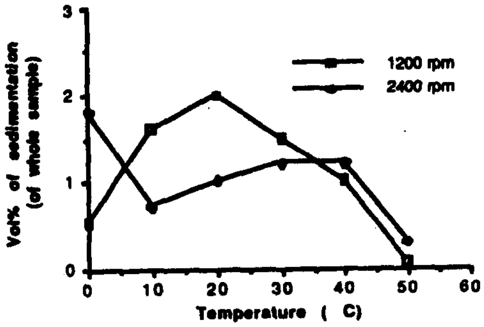


Figure 3. The same as in Figure 2 but for Pol-73 crude.

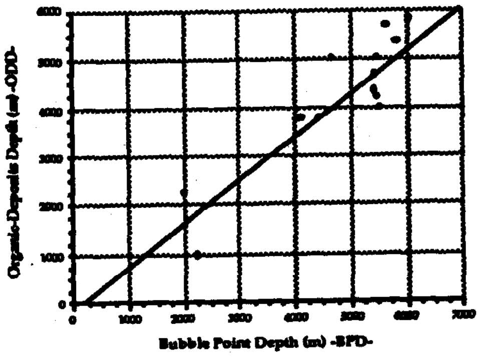
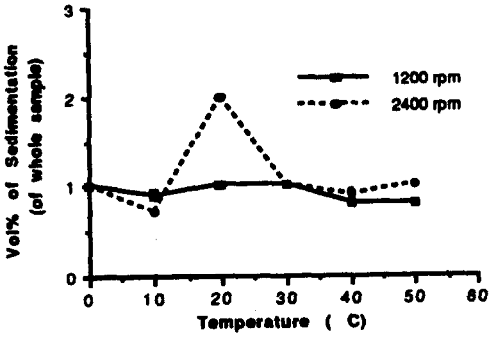


Figure 6. Linear relationship between Bubble point depth and Organic deposits depth from field data.



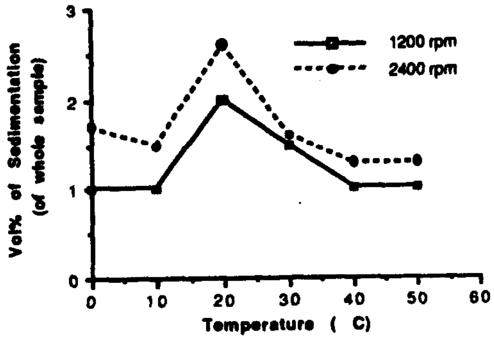


Figure 4. The same as in Figure 2 but for a 50/50 mixture (by volume) of Abkatun-93 and Pol-73 crudes.

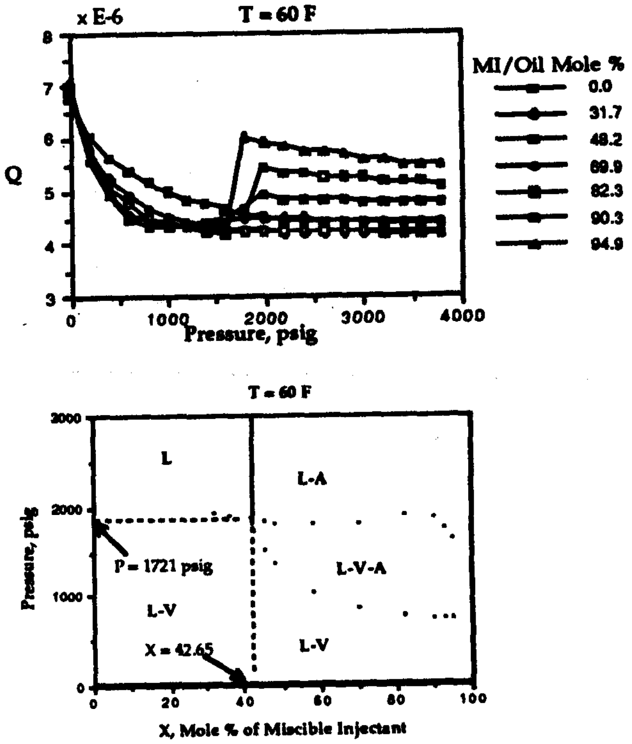


Figure 7. Effect of flow conditions, pressure, and concentration of a miscible injectant (MI) on the onset of deposition of asphaltene from a flowing crude oil in conduits at 60oF

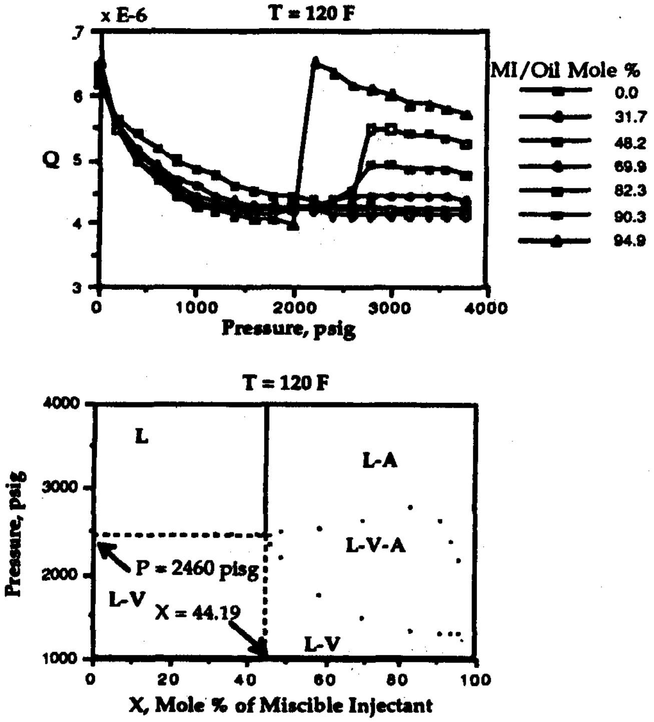


Figure 8. The same as Figure 7 except at 120°F

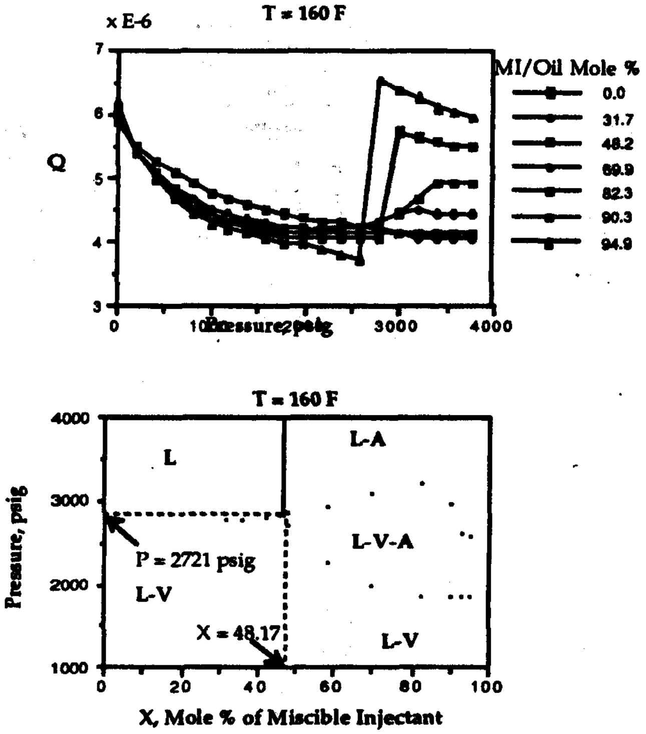


Figure 9. The same as Figure 7 except at 160°F.