n-Alkane Distributions in Wax Deposits

vs.

Temperature of Deposition

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Abstract

Temperature, pressure and oil compositions are commonly considered as main factors controlling petroleum wax deposition. The present study explores the changes in molecular weight distributions of n-alkane mixtures in wax deposits formed under different temperature conditions. Presented results are based on HTGC analysis of both wax deposits formed during laboratory simulated wax deposition using a cold-finger apparatus, and field formed wax deposits along the same oil producing well and a pipeline. A consistency between experimental and field results is found, demonstrating that at increasing temperatures of deposition below the cloud point of the oil, hydrocarbon distributions in wax deposits shift towards higher molecular weight mixtures compared to those formed at lower temperatures. The results suggest a significant variability in the composition of formed wax deposit profile along the same well/pipeline, and related to that variability in the physical properties of deposits. It is proposed that an efficient chemical treatment of wax deposits formed in the same well or pipeline should account for this variability in the deposits.

Introduction

The solid material precipitation and deposition in production and transportation facilities and reservoirs have been presenting problems to petroleum production practices for over a century and occurs in petroleum producing regions worldwide. Solid material deposition, often referred to as "paraffin" or "wax" deposition, presents a problem to petroleum production by reducing reservoir permeability and/or causing formation damage, by plugging and reducing well tubing and pipeline diameters, all of them resulting in deferred and/or decreased oil production and additional costs for cleaning and remediation. Although the wax deposition phenomenon has been known for over a century, it is a recurrent problem even today, and the remediation costs continue to escalate, especially with the expansion in offshore petroleum exploration and production. It has been recognized, and there is a consensus now, that the understanding of and the predictive methods for paraffin deposition are still to large extent unsatisfactory for efficient prevention and treatment of the problem (e.g., Monger-McClure et al., 1999).

One reason for the difficulties in treating the wax deposition problem is the compositional variability of wax deposits formed in different fields, or even in different wells of the same field (Westrich et al., 2000). This variability relates to differences in the origin of the oils and the petroleum system, including kerogen type and depositional environment of the source rocks, petroleum generation, primary and secondary migration, post-accumulation reservoir history, and the pressure-temperature production and transportation conditions (e.g., Hunt, 1954; Martin et al., 1963; Hedberg, 1968; Tegelaar et al., 1989; Hunt, 1991; Carlson et al., 1991; del Rio and Philp, 1992; Carlson et al., 1993; Manning and Gize, 1993; Hunt, 1995; Ruble et al., 1997; Carlson et al., 1997;

Killops et al., 1998; Inan et al., 1998; Isaksen et al., 1998). The composition of wax deposits is a complex mixture dominated by hydrocarbons (mainly n-alkanes, with various amounts of cycloalkanes, isoalkanes, alkylaromatics) and non-hydrocarbons (resins and asphaltenes), with additional trapped oil, inorganic material and water in various proportions (e.g., Reistle, 1932; Carnahan, 1989; Misra et al., 1995). Both the hydrocarbons and non-hydrocarbons in wax deposits represent a large variety of individual compounds and homologues series with different molecular weights and often-unknown structures and physical properties. Thus, the properties of the complex mixtures they form are even more obscure, which presents a major obstacle to the development of more effective and less costly remediation methods for wax deposition problems. The use of terms such as "wax" or "paraffin" deposits to refer to the complex composition of petroleum formed solid deposits could be confusing because these terms imply that the deposits exclusively consist of hydrocarbons or n-alkanes (n-paraffins), respectively. "Wax" deposits and deposition are used in the present study being aware of the broader compositional range that the solid deposits represent. Temperature, pressure and oil composition are commonly considered as the main factors controlling petroleum wax deposition (e.g., Reistle, 1932; Mozes, 1982; Hansen et al., 1991; Misra et al., 1995; Leontaritis, 1997). Changes in these conditions during production/transportation of petroleum closely relate to variability in the composition of formed deposits. The present study mainly focuses on the effect of temperature on composition of wax deposits, and specifically on the variations in carbon number distributions of n-alkane mixtures in the deposits. The experimental results discussed in this study are obtained under controlled conditions, with pressure and oil composition being kept constant, and the effect of

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temperature on the distribution of n-alkanes in wax deposits is mainly explored. In addition, a comparison is performed with the composition of wax deposits formed under field conditions at different temperatures of the same oil producing well and a pipeline.

Experimental

Samples

Oil used in cold finger experiments. A five-gallon stock tank oil sample produced from Gulf of Mexico was provided by Mobil Technology Company for the cold finger experiments. Further information regarding well name, location, reservoir and production conditions has not been released. The five-gallon oil sample was transported to laboratory in a closed contained. At room temperature, the oil represented a black liquid. The initial five-gallon oil was subdivided into aliquots of 450 ml for use in the cold finger experiments after applying a thermal pre-treatment directed to dissolve and homogenize the wax in the oil as much as possible. The procedure consisted of heating the five-gallon oil container in an oven at 70°C for 7 hours, with applied manual shaking of the oil container for 10-15 minutes every hour. During the thermal pre-treatment, a plastic glove was attached to the container opening in order to reduce the pressure build-up resulting from gases released during the heating and confined to a fixed volume. The glove was removed before taking the 450-ml aliquots, without attempting to collect the light components accumulated there. Aliquots were taken from the heated oil directly into the bottles (500 ml) used in cold finger experiments and stored at 5-10°C before use in the cold finger experiments.

Pipeline wax deposit samples (called # 9 and # 10 in the present study) were collected at two different locations of the same pipeline and provided by Mobil Technology Company. Any additional information regarding the sample and pipeline locations, gathering system, composition of oil(s) flowing through the pipeline has not been released. The wax deposit samples were stored in plastic bags at ambient conditions and represented medium to dark brown solids.

Rod wax deposits formed in a Mosteller 1-21 well were collected at different depths. The well is located at the easternmost part of Anadarko Basin, Cleveland Co., Oklahoma (T10N, R3W, section 21). The well is considered to produce oil only from the Viola Formation (Ordovician) and the possibility of commingled oil production with other reservoirs is very low. The samples were collected when the rods were taken to the surface for cleaning operations after a wax deposition problem occurred in this well and stopped the production. Two samples used in the present study are designated as "deeper" and "shallower" deposits. Maximum depth of the well is approximately 8000 feet. Since bottom hole temperature measurements were not available for the well, an attempt was made to calculate the temperature corresponding to this depth by using published data of geothermal gradients for the eastern part of Anadarko Basin. The maximum depth of the well would correspond to a temperature interval of 36-44°C if considering the regional geothermal gradients of 2.1°C/100 m to 2.4°C/100 m suggested by Lee and Deