

THE EXPERIENCE OF PETROBRAS WITH CHARACTERIZATION AND CLASSIFICATION OF DEPOSITED MATERIALS FOUND IN OIL PRODUCTION

Marco Antonio Gomes Teixeira, Fátima Regina Dutra Faria and Maria Luísa Aleixo Gonçalves
PETROBRAS Research & Development Center-Division of Chemistry
Av. Um, Quadra 7, Cidade Universitária, Rio de Janeiro, Brazil - CEP:21949-900
E-Mail: marco@cenpes.petrobras.com.br

Keywords: PARAFFIN WAX, ASPHALTENES, CHARACTERIZATION

ABSTRACT

Experimental characterization of some deposited materials collected in Brazilian oil fields and transportation pipelines are presented, to point out limitations of data generated by fractional solubilization, which is normally employed for classification of deposits into paraffin waxes or asphaltenes. Gas chromatography, which is a reference technique for paraffinic materials, has its data compared to molecular weight by VPO, being clearly characterized the difficulties of elution for heavy fractions. It is also shown that most characteristic compositional properties for asphaltenes, like elemental analyses and aromaticity, are not conclusive for the definition of deposits as asphaltenic materials.

So, it is proposed that chemical analysis of deposited materials should aim ready classification of deposited material, since all of the techniques have limitations and yield information that should be considered qualitative and for comparison purposes. And since classification should be a way to provide quick responses to field problems, another concept was sought.

A classification technique based on *thermogravimetry* has been proposed to improve the capacity of PETROBRAS to determine the nature of some deposits verified in production equipment. It is based on the fact that asphaltenes yield considerable amounts of coke by pyrolysis, while paraffinic material do not. The method has been validated with several reference samples, and it is being used successfully in various field situations in Brazil

INTRODUCTION

Concerning to deposition problems, analytical techniques employed for characterization yield data to provide information about chemical nature of deposited material, which are also used to feed mathematical simulators of deposition used by production engineers. These computer programs support operational decisions that try to minimize or avoid deposition phenomena. Of course, due to the economical magnitude of problems brought by deposition, much is expected of these simulators, and therefore much is charged of analytical data. However, usual analytical techniques have some limitations, and careful interpretation of results is necessary.

Of course, it is normally easy to tell inorganic and organic (main focus of interest of this work) materials apart. And operational culture may be frequently employed for a successful pre-classification of organic ones into the two main classes normally recognized, i. e., paraffinic or asphaltenic deposits. In these cases, simulators may need some temperature or pressure dependent measurements, being a minimum characterization required. Sometimes, however, it is not possible to affirm anything previously. Our work has been showing this is the case of deposits found in production columns. Past experience shows that asphaltene precipitation frequently happens in pressure disturbance zones, mainly in bubble point regions of oils in production columns, as observed for example by IZQUIERDO and RIVAS (1995). Differently, paraffin deposition may possibly be observed in almost all pipes and tanks used in petroleum industry. So column deposits are an application of particular interest for any work on characterization, because both classes are possibly found. When the nature of deposited material is an uncertainty, its definition is the first necessary input. It should be remarked that, for analytical purposes, an operational definition for paraffin waxes or asphaltenes is based on solubility. It is normally accepted that paraffin waxes are a fraction insoluble in ketones at low temperatures (according for example to Shell SMS 1769) and asphaltenes are a fraction insoluble in light n-alkanes and soluble in aromatic solvents (according for example to IP-143). This definition may be used for classification of deposited material, being normally employed a sequential solubilization with a light alkane (which would solve paraffinic components) and an aromatic (which would solve asphaltenic components), as performed by ABUL FAZAL et al. (1995).

If further characterization is required, analytical techniques employed for deposited material are normally gas chromatography and nuclear magnetic resonance. Since they are both well known by analytical chemists, there is no need for considerations about their fundamentals. Interpretation of results from these two techniques are normally supported by other information, like elemental analyses or infrared spectra. It is impossible, however, to achieve a complete characterization, *stricto sensu*, of all components of deposits because there is an uncountable number of heavy components from

petroleum, and chemical analysis can not resolve heavy components.

Careful investigation of results obtained, shown below, indicates that these data may be inadequate for non equivocal conclusions about the nature of deposits. So, a new approach has been proposed, based on the fact that asphaltenes have large aromatic nuclei (BESTOUGEFF e BYRAMJEE, 1994). Those nuclei yield coke when pyrolysed, and this may be detected by thermogravimetry. This approach has been employed successfully for several field cases in Brazil.

EXPERIMENTAL

Sequential solubilization experiments were performed in a Soxhlet apparatus, and solvents chosen were n-heptane and toluene. After extraction, solvents were evaporated and weighed. All the procedure was repeated to constant weight with each solvent. Number molecular weights were determined by vapor pressure osmometry (VPO; a Wescan model 233 apparatus was employed), in toluene solutions at 88°C, with benzyl as a calibration standard. GC chromatograms were obtained in an HP 5890-2, with the following analytical conditions: 0.53 mm i. d. methyl silicon column (5 m length), programation for inlet temperature from 60 to 430°C at 70°/min, for the oven -20 to 430°C at 10°/min, then 5 min at final temperature, flame ionization detector at 430°C. TG curves were obtained in a DuPont 951 thermal balance with TA Instruments 2100 control system: 10 mg of sample heated firstly at 10°C/min up to 700°C under a 60 mL/min nitrogen flow, then at 10°C/min up to 1000°C under a 60 mL/min air flow.

RESULTS AND DISCUSSION

Sequential solubilization

To determine and follow the nature of deposited material found in the column production of a Brazilian off-shore well throughout 3 months in 1996, sequential solubilization was firstly employed. Samples were obtained on different days. Some samples demanded a 72 h reflux to constant weight, showing that even if the result is very conclusive, that procedure could not be considered practical. However, abundant insoluble material in both solvents was obtained, what makes impossible a classification by this approach. The presence of inorganics was considered, but low ash yields after burning did not confirm this possibility. Table 1 shows these results, which stress the need of further work in some cases.

Some possibilities were sought for a conclusive characterization. However, since deposits are normally complex mixtures, average parameters obtained by NMR, like amount of aromatic carbons (the most relevant one), are frequently found in intermediate values, which do not assign a clear classification, and the same happens to the C/H ratio from ultimate analysis. Fractionated precipitation and liquid chromatography (LC) show in some cases poor resolution of fractions obtained, and for LC fractions (normally saturates, aromatics, resins and asphaltenes) there is also loss of polar compounds that stay strongly adsorbed onto the stationary phase.

Gas chromatography and vapour pressure osmometry

An alternative that is very useful for several characterizations in petroleum industry is gas chromatography. So, the possibility of determination of paraffinic material by this technique was considered. Since one can accept two classes of materials in deposits, low contents of paraffins would characterize asphaltene deposition.

Typically, a gas chromatogram of paraffinic material is similar to the picture presented in figure 1, for a paraffin wax obtained from a Brazilian oil by Shell SMS 1769/88. This oil was chosen for the study because it has deposition of paraffin wax proved by field experience. Clear separation is achieved for lighter linear alkanes, and peaks between them are attributed to other saturated hydrocarbons. In high temperature GC, this task is easily done up to 40 carbon atom alkanes, normally. After that, the number of carbon atoms after which no resolution is obtained (called in this work C^*) is a subjective parameter. If eluted material represented the whole sample, the distribution of linear alkanes and other components would be an important characteristic, since linear molecules have more ease to overlap their chains, propiciating deposition.

Table 2 shows main interpretation data for the chromatogram in figure 1, and, for comparison, for the GC analysis of a natural deposit. Naturally, one should expect that deposits would have longer components than laboratory precipitated paraffin wax, since this material was stable in oil before intervention, while the components of deposits were not. However, that is not what was found in the comparison, since the chromatogram of deposited material could be resolved up to 50 carbon atoms, while the other one could be up to 45, only, being also the amount of material up to C^* larger for the deposit. The non resolved fraction (from figure 1, one can consider after 60 carbon

atoms) was larger for the laboratorial wax. The only information that agreed with previous expectance was the ratio of linear alkanes to other components, which was slightly superior in natural deposit. The possibility of components of the oil that could be occluded in the natural deposit and would not be in the laboratorial one, because of washing by the ketone used as precipitant, was considered but not confirmed, since the first hydrocarbon present in both samples had the same carbon number, 16. These results are better explained in a comparison to molecular weight data by VPO. This technique, itself, yielded values of 554 and 506 for the number molecular weights of the laboratorial and natural waxes, respectively, leading to the same trend given by GC. However, from compositional distribution in the chromatogram, it is possible to obtain the molecular weight and thus a carbon number for a pseudo-alkane component that would represent the C_{60}^+ fraction ($\#C_{60}^+$). The equation for that is readily deduced:

$$M_n = 100 / \sum (\% / M_i) \quad (\text{Eq. 1})$$

where M_n stands for the average molecular weight of the whole deposit, and $\%$ and M_i for the weight fraction in the material and the molecular weight of each individual component, respectively. Using equation 1, one gets a value for $\#C_{60}^+$ of 76 for the laboratorial wax, while for the natural deposit even an infinite carbon numbered pseudo component would yield the value from VPO. After substitution of all $\%$'s and M_i 's from the chromatogram of this sample, the value of M_n by equation 1 has a limit of 498 as the $M_n C_{60}^+$ increases. One can deduce that non eluted material is much more representative for the natural deposit than it is for the laboratorial wax, and that evidences the limitation of GC for the analysis of field material. Qualitative analysis of eluted material does not help very much either, since it has been found that asphaltenes yield chromatograms similar to other petroleum fractions (AQUINO NETO et al., 1995).

Approach proposed - use of thermogravimetry

Based on the need of an approach that would not have all limitations detected by other techniques, we have conceived a quick experiment by thermogravimetry (TEIXEIRA and GONÇALVES, 1977). Basically the sample is heated under inert atmosphere, for distillation and pyrolysis of some constituents, then under oxidative atmosphere, which allows the burning of remaining material.

Behaviours of paraffins and asphaltenes submitted to those conditions were evaluated. Asphaltenes have as a remarkable characteristic relatively large alkyl side chains and aromatic nuclei (BESTOUGEFF e BYRAMJEE, 1994). We believe that branches may be thermally eliminated from the major structure, but aromatic nuclei will be thermally stable under inert atmosphere, maybe by the generation of coke. Paraffins should be either distilled or pyrolysed, so their TG would show different profiles in relation to asphaltenes, which would be enough since only classification of the predominant class of constituents of the sample is aimed. Inorganics would yield stable material at 1000°C under air, so they would be also evaluated.

TG would also have the advantage of analysis of the whole deposit without any pre-treatment, since water and excess occluded oil would be distilled before the temperatures of interest. It should be emphasized, however, that classification by the methodology studied necessarily presupposes that there are only the three possible classes cited above in deposited material, but that assumption is normally good for classification purposes.

Figure 2 shows a TG curve of a standard paraffin. It can be seen that before 700°C the distillation (or maybe pyrolysis) of the materials is already complete. In these TG curves, and in all the other ones in this work, mass loss is indicated by the monotonically decreasing curve, while the other curve is its first derivative. Figure 3 shows a TG curve of an asphaltene sample obtained by a standard method (IP-143), from which a typical profile of this class of material may be determined. There is effectively mass loss before air introduction, but the main remark, which will make possible the differentiation from paraffinic material, is mass loss after air introduction that is clearly seen. From these facts a classification scheme is proposed: paraffins are characterized by complete volatilization under inert atmosphere up to 700°C, asphaltenes by burning with air injection from 700°C, and inorganics by the burning residue at 1000°C.

The methodology has been employed for the classification of several real field deposits. Examples that prove consistency of the proposed approach are its applications to column deposits. Figures 4 and 5 show TG curves of two ones, from different wells from Brazilian fields, whose nature was found to be very distinct by the methodology proposed here.

CONCLUSIONS

Thermogravimetry may be used successfully to overcome a major problem in the study of

depositions, which is to reach a clear qualitative definition of the nature of deposited material. It does not yield properties of the deposits that are necessary inputs for simulation work, but it provides the ways to determine which phenomenon is to be modeled in each case.

REFERENCES

ABUL FAZAL, S.; ZARAPKAR, S. S.; JOSHI, G. C. (1995) "Studies on Sludge from Waxy Crude Oil Storage Tank.II.Solvent Fractionation", *Fuel Science and Technology Int'l.*, vol. 13(10), 1239-49

AQUINO NETO, F. R. et al. (1995) "High Temperature - High Resolution Gas Chromatography (HT-HRGC) of Paraffinic and Asphaltenic Crudes and Related Deposits", *Proceedings of the First International Symposium on Colloid Chemistry in Oil Production-ISCOP'95* (Rio de Janeiro), pp. 63-7

BESTOUGEFF, M. A. & BYRAMJEE, R. J. (1994) "Chemical Constitution of Asphaltenes" in YEN, T. F. & CHILINGARIAN, G. V. (Editors), *Asphaltenes and Asphalts, I. Developments in Petroleum Science*, 40, pp. 67-93

IP Standard Methods for Petroleum and its Products, The Institute of Petroleum, London (1965), Part I, Section 2, Standard 143, p. 596

IZQUIERDO, A. & RIVAS, O. (1995) "INTEVEP's Overall Approach to Asphaltenes Deposition Problem", *Proceedings of the First International Symposium on Colloid Chemistry in Oil Production-ISCOP'95*, pp. 155-8

SHELL. "Wax contains of petroleum and its products", SMS 1769/88 (1988), 7 p.

TEIXEIRA, M. A. G. & GONÇALVES, M. L. A. (1997) "Use of Thermogravimetry for Classification of Chemical Nature of Deposits of Petroleum Industry", *Petroleum Science & Technology International*, submitted

Table 1. Characterization of deposits of the same well (weight %)

Sample collected on	n-heptane solubles	toluene solubles	burning residue
January 11th	28.01	1.25	13.25
January 16th	2.85	6.31	11.65
February 9th	23.73	0.68	9.81
March 9th	24.39	1.16	5.62

Table 2. Comparison of a laboratorial paraffin wax of a Brazilian oil and a natural deposit

Sample	C*	%up to C*	%C ₆₀₊	%linear up to C* % other up to C*	#C ₆₀₊
Paraffin wax by Shell SMS 1769/88	45	55.53	27.53	1.83	76
Natural paraffinic deposit	50	69.01	11.90	1.93	∞

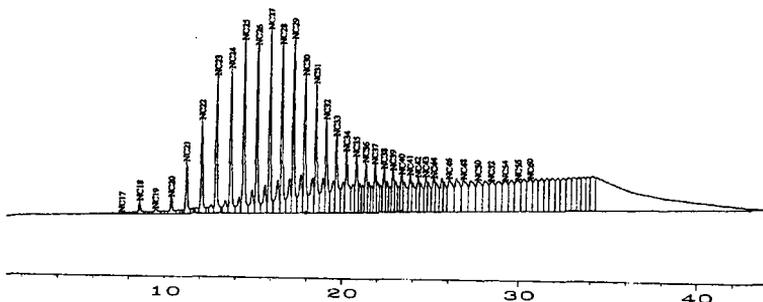


Figure 1. Gas chromatogram of a sample of laboratorial paraffin wax of a Brazilian oil

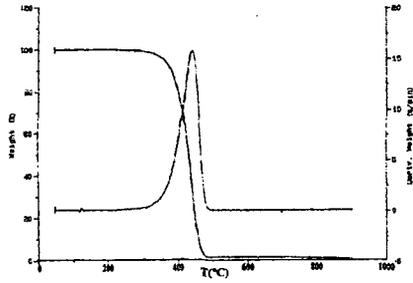


Figure 2. TG curve of a standard paraffin of average molecular weight 1000

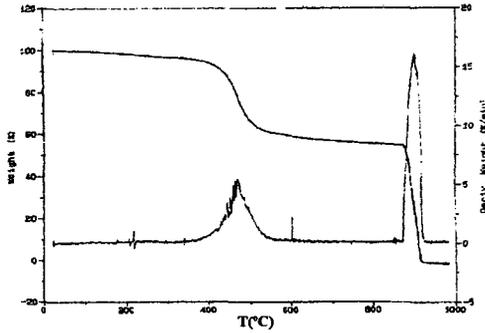


Figure 3. TG curve of asphaltene from light arabian oil

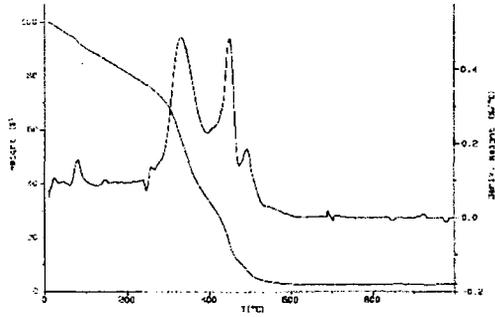


Figure 4. TG curve of a paraffinic production column deposit

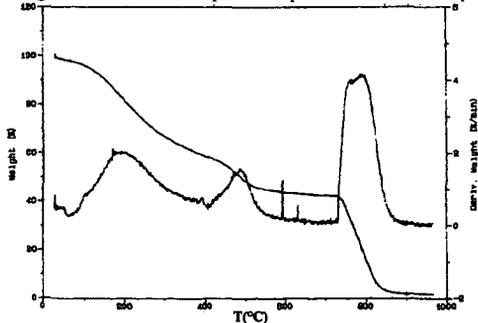


Figure 5. TG curve of an asphaltenic production column deposit

PARAFFIN AND ASPHALTENE DEPOSITION RESULTING FROM COMMINGLING OF OILS DURING PIPELINE TRANSPORTATION AND STORAGE.

N. Thanh, M. Hsieh, J. Allen, and R. P. Philp, School of Geology and Geophysics,
University of Oklahoma, Norman, OK. 73019.

ABSTRACT

Commingling of oils from different reservoirs and different sources is a common process during production and transportation. In certain situations, this may lead to the precipitation of solid residues and cause serious production problems. The question arises as to the nature of the solid residues produced in this manner. Are they waxes or asphaltenes or mixtures? In this paper we will describe a recent study of such a problem. Using recently developed processes in our laboratory the characterization of such a residue in a storage tank in terms of its asphaltene and paraffin content will be described. In addition high temperature gas chromatography has been used to document high concentrations of hydrocarbons up to C_{30} in the wax despite their relatively low concentration of these components in the original sample. Laboratory mixing experiments have also been undertaken in an effort to simulate the production of such residues in the storage tanks to determine whether or not such problems could have been avoided by adjusting the relative proportions of the two oils prior to mixing in the pipeline.

INTRODUCTION

In many cases crude oils produced from different wells in the same field have to be commingled during production or in pipelines to storage facilities prior to shipping. In certain situations oils, which when transported independently may not produce any problems, may have significant problems resulting from paraffin or asphaltene deposition when commingled with other oils with slightly different properties but produced from the same field. In a recent study we had the opportunity to examine such a situation from a geochemical perspective. In this study, two oils being produced from a certain field had to be commingled and transported via pipeline to a storage tank prior to shipping. Neither of these oils showed any signs of paraffin or asphaltene deposition when transported individually. However when commingled, it was observed that within a relatively short period of time, the storage tank containing the commingled oils was filled to about 30% of its capacity with a black residue. Characterization of this residue demonstrated that it consisted of predominantly paraffins with a small amount of asphaltenes. In this paper it is proposed to discuss the characteristics of the original oils, particularly in terms of their wax contents as determined by high temperature gas chromatography, as well as the characteristics of the black residue and the liquid oil in the storage tank. It is also anticipated that by the time of the meeting additional laboratory data will be available to show the nature of the residues formed as a result of mixing various proportions of these two oils in the laboratory and permitting them to stand for different periods of time.

DISCUSSION

In the initial part of this study oils from the two sources were characterized by high temperature gas chromatography. The resulting chromatograms obtained in this way suggested that the oils contained some high molecular weight hydrocarbons above C_{35} , although the concentrations of these compounds were relatively low. In order to get a better indication of the distribution of hydrocarbons in these samples a wax concentrate was isolated from each sample and using a method developed in our laboratory the asphaltenes were quantitatively separated from the wax components. HTGC analysis of the asphaltene fraction clearly showed that there were no hydrocarbons in the wax fraction. HTGC analysis of the wax concentrate gave a clearer picture of the HMWHC distribution but clearly the relative concentrations of these compounds was still relatively low in the individual oils.

As mentioned above mixing of the two oils in question did not produce any paraffin deposition problems in the pipeline transporting the mixture to the storage tanks. IN Fig. 1 the top chromatogram shows the oil mixture from the pipeline and the relatively low concentration of HMWHCs present in this mixture. However in the storage tanks a considerable quantity of a heavy black residue accumulated over a relatively short period

of time. This residue was treated in the same way as the oils, with the separation of a wax concentrate and removal of the small quantity of asphaltenes in the sample. The wax content in this sample was around 34%, asphaltenes 0.5% and the remaining part of the sample was low molecular weight hydrocarbons. Fig. 1c shows the HTGC chromatogram for the residue and it can be seen very clearly that there has been significant concentration of the hydrocarbons in the region above C_{40} , and in view of the relatively low concentrations of these compounds in the original oils this clearly represents the accumulation from several filling episodes of the tank. Quantitation of individual components in this wax concentrate and comparison with their concentrations in the original sample should permit one to determine the volumes of oils necessary to produce this amount of residue.

Fig. 1b shows the HTGC chromatograms of the oil produced from the storage tank. A comparison of the chromatogram for the pipeline mixture and the produced oil from the storage tank shows that the difference in the envelope of these two chromatograms represents the wax material that has precipitated in the storage tank. Over time significantly higher concentrations of the compounds above C_{40} have accumulated.

SUMMARY

Whilst HTGC could not prevent this type of wax accumulation it does provide us with the ability to quantitatively assess what is happening in this particular situation and determine the amount of material that is basically being lost as a result of mixing these two oil samples. Furthermore it is anticipated that careful and detailed laboratory mixing studies should permit one to determine the optimum mixture of these two oils which will minimize the amount of wax precipitation occurring in the storage tank as a result of mixing the two oils. Finally it is also suggested that no wax problems are observed in the pipeline transporting the mixture of these two oils simply because of the turbulence and shearing effects in the pipeline preventing such deposition. The wax crystals in this particular case are of a microcrystalline nature and relatively fine. Hence it is only when the oil has reached the storage tank that these crystals can finally undergo separation as a result of gravitational segregation. The use of HTGC is also vitally important in these types of studies since it permits one to clearly differentiate between the waxes and asphaltenes and also on the purity of these different fractions which can have a significant impact in any purification or remedial steps that may be used at a later stage of the process.

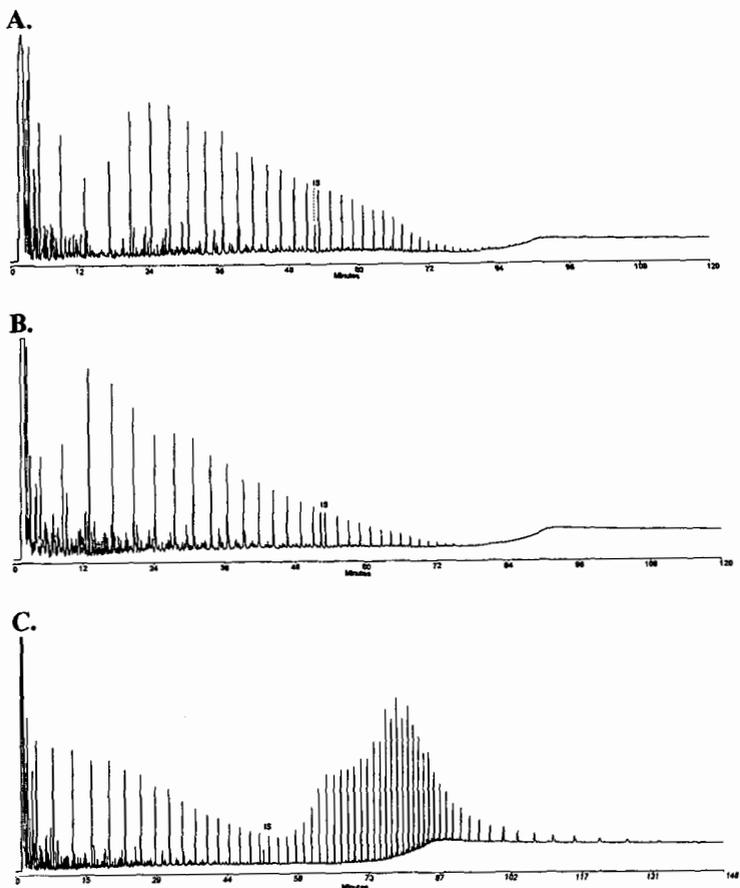


Fig. 1. Chromatograms showing (a) the pipeline mixture (note-IS is the internal standard and is $C_{24}D_{50}$); (b) the liquid crude in the tank; and (c) the solid residue in the tank (note also that the top two chromatograms have total run times of 120 mins and the bottom chromatogram has a run time of 146mins).

A STUDY OF MAGNETIC EFFECTS ON THE PHYSICOCHEMICAL PROPERTIES OF INDIVIDUAL HYDROCARBONS

Hejun Guo, Zhizhong Liu, Yunchao Chen, Rujie Yao
Logistical Engineering College, Chongqing 400042, P.R.China

Keywords: magnetic treatment, hydrocarbon, IR and UV spectra

INTRODUCTION

There have occurred a great number of experimental studies which present evidences of the benefits of magnetic treatment on many occasions. Some eye-catching proto-industrial examples ever reported include: the enhancement of oil recovery[1] and prevention of wax deposition[2-4] in petroleum production, transportation and refining; the improvement of fluidity of crude oils[5-7], and the demulsification of oil-water mixtures[1,8]. Even for motor vehicles and industrial boilers, much fuel economy and noticeable soot suppressions could be approached when the magnetic treatment was introduced[9-11]. Over the last decade or so, the magnetic treatment, as a novel technique with great economic potentiality, has been strenuously exploited and widely adopted in the domain of petroleum chemical engineering. However, there remain some blurring issues waiting eagerly for early answers, with the core of the uncertainties being the unfolding of the molecular interaction mechanism(s) governing the macro-behaviors of the magnetically treated hydrocarbons and fuels. In our study, focus has been laid on the understanding of magnetic action modes which have led to the fuel economy and soot abatement in engine applications.

In the present research, measurement was made about the properties of some typical individual hydrocarbons such as viscosity, surface tension and maximum smokeless flame height(MSFH) after they have been treated in the magnetic fields of different intensities. The IR and UV spectra of the magnetized hydrocarbons were employed to elucidate the property changes in terms of molecular structures.

EXPERIMENTAL

An electromagnet of double yokes was devised and utilized. Each of its two poles is 80mm in diameter and the distance between the poles is 11mm. The intensity of the magnetic field was displayed by a Tesla gauge of CT3 type and could be adjusted from 0 T to 1.0 T.

An L-type quartz glass tube of 10mm in diameter was positioned in the center of the magnetic field. The tube had a rotatable piston in one end just like that of the acid buret to be used to control the flowing rate of liquid samples. In the experiment, the liquid samples of individual hydrocarbons were conducted into the glass tube and flowed transversely through the magnetic field to be magnetized at the rate of 7.5 ~ 10.0ml per minute.

The individual hydrocarbons selected were as follows: n-heptane, n-hendecane, n-hexadecane, cyclohexane, methylcyclohexane, toluene, m-xylene, n-butylbenzene and isopropylbenzene. All of them were in analytical pure. The UV analytical samples were the n-heptane solution of individual aromatic hydrocarbon.

After being magnetized the sample was immediately tested at room temperature in strict accordance with China National Standard Test Method of Petroleum Products. For comparison, measurements were also made on the same untreated samples. Of the tests, the viscosity was determined with a capillary viscosimeter, and the surface tension with the DuNouy ring method described in previous studies[12,14]. The MSFH was measured on an apparatus specified by GB5539-86. In data processing, suspected data were judged with the statistic method of t-check test.

The HITACHI 260-50 type IR spectrometer was employed; its sample cell was KBr crystal. The UV spectra were measured on a UV spectrometer of LAMBDA-Q type, and the sample cell was 1cm in width. In the analysis procedure, blank tests were conducted to adjust the absorbance of n-heptane in UV region to be equal to zero for measurement of the real absorbances of each of the tested individual hydrocarbons.

RESULTS AND DISCUSSION

In Figure 1 is listed the changes of the viscosities of three magnetized normal paraffinic hydrocarbons. As is easily seen, there occur slight decreases of the viscosity of the magnetized normal hydrocarbons. The magnitude of the change becomes larger as strength of the magnetic field increases, with more obvious change pace below 0.3T than above 0.3T. Such a phenomenon is very similar to those of the magnetized petroleum fuels[13]. It can also be noticed that, approximately below 0.2T, the viscosity decreases of the studied normal paraffinic hydrocarbons

are almost the same while above 0.2T, they are different and follow the order of n-hexadecane > n-hendecane > n-heptane. In other words, the more the carbon numbers of the normal paraffinic hydrocarbons, the more obvious of the decrease rate of their viscosity after magnetized.

Figure 2 shows the viscosity decrease of the magnetized methylcyclohexane and cyclohexane. It is apparent that the viscosity decrease of the magnetized cycloalkanes also becomes bigger with the increase of the applied magnetic field. Comparatively, the viscosity decreases more rapidly below 0.2T than above it, a very resemblance to those identified for the normal paraffins stated above.

Figure 3 displays the viscosity decreases of aromatics such as n-butylbenzene and m-xylene. Evidently, similar features to those of normal paraffins and cycloalkanes have been demonstrated between their viscosity decrease rates and the strength of the applied magnetic fields. It can be observed that there occur rapid decreases of viscosity below 0.5T, while above 0.5T the decrease of the viscosity becomes more and more slowly with the increase of the magnetic field strength. This indicates that the decrease of the viscosity of the magnetized individual hydrocarbons is not directly proportional to the strength of the applied magnetic field.

Figure 4 displays the relationship between the decrease rates of the surface tension of magnetized n-octane and the applied magnetic intensities, and Table 1 lists the decrease magnitudes of the surface tensions of n-hexadecane, cyclohexane and isopropylbenzene. The results show that, after magnetized, the surface tension of the individual hydrocarbons decreases. However, the decrease rates or the decrease magnitudes do not increase accordingly very well as the strength of the magnetic field increases. At some certain magnetic fields, the surface tension decreases comparatively considerably while at others it decreases comparatively unnoticeably. So, it can be easily concluded that the surface tension of the individual hydrocarbons decreases fluctuately with the increase of the magnetic field strength.

The value of surface tension is determined not only by molecular attraction force but also by molecular orientation state on the liquid surface[15]. It is suggested that the oriented distribution state of hydrocarbon molecules on the liquid surface must have changed after they have been magnetized, and that the oriented distribution state must have changed differently at different magnetic field strength. This can result in high decrease rate of surface tension compared with that of viscosity, and the fluctuation of the decrease of surface tension.

Table 4 exhibits the changes of the MSFH of magnetized toluene and its mixture with n-heptane and methylcyclohexane. It is shown that, after being magnetized, the MSFH of the individual hydrocarbons rises with the increase of the magnetic field strength. This indicates that soot formation has been suppressed after the hydrocarbons are magnetized, implying that the combustion efficiency of the hydrocarbons has been improved.

Theoretical researches have been done to unfold the magnetization mechanism of hydrocarbons. It is proposed that the magnetic treatment can depolymerize molecular aggregates of hydrocarbons in normal conditions[16,17]. In the present study, the molecular structure changes of the magnetized hydrocarbons were analyzed which could reveal the mechanism of the changes of the above physico-chemical properties in terms of microstructure.

From Figure 5 it can be easily seen that, after 1,3,5-trimethyl benzene is magnetized at 1.0T, the absorption peaks of its methyl stretching vibration ($2860\text{cm}^{-1} \sim 2920\text{cm}^{-1}$), skeleton vibration of aromatic ring ($1456\text{cm}^{-1} \sim 1616\text{cm}^{-1}$), methyl symmetrical deformation vibration (1384cm^{-1}), in-plane bending vibration of $\text{C}=\text{CH}$ (1035cm^{-1}), out-of-plane bending vibration of $\text{C}=\text{CH}$ (840cm^{-1}) and out-of-plane vibration of aromatic ring (685cm^{-1}) all shift toward higher wavenumber regions. Also, the peaks of the overtone and combination bands in the region of $2000\text{cm}^{-1} \sim 1660\text{cm}^{-1}$ due to the C-H out-of-plane deformation vibrations are clearly observed in the higher wavenumber regions. Since the frequency is determined by the energy difference between the excited vibration state and the ground vibration state, the vibrational energy levels of above groups must have changed. Because the molecular attraction energy (Vl) of nonpolar hydrocarbon is determined by group vibrational frequency (ν) according to the formula of $Vl = -3/4 \cdot (h \nu e^4) / (K^2 R^6)$ (where $\nu = 1 / (2\pi) \cdot (K/\mu)^{1/2}$), so a conclusion can be easily reached that the higher the frequency the lower the absolute value of Vl, or, the lower the group attraction energy. Thus, it can be deduced that the molecular attraction force among hydrocarbons decreases after they are magnetized. This is why the property indices of hydrocarbons, such as viscosity and surface tension which are influenced by the molecular attraction force, decline after the hydrocarbons flow through magnetic field.

Table 2 and Table 3 list the changes of the UV absorptions of toluene and n-butylbenzene respectively. Figure 6 shows the UV absorption spectra of the magnetized and unmagnetized naphthalene. It is evident that the UV absorption strength increases remarkably after the aromatic hydrocarbons have been magnetized. This means that the transition probability of electrons in the π -bond conjugated system among different energy levels has become higher. Since the transition of the bond electrons from the ground level to the excited level is the main process of molecule

radicalization. This may enhance the splitting of the C=C bonds in the aromatic rings in the course of combustion under intense actions of light and heat, and therefore the oxidation of the aromatic rings can be accelerated and easily completed thoroughly. As a result, the combustion efficiency of aromatic hydrocarbons could be boosted, which gives rise to the noticeable increase of their MSFH.

CONCLUSION

- (1) After individual hydrocarbons are magnetized, viscosity and surface tension decrease slightly and weakly respectively, MSFH rises noticeably. The decrease rate of viscosity increases more and more slowly accompanying the increase of the magnetic field strength, and also increases with molecular carbon atom number increasing, while surface tension decreases fluctuately.
- (2) IR absorption peaks shift toward higher wavenumber regions, and UV absorptions of aromatics increase remarkably in strength, which grants the explanations to the changes of above physico-chemical properties.

REFERENCES

1. Yu Zhaoxian et al, "The Application of Intense Magnetic Technique in Petrochemical Industry," *Physics(China)*, 1992,21(3).
2. JAY, "Magnets Utilized for Paraffin Control Appear to Be Effective," *Amoco Oil Company Newsletter*, Dec.1981.
3. Chen Lidian et al, "Magnetic Treatment for Scale and Paraffin Deposits Prevention --- An Promising Technique," *Oil-Field Chemistry(China)*, 1986,6(3).
4. Ye Yazhong, "The Applied Test of Wax Protection by Intensive Magnetism," *Oil & Gas Storage and Transportation(China)*, 1990,9(2).
5. Liang Changqing et al, "Experimental Study of the Effect of Magnetic Treatment on Crude Oil in Pipeline," *Oil & Gas Storage and Transportation(China)*, 1990,9(1).
6. Zhang Yuxian, "The Applicable Research of Magnetic Technology in the Pipeline Transportation of Crude Oil," *Oil & Gas Storage and Transportation(China)*, 1989,8(1).
7. Cao Yujian et al, "Reduction of Viscosity of Crude Oil by A Strong Magnetic Field and Its Application," *Acta Petrolei Sinica*, 1989,10(1).
8. Liu Wenping et al, "The Effect of Magnetic Treatment on the Breaking of Heavy Oil Emulsions," *Oil-field Chemistry(China)*, 1990,7(3).
9. 吉村克郎, "The Effect of Fuel Oil Combustion through Magnetic Treatment Device," *Fuel and Combustion (Japan)*,49(3).
10. 藤田越文, "The Combustion Efficiency Improving of Magnetized Fuel Oil," *Fuel and Combustion*, 45(1).
11. Sun Mingdong et al, "Study on the Combustion Efficiency of Magnetized Petroleum Fuels," *Chinese Science Bulletin*, 1984. 3.
12. Zhao Yang et al, "Effect of Magnetic Fields on Physico-chemical Properties of Surfactant Solutions," *Oil-field Chemistry(China)*, 1989,6(3).
13. Guo Hejun et al, "Discussion on Energy Saving Mechanism of Magnetized Fuel Oil," *Energy Conservation(China)*,1997.4.
14. Zhao Liang et al, "Effect of Magnetic Field on the Surface Tension of Alkanes and Alcohols," *Chemistry(China)*, 1989. 1.
15. A.W.Adamson, *Physical chemistry of Surfaces, VOL ONE (Chinese Version)*, Science Publishing House of China, 1983, P63.
16. Tong Jingshan et al, "The Molecular Thermodynamics Model of Magnetized Fluid and the Study of Combustion Performance of Magnetized Oil Fuels," *Energy Conservation Technology(China)*, 1989.9.
17. Chen Guoxian, Yi Zhiying, "Microscopical Analyses of Magnetically Treated Fuel Oil," *Physics(China)*, 1992,21(3).

