Characterization of high molecular weight hydrocarbons ($>C_{40}$) in oils and reservoir rocks

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Abstract: The presence of high molecular weight hydrocarbons in crude oils has been known for some time, particularly in view of their ability to precipitate and form barriers and blockages in pipelines. Recent advances in analytical technology have led to the development of capillary columns for gas chromatography capable of withstanding high temperatures (350 to 450°C), which allow the characterization of hydrocarbons with carbon numbers as great as C_{100} and above. Consequently, the individual high molecular weight hydrocarbon compounds in oils and waxes can now be identified. In the present paper, results are presented from high temperature gas chromatographic analyses of naturally occurring waxes. These clearly show the presence of significant concentrations of hydrocarbons with carbon numbers in excess of C_{40} in many of these samples. In order to assist in the quantification of these high molecular weight hydrocarbons, we have also assessed the potential of thermal microdistillation coupled with a field ionization detector, to obtain more accurate molecular weight distributions in wax samples. This is based on the concept that high temperature gas chromatography has an upper carbon number limit in the range C_{100} to C_{120} . Thermal distillation may provide the ability to exceed that limit and determine the presence of compounds above C_{120} . More detailed characterization of the wax fractions on a molecular level has the potential to provide clues as to the composition and origin of the residual components left in a petroleum reservoir at the end of its production history. A better understanding of the nature of this material will lead to improved secondary and tertiary recovery mechanisms, and other enhanced oil recovery procedures.

Petroleum geochemistry has developed rapidly over the past two or three decades (Peters & Moldowan 1992) and until recently most of the emphasis was directed towards exploration problems. However, the pace of this development has now inevitably slowed, resulting in a tendency to apply geochemistry to areas that are concerned more with the exploitation and production of fossil fuels, which has led to the development of reservoir geochemistry. Typically, two-thirds of the oil in place in a reservoir is not produced, even following secondary and tertiary recovery techniques. A number of processes are responsible for poor production, including reservoir heterogeneity, the formation of petroleum-derived barriers, either during accumulation or production (e.g. tar mats, asphaltenes, waxes), interaction of petroleum with surrounding minerals, low viscosity of waxy oils and petroleum biodegradation. An understanding of the processes by which oil entered the reservoir, the nature of inorganic/organic interactions and how petroleum compositions vary with respect to time, should lead to an improvement in methods available for the recovery of these residual oils.

A reservoir, in the context of petroleum, is simply defined as a rock containing petroleum (North 1985). Consequently, reservoir geochemistry can be considered as the study of the

geochemical processes that take place in a porous sediment, following the commencement of petroleum accumulation. In a number of petroleum-producing regions, the precipitation of solids from the oil, either during accumulation or production, is a major problem. The composition of the precipitated solids ranges from high molecular weight hydrocarbons to bitumens and asphaltenes (Carnahan 1989). Use of the term 'reservoir bitumens' to describe petroleum-derived solids should not be encouraged, as this will simply lead to confusion with the bitumen of organic extracts and native bitumens such as the gilsonite veins of the Uinta Basin.

Precipitation may occur either in the reservoir or in the production string, as far up as the storage tanks. As a result, barriers may form within the reservoir and/or blockages develop in the pipelines themselves. By infilling the pores, the solids may restrict the pore throats and change the wettability characteristics of the mineral surfaces, which in turn will influence reservoir-quality predictions in play assessments and basin evaluations. Consequently, petroleum-derived solids are as significant as carbonate cements, silicate cements or authigenic clays, when it comes to the characterization and evaluation of petroleum reservoir systems (Lomando 1992). Finally the presence of

these materials can also cause reservoir damage through the migration of fines leading to reduction of porosity.