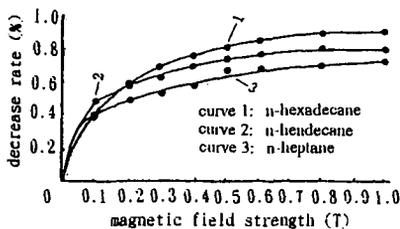


Figure 1. Viscosity decrease rate of normal paraffin versus magnetic field strength

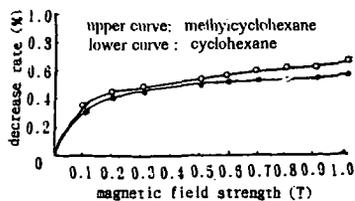


Figure 2. Viscosity decrease rate of cycloalkane versus magnetic field strength

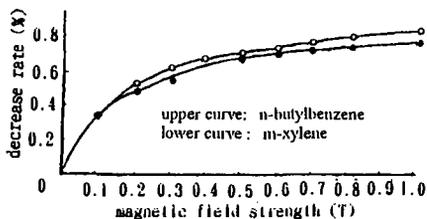


Figure 3. Viscosity decrease rate of aromatics versus magnetic field strength

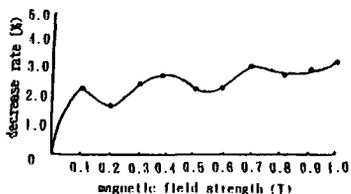


Figure 4. Surface tension decrease rate of n-octane versus magnetic field strength

Table 1 The Surface Tension Changes of Magnetized Individual Hydrocarbons ($\Delta \gamma$, dyn/cm)

sample	B(T)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1.0
n-hexadecane		-0.5	-0.4	-0.6	-0.5	-0.6	-0.7	-0.8	-0.9	-1.1
cyclohexane		-0.2	-0.4	-0.4	-0.4	-0.5	-0.5	-0.7	-0.5	-0.6
isopropylbenzene		-0.4	-0.6	-0.6	-0.7	-0.8	-0.5	-0.5	-0.6	-1.0

Table 2 The MSFH Increases of Magnetized Toluene and Its Mixture (Δh)

sample	B	1.8 T	5.0 T	1.0 T
toluene		1.2mm	1.6mm	1.9mm
toluene + methylcyclohexane		1.7mm	2.1mm	2.5mm
+ n-heptane(1:1:1, vol)				

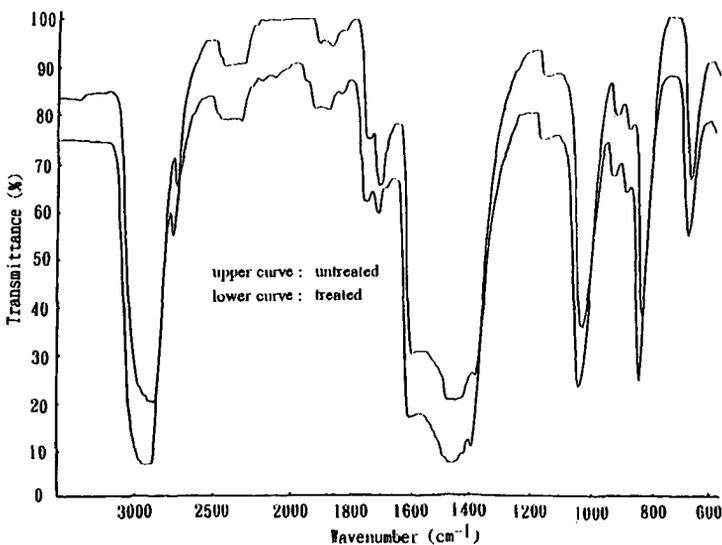


Figure 5. The IR spectra of magnetically treated and untreated 1,3,5-trimethylbenzene at 1.0T

Table 3 The absorbance increase rates of magnetized toluene UV absorption

wavelength	220.4 nm	257.2 nm	263.0 nm
1.0 T	18.1%	6.4%	6.0%
0.3 T	21.1%	5.0%	5.0%

Table 4 The absorbance increase rates of magnetized n-butylbenzene UV absorption

wavelength	220.6 nm	253.0 nm	259.2 nm
1.0 T	16.6%	6.1%	6.8%
0.3 T	11.6%	4.2%	5.6%

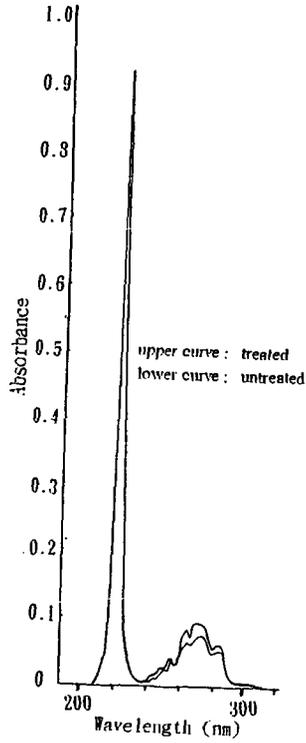


Figure 5. The UV spectra of magnetically treated and untreated naphthalene at the strength of 1.0 T

notes: sample concentration: 1.5 μ g/ml
 The very similar graph was also achieved at the conditions of 3 cm in width of sample cell and 0.5 μ g/ml in sample concentration

COMPOSITIONAL MODELLING OF GENERATION AND MIGRATION OF PETROLEUM COMPOUNDS IN A HIGH PRESSURE/ HIGH TEMPERATURE ZONE IN THE CENTRAL GRABEN (NORTH SEA): INFLUENCE OF THE THERMAL STABILITY OF CHEMICAL CLASSES ON THE OIL PREDICTION.

M. Vandembroucke, F. Behar, J.L. Rudkiewicz, J. Wendebourg, J.M. Gaulier, IFP 92500 Rueil-Malmaison, FRANCE; A. Vear, N. Beveridge, BP Sunbury TW16 7LN, U.K.; S. Düppenbecker, BP Houston TX77079, U.S.A; F. Brigaud, EEP 64018 Pau, FRANCE, D. Grauls, EEP 64018 Pau, FRANCE.

Keywords: petroleum system modelling, compositional kinetics, high pressure/ high temperature reservoirs, Temispack.

INTRODUCTION

Basin simulators that predict oil and gas generation and migration in petroleum systems use kinetic schemes of oil and gas production based on pyrolysis of source rock samples for simulating their natural maturation. The organic matter decomposition with increasing temperature due to burial in geological conditions is governed by kinetics, the thermodynamically stable ends being methane and almost pure carbon. As millions of reactions occur in source rocks, a number of product groupings and assumptions have to be done for modelling cracking kinetics, and several models have been described in the literature (1-7). The present study is a part of an European Union sponsored project associating BP, EEP and IFP. In this paper we simulate the generation, migration and cracking of fluids until present on the high pressure (1100 bars) high temperature (190°C) Elgin field in the North sea with the 2D simulator Temispack. We compared in the same 2D cross section a kinetic model 1 calibrated on pyrolysis and field data, describing kerogen cracking into two classes, oil and gas, and another kinetic model 2 calibrated on pyrolysis data only, based on various chemical classes with different thermal stabilities. Oil cracking is calibrated on pyrolysis data, giving gas and coke in model 1 and a chemical class distribution in model 2. The two models compute the genesis and secondary cracking of hydrocarbons in the source rocks, their expulsion, migration and secondary cracking in carriers and reservoirs, the saturations and number of phases in each element of the section. The present hydrocarbon composition observed in Elgin Fulmar sands reservoirs is compared with the corresponding results of these models and thus accounts for their difference in kinetic modelling.

EXPERIMENTAL AND MODEL SETTINGS

Geological context modelling

The studied zone is located in the 'four corners' high pressure high temperature area in the North Sea Central Graben. The choice of this zone was guided by the will to test the models in an unusual geological setting where present day conditions may seem a priori unfavorable to oil preservation, leading to question the kinetic schemes currently used in basin simulators. A 2D cross section intersecting the structural crest of the Elgin field as well as the relevant kitchen areas was reconstructed through time, the geological history of sediment deposition being described by a series of 31 events corresponding to stratigraphic markers. To each formation is associated during burial a lithology describing the compaction (porosity vs. depth), the conductivity and the permeability of the rock. The stratigraphic and lithologic parameters of the 2D cross section are given in Table 1. The parameters of lithologies and the thermal boundary conditions were calibrated on present day temperatures and pressures coming from well data, and on vitrinite reflectance measurements. The present day geometry and source rock position as reconstructed by Temispack is shown on Fig. 1.

Geochemical parameters

a) source rock distribution

Pertinent information on the sedimentology of source rocks is crucial for a good prediction of oil and gas potentials. Previous geochemical studies in the Elgin area showed that main source rocks are within the Kimmeridge and Heather formations and contain marine organic matter (Type II of Tissot and Welte (8); organofacies B of Pepper and Corvi (6)). A second source rock can be found in the Pentland formation (Middle Jurassic). However its organofacies varies according to the studied zone from algal lacustrine (Type I/organofacies C) to coaly (Type III/organofacies F), making difficult to estimate at a regional scale the amount and petroleum potential of the formation. In the Elgin area, the Pentland source rock is considered as Type III organic matter bearing.

b) kerogen cracking parameters

As primary cracking of kerogen consists mainly in breaking of functional bonds, the kinetic parameters depend on the kerogen type. Both models describe kerogen and oil cracking by a set of parallel reactions, assuming that the order of all reactions is one and the rate constants follow the Arrhenius law. The distribution of partial potentials according to activation energies is Gaussian in model 1, thus defined by its mean and standard deviation and one preexponential factor; it is calibrated on pyrolysis experiments and field data. Oil (C₆) and gas (C₁-C₂) generation are modelled separately. For model 2, a discrete distribution of partial potentials for increasing activation energies is calculated by an optimization procedure (9) to account for the Rock Eval

pyrolysis curve obtained with different heating rates; the preexponential factor is the same for all reactions and a reactive fraction of the total hydrogen index is calculated for each activation energy. In order to simulate hydrocarbon generation and migration, once geochemical types and amounts of possible source rocks are mapped, two options can be chosen. Either default cracking parameters are used on the basis of known geochemical data on the modelled area, or cracking parameters are adjusted on the pyrolysis study of representative samples. The first option is the only one possible for model 1. For using the second option, samples at the beginning of the catagenesis zone (oil generation) have to be recovered in sufficient amount. Their organic matter must be isolated from minerals to avoid undesirable catalytic effects due to the increase in temperature necessary for compensating geological time during the pyrolysis procedure. For calibration of the Kimmeridge and Heather source rock in model 2, an immature Kimmeridge clay from the Yorkshire coast was used for pyrolysis experiments. The immature equivalent of the Pentland Type III was not available, thus default kinetic parameters were used for this source rock. The complete methodology for determining the kinetic parameters of reference kerogens is defined in (10). The derived procedure used here for Type II kerogen in model 2 is summarized hereunder.

A first step is to perform compositional Rock Eval according to the method described by Espitalié et al. (11). Briefly, kinetic parameters are derived from pyrolyses at various heating rates in open system using an optimization procedure which determines for each kerogen an unique frequency factor and a weight distribution, for a discrete series of activation energies, of C_1 , C_2 - C_5 , C_6 - C_{14} and C_{15+} classes, using various cold traps. This step allows to compare the primary cracking of the type II kerogen into gas (C_1 - C_4) and oil (C_{6+}) between models 1 and 2. Model 1 is centered on $E = 51$ Kcal/mol with a preexponential factor $A = 8.14 \cdot 10^{13}$ s⁻¹ for oil and on $E = 67$ Kcal/mol with a preexponential factor $A = 2.17 \cdot 10^{18}$ s⁻¹ for gas. Model 2 is strongly asymmetrical and maximizes on $E = 52$ - 54 Kcal/mol for oil and on $E = 54$ Kcal/mol for gas with a same preexponential factor $A = 1.6 \cdot 10^{14}$ s⁻¹ for oil and gas. Although these models give very close generation curves in the laboratory conditions, it can be seen on Fig. 2 that it is no longer true in basin conditions, where the proportion of gas and oil are calculated for a constant sediment burial of 50 m/My and a geothermal gradient of 25 °C/km.

The second step consists in running preparative pyrolysis as described in (10), in order to quantify by gas chromatography the C_6 - C_{14} fraction into saturates and aromatics, and by weighing the C_{15+} compounds after fractionation by liquid chromatography into C_{15+} saturates, C_{15+} aromatics and NSO compounds. These proportions are applied evenly to the C_6 - C_{14} and C_{15+} classes obtained in the first step whatever the activation energy, as it was shown (10) that the pyrolysate composition does not change during open system pyrolysis.

A third step is to run gas chromatography on the C_{15+} saturates and to measure in the same carbon interval the total area of the chromatogram once the blank is subtracted, and the total area of *n*-alkanes and 1*n*-alkenes. The ratio of these areas gives the proportions of *n*-alkanes and *iso*-*cyclo*-alkanes in the C_{15+} saturates. Separation of these compounds in the kinetic scheme results from a recent study (12) on the effect of pressure on cracking of pure *n*- C_{25} , showing that pressure in the range 100-800 bars has little influence on cracking kinetics compared to temperature. The influence of pressure was assumed to be small for all chemical classes. Absolute kinetic parameters were obtained, showing that *n*-alkanes are more stable than *iso*-*cyclo*-alkanes. These kinetic parameters are used for all C_{15+} *n*-alkanes. Because using pure compounds does not automatically take into account the mixture effect (hydrogen donors/acceptors), another study was performed to test this parameter (13), indicating that this effect does not change significantly the kinetic parameters and tends to delay cracking.

The final step is to perform an isothermal pyrolysis in closed system at 550°C during 24 hours on a kerogen at the beginning of the metagenesis stage. It was in fact shown (10) that open and closed system pyrolyses give fairly similar results for stoichiometric coefficients of primary cracking except for methane. In the open system the final pyrolysis temperature is higher than in the closed system and results in a competition between C-C and C-H bond cracking in the kerogen. The molecular hydrogen that is generated lowers the amount of methane. The kerogen at the beginning of the metagenesis stage may be either prepared on a natural sample, or preferably by performing a first pyrolysis on the immature sample at 350°C during 48 hours to generate all the oil from primary cracking, then extracting the remaining kerogen. The C_1 and C_2 gases being stable in geological conditions can be quantified after the second pyrolysis, allowing to split the gas into C_1 , C_2 and C_3 - C_5 .

This methodology results in a complete compositional description of the products of kerogen cracking into chemical classes of compounds. Even if these chemical classes represent the lumping of a great number of compounds, they behave similarly during secondary cracking because of similar chemical structures and bonds. The kinetic scheme for secondary cracking can thus be better constrained. In basins where source rocks do not experience a strong secondary cracking, this kinetic model can be highly simplified.

c) oil cracking parameters

Secondary cracking of oil consists mainly in breaking of C-C bonds, hence it does not depend on the kerogen type. In our work, we used standard secondary cracking schemes that were calibrated on pyrolysis experiments on isolated oils and mixtures of kerogen and its cracking products.

Model 1 uses as for kerogen a Gaussian distribution of activation energies, thus secondary cracking is defined by three parameters, the mean energy $E = 58$ Kcal/mol and its standard deviation and a preexponential factor $A = 10^{14}$ s⁻¹ (7). Oil cracks into gas and coke. Model 2,

presented in detail in (5), describes cracking of each chemical class defined previously by a reaction producing other chemical classes. The kinetic parameters, E, A and the stoichiometric coefficients are fitted on experimental pyrolysis values, and constrained by mass and atomic balances; the model is simplified by choosing the same preexponential factor for all reactions. This kinetic scheme (5) was modified in the present study by adding the cracking reaction of *n*-alkanes with its own E and A (12).

RESULTS AND DISCUSSION

Once the 2D cross section was calibrated to match the pressure and temperature data, several compositional runs tested the influence of geochemical parameters on the saturation and composition of fluids in possible reservoirs. Typically, runs with model 1 need 10 hours and runs with model 2 need 25 hours of CPU on a Sun Spark Ultra 1 workstation. This difference is linked to the number of unknowns that have to be computed.

Geological events

As shown on Fig. 1, during the Quaternary (1.64 My), over 1000 meters of silty shales were deposited. This large input of sediments resulted in a very rapid burial of the petroleum system. Fig. 3 shows the thermal history of the Fulmar sands, the reservoir of the Elgin field located just under the Kimmeridge and Heather source rocks. In this reservoir, the temperature increased from 160 to more than 180°C in the last million years. Due to the very low permeability of the carbonates in the Hod formation, the fluid expulsion was not quick enough to accommodate the rapid burial, enabling fluid pressures close to lithostatic pressure in the underlying sediments.

Saturations and phase behaviour

The petroleum system modelling through time indicates that the Elgin reservoir filling begins around - 50 My. The petroleum fluid is monophasic during migration, thus all hydrocarbons, either C₆, or C₁-C₅, move with the same speed.

Primary cracking

The separate contribution of each source rock to the reservoir filling was tested. The results show that primary cracking is completed whatever the source rock considered, hence the oil composition does not depend much on the kerogen type. However as *n*-alkanes are fairly stable, their characteristic carbon distribution according to the source rock contribution, particularly in the Type I Pentland in other zones of the study, can still be recognized in the oil analyses.

Secondary cracking

Its kinetic parameters determine the hydrocarbon composition in the Elgin reservoir. Model 1 predicts only gas; model 2 predicts both oil and gas. The oil composition predicted by model 2 and observed in the Elgin oil is shown on Fig 4. The prediction is fairly good for all chemical classes except for methane which is underestimated, and condensed aromatics which are overestimated.

The reason why model 1 overestimates secondary cracking can be found in the way it is mathematically expressed and calibrated. The Gaussian distribution of activation energies may be a reason as in many oils, saturates are both the most abundant and the most stable compounds. The calibration of cracking experiments is done by pyrolysis-gas chromatography. This technique allows the analysis of small amounts of hydrocarbon compounds to be performed but no mass balance can be made: only compounds able to cross the chromatographic column are detected. Heavy fractions are thus not taken into account, and this may bias the description of cracking, thus the mean activation energy, towards the light ends.

The methane underestimation of model 2 could be due in part to its quantification in primary cracking. Although the Rock Eval value has been corrected using the result of a closed system pyrolysis at 550°C/24h, a currently performed research shows that this correction represents only 60% of the total methane potential of the kerogen. Condensed aromatics are probably the least constrained chemical class in the secondary cracking scheme (6). Their definition was based on elemental analysis but the low amounts obtained during pyrolyses made it difficult to calibrate correctly the stoichiometric coefficients, and the activation energy may be too high, as already noticed in (6): 59.1 Kcal/mol for type II and III kerogens as compared with 57.1 for Boscan oil.

Evolution of the petroleum system

The petroleum system modelling shows that the occurrence of oil in Elgin despite the presently high temperature is due to its very recent increase from 160 to 190°C in the last million years. This situation evolves rapidly as shown both by the model and by optical studies on reservoir cores proving that pyrobitumen due to the oil cracking is currently forming.

CONCLUSION

Simulating generation, migration and entrapment of hydrocarbons in a petroleum system is the only way to handle its numerous variables and to be able to test the influence of selected parameters. Many of them depend upon assumptions which are sometimes uncertain; however the simulation allows us to check the current hypotheses, to measure the sensitivity to parameter changes and to calibrate the entry parameters against field data.

In this respect the present study shows that in a petroleum system where high temperature causes a large amount of secondary cracking both in source rocks and in reservoirs, it seems difficult to predict the occurrence of oil or gas without taking into account the detailed chemical composition of products, linked to their thermal stability, as done in model 2. It shows also that in this latter, the calibration of secondary cracking should be improved to better account for a higher proportion of

methane and a lower proportion of condensed aromatics. Future work will be performed in two directions: one is to run new pyrolyses on the oil constituents generating condensed aromatics, such as NSO compounds; it seems also necessary to check again the database and the optimisation procedure used to establish the secondary cracking scheme. The second consists in adjusting modified cracking parameters to the present study and then checking whether they are able to account for observed compositions in reservoirs from various sedimentary basins.

REFERENCES

1. LOPATIN N.V. (1971) Temperature and geologic time as factors in coalification. Akad. Nauk SSSR Izv. Ser. Geol. 3,95-106 (in Russian).
2. TISSOT B.P. and ESPITALIE J. (1975) L'évolution de la matière organique des sédiments: application d'une simulation mathématique. Rev. Inst. Fr. Petrol., 30, 743-777.
3. QUIGLEY T.M., MACKENZIE A.S. and GRAY J.R. (1987) Kinetic theory of petroleum generation In: "Migration of hydrocarbons in sedimentary basins" (Ed. B. Doligez). Editions Technip, Paris, 649-665.
4. BURNHAM A.K. and BRAUN R. L.(1990) Development of a detailed model of petroleum formation, destruction and expulsion from lacustrine and marine source rocks. Org. Geochem., 16, 1-3, 27-39.
5. BEHAR F., KRESSMANN S., RUDKIEWICZ J.L. and VANDENBROUCKE M. (1991) Experimental simulation in a confined system and kinetic modelling of kerogen and oil cracking. Org. Geochem., 19, 1-3, 173-189.
6. PEPPER A.S. and P.J. CORVI (1995) Simple kinetic models of petroleum formation. part 1: oil and gas generation from kerogen. Marine and Petroleum Geology, 12, 3 , 291-319.
7. PEPPER A.S. and T.A. DODD (1995) Simple kinetic models of petroleum formation. part 2: oil - gas cracking. Marine and Petroleum Geology, 12, 3 , 321-340.
8. TISSOT B.P. et WELTE D.H. (1984) Petroleum formation and occurrence. Springer Verlag, Berlin
9. UNGERER P. and R. PELET (1987) Extrapolation of the kinetics of oil and gas formation from laboratory experiments to sedimentary basins. Nature, 327, 6117, 52-54.
10. BEHAR F., VANDENBROUCKE M., TANG Y., MARQUIS F. and ESPITALIE J. (1997) Thermal cracking of kerogen in open and closed systems: determination of kinetic parameters and stoichiometric coefficients for oil and gas generation. Org. Geochem., 26,321-339.
11. ESPITALIE J., UNGERER P., IRWIN H. and MARQUIS F. (1988) Primary cracking of kerogens. Experimenting and modelling C₁, C₂-C₅, C₆-C₁₅ and C₁₅₊ classes of hydrocarbons formed. Org. Geochem., 13, 893-899.
12. BEHAR F. and VANDENBROUCKE M. (1996) Experimental determination of the rate constants of the n-C₂₅ thermal cracking at 120. 400. and 800 bar: implications for high-pressure/high-temperature prospects. Energy Fuels, 10, 932-940.
13. MCKINNEY D.E., BEHAR F. and HATCHER P.G. (1998) Reaction kinetics and product distribution of ¹³C labeled n-C₂₅ in Arabian Light marine oil as determined by SIM/GC/MS: are mixture effects important? Submitted to Energy Fuels.

n°	stratigr. markers	Age (My) (Top)	Stratigraphy	Lithology
1	Seabed	0	Quaternary	Shale_silty
2	T_Plio	1.64	Pliocene	Shale_silty
3	TE_Plio	3.4	Pliocene	Shale_silty
4	T_Miocene	5.2	Miocene	Shale_silty
5	T_Mid_Mio	10.4	Miocene	Shale_silty
6	T_Oligoc	23.3	Oligocene	Shale_silty
7	TMid_Eocene	38.6	Eocene	Shale_silty
8	TEar_Eocene	50	Eocene	Shale_silty
9	T_Balder	54.5	Palaeocene	Shale
10	T_Forties sd	57	Palaeocene	Sand
11	T_Maureen	61	Palaeocene	Shale_silty
12	T_Ekofisk	63	Maastricht.	Chalk
13	T_Chalk	65	Campanian	Chalk
14	Intra Chalk	71	Campanian	Chalk
15	T_Hod	78	Turon/Campan.	Arg_Lmst.
16	Intra Hod	81	Turon/Campan.	Hardgrds
17	int_Hod	83	Turon/Campan.	Arg_Lmst.
18	T_Herring	85	Cenom/Turon.	Plns_Marl
19	T_PlensMrl	90.4	Cenom/Turon.	Plns_Marl
20	T_Rodby	97	Albian	Tight_shale
21	T_Sola	112	Apitian	Shale
22	Kim_Clay	145.6	Portland/Berria.	KCF
23	Heather_shly	152	Oxford/Kimmeri.	Heather_src
24	int_Heather	153.5	Oxfordian	Shale_silty
25	Fulmar sdy	155	Callov/Oxford	Sand
26	Pentlnd-sdy	157	Bathon./Callov.	Shale&Sand
27	Pentlnd-shly	182	Bathon./Callov.	Pentland_src
28	Tr_Skagerrak	208	U.Triassic	Shale&Sand
29	Tr_Smithbank	222	L.Triassic	Shale_silty
30	Top_Salt	245	Zechstein	Salt
31	Rotliegend	256	M-L.Perm.	

Table 1: Stratigraphic and lithologic parameters of the 2D section

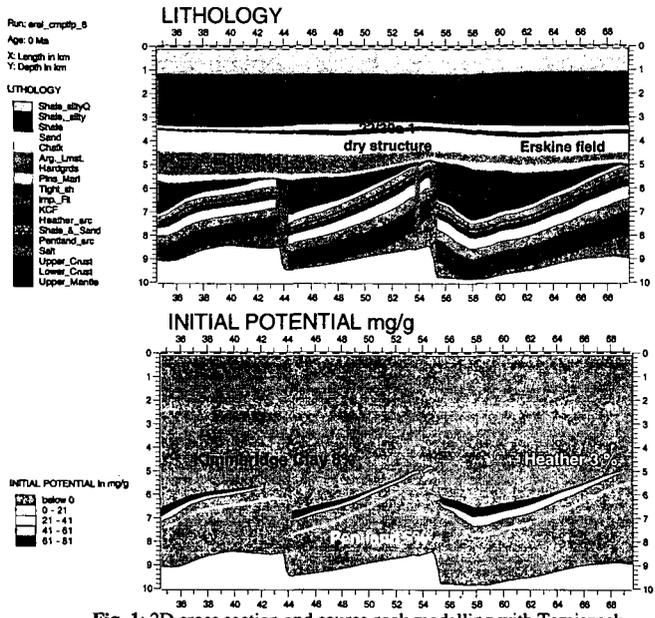


Fig. 1: 2D cross section and source rock modelling with Temispack.

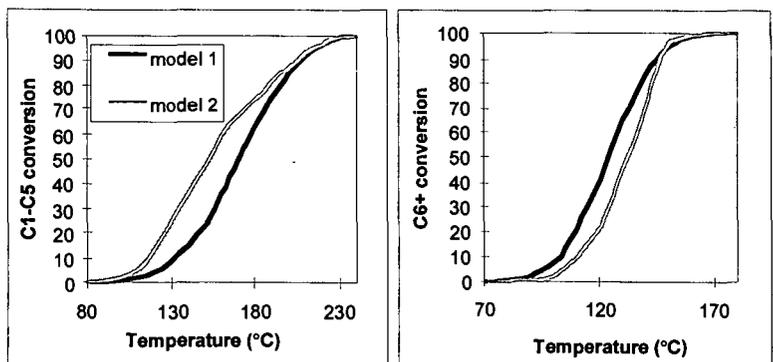


Fig. 2: Comparison of primary cracking kinetics in model 1 and model 2 calculated for a constant sediment burial of 50 m/My and a geothermal gradient of 25 °C/km.

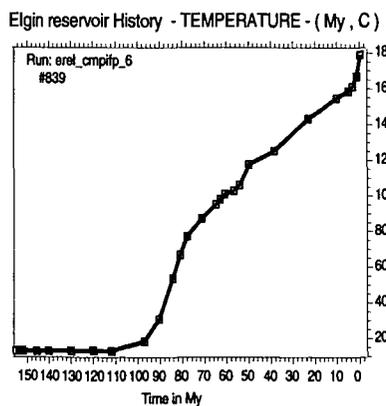


Fig. 3: Thermal history of the Elgin reservoir.

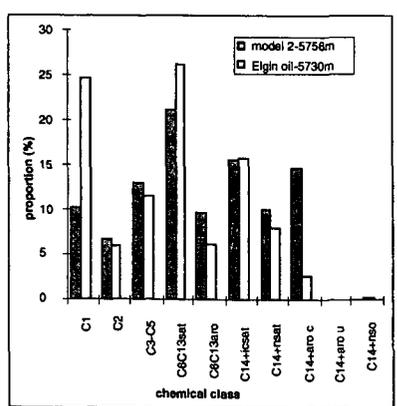


Fig. 4: Comparison of calculated and observed oil composition.

Analysis of High Pressure Samples by Gas Chromatography

Paul A. Peadar

APTI Geosciences, 10450 Stancliff Road, Houston TX 77099

Gas Analysis, Adamantanes, Hydrocarbons

ABSTRACT

High molecular weight compounds dissolved in gases at elevated pressures and temperatures in reservoirs often present production problems. These can range from precipitation of solids which foul chillers and tubing to plasticizing membranes used for gas component separations. Quantitative analysis of such samples is problematic because they are frequently present in sample vessels as two phases (gas and solid or liquid). This paper describes a technique for rendering samples collected at high temperature and pressure single phase and analysis by gas chromatography. Results of this technique to the analysis of gases containing diamondoids and other high molecular weight hydrocarbons are presented.

INTRODUCTION

The analysis of hydrocarbon gases is usually done by gas chromatography. Common analyses performed include a natural gas analysis which provides the hydrocarbon composition through n-pentane, a hexanes plus value, nitrogen, oxygen, and carbon dioxide. The analysis of these hydrocarbon gases by gas chromatography using a flame ionization detector is also often used to provide details about the hydrocarbons present in the C1 to C8 range. If it is necessary to extend the analysis range to C12, or in the extreme to C28, this can be done by careful heating of the sample and sampling lines to the appropriate temperatures to make sure that the higher boiling hydrocarbons are not lost due to adsorption or cold spots. It is possible to get around these sampling problems which lead to discrimination by sampling under supercritical conditions.

EXPERIMENTAL

SFC grade carbon dioxide was obtained from Air Liquid. An Isco syringe pump was used to pressurize samples with the carbon dioxide. A 6 port valve allowing sample pressures up to 6000 psi with a 30 μ L sample loop was used. The sample inlet line and valve was heated to about 60°C. The restrictor used between the valve and the injection port was between 5 and 10 cm of 50 μ m id fused silica tubing. This is similar to the approaches taken in SFE/GC techniques (1). The gas chromatograph was a Hewlett-Packard 5890 equipped with both FID and FPD detectors. A high pressure gauge reading from 0 to 10,000 psi was positioned between the valve and the waste outlet. Flow at the outlet was controlled with a needle valve (see Figure 1). Samples were in stainless steel cylinders ranging from 150 cc to 500 cc.

To do the extended hydrocarbon analysis first a conventional natural gas analysis was obtained. This was done in order to get the concentrations of nitrogen, oxygen, carbon dioxide, and the C1 to C4 hydrocarbons. At this time the sample pressure was also measured along with the cylinder weight. Based on the amount of methane and carbon dioxide present the quantity of carbon dioxide necessary to bring the sample to a reduced density of 1 or greater was calculated. Using the syringe pump this quantity of carbon dioxide was added to the sample and the sample was reweighed. The weighing helped verify that the right amount of carbon dioxide really was added to the cylinder. The sample was then allowed to equilibrate (usually overnight) at 60°C until sampling.

Sampling was done at cylinder pressure and temperature. The sampling line was heat traced along with the valve. Another high pressure line to the valve from the ISCO pump supplied carbon dioxide at or slightly above the cylinder pressure as measured by the pressure gauge. Prior to sampling the sample was allowed to flow through the sampling system for at least 2 to 3 minutes at about 100 mL/min. In order to keep methane through butane on scale a range change from lower to higher sensitivity was done automatically after the elution of n-butane. The magnitude of this change was generally a factor of 512, but for some samples with high concentrations of hydrocarbons it was lower.

RESULTS AND DISCUSSION

The data indicate that reduced densities of at least one are sufficient to give quantitative results for most samples. This is shown by the results in figures 2-4. Most importantly this data indicates that by sampling under the proper conditions it is possible to significantly reduce or eliminate any discrimination between low boiling and high boiling hydrocarbons. Quantitative results for the hydrocarbons are calculated by using the natural gas results for the amount of methane through butanes in the sample. Using this value as an internal standard amount the quantities of other hydrocarbons in the sample can be calculated based on a carbon equivalent response for the FID (2). It is possible to determine adamantanes and other hydrocarbons quantitatively at concentrations of 1 ppm with detection limits around 0.05 ppm. The actual quantitative limits depend on the initial state of the sample. Samples which require the addition of large amounts of carbon dioxide will have higher detection limits, and those requiring little carbon dioxide will have lower detection limits. Obviously this analysis excludes water. If water is present is not expected to significantly impact the results obtained except for its exclusion.

REFERENCES

- (1) Lee, M. L.; Markides, K. E. *Analytical Supercritical Fluid Chromatography and Extraction*; Chromatography Conferences, Inc.: Provo, Utah, 1990; PP 335-344.
- (2) Scanlon, J. T. Willis, D. E. *J. Chromatogr. Sci.* 1985, 23, 333.

FIGURES

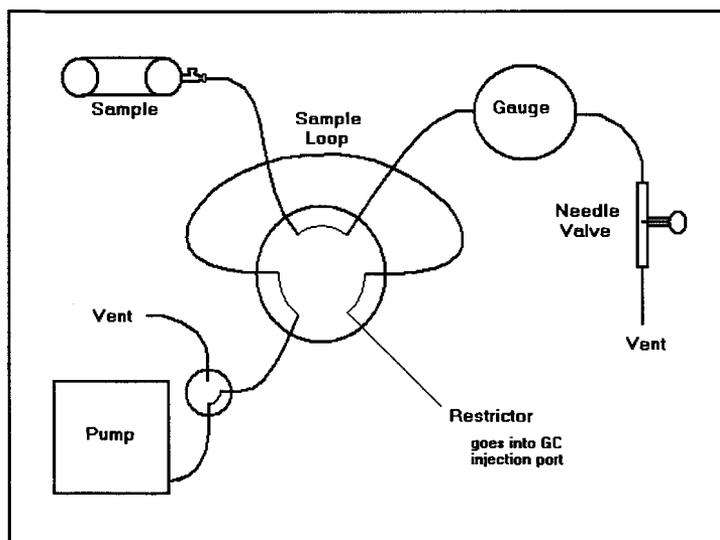


Figure 1. Diagram of the sampling system.