Waxes consisting primarily of high molecular weight hydrocarbons (i.e. $> C_{40}$), often referred to as paraffins or paraffin waxes, are a major problem in some fields. The factors controlling the deposition of such waxes have been reviewed by Carnahan (1989). Wax deposition is related to changes in the supercritical character of petroleum fluids during accumulation and production. The temperature in deeper reservoirs can exceed the critical temperature of the low molecular weight petroleum constituents, for example, methane or ethane. Hence these compounds may act as supercritical solvents for the high molecular weight hydrocarbons. Petroleum production inevitably results in a loss of reservoir pressure, which results in a reduction in the carrying capacity of the supercritical solvent system. This leads to the precipitation and deposition of the high molecular weight hydrocarbons. Deposition in the production facilities is a result of the drop in temperature of the petroleum after it has left the reservoir (Carnahan 1989).

A number of approaches have been utilized to remediate the effects of wax deposition (Tuttle 1983; Ashford *et al.* 1990), including hot oiling, wireline cutting and chemical treatments to prevent formation of wax deposits. In higher latitudes and beneath the sea, insulation may be necessary to prevent deposits forming in the well and transfer pipelines (Ashford *et al.* 1990). However, the application of such techniques clearly results in additional production costs, the actual amounts being linked to the wax content of the petroleum (Tuttle 1983).

Analytical developments

Despite the analytical advances made in the past few decades, the study of higher molecular weight ($> C_{40}$) hydrocarbons has been largely overlooked for two main reasons. The first has been the lack of appropriate techniques, because traditional gas chromatographic methods are limited to species with sufficient volatility. The second, particularly in the case of oils, is that high molecular weight hydrocarbons are often not present, or occur in low concentrations, in the oils collected at the well head. Rather, these compounds may precipitate due to their low solubility and mobility at surface temperatures and pressures.

With the recent development of columns suitable for high temperature gas chromatography (HTGC) (Lipsky & Duffy 1986a,b), and the introduction of supercritical fluid chromatography (SFC)

(Hawthorne & Miller 1987, 1989; Smith *et al.* 1987), it has been possible to extend the carbon number range of the compounds that can be analysed and identified. Gas chromatographic capillary columns have been produced (made from fused silica, aluminium and stainless steel) containing thin films of thermostable, bonded and crosslinked stationary phases which can be maintained isothermally at 400 to 425°C and temperature programmed from 425 to 440°C. Lipsky & Duffy (1986a,b) first described the use of fused-silica columns for HTGC, showing that they were capable of analysing alkanes with carbon numbers up to C_{100} .

Capillary SFC can also be used for the separation of compounds that lack sufficient volatility to be separated by GC, and the use of SFC to separate high molecular weight compounds has been demonstrated (Hawthorne & Miller 1987, 1989). SFC is now recognized as an important method for analytical separation, because the physico-chemical properties of supercritical fluids impart significant chromatographic advantages for the analysis of thermally labile and higher molecular weight compounds. In addition, the use of small-diameter capillary columns (25–100 μm i.d.) for SFC, which have negligible pressure drops, permits exploitation of the full potential of pressure programming methods to obtain high-resolution separation, approaching that achievable with capillary gas chromatography.

The coupling of SFC or HTGC with mass spectrometry (MS) offers the potential to provide high-resolution separation of high molecular weight compounds with selective detection (Blum *et al.* 1990; Olesik 1991), and are thus the appropriate techniques required to deal with the characterization of high molecular weight biomarkers. HTGC–field ionization mass spectrometry (FIMS) has also been successfully applied to the analysis of porphyrins and complex mixtures of high molecular weight saturated and aromatic hydrocarbons (Gallegos *et al.* 1991; Carlson *et al.* 1993). The FIMS method permits the identification of molecular weights (and thus ring number) of high molecular weight hydrocarbons which exhibit no molecular ions in mass spectrometric studies employing other ionization methods. Hawthorne & Miller (1987) used SFC–MS to analyse several commercial waxes, including a microcrystalline wax, consisting of alkanes ranging up to C_{75} , and a synthetic Fischer–Tropsch wax, with hydrocarbons up to C_{100} . The potential of SFC–MS will continue to grow as SFC techniques are extended by the introduction of new mobile and stationary phases and as improved mass spectrometric detectors for higher molecular weight compounds (> 1000) become available.

Practical examples of high molecular weight hydrocarbon determinations

Experimental

A bitumen sample, ozocerite, from the Uinta Basin, Utah, a microcrystalline wax (Micro 195) and a synthetic wax obtained via a Fischer-Tropsch synthesis (FT H-1) were used as standards for this study along with various wax deposits and waxy oils collected from the Anadarko Basin, Oklahoma and the Uinta Basin, Utah. Where necessary, the

saturate fractions of the oils were isolated by alumina column chromatography and elution with cyclohexane. Concentration of the high molecular weight hydrocarbon (HMWHC) fraction was also achieved by precipitation prior to asphaltene isolation by addition of hot tetrahydrofuran (THF) followed by cooling overnight at 0°C. The HMWHC precipitate could then be removed by filtration. Asphaltenes were isolated from the oils by precipitation with excess *n*-pentane and subsequent centrifugation followed by reprecipitation with *n*-pentane to purify the asphaltenes.

Fig. 1. Gas chromatograms obtained from analysis of two standard wax samples, (a) Microwax 195 and (b) Fischer-Tropsch wax sample, by high temperature gas chromatography.

High temperature gas chromatography analyses were performed using a Carlo Erba gas chromatograph equipped with a short 6 m aluminium-clad capillary column coated with HT-5 liquid film. The conditions were on-column injector and flame ionization detector at 400°C; column heated from 60 to 440°C at a rate of 8°C min⁻¹ with 50 min final hold time. The samples were dissolved in warm *p*-xylene before injection.

Pyrolysis gas chromatography analyses of the asphaltenes were performed with a CDS

Pyroprobe. The pyrolysis interface was held at 350°C and interfaced to a Varian 3300 GC. The gas chromatograph was equipped with an aluminium-coated column (6 m or 25 m) and temperature programmed from 0 to 400°C at 8°C min⁻¹.

Thermal distillation experiments of standards, wax samples and HMWHC concentrates were undertaken using a Pyran Level I pyrolysis system. The pyrocell was temperature programmed from 100 to 600°C at a rate of 10°C min⁻¹ with 50 min hold time.

Fig. 2. Chromatograms showing a comparison between the *n*-alkane distribution in (a) an oil and (b) associated wax collected from the same well.

Characterization of natural and synthetic waxes

Chromatograms of the commercial waxes obtained from the analyses by HTGC using short aluminium-coated capillary columns produced the chromatograms shown in Fig. 1. The Micro 195 wax showed a distribution of *n*-alkanes up to C_{70} , with a maximum around C_{40} and a marked predominance of even over odd carbon number (Fig. 1a). The FT H-1 wax (Fig. 1b) showed an *n*-alkane distribution from C_{20} to C_{75} without any pronounced even/odd predominance as expected from a synthetic product of Fischer-Tropsch synthesis. Similar distributions of hydrocarbons

were obtained by SFC, although the FT H-1 showed hydrocarbons extending up to C_{100} (Hawthorne & Miller 1987).

The saturate fractions of a number of oils and their associated waxes isolated from the oil-well drill-stem pipes have also been analysed by HTGC (Del Rio *et al.* 1992; Del Rio & Philp 1992a). A relatively high concentration of high molecular weight hydrocarbons (up to at least C_{60}) was observed in waxes but not in oils collected at the well-head (Fig. 2). The waxes dominated by *n*-alkanes also contain complex mixtures of branched/cyclic hydrocarbons, mainly alkylcyclohexanes and mid-chain methyl alkanes, probably formed by condensation reactions of fatty acids

Fig. 3. Comparison between the hydrocarbons of ozocerite analysed on (a) a conventional GC column and (b) a higher temperature GC column.

(Del Rio & Philp 1992b). Similar results have also been reported by other authors (Carlson *et al.* 1993) who identified series of co-eluting monocyclic and acyclic saturated hydrocarbons extending to the C_{60} molecular weight range in a variety of crude oils. These cyclic compounds were observed to show an odd carbon number preference for marine-sourced oils and an even number preference for lacustrine-sourced oils. The oils produced a fairly typical n -alkane distribution ranging up to C_{35} . The presence of high concentrations of these hydrocarbons in wax deposits collected from drill-stem pipes was not altogether surprising, but the results demonstrate that high molecular weight hydrocarbons are absent, or present in low concentrations, from oils collected at the well-head. These components precipitate out in the drill-stem pipes due to changes in temperatures and pressures or remain in the reservoir rocks due to their low mobility.