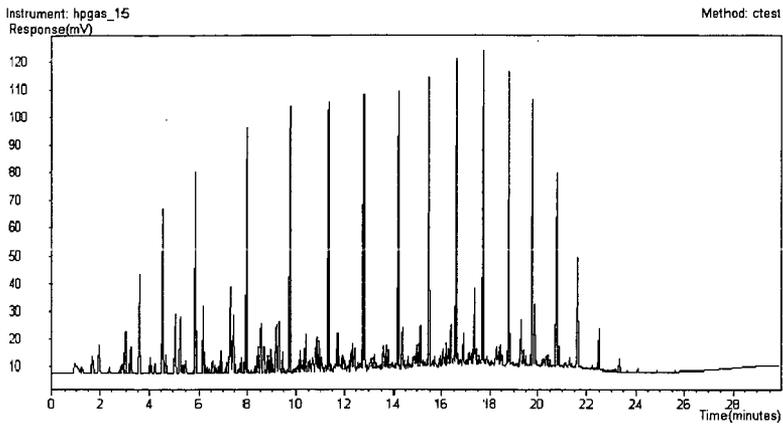


Figure 2. Results at a reduced density of 0.5.

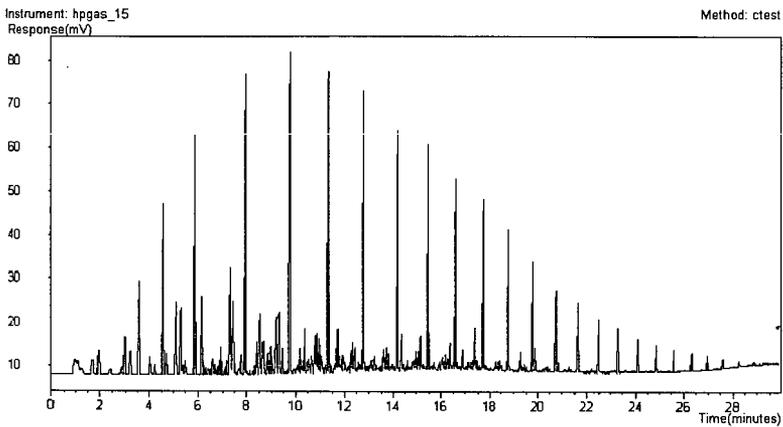


Figure 3. Results at a reduced density of 1.0.

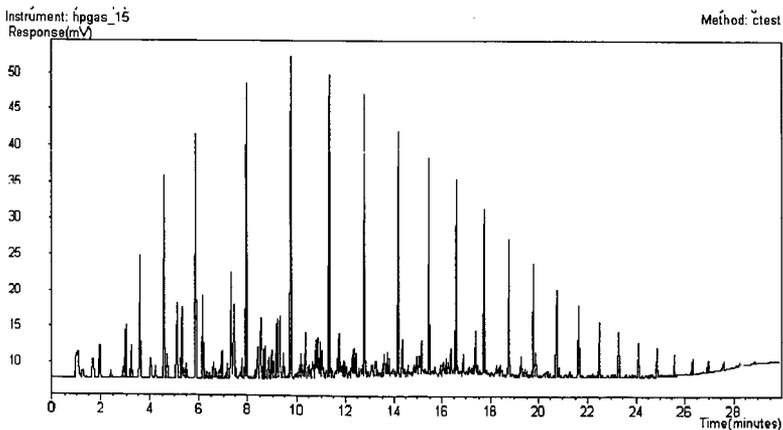


Figure 4. Results at a reduced density of 1.2.

CONCENTRATION OF HYDROCARBONS ADSORBED ON SOIL AND ROCK SAMPLES BY SUPERCRITICAL FLUID CHROMATOGRAPHY

Bruce W. Bromley, Victoria Corona, Paul A. Peadar

APTI Geosciences, 10450 Stancliff Road, Houston, Texas 77099

Extraction, Supercritical Fluid, Drilling Mud

ABSTRACT

A procedure for quantitatively extracting hydrocarbons ranging from C5 to C44 using carbon dioxide at supercritical conditions to yield a concentrated extract suitable for analysis by GC or GC-MS is described. Examples are presented of the application of this technique for the detection of petroleum hydrocarbons in samples from wells drilled with oil based mud and for the characterization of gasoline range contamination in water saturated soils.

INTRODUCTION

Isolation and concentration of hydrocarbons contained in soil and rock matrices by solvent extraction frequently results in the loss of low boiling components. Much of this loss results from the process of solvent removal by evaporation that must be performed in order to concentrate components prior to analysis. Also, presence of high concentrations of water in samples can interfere with the solvent extraction process. Supercritical fluid extraction (SFE) is the process by which a supercritical fluid removes analytes from a matrix and transfers them to a trap where the supercritical fluid is returned to a gaseous state and escapes, leaving the sample components behind. The sample is then rinsed from the trap with a small amount of solvent and transferred to output vials. A SFE procedure that overcomes difficulties of light end retention and water interference is described.

EXPERIMENTAL

A Hewlett Packard Model 7680T Supercritical Fluid Extractor was employed (1) using SFC grade carbon dioxide. The SFE trap was packed with a porous polymer selected to retain hydrocarbons while being inert to CO₂. If samples were wet, desiccant was mixed with the sample prior to extraction. Extractions described here were performed in two steps as follows:

Step 1

Density = 0.25 g/cc, sample cell temperature = 40°C

Static (closed cell) extraction time = 1 minute

Dynamic (open cell) extraction time = 5 minutes (5.3 cell volumes)

Rinse trap to collection vial with 500 µl dichloromethane

Step 2

Density = 0.84 g/cc, sample cell temperature = 40°C

Static (closed cell) extraction time = 1 minute

Dynamic (open cell) extraction time = 10 minutes (3.1 cell volumes)

Rinse trap to collection vial with 500 µl dichloromethane

RESULTS AND DISCUSSION

As the use of oil based muds becomes more prevalent in drilling oil wells, detecting oil shows can be problematic. Hydrocarbons ranging from C5 to C44 can be readily extracted from rock samples (conventional cores, sidewall cores, or cuttings) using SFE and examined for non-mud hydrocarbon presence by gas chromatography of the extract.

The restricted boiling range of oil based muds, as shown in Figure 1, allows detection of hydrocarbons boiling at higher or lower temperatures than those of compounds present in the mud. Figure 2 contains expansions of gas chromatograms of supercritical fluid extracts of sidewall cores from a single well; one containing only oil based drilling mud and the other containing mud and hydrocarbons contributed from the core. A profile of the data down this well yielded the results in Figure 3, showing the presence of non-mud hydrocarbons at approximately 11,250 ft. Testing of this well from the interval identified by SFE produced oil with the composition shown in Figure 4. This oil likely could not have been detected using conventional solvent extraction methods as solvent evaporation would likely have resulted in loss of most of this particularly volatile oil.

Hydrocarbon contamination in soils can be very difficult to quantitatively extract and characterize, especially when water or low boiling components are present. Hydrocarbons ranging from C5 to C44 can be readily extracted from soil samples using SFE (even if the soils are wet) and the resulting extract characterized by gas chromatography.

Figure 5 is a chromatogram of a hydrocarbon "free product" collected from a severely contaminated site. The goal of this investigation was to evaluate soil core samples surrounding this free product accumulation to determine the extent of contamination and to ascertain if more than one source may have contributed to the main accumulation.

The character of the soil in this site was sandy with small pebbles. In order to test the effectiveness of the SFE method, a sample of clean sand was soaked with water and then spiked with the free product illustrated in Figure 5. A chromatogram of the resulting SFE extract, shown in Figure 6, is indistinguishable from the original material. Segments from multiple cores were extracted by SFE and analyzed by GC. Sample amounts, SFE and GC conditions were held constant. Figure 7 is an example chromatogram of an actual core extract. Using the results of these analyses the extent of the contamination was clearly defined and significant differences in origin of material contributing to the free product were observed.

REFERENCES

- (1) Hewlett Packard 7680A Supercritical Fluid Extractor Operational Manual: Part Number 07680-90320. Edition 2, November, 1991.

FIGURES

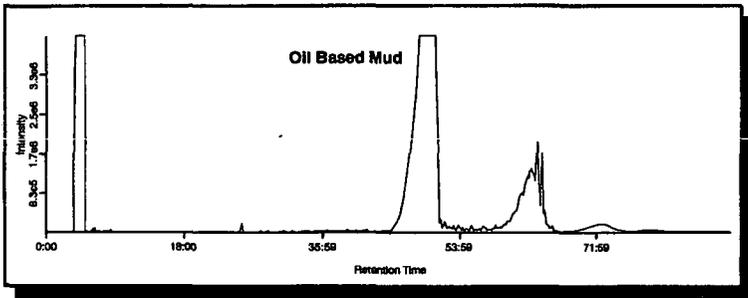


Figure 1 - Oil based Mud, Gulf of Mexico

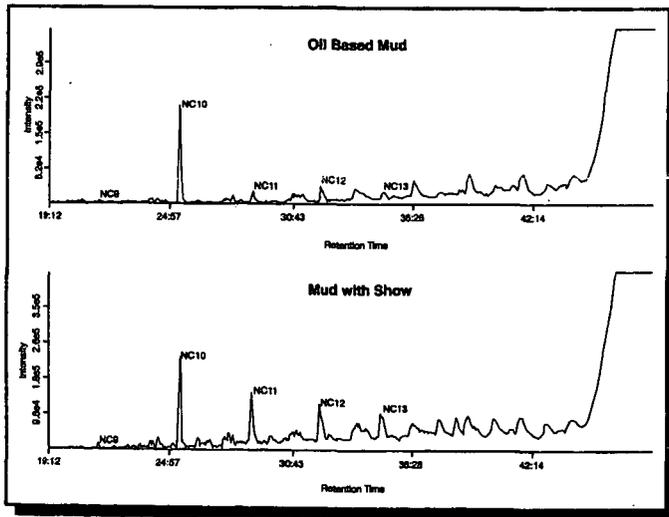


Figure 2 - Oil Based Mud and Mud with Show

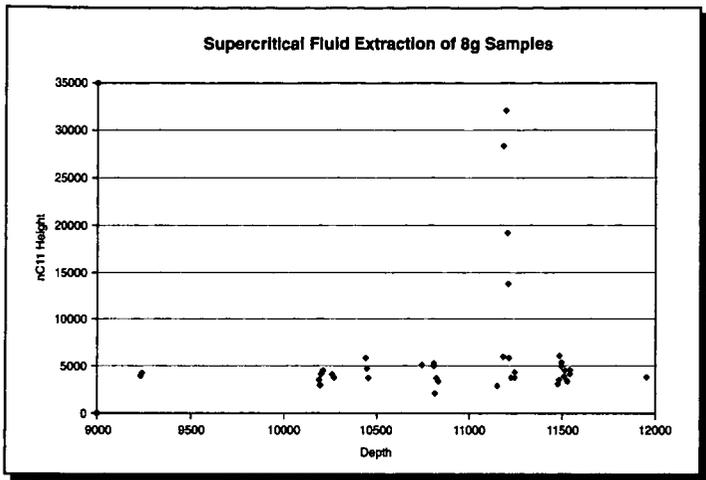


Figure 3 - Supercritical Fluid Extraction of 8 gram Core Samples

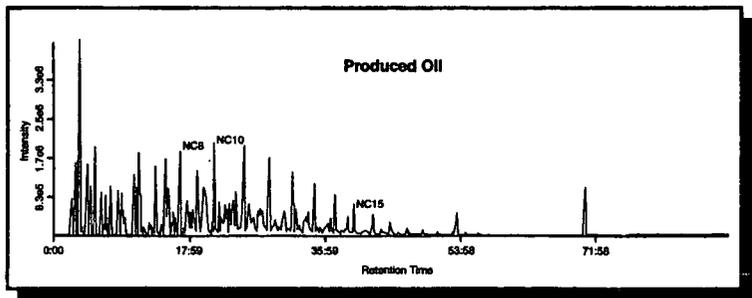


Figure 4 - Produced Oil

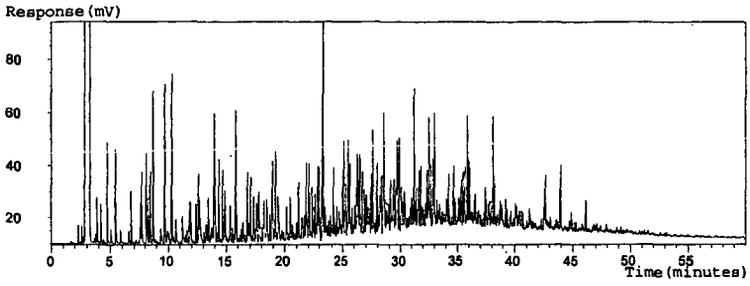


Figure 5 - Free Product

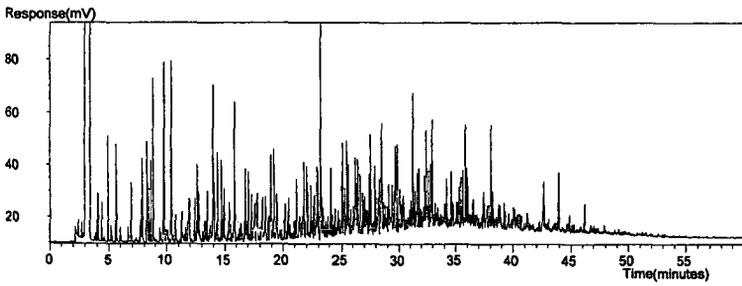


Figure 6 - Test of SFE Method to Remove Free Product From Similar Soil Matrix: 100ul Free Product on Water Saturated Sand

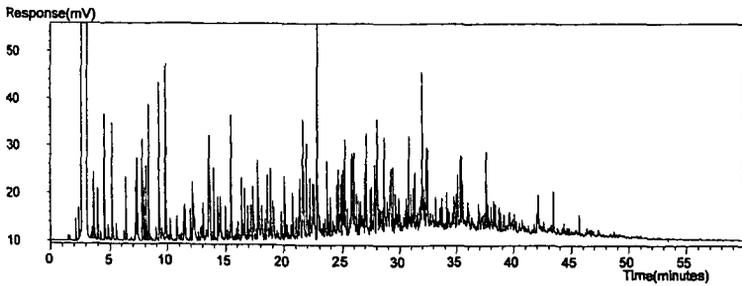


Figure 7 - Core Extract

THE USE OF SYNTHETICS IN WELL DRILLING FLUIDS FOR THE FOR OFFSHORE OIL FIELD

Burney Lee
Amoco Chemicals
Building 503-1330
150 West Warrenville Road
Naperville, IL 60563-8460

KEYWORDS: Synthetic Based Mud, Drilling Mud, Offshore Drilling

ABSTRACT

As Gulf of Mexico offshore drilling moves into deeper water and into more demanding conditions in terms of the depth and type of wells (deviated and horizontal), drilling muds providing higher lubricity and better hole stability are needed. Previously, oil based muds (OBMs) which are primarily based on diesel oil met this need. However, the on site discharge of cuttings from wells drilled using OBMs was banned in the early 1990's. At this time, synthetic based muds (SBMs) were introduced that are prepared using synthetically derived base fluids. SBMs were developed to provide an environmentally safe alternative drilling mud that would meet both the severe drilling mud requirements and the need for cuttings discharge into the ocean. These base fluids are chemically synthesized from the reaction of specific purified chemical feedstocks to give readily characterized products. The synthetic fluids used in the Gulf of Mexico today are linear alpha olefins (LAOs), isomerized olefins (IOs), polyalphaolefins (PAOs) and esters. A description of their chemistry, the benefits they provide and the regulatory issues surrounding their use is discussed.

INTRODUCTION

Oil exploration and production offshore continues at high rates today all around the globe. It is expected to continue at these rates for the next 5 years. In the Gulf of Mexico, this activity has moved out onto the continental slope and beyond to water depths over 6000 feet at locations that are many miles from shore support. These severe conditions coupled with difficult drilling through water sensitive formations push drilling technology to the limit and demand maximum performance in all aspects of the oil exploration process. To minimize difficulties encountered from drilling through water sensitive formations, invert emulsion based drilling muds are often used today.

Drilling muds are materials that are pumped through the rig's drill string and drill bit to remove drill cuttings from the bore hole during drilling operations. They also clean the bit, maintain desired pressure differential between the formation and mud and serve to stabilize the hole. For most drilling, the muds used are prepared by dispersing finely divided clays in water and are called water based muds (WBMs). These solids provide the desired suspending power to assist with cuttings removal and mud density to control pressure. However, WBMs tend to interact with water sensitive formations during drilling operations leading to bit balling and hole stability problems. These conditions can lead to a variety of costly difficulties for operators such as stuck pipe and reduced drilling rates.

To combat these problems when drilling through difficult or unknown formation conditions, an invert emulsion based mud is used. In an invert emulsion mud an organic based fluid forms a continuous outer phase surrounding an internal aqueous phase of finely dispersed droplets (an emulsion). The mud solids and other additives are also suspended in the organic phase. Because the external phase is insoluble in water, interactions with water sensitive formations are reduced. For this reason invert muds reduce sloughing problems, form better filter cakes and produce more stable bore holes. These attributes lead to formation of in-gauge holes that provide higher space velocity of the mud and thus better removal of cuttings. Cutting fines are also less likely to disperse in an organic phase, leading to fewer solids control problems. Lubricity, heat transfer and bit wear performance are also improved leading to enhanced drilling rates.

Invert muds are generally based on diesel or mineral oil and called oil base muds (OBMs). In the early 1990's, however, the discharge of drill cuttings into the ocean from wells drilled using

OBMs was prohibited. The inability to discharge cuttings greatly increased cost as they now had to be transported to a safe disposal site. This quickly produced a need for a high performance environmentally safe mud to allow for cuttings discharge. To meet this need, alternative inverse emulsion muds were developed using less toxic synthetic based organic fluids so that drill cuttings discharge would be allowed. These synthetic based muds (SBMs) are produced using synthetic fluids prepared from specific purified starting materials, and they lead to defined products that are essentially free of undesirable polycyclic aromatic hydrocarbons (PAHs). These materials are less toxic and more biodegradable than refined mineral oil products such as diesel oil. Synthetic fluids used today in the Gulf of Mexico to make SBMs include linear alpha-olefins, isomerized olefins, polyalphaolefins, and esters.

EXPERIMENTAL

In this section a brief description is given of the various chemistries used to produce synthetic fluids.

Synthesis of Linear Alpha Olefins (LAOs) and Isomerized Olefins (IOs)

Linear alpha olefins (LAOs) are prepared from the catalytic chain growth of ethylene on triethyl aluminum. After the chain growth step the larger alkyl groups are displaced from the aluminum either simultaneously with the chain growth step or in a separate step to give even numbered linear olefin products with carbon numbers from C₄ - C₂₀+ (Figure 1). The olefin double bond is formed between the first and second carbons of the alkyl chain (the alpha position) during the displacement step. Distillation provides clean cuts of the desired olefin products.

Isomerized Olefins (IOs) are produced from LAOs using an isomerization catalyst to move the olefin double bond from the alpha position to an internal position along the carbon chain (Figure 1). The internal double bond is distributed throughout the linear chain. Isomerizing an LAO lowers the pour point of the fluid.

Synthesis of Polyalphaolefins (PAOs)

Polyalphaolefins are prepared by the catalytic oligomerization of LAOs followed by hydrogenation of the material to remove the double bond (Figure 2). The oligomerization reaction produces dimers, trimers, tetramers, ... of the LAO. These oligomers have many different types of branched structures due to olefin rearrangements occurring during the oligomerization reaction. The structure in Figure 2 represents one possibility for a dimer oligomer.

Synthesis of Esters

Esters are prepared from the condensation reaction of alcohols and organic acids generally under acid catalysis conditions (Figure 3). Because the alkyl group associated with the alcohol or acid can be obtained from a variety of sources, many structures of esters are possible. For drilling mud applications the starting materials generally come from vegetable oils.¹

Refining of Mineral Oils

In contrast to the synthesis of organic fluids for invert emulsions, diesel and mineral oils are refined from crude oil (Figure 4). These traditional fluids are produced solely through physical separation processes and/or minor chemical reactions such as cracking and hydroprocessing. Refining eliminates most of the undesirable components of these mixtures but they still can contain significant amounts of PAHs.

DISCUSSION

The different chemistries available for making SBMs allows the operator choices when using the muds for drilling a well. The properties of synthetic fluids used in the Gulf of Mexico today to make drilling muds are given in Table I. The first generation of synthetic fluids were PAOs and esters. These materials provided technical performance that was equal to or better than that of an OBM, and because of their low toxicity, the drill cuttings could be discharged into the ocean. A second generation of synthetic fluids, LAOs and IOs, are used singularly or as blends with other synthetics. Cuttings produced when using these muds can also be discharged on site.

The lower viscosity of the second generation synthetic fluids leads to better rheological control in the muds and they have become the preferred materials of use. The ability to control low temperature viscosity becomes more important at deeper water depths where temperatures are in the low 30's (°F). Low temperature results in viscosity increases in the mud as it travels through the water column to the surface. IOs have lower pour points than LAOs (Table I) which allows for more rheological flexibility at lower temperatures.

SBMs are invert emulsion muds and thus are less reactive to water sensitive formations providing better hole stability, filter cake formation and drill rates. Enhanced hole stability provides better solids removal because of better mud velocities due to in-gauge hole and reduces maintenance time while tripping (moving in and out of the hole), casing and cementing. Stable filter cake provides lower drag and torque and less stuck pipe particularly while drilling deviated wells.

These benefits result in less nonproductive down time during drilling which can lower costs more than the enhanced rate of penetration SBMs provide. Operators choose SBMs to reduce risks and save time when drilling offshore through difficult water sensitive formations. With expensive drill rig day costs for these offshore operations, SBMs have proven themselves to have substantial economic benefits.²

The environmental properties of synthetic fluids used in SBMs are excellent because of their low toxicity and biodegradability. This is due to their controlled synthesis from purified feedstocks to provide products that are typically free of PAHs. Removal of these priority pollutants greatly reduces fugitive emissions and worker exposure.

The use of SBMs and cuttings discharge criteria are currently piggy backed onto EPA regulations governing WBMs. Because of this, SBM well drill cuttings can be discharged at the well site provided they pass the mysid shrimp toxicity test and are free of crude and diesel oil contaminants. The EPA has now defined synthetics as materials produced by the reaction of specific purified chemical feedstocks, as opposed to traditional base fluids obtained through refining processes. Also the EPA is working to develop regulations specific to their use.

All synthetic materials used to produce SBMs meet the EPA's current toxicity effluent limit guideline for cuttings disposal with a mysid shrimp LC₅₀ of 30,000 ppm suspended particulate phase. Because SBMs are invert emulsions, the organic phase tends to stick to the drill cutting's surface and can be carried to the sea floor. This changes the focus of toxicity concerns to the benthic communities that are exposed to these cuttings. There is currently no test accepted by the EPA to measure benthic toxicity of SBMs in the Gulf of Mexico.

The invert emulsion nature of SBMs also causes a problem measuring crude oil contamination in drilling muds using the current static sheen test developed for WBMs. The synthetic itself is lighter than water and can form a sheen giving a false positive, or stick to the cuttings and carry crude oil contamination to the sea floor producing a false negative. In contaminated SBM lab samples crude levels of up to 20 wt % have passed the sheen test.

The EPA recognizes the problems with the current regulatory toxicity and compliance monitoring tests developed for WBMs do not adequately address SBMs. The EPA is now working with the National Oceans Industry Association and the American Petroleum Institute to develop tests to measure the benthic toxicity for muds and crude oil contamination.

Synthetic fluids are biodegradable as measured by the difficult BODIS marine aerobic assay test. These studies show a trend that generally follows the molecular weight (MW) of the fluids for LAOs and IOs. The order of biodegradability generally increases as the MW decreases from that of PAOs to LAOs and IOs, PAOs < LAOs < IOs < esters (Figure 5). This trend is opposite that for mysid shrimp toxicity where toxicity tends to increase as MW decreases. When choosing a synthetic fluid for preparing a drilling mud a balance between biodegradability and toxicity must be reached. This balance is set by regulations governing the drilling area.

Other trends that follow the MW of synthetic fluids are skin compatibility and flash point, which increase as MW increases, and pour point and viscosity both decrease with decreasing MW.

CONCLUSIONS

Synthetic fluids have excellent physical properties suitable for producing invert emulsion based muds, SBMs. Their low toxicity provides improved worker safety, reduces environmental hazards and lessens fugitive emissions of PAHs. The number and type of synthetic fluids available give operators choices of performance when considering the use of SBMs for drilling wells. These materials are also marketed globally to meet drilling needs in the Gulf of Mexico and around the world.

REFERENCES

1. Peresich, R.L., Burrell, B.R. and Prentice, G.M., "Development and Field Trial of a Biodegradable Invert Emulsion Fluid," paper SPE/IADC 21935 presented at the 1991 SPE/IADC Drilling Conference, Amsterdam, Mar. 11-14, 1991.
2. Burke, C. and Veil, J.A.: "Synthetic-based Drilling Fluids have many Environmental Pluses," paper presented at the 1995 SPE/EPA Environmental Conference, Houston, TX, Mar. 27-29.

Figure 1: Synthesis of LAOs and IOs

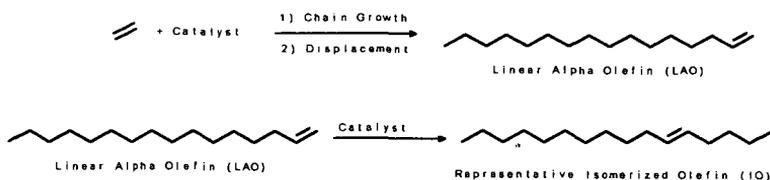


Figure 2: Synthesis of Polyalphaolefins

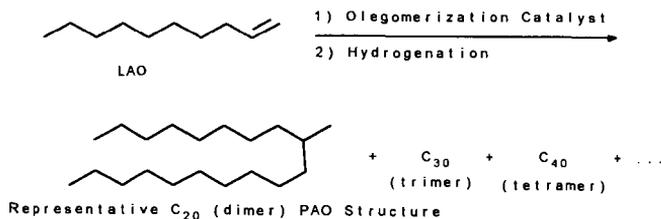


Figure 3: Synthesis of Esters

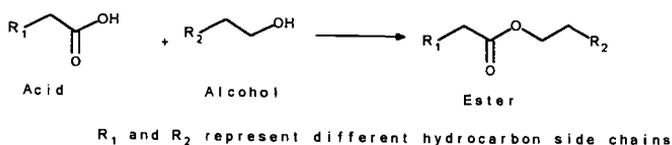


Figure 4: Refining of Diesel and Mineral Oils

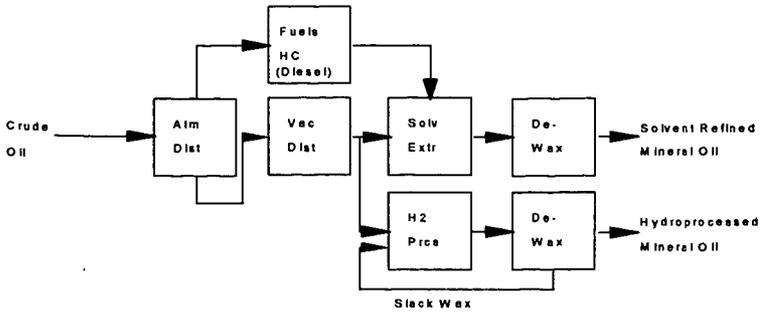
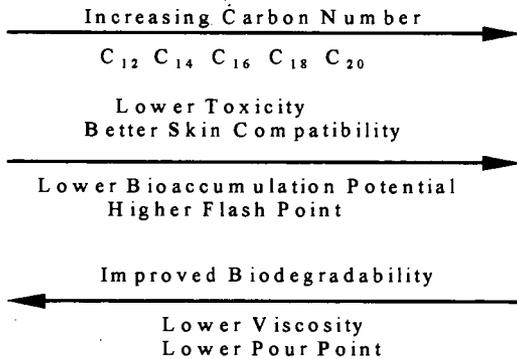


Table I: Physical Properties of Synthetic Fluids

	Viscosity (cSt)		Pour Point (°C)	Flash Point (°C)
	@ 40 °C	@ 100 °C		
2 cSt PAO	5.50	1.80	<-65	155
4 cSt PAO	16.8	3.90	<-65	215
Ester	5.13	1.82	-33	170
C1416 LAO	2.09-2.11	0.97	-12 to -9	114
C1618 IO	3.09-3.37	1.30-1.39	-24 to -14	134-137
C1618 LAO	2.98-3.08	1.27-1.29	3-9	146

Figure 5: Trends in Synthetics for Biodegradability and Toxicity with Carbon Number



THE DETECTION OF CRUDE OIL CONTAMINATION IN SYNTHETIC BASED DRILLING MUDS

Jim Story
Amoco Corporation
Building 600-2034
150 West Warrenville Road
Naperville, IL 60563-8460

Burney Lee
Amoco Chemicals
Building 503-1330
150 West Warrenville Road
Naperville, IL 60563-8460

KEYWORDS: Synthetic Based Mud, Crude Oil Contamination, Detection

ABSTRACT

In response to a need for a simple compliance monitoring test for crude oil contamination in synthetic drilling muds an inexpensive and rig-worthy ultraviolet (UV)/chromatography method was developed. The method utilizes prepackaged silica gel solid phase extraction columns to separate various mud components from the synthetic base and crude oil contaminants using common organic solvents. The synthetic fluids along with any crude oil are eluted down the column. Observance of any UV induced fluorescence along the column can be attributed to crude oil contamination as synthetic base fluids do not contain fluorescent entities. Detection limits to 0.05 wt% crude oil contamination were found.

INTRODUCTION

The offshore drilling conditions in the Gulf of Mexico are demanding with water depths up to 6,000 feet through reactive clays and around salt formations often using deviated drilling techniques. These severe conditions require the use of inverse emulsion drilling muds or oil based muds (OBMs) that provide optimum drilling performance. In an invert emulsion mud, there is continuous outer organic phase that contains the mud solids and an internal aqueous phase dispersed (emulsified) as separate droplets. The continuous organic outer phase is water insoluble and thus reduces the amount of interaction of the drilling mud with water sensitive formations leading to better solids control, cuttings removal, hole stability and drilling rates.

Traditionally the invert emulsion muds used diesel or mineral oil for the organic phase, OBMs. However, on site discharge of drill cuttings from drilling rigs produced from wells using OBMs was banned in the early 1990's. This created a need and lead to the development of synthetic based muds (SBMs). These drilling muds are also inverse emulsions and provide the same or improved drilling characteristics as an OBM. A key advantage to their use is that the low toxicity of the synthetic fluid resolves many of the environmental issues associated with the use of invert muds and in particular allows for discharge of the drill cuttings. The low toxicity also reduces pollution hazards and worker exposure to diesel oil.

Current EPA regulations do not specifically address SBMs today but the EPA is working with industry groups, the American Petroleum Institute (API) and the National Oceans Industries Association (NOIA), to develop these regulations. An important compliance test needed for WBMs is one to detect crude oil contamination. The static sheen test developed for water based muds (WBMs) is ineffective for SBMs. The synthetic itself is lighter than water and can form a sheen giving a false positive. Also because the mud is an invert emulsion mud with a water insoluble external phase, the mud can stick to the drill cutting's surface and be carried to the seafloor hiding any contamination to produce a false negative. SBMs containing up to 20 wt% crude oil contamination have shown negative static sheen tests in lab tests. A joint API/NOIA analytical work group with EPA participation was formed to find a suitable test to determine crude oil contamination in SBMs. The suggested requirements for the analytical method were:

- comparable detection limits to static sheen test, 1 wt% crude
- suitable for rig site (rig motion, power fluctuations, rugged, small spaces)
- single pass/fail limit
- minimal false positives
- works with a variety of crude oils and synthetic base oils
- easy operation (minimal training required)
- reasonable costs.

Using these criteria, a simple effective chromatographic test method using black light fluorescence detection for crude oils was developed. It uses readily available rugged equipment, prepackaged activated silica solid phase extraction columns, and common solvents. The test meets the detection requirements and is easy to run using minimal space and simple equipment.

EXPERIMENTAL

Determination of Crude Oil Contamination in Drilling Fluids - Field Method

The method is intended for the on-site measurement of total crude oil in new or contaminated drilling fluids. It relies upon fluorescence of the aromatics in the crude oil for detection and measurement of crude oil contamination. Aromatics are visualized by fluorescence on an active silica column during separation from other components of the sample. The liquid portion of the drilling fluid is separated from the mud solids by settling. Centrifugation may be necessary in rare cases to separate the liquid and solids. One drop of the liquid is carefully placed on an active silica solid phase extraction (SPE) column using a pipet or medicine dropper. One half ml. of isopropanol is added and the column is placed under a black (mercury vapor UV) light. The fluorescing aromatics in the sample are observed as they move down the column and the concentration of crude is determined by visual comparison of the sample fluorescence with that of standards prepared in hexadecane solvent from the suspect crude. Alternatively the fluorescence intensity can be compared to a polynuclear aromatic standard reference, such as phenanthrene. This might be done in those cases where no samples of the potential crude contaminant exist, as is the case when drilling through new formations.

The apparatus consists of solid phase extraction (SPE) columns packed with active silica. For this work we used SPE columns manufactured by J.T. Baker and marketed by a number of distributors. They were used as received. These columns will become deactivated if saturated by water, so they should be kept carefully sealed from atmospheric humidity until a few minutes before use. A 300mw black light emitting wavelength 254 nm was used for visualization. Isopropanol was purchased as chromatographic grade. Phenanthrene and hexadecane were reagent grade.

This work was part of a collaborative test study to determine the best ways to identify crude contamination of drilling muds. Sixty samples of muds were prepared from five different crude oils and three different fluids by a drilling company. The fluids used to prepare the samples were enhanced mineral oil fluids (EMO), internal olefin fluids (IO), and linear alpha olefin-ester fluids (LAO). Crude oil concentrations in the prepared samples were 0.5%, 1%, 2% and 5% v/v. Samples of the presumably crude-oil free mud were also provided. The crudes were chosen for variety. Four of the five crudes were fairly typical, fluoresced strongly, and could be easily detected. Most crudes would be expected to behave in this way. The fifth crude, labeled crude D, was extremely light and possessed little aromatic content. Instead of the normal brown to black color it was yellow, suggesting that it was more typical of a condensate than a real crude. Gas chromatographic analysis confirmed that the crude contained only the light fraction, and was thus not typical of what might be encountered while drilling.

In this work the fluorescence intensity was used to determine the presence or absence of crude oil, and to rank the samples in order of crude concentration. Presence of crude was defined as observing a fluorescence intensity equal to or greater than that of a 0.5% solution of the same crude diluted with hexadecane and analyzed in the same way. A sample of the uncontaminated mud was also run to define a blank level.

RESULTS

In order to define a detection limit for the method, a series of dilutions of phenanthrene in hexadecane were run. These experiments showed the limit of detectability for the method to be approximately 50ppmw/v phenanthrene.

As mentioned above, one of the crudes, the crude labeled D, used in preparing the samples was, in actuality, a condensate and not a realistic sample. The aromatics level in this crude was very low and greater difficulty was encountered in detection of this crude than any of the others.

Drilling fluids typically also contain additives which may fluoresce. These additives are often very polar structures. Samples of all three fluids showed varying levels of a fluorescing material which was strongly retained at the top of the silica column and resolved chromatographically in the SPE column from the crude oil aromatics. All twenty spiked samples of the enhanced mineral oil fluids tested positive for at least 0.5% crude oil. All of the samples fluoresced at levels consistent with their crude oil concentration. The blank mud showed no fluorescence, except for the small band at the top of the column, presumably due to the additive fluorescence. Each of the crude oil/mud samples also showed the additive fluorescence band at the top of the column.

When the internal olefin (IO) based mud was analyzed, it was found that the blank mud containing supposedly no crude actually contained a small amount of fluorescing material. Analysis of the mud liquid phase by GC-MS showed that the mud was contaminated with polycyclic aromatics (PAH's). It was later discovered that this mud actually was a field mud. The presence of PAH's created a significant blank fluorescence which had to be considered in evaluating the actual samples. However interference was minimal and analysis of all twenty spiked IO samples showed all samples to test positive for at least 0.5% crude, except for 2 of the 0.5% samples, which were only marginally positive. One of the two samples was the 0.5% sample of the condensate, crude D.