Ozocerite, a fossil bitumen known from previous studies to be waxy, when analysed by conventional GC showed an n -alkane distribution maximizing around C_{35} – C_{40} (Fig. 3a). Analysis of the total

saturate fraction by HTGC showed a distribution of n -alkanes ranging up to C_{75} , with a maximum at C_{32} and another at around C_{42} and no even/odd predominance (Fig. 3b). The saturate fraction was dominated by n -alkanes and relatively small amounts of branched/cyclic hydrocarbons, which after molecular sieving were found to be concentrated in the C_{50} – C_{75} n -alkane region. Electron impact mass spectra for both the total saturate and branched/cyclic fractions from the ozocerite, obtained using the direct insertion probe, showed the presence of molecular ions of hydrocarbons ranging up to C_{80} in the spectrum of the total saturate hydrocarbons (Del Rio *et al.* 1992). Note that in the higher molecular weight region of the chromatogram (i.e. $>C_{65}$) the alkanes at every second carbon atom are absent, which may be a product of the biosynthetic pathway responsible in their formation.

In one of the few reported applications of both HTGC and SFC for the analysis of HMWHC, Thomson & Rynaski (1992) reported a use for the simulated distillation of wax samples. The object of their study was to compare the degree of variation

Fig. 4. Chromatograms obtained from analysis of a mixture containing equal concentrations of five n -alkanes. Note the decrease in response with increasing carbon number and decrease in retention-time differences with increasing carbon number.

in simulated distillation boiling range distributions from HTGC and SFC. The wax samples used in the study were obtained from the distillation and dewaxing of sludge from underground oil storage caverns. Previous studies have suggested that there are problems with both the HTGC and SFC approach for this type of analysis. Problems include thermal cracking at temperatures above 370°C as observed during thermogravimetric analysis, although in our own HTGC studies we have not observed this to be a problem. Sample introduction in SFC, particularly of these high molecular weight samples, has also caused problems in terms of compound discrimination, although this has now been rectified through the use of heated sample introduction units. Analyses of standard compounds and comparisons between the two techniques clearly showed that it was possible to get compounds up to C_{100} through both types of analytical systems. Results from the two techniques showed little difference and the authors concluded that, for the hydrocarbons at least, the preferred method will depend as much on instrument availability as anything else.

A key problem in the HTGC of HMWHCs is the bias of response towards the shorter-chain homologues. This is demonstrated in Fig. 4 where a number of n -alkanes of equal concentration are shown analysed by HTGC. Clearly, the apparent concentration decreases with increasing carbon number, such that the response of C_{60} is approximately one-third that of C_{30} . A number of factors are responsible for this discrimination, including

the poor solubility of the HMWHCs in the solvent and the difficulty in eluting such high boiling compounds even at 440°C. The relationship between n -alkane carbon number, boiling point, and melting point is shown in Fig. 5. The boiling point of the n -alkanes begins to level off at approximately C_{50} , although it should be mentioned that these values were determined in a static atmosphere, whereas in HTGC a constant flow of He is present which will affect the boiling behaviour of the n -alkanes. Thus it is uncertain at which GC oven temperature the boiling point of the high molecular weight n -alkanes will be equivalent. The overall implication of these processes is that the concentrations of the HMWHCs are likely to be underestimated in HTGC. Consequently, the presence of a small peak at C_{100} may actually represent the largest n -alkane component in that sample.

High molecular weight hydrocarbons in asphaltene pyrolysates

The asphaltenes isolated from a number of waxy oils were characterized by flash pyrolysis-gas chromatography using an aluminium-coated fused-silica high temperature capillary column. (Note: It is important to emphasize here that the asphaltene fractions were prepared in the classical sense by precipitation with pentane and purification by reprecipitation with additional n -pentane. It is entirely possible that during this isolation process, HMWHCs also precipitate due to lack of solubility

Fig. 5. Relationship between the n -alkane carbon number, boiling point and melting point.

in pentane. Despite not being chemically bound within the asphaltene structure, these hydrocarbons are by definition still a part of the so-called asphaltene fraction.) The results of these analyses showed that the pyrolysis products, for these particular asphaltenes, were dominated by *n*-alkanes extending to C_{60} , with a predominance of the higher molecular weight hydrocarbons (Fig. 6). As with the extractable material, these higher molecular weight compounds have been overlooked in the past owing to temperature limitations

with the chromatographic columns. The question surrounding these compounds produced by pyrolysis is whether they are actually part of the asphaltene structure or simply trapped in the asphaltenes during the isolation process. Attempts to clarify this situation have led to the use of RuO_4 , a mild and selective oxidizing reagent which preferentially destroys aromatic rings leaving the aliphatic and alicyclic portion intact, to degrade the asphaltenes. The carboxylic acid function in the aliphatic and acyclic structures produced marks the

Fig. 6. Asphaltene pyrolysis products from oils containing no apparent high molecular weight hydrocarbons components.

Fig. 7. Carboxylic acid oxidation products obtained from RuO₄ oxidation of an isolated asphaltene fraction compared with a standard wax sample in order to obtain the carbon distribution of degradation products.

point of attachment in the asphaltene structure. The products obtained in this way consist of carboxylic acids up to C₇₅ (Fig. 7), supporting the idea that these long-chain compounds were indeed part of the asphaltene structure.

Alternative methods for the analysis of high molecular weight hydrocarbons

In an effort to extend the molecular weight range of compounds that may be determined in the crude

oils or rock samples, a number of alternative approaches have been investigated for their applicability to this problem. In particular, the use of thermal distillation of samples directly into a flame ionization detector with no GC separation has been utilized to analyse both standards and samples with varying degrees of success. In the initial approach, a number of standard *n*-alkanes were analysed in this manner and it was noted that good separation could be obtained under the conditions being utilized as shown in Fig. 8. With

Fig. 8. Analyses of standard hydrocarbons by thermal distillation coupled directly to a flame ionization detector with no GC separation.

increasing carbon number, the amount of separation decreases because differences in the boiling points of these compounds decrease with increasing molecular weight, as shown in Fig. 5 and discussed previously. Following the initial success in separating the individual standards, the samples of the standard polywaxes were analysed in the same manner and it can be seen from Fig. 9 that the three standards can be differentiated on the basis of their molecular weights. Furthermore, these waxes can be used as a means of calibrating the molecular weight of unknown waxes isolated from the oils or extracts. The chromatogram for the ozocerite (Fig. 9d) has a trimodal distribution, and when compared with standards, displays hydrocarbon molecular weights ranging up to C_{80} , which agrees well with the gas chromatogram shown previously in Fig. 3. Other waxes analysed in this way showed that when used in conjunction with calibration standards, a good indication of the molecular weight distribution can be obtained.

In many of the oil samples analysed, concentrations of the high molecular weight fractions are relatively low because many of these HMWHCs have precipitated from solution during the production process or have remained in the reservoir. Therefore, if only oil samples are available

for analysis, it is desirable to have a method of concentrating whatever alkanes are present in the samples. One approach involves taking advantage of the solubility differences of the HMWHC. Addition of warm THF to the waxy oil followed by cooling will lead to precipitation of the HMWHC which can then be removed by filtration. An example of this approach is shown in Fig. 10 where one of the waxy crudes from the Uinta Basin has been treated in this way. The chromatograms of the original oil and the HMWHC concentrate are shown. The use of this approach provides a rapid means of concentrating these compounds, enabling their characterization and analysis.

Origin of the high molecular weight hydrocarbons

In discussing the source of these compounds, the presence of natural precursors must be included, because polyisoprenyl alcohols up to C_{100} have been reported in several organisms (Hemming 1983; Lehle & Tanner 1983; Chojnacki & Vogtman 1984; Chojnacki *et al.* 1987; Swiezewska & Chojnacki 1988, 1989) and bacterial carotenoid skeletons containing up to C_{50} are well known

Fig. 9. Analysis of three standard wax samples and ozocerite by thermal distillation coupled to a flame ionization detector, showing variations resulting from differences in molecular weight distributions.