The LAO-ester fluid mud samples were also prepared from the same used mud as the IO samples. All spiked LAO samples tested clearly positive again with the exception of the 0.5% sample of crude condensate D.

CONCLUSIONS

All samples correctly tested positive at the required 1.0% level. The test resulted in clear positive results for all but three of the sixty spiked samples at the 0.5% level. Two of the three questionable results were for the atypical crude D, in reality a condensate. Only one of the sixty spiked samples would have been judged erroneously to be below the 0.5% level, and that was the 0.5% LAO sample of crude D. Two of the three supposedly clean muds were found by this method in fact to be contaminated with low levels of crude oil. This was confirmed by GC-MS analysis of the mud fluid and by admission of the preparer that the mud had already been used in a formation. The test is thus very sensitive, sensitive enough to detect ppm levels of crude oil in muds. For accuracy in predicting contamination at or above a certain level, a comparison or reference standard, such as a solution of crude oil or phenanthrene, must be used. Any sample producing fluorescence above that standard is judged to test positive.

This method has several advantages:

- It is capable of being used at the drilling site since it requires minimal equipment and training and uses inexpensive and safe equipment and material
- It is rapid (<5 minutes), simple, and inexpensive
- It works with all synthetic fluids and gives no false positives at the 0.5% level. Polar surfactants which fluoresce do not interfere because they are chromatographically separated from the fluorescing crude components.
- The threshold limit for positive report can be set at any level above about 0.1% crude oil because of the sensitivity of the method.

REVERSE PHASE EXTRACTION METHOD FOR DETECTING OIL CONTAMINATION IN SBM

Jerry L. Sides and Kerry Spilker
Texaco EPTD, Briarpark Technical Facility
Houston, TX

Keywords: synthetic base drilling mud, static sheen test, C₁₈ SEP PAK®.

ABSTRACT

Waters Associates SEP PAK® reverse phase cartridges are used to separate and collect crude oil contamination from synthetic base drilling mud (SBM) in a quick and easy procedure for subsequent blacklight (ultraviolet) detection. The method is intended as a positive/negative test to determine the presence of crude oil in SBM prior to dumping drill cuttings overboard in the offshore environment. The test should be comparable to the accepted static sheen test presently used for water base muds.

INTRODUCTION

The regulatory permitting agencies that oversee the offshore oil and gas operations depend on a static sheen test (1) to determine if drill cuttings recovered from the drilling mud are contaminated with crude oil prior to dumping cuttings in the open sea environment. Crude oil contamination can result when an oil bearing geologic formation has been penetrated during the drilling operation. The static sheen test is simple and will indicate if the cuttings contain oil that could cause a sheen on the sea surface. The test is adequate when conventional water based drilling muds (WBM) are used. If the water based mud is replaced with an oil based mud (OBM), the drilling operation is greatly enhanced when drilling certain geologic structures, deviated wells and horizontal wells. Such muds have crude oil or a refined oil as the continuous phase. These OBM's and the cuttings separated from them can not be dumped in the offshore environment because of their toxicity. The industry has found certain synthetic solvents such as internal olefins (IO), esters, linear alpha-olefins (LAO) and enhanced mineral oil (EMO), to be environmentally friendly substitutes for conventional OBM's which are not environmentally acceptable. Industry studies have shown that crude oil contaminated cuttings in SBM systems do not produce a static sheen as normally seen for oil contaminated cuttings from WBM. These synthetic base mud (SBM) systems contain chemical additive packages to stabilize the drilling fluid emulsion and to maintain proper drilling mud properties such as viscosity and gel strength. The emulsifier package interferes with the static sheen test by emulsifying any oil contamination on cuttings from the SBM systems. A test that is similar to the static sheen test for WBM systems is needed by the industry to insure that oil contaminated cuttings from SBM systems are not dumped into the sea.

An industry work group (API-Synthetic Based Mud Analytical Work Group) has determined that the new test should have certain desirable characteristics. The test should work well on an offshore platform; have a detection limit comparable to the static sheen test ($\geq 0.5\%$ crude oil contamination); have reasonable cost; be reproducible; use equipment that is easy to operate with a minimum of expertise; work well with a variety of crude oils and SBM's; not be prone to false positives; and have a pass/fail limit.

EXPERIMENTAL

A whole mud sample is taken at the drilling site for this test. It is necessary to have the nonaqueous phase in a polar solvent to pass through the C₁₈ SEP PAK® for separation of the emulsifier from the crude oil components. After looking at several solvents, it was found that extraction of the whole mud with isopropyl alcohol (IPA) uniformly extracts the crude oil from the mud system and also has enough polarity to carry the emulsifiers through the C₁₈ SEP PAK® while leaving the crude oil behind. IPA also has the added benefit of being a familiar, available and relatively safe solvent for on-site use.

The developed procedure has the following steps for extraction.

1. Transfer 0.10 ml of SBM sample to a large (16x125-mm) test tube and add 10 ml of solvent grade IPA. Stir the solvent and SBM thoroughly (10 sec. on a Vortex mixer) and let stand to allow the solids to separate.
2. Filter about 4 ml of the extract from the test tube through a syringe cartridge filter (PTFE syringe type filter, 25-mm, 0.45- μ m) into a second test tube.
3. Precondition a C₁₈ SEP PAK® cartridge by attaching to a five-ml syringe and pushing 3 ml of solvent grade IPA via the syringe through the SEP PAK®.
4. Transfer 0.50 ml of the extract (Step 2) to the syringe barrel and add 3 ml of IPA. Push the extract and IPA through the preconditioned C₁₈ SEP PAK® cartridge to separate any crude oil contamination from the extract. Push another 2 ml of solvent grade IPA through the SEP PAK®.

5. Place the C₁₈ SEP PAK[®] cartridge under the blacklight and observe the absence or presence of fluorescence as compared to a blank. Presence of fluorescence is a positive test for crude oil.
6. A blank is prepared by carrying out the procedure on a sample of the SBM as sent from the supplier (has not been circulated downhole).

To assure the quality of the IPA and filters, a reagent blank is prepared by passing 5 ml of the IPA through a PTFE cartridge filter and collected in a small test tube. Add 0.5 ml of the filtered IPA and 3 ml of IPA to a syringe and push through a preconditioned SEP PAK[®] cartridge (step 3 above). Add 2 ml of IPA to the syringe barrel and push it through the cartridge. Check the SEP PAK[®] cartridge under the black light for fluorescence. No fluorescence should be observed if the IPA and the filter are of good quality.

The procedure was carried through on laboratory prepared SBM drilling fluids that had been spiked with known amounts of crude oil. The laboratory samples were comprised of sets of three SBM types, an EMO, an IO, and a mixed Ester/LAO. Each SBM was spiked with five different crude oils at four different oil concentrations (0.5, 1.0, 2.0, 5.0 % by wt) resulting in 20 spikes and a base mud blank for each of the three SBM sample sets. The sample designations and API gravities for the crude oils are: A, 28°API; B, 31°API; C, 36°API; D, 51°API; E, 24°API. Simulated distillations of the five crude oils by gas chromatography (ASTM D2887) were performed to characterize and compare the relative boiling point and molecular size distributions.

Five observers independently determined the presence or absence of fluorescence by comparing the SEP PAK[®] cartridges developed for each of the prepared oil spiked SBM's to a blank in a view box with a built in UV light source. The observation was made by placing the test cartridge next to a blank cartridge corresponding to the SBM with no oil spike.

RESULTS AND DISCUSSION

Fluorescence of crude oil by ultra-violet electromagnetic energy is due to molecular excitation of multi-ring aromatic hydrocarbons and heterocyclic compounds. Non-aromatic, but highly conjugated compounds may also fluoresce (2), and such compounds and smaller heterocyclics may exist in the SBM emulsifier packages. The reverse phase extraction method passes these more polar emulsifiers through the SEP PAK[®] cartridge while retaining the less polar aromatics and heterocyclics found in crude oil. This test assumes that crude oil compounds are retained on the SEP PAK[®] cartridge, and that the concentration of fluorescent compounds in the crude oil are high enough for detection at about 0.5% or higher concentration of crude oil in the SBM.

The observation of fluorescence by comparing cartridges is somewhat subjective when there is a very low concentration of oil on the developed cartridge. Absence of fluorescence was indicated by a "0" (negative test result) and presence by a "1" (positive test result). Five observers were selected to see if a consensus result would be found in each case. The observers were to report a positive test if the sample cartridge showed "more fluorescence" than the blank. Three of the observers were experienced laboratory experimentalists while two were contract technicians with about one-year laboratory experience. Tables 1 through 3 are summaries of the results of the five observers' readings for each of the three sets of SBM samples. Each sample was given the sum of the five observers' readings. Therefore, a summary value of "0" indicates that the reading was "0" (negative) for all five observers; and a "5" indicates the reading was "1" (positive) by all five observers. Values of 1, 2, 3, and 4 show non-agreement among the observers and indicate the difficulty in determining fluorescence for these samples.

The tabulated results show the test summary by SBM. The IO based mud (Table 2) appears to be slightly more sensitive to crude oil detection than the other two systems (Tables 2 and 3), since fluorescence was more often observed at the 0.5 % concentration.

Crude oil D (51°API) was only detected once at concentrations up to and including 5% in any of the SBM systems. The API gravity and lack of fluorescence leads to the belief that the oil is paraffinic with a low concentration of multi-ring aromatic molecules present. The gas chromatogram (Figure 1) of crude oil D confirms this idea. The chromatogram shows the relative carbon numbers for the straight chain paraffins. The carbon numbers and retention times are consistent in all of the figures. Crude oil D shows very little material after C 24.

Contamination of 2% or higher is consistently detected for crude oils A, B, C, and E in all of the drilling muds. The crude oils A, B, C, and E are similar in fluorescence sensitivity as shown by the split negative and positive readings by the observers at the 0.5% and 1.0% concentrations in the various SBM's. Gas chromatograms (Figures 2-5) for these oils are similar and contain significant amounts of high molecular weight oil (>C 24) that probably contains multi-ring aromatic compounds.

IV. Conclusions

The reverse phase extraction method for determining crude oil contamination in SBM's appears to have merit as a possible field test. The inability to detect the high API gravity paraffinic oil is obvious. Aside from this, the test meets the desirable characteristics determined by the industry

study group. It is comparable to the static sheen test in detection limits, can be performed offshore with reliable equipment by field personnel, is reasonably low cost, and has a single pass/fail end point.

The inconsistency of this test from one crude oil to the next is not unexpected. There is no standard crude oil that can be representative of all crude oils. This field test is to be applied during exploratory drilling where the oil encountered will be unknown. It is important to note that the toxic components in petroleum hydrocarbons are generally thought to be the multi-ring aromatics or polycyclic aromatic hydrocarbons (3). These components produce fluorescence. The paraffinic components do not fluoresce under the blacklight, but the paraffinic compounds are not detrimental to the environment. Effectively, the test could be determining the presence of the components that are environmentally unfriendly. The inability to detect high API gravity oils that are primarily paraffinic may not be a draw back to using this test.

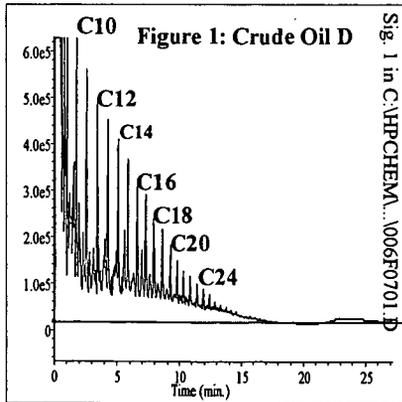
REFERENCES

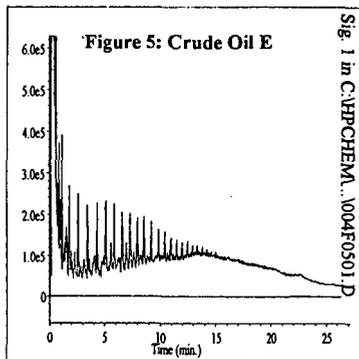
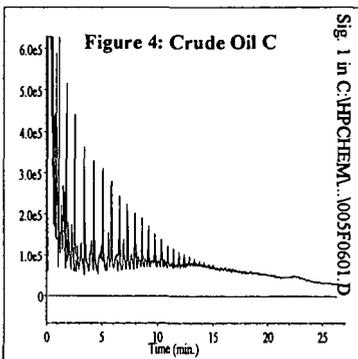
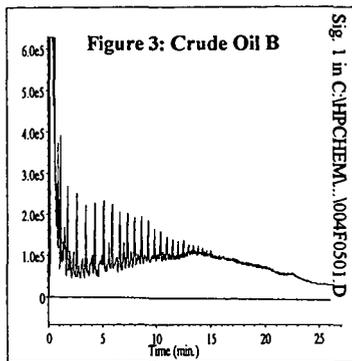
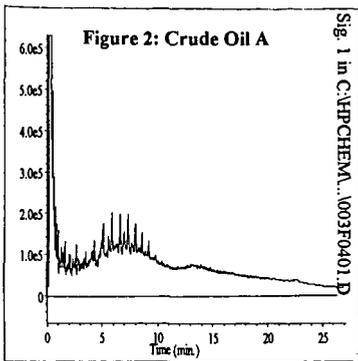
- (1) Weintritt, D. J.; Qaisieh, N. S.; and Otto, G. H. *Oil & Gas Journal* 1993, 91, No. 18, 77-78, 80, 82, 84.
- (2) Guilbault, G. C.; *Practical Fluorescence*; Marcel Dekker, Inc.; New York, 1990.
- (3) Neff, J. M.; *Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*; Applied Science Publishers Ltd.; London, 1979.

Table 1: EMO SBM					
Oil	0% Oil	0.5% Oil	1.0% Oil	2.0% Oil	5.0% Oil
A	0	0	4	4	5
B	0	0	0	4	5
C	0	0	2	3	5
D	0	0	0	0	0
E	0	1	3	5	5

Table 2: IO SBM					
Oil	0% Oil	0.5% Oil	1.0% Oil	2.0% Oil	5.0% Oil
A	0	2	1	5	5
B	0	4	2	5	5
C	0	2	5	5	5
D	0	0	0	0	0
E	0	2	5	5	5

Table 3: Ester/LAO SBM					
Oil	0% Oil	0.5% Oil	1.0% Oil	2.0% Oil	5.0% Oil
A	0	0	3	5	5
B	0	0	3	5	5
C	0	2	3	5	5
D	0	0	1	0	0
E	0	1	5	5	5





THE FATE OF SCALE INHIBITORS IN OIL/GAS PRODUCTION

Jianjun Xiao, Amy T. Kan, Mason B. Tomson

Department of Environmental Science and Engineering, Rice University, Houston, TX 77005

Keywords: Phosphino-polycarboxylic acid (PPCA); Potentiometric titration; Calcium phosphino-polycarboxylate.

ABSTRACT

The thermodynamic properties of the scale inhibitor, phosphino-polycarboxylic acid (PPCA) and of its calcium complexes under conditions of high ionic strength and high temperature have been studied by potentiometric titration. Applying the electrostatic theory for polymers gives dissociation constant K_M for $ML \leftrightarrow M + L$ as $pK_M = pK_{Mint} + zf\theta_u$ where L stands for polymer ions, pK_{Mint} stands for intrinsic constant, z is the charge of the small ion M which can be H^+ and any metal ion, f is a parameter related with polymer characteristics and θ_u stands for the dissociation fraction of the polymer ion. A general equation for f is obtained: $f = 2.757 - 1.056I^{1/2} + 0.220I$ where I stands for ionic strength. The intrinsic constant for proton dissociation pK_{Hint} (when M is proton) is assumed to be: $pK_{Hint} = 4.798 - 0.954I^{1/2} + 0.2461 - 187.8/T$ where T stands for temperature in Kelvin. For calcium ion (M is Ca^{2+}), the intrinsic constant is: $pK_{Mint} = 3.928 - 2.631I^{1/2} + 0.7381 - 1099.4/T$. Also investigated are calcium-PPCA precipitation and dissolution. An empirical dissolution reaction is observed as: $Ca_3(A-A-A)_2(s) \leftrightarrow 3Ca^{2+} + 2(A-A-A)$, of which the solubility product $K_{sp} = [Ca]_3[A-A-A]^2$ can be expressed as: $pK_{sp} = 34.02 - 0.832I^{1/2} + 0.7621 - 6839.5/T$. Here, $(A-A-A)$ stands for an arbitrary unit of three functional groups (A). Therefore, PPCA concentration and its species distribution in any oil/gas production can be predicted by these equations and consequently the efficiency of PPCA as a scale inhibitor for a specific well can be evaluated and can be applied in squeeze design.

INTRODUCTION

Phosphino-polycarboxylic acid (PPCA), $H-(CH_2CHCOOH)_x-POOH-(CH_2CHCOOH)_y-H$, is different by only one group (phosphino group) from polyacrylic acid (PAA). It is widely used in oil fields as a scale inhibitor because of its good quality, low cost and environmental acceptability. Chang and Patel (1) have studied PPCA under typical boiler conditions and found that as a scale inhibitor (for $CaCO_3$, calcium hydroxyapatite and iron oxide), PPCA has advantages over PAA and phosphonates in thermal stability, dispersion and iron transport. Some other research (2,3) implies that PPCA or its derivatives have potential to be multifunctional inhibitors in boilers, cooling water formulations and oil wells. Rabaoli and Lockhart (4) have investigated the precipitation conditions and precipitate yield of CaPPCA and its solubility in a brine system. The sharp contrast of high solubility to the observed very low concentration of inhibitors in the return produced water of oil wells was explained as a kinetically controlled dissolution.

Taking into consideration the great potential of application of PPCA in many aspects and the variety of the conditions of those applications, this paper tries to explore the fundamental aspects of the solution chemistry of PPCA under various harsh conditions and to provide basic data for its application. This includes constants of proton dissociation, metal complexation of PPCA, and precipitation/dissolution of CaPPCA. They all together determine the efficiency of PPCA as a scale inhibitor and the lifetime of a squeeze.