Fig. 9 continued overleaf.

Fig. 9. continued

Fig. 10. Chromatograms showing the effects of concentrating the high molecular weight hydrocarbons in a yellow crude from the Bluebell Field by the addition of tetrahydrofuran to the saturate hydrocarbon fraction.

(Liaenen-Jensen 1990). Although detailed structures have not yet been determined, it is possible that some of the high molecular weight compounds in the oils could be formed by intramolecular cyclization of high molecular weight polyisoprenoid alcohols. Moldowan *et al.* (1983) proposed that cyclization of solanesol (a C_{45} polyprenol) could lead to the extended series of tricyclic terpenoids up to C_{45} , and Albaiges (1980) also proposed polyprenols as precursors of isoprenoids extending up to C_{45} . These alcohols may be converted into high molecular weight isoprenoid alkanes just as the low molecular weight analogues (i.e. phytol) are converted into hydrocarbons by attack at the alcohol moiety, followed by reduction and thermal cracking.

Another possibility is that the high molecular weight hydrocarbons are di- and trimerization products of lower molecular weight precursors (Del Rio & Philp 1992b). Previous papers strongly support this hypothesis. For instance, De Leeuw *et al.* (1980) obtained di- and trimerization products of phytol after heating it in the presence of clay minerals. Rubinstein & Strausz (1979) reported the formation of dimerization products of fatty acids when heating them in the presence of clay

minerals. More recently, Van Aarssen *et al.* (1992) discovered some C_{45} hydrocarbons, thought to be trimeric cadinanes, in crude oils and sediments from South East Asia, suggesting that sesquiterpenes may dimerize or oligomerize under appropriate conditions by an abiotic process.

Conclusions

High molecular weight hydrocarbons have been found to be concentrated in the wax deposits that frequently occur in drill-stem pipes of producing oil wells. Pyrolysis of the asphaltene isolated from the oils suggests that thermal breakdown under reservoir conditions may be one mechanism leading to the formation of these high molecular weight hydrocarbons. The presence of high molecular weight hydrocarbons has been observed in the saturated fraction of ozocerite, a fossil bitumen. Cyclic structures ranging up to C_{80} could be observed in the ozocerite, although no detailed structures were confirmed for these compounds.

It is suggested that the study of high molecular weight hydrocarbons has been overlooked in the past for two main reasons: the first is the lack of

appropriate analytical techniques; the second is that, particularly in the case of produced oils, the higher molecular weight components are often absent in the oil collected at the well-head. Rather, these components precipitate out in the drill-stem pipes or remain in the reservoir rocks due to their low mobility. In view of the results presented herein it is proposed that continued study of these high molecular weight fractions will provide additional insights into the origin and types of organic source materials responsible for various types of oils. Major advances can be expected in this area over the next few years, largely because of improvements in analytical techniques that will make it easier to identify the high molecular weight compounds on a molecular level.

Traditional gas chromatographic methods are limited to species with sufficient volatility. High temperature gas chromatography and supercritical fluid chromatography coupled with mass spectrometry offer the potential to provide high-resolution separation of high molecular weight compounds

with selective mass spectrometric analysis. This could be the appropriate technique to analyse these new high molecular weight compounds, which may be potential biomarkers, although instrumentation and interfaces are still being developed. The potential of HTGC-MS and SFC-MS will continue to grow as HTGC and SFC techniques are extended by the introduction of new mobile and stationary phases, new approaches for the interfaces are developed and as improved mass spectrometric detectors continue to become available.

Finally, the importance of developing techniques to analyse for these high molecular weight compounds in the context of reservoir geochemistry cannot be overemphasized. These high molecular weight hydrocarbons will, in certain cases, be responsible for significant amounts of the residual components left in a reservoir. A better understanding of the nature of this fraction has the potential to improve current secondary and tertiary recovery processes and other enhanced oil recovery methods.

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