In structure, PPCA is similar to PAA which is used as a standard polymer for studying properties of linear polyelectrolytes. For this reason, the basic concept in this study is transplanted from those developed for PAA. On the base of research by Debye and Huckel (5), Falkenhagen (6), Kirkwood and Poirier (7), Hill (8), Hermans and Overbeek (9), Tanford (10,11) et al, applying electrostatic theory to PPCA, one can easily derive the following hypothetical reaction and their constant expressions:



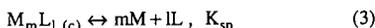
$$\begin{aligned} pK_M &= -\log \frac{[M][L]}{[ML]} = pM - \log \frac{\theta_u}{\theta_M} \\ &= pK_{Mint} + zf(R, r, \kappa)\theta_u \end{aligned} \quad (2)$$

where L is an arbitrary combined unit of z functional groups (monoacids, A), $L = zA$ and $[L] = [A]/z$, and ML is electroneutral. M with charge z represents any cation which can associate with PPCA. For instance, when M stands for proton, H^+ , $z=1$ and L is just one group while for Ca^{2+} , $z=2$ and L is an arbitrary unit of any two groups. The parameter f is a function of the polymer size R , small cation (M) size r and Debye-Huckel parameter κ which is then related with ionic strength. Of course f is also a function of temperature. pK_{Mint} is the so-called intrinsic constant. θ_u stands for dissociation fraction of PPCA, $\theta_u = z[L]/C_A = [A]/C_A$ while θ_M stands for

the association fraction of PPCA by M, $\theta_M = z[ML]/C_A$ with C_A meaning total PPCA concentration in normality.

The second term in equation 2 represents the electrostatic effect of neighboring dissociated groups on the given group. Under certain conditions, R might be independent of the dissociation fraction so that $zf(R, r, \kappa)$ in the second term of equation 2 might be a constant through a titration. Therefore, pK_M is linear to dissociation fraction θ_u . Applying this to titration data can yield pK_{Mint} and $f(R, r, \kappa)$ from a plot of pK_M versus θ_u .

After pK_M s are available, precipitation/dissolution of metal polymer precipitates can be analyzed. However, this equilibrium is very complicated and no definition of solubility product for metal polymer precipitates is available from literature. Therefore, a hypothetical precipitate and its dissolution equilibrium are assumed to be:



$$K_{sp} = [M]^m [L]^l \quad (4)$$

where L is an arbitrary unit (statistically) of x As (univalent). Therefore, $L=xA$ and $[L]=[A]/x$. Furthermore, the electroneutrality requires $xl=mz$. Thus equation (4) becomes:

$$K_{sp} = [M]^m [A]^l \left(\frac{1}{mz}\right)^l \quad (5)$$

or

$$\begin{aligned} \log[A] &= \left\{ \frac{\log(K_{sp})}{l} - \log\left(\frac{1}{mz}\right) \right\} - \frac{m}{l} \log[M] \\ &= \text{constant} - \frac{m}{l} \log[M] \quad (6) \end{aligned}$$

Equation (6) shows that m and l can be obtained from the plot of $\log[A]$ vs. $\log[M]$. In this plot, the slope is $-m/l$. Since m, l and x should be integral, m/l is the common fraction of the slope. For example, if the slope is $-m/l=-0.33$, take $l=3$, $m=1$, and $x=0.33z$, thus z must be 3; if $-m/l=-1.5$, then take $l=2$, $m=3$, and $x=1.5z$.

EXPERIMENTAL

Chemicals: Phosphino-polycarboxylic acid (PPCA) was from FMC Co., 50%, MW ~3600. NaCl, used for adjusting ionic strength, was from Fisher Scientific Co., 99.4%. $CaCl_2 \cdot 2H_2O$, used for titration, precipitation and stock solution, was from Fisher Scientific Co., 76.1% ($CaCl_2$). Acid/base titrant of 1.600 ± 0.008 N and 0.1600 ± 0.0007 N NaOH cartridges and EDTA titrant cartridges were from HACH Co. All stock solutions were made with deionized water.

Potentiometric titration: Solutions of different concentration of PPCA with or without Ca^{2+} were titrated by NaOH in a jacketed beaker. The ionic strength of the solutions was adjusted by NaCl and the temperature was monitored by a temperature circulator within ± 0.1 °C. Each titration was finished under a fixed condition. pH was measured by an Accumet model 15 pH meter (Fisher Scientific Co.) with a Ross combination pH electrode (Orion Inc.). Before each titration, the pH electrode was refilled with new filling solution (Orion Inc.) and was kept in a storage solution at the same temperature for about 2 hours to be stabilized. Immediately before and after each titration, the stabilized pH electrode was calibrated. All operations relevant to titrations were run under N_2 atmosphere.

Precipitation/solubility product: Precipitation was carried out by slowly titrating PPCA solution [using a syringe pump (Harvard Co.)] into a bulk solution of 1N NaCl- $CaCl_2$ -1mM NaAc at pH5.5 and 70°C under stirring. The Ca^{2+} concentration was made so that after equivalent precipitation, the remaining Ca^{2+} concentration in solution was 0.1M. pH was simultaneously monitored at pH 5.5. After the titration precipitation was finished, the slurry was kept stirring about 5 hours and then transferred into an Amicon cell fitted with an Amicon YM 10 membrane to do diafiltration/maturation under 70°C and stirring for a week with an inflow of stock solution of 1N NaCl-0.1M $CaCl_2$ -1mM NaAc at pH5.5 and 70°C. The flow was monitored by a pump (Pharmacia LKB) at about 90 ml/hr. After a week, the produced solids-solution mixture was kept in a 70°C oven for static maturation. Samples were taken at different stages to study the evolution of the stoichiometry of the precipitate and its solubility. All solid samples were put through a 0.2 μ m microfilter and washed with deionized water many times at the same temperature. Solids collected in this manner were used to study the stoichiometry while the filtrates were collected for quantitative analyses to provide data for the study of thermodynamic properties. Also the samples at different stages were used to explore the relationship between the solubility and other condition variables, such as ionic strength, temperature and different Ca^{2+} concentrations.

RESULTS AND DISCUSSION

The plots of acid/base titration curves (pH vs. dissociation fraction, θ_u) at different ionic strength and temperature in the absence of Ca^{2+} are shown in figures 1 and 2, respectively. As the figures show, with an increase of ionic strength, pH decreases (figure 1) with the same dissociation fraction, implying that the dissociation constant decreases. While temperature has little effect on the PPCA association/dissociation (figure 2). Data treatment shows that $\text{p}K_H$ is linear with θ_u in the range of dissociation fraction 0.3 to 0.95, especially at higher ionic strength ($[\text{NaCl}] > 0.05\text{M}$). This observation is consistent with that by Miyajima et al (12) for PAA and other observations (13,14,15,16). It was also observed that the concentration of polyacid has a slight influence on the dissociation constant but at a higher concentration and higher ionic strength, $\text{p}K_H$ has no significant change with concentration, which is consistent with findings for PAA by Nagasawa et al (12), Arnold and Overbeek (17), and Samelson (18). Quantifying all relationships between the dissociation constant and condition variables by the nonlinear regression method, a general equation for proton dissociation of PPCA acid was obtained:

$$\text{p}K_H = (4.798 - 0.954\sqrt{I} + 0.245I - \frac{187.8}{T}) + (2.757 - 1.056\sqrt{I} + 0.220I) * \theta_u \quad (7)$$

From this equation, it is easy to get $\text{p}K_{H\text{int}}(I=0, T=298\text{K})=4.17$ for PPCA which is smaller than $\text{p}K_{H\text{int}}=4.28$ for PAA by other researchers (13), $\text{p}K_H=4.76$ for acetic acid and $\text{p}K_{H\text{int}}=4.64$ for glutaric acid under the same conditions.

Figures 3 and 4 show the similar titration curves but at the presence of Ca^{2+} . Applying equation 2 and equation 7 to these titration curves, a general equation was then obtained by least square method:

$$\text{p}K_M = (3.928 - 2.631\sqrt{I} + 0.738I - \frac{1099.4}{T}) + 2(2.757 - 1.056\sqrt{I} + 0.220I) * \theta_u \quad (8)$$

This equation gives $\text{p}K_{M\text{int}}(I=0, 298\text{K})=0.24$, comparing with $\text{p}K_M=1.06$ for glutaric acid (H_2L -calcium complexation (19) and 1.16 for succinic acid-calcium (20). But extrapolation to $I=0$ for both $\text{p}K_{H\text{int}}$ and $\text{p}K_{M\text{int}}$ should be careful since no titration is carried out at very low ionic strength where constants are extremely sensitive to that.

Once both $\text{p}K_H$ and $\text{p}K_M$ are set up, solution equilibria analysis can be done for a Ca-PPCA solution system. Sampling the long-time matured precipitates, solubility experiments under wide diverse conditions were carried out. The solid speciation indicated that these long-matured precipitates are composed of only Ca and PPCA and the ratio is: Ca:PPCA=1:1 (in equivalence). The formula can thus be written as: $[\text{Ca}(\text{CH}_2\text{CHCOO})_2 \cdot x\text{H}_2\text{O}]_n$ (-POO-). Figure 5 shows the results of the dissolution experiments on these precipitates designed for solubility product at pH 5.5, 70°C and in 1.0M NaCl solution. It implies that the product $[\text{Ca}]^{1.5}[\text{A}]$ or $[\text{Ca}]^3[\text{L}]^2$ is constant (A represents free monomer, L represents a unit of certain monomers). Considering electroneutrality and applying equations (5) and (6), we let $l=2$, $m=3$, and $x=3$ and the precipitate of CaPPCA behaves like the simple crystals of calcium-trimer precipitate. Applying this semi-empirical definition of solubility product to solubility data, a plot of $\text{p}K_{\text{sp}}$ vs. ionic strength at differing temperature was obtained as in figure 6. And further nonlinear regression analyses yield the equation:

$$\text{p}K_{\text{sp}} = 34.02 - 0.832\sqrt{I} + 0.762I - \frac{6839.5}{T} \quad (9)$$

It should be pointed out that at a different temperature, the crystalline morphology of the precipitates might be different. This equation might therefore not reflect the real physical details of $\text{p}K_{\text{sp}}$ but just a mathematical expression. However, the equilibria calculations showed that the calculated solubility of CaPPCA is very close to the experimental result, and more than that, is reasonably consistent with that of CaPAA from literature (21).

The predicted titration curves by these numerical equations also show the very good consistency with titration data, as shown by lines in figures 1 and 3.

With these constants, one can evaluate the feasibility of PPCA as a scale inhibitor in a specific well. Table 1 gives 3 field case studies. In this table, 'equil PPCA' means the equilibrium concentration of PPCA calculated from those equations above under the well condition and 'min PPCA' means the minimum PPCA concentration required for inhibiting scale formation in this specific well and is calculated from the Scalesoft™ (A scale control and treatment software produced by the Brine Chemistry Consortium in Rice University). In well #1,

PPCA can not be applied as an inhibitor in a precipitation squeeze because the equilibrium concentration can not meet the minimum concentration needed. Well #2 doesn't need any inhibitor. PPCA can work well as a scale inhibitor in Well #3. However, further research need to be done at extremely high temperature where the polymer properties might change and extended application of these equations might be inappropriate.

Table 1. The equilibrium concentration (available) and the minimum concentration (required) of PPCA as a scale inhibitor in three oil wells' production assuming precipitation squeeze.

Well	Ca (M)	I (M)	T (K)	pH	equil PPCA, (ppm)	min PPCA, (ppm)
#1	0.240	2.91	424.7	5.5	0.0012	11.15
#2	0.0307	1.20	411.9	6.0	0.10	0
#3	0.0112	0.74	371.9	6.5	3.92	3.51

ACKNOWLEDGEMENTS

The authors are grateful for the financial support of the Brine Chemistry Consortium in Rice University.

REFERENCE

- [1]. Kelvin Y. Chang and Suresh Patel. A Mechanistic Study of Phosphinocarboxylic Acid for Boiler Deposit Control. MP/July 1996, p.48-53.
- [2]. T. Grchev, M. Cvetkovska and J. W. Schultze. The Electrochemical Testing of Polyacrylic Acid and Its Derivatives as inhibitors of Corrosion. Corrosion Science, Vol 32, No 1, 103-112, 1991.
- [3]. S. Patel and A.J. Nicol. Developing a Cooling Water Inhibitor with Multifunctional Deposit Control Properties. MP/June 1996, p.41-47.
- [4]. M.R. Rabaioli, Thomas P. Lockhart. Solubility and phase Behavior of Polyacrylate scale inhibitors. J. petroleum Sci and Engin 15(1996) 115-126.
- [5]. P. Debye and E. Huckel, Physik. Z., 24, 185 (1923).
- [6]. H.S.Harned and B.B. Owen, Physical Chemistry of Electrolytes, 2nd ed., Reinhold Publishing Corp., New York, 1950, Chs2,3.
- [7]. J.G. Kirkwood and J.C. Poirie, J. Phys. Chem., 58, 591 (1954).
- [8]. T.L. Hill, Arch. Biochem. Biophys., 57, 229 (1955).
- [9]. J.J. Hermans and J. Th. G. Overbeek, Rec. trav. chim., 67, 761 (1948).
- [10]. C. Tanford, J. Phys. Chem., 57, 229 (1955).
- [11]. Charles Tanford, Physical Chemistry of Macromolecules, Joh Wiley & Sons, Inc., 1967.
- [12]. Tohru Miyajima, Megumi Mori and Shin-ichi Ishiguro, Journal of Colloid and Interface Science, 187, 259-266 (1997).
- [13]. R. Arnold and J.Th.G. Overbeek, Rec. trav. chim., 69,192(1950)
- [14]. D.T.F. Pals and J.J.Hermans, Rec. trav. chim., 71, 433 (1952)
- [15]. V.Ya. Kabo, L.A. Itskovich and V.P.Budtov, Polym Sci USSR 31,10, 2217(1989)
- [16]. K.R.Rogan, Colloid Plym Sci 273: 364-369 (1995)
- [17]. R. Arnold and J.Th.G. Overbeek, Rec. trav. chim., 69,192(1950)
- [18]. Samelson,H., Columbia Univ. thesis; Univ. Microfilms (Ann Arbor, Michigan), Publ. No. 9531 (1954).
- [19]. R.K. Cannan and A. Kibrick, J. Amer. Chem. Soc., 1938, 60, 2314.
- [20]. H. morawetz, A.M. Kotliar and H. Mark, J. Phys. Chem., 58, 619 (1954).
- [21]. Tsuneo Okubo and Nobuyuki Mohri, The Solubility of Polyelectrolyte Complexes. CalciumPolyacrylate and the Poly(4-Vinyl-N-pentylpyridinium) Salt of Poly(styrenesulfonic Acid). Macromolecules 1988, 21, 2744-2747.

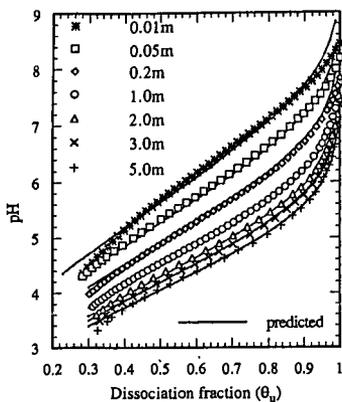


Figure 1. Plot of pH vs θ_H for acid-base titration of 0.0025N PPCA at 70°C and different NaCl concentration

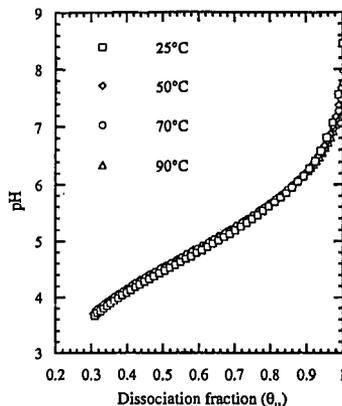


Figure 2. pH vs θ_H for acid-base titration of PPCA solution: 0.0025N PPCA-1.0m NaCl at different temperatures.

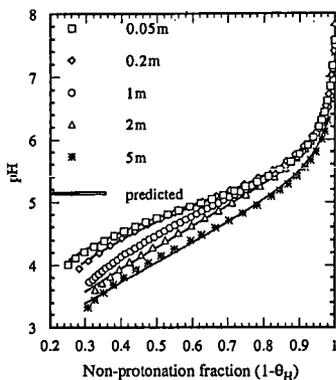


Figure 3. Plot of pH vs $(1-\theta_H)$ for the acid-base titration of 0.0025N PPCA-0.005M Ca solution at 70°C and different NaCl concentration.

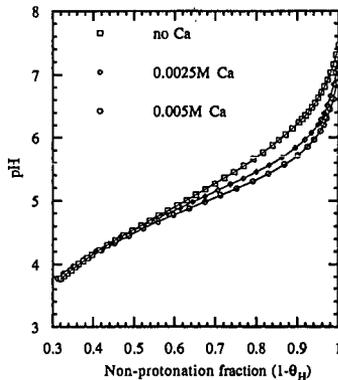


Figure 4. pH vs $(1-\theta_H)$ for acid-base titration of 0.0025 N PPCA solution at 90°C and 1m NaCl.

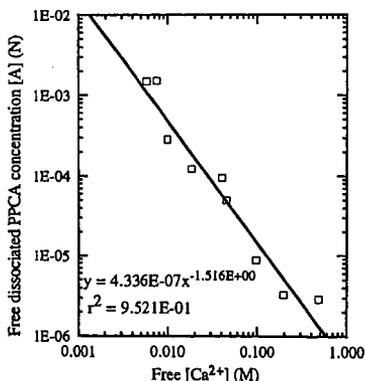


Figure 5. Diagram of $[A]$ and $[Ca^{2+}]$ to define solubility product of Ca-PPCA.

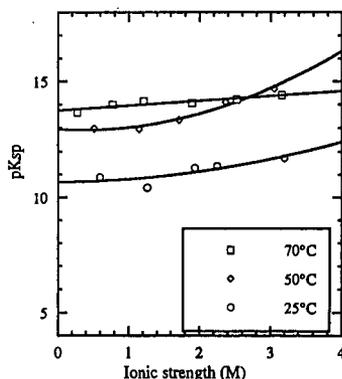


Figure 6. Diagram of pK_{sp} of Ca-PPCA vs. ionic strength at three different temperatures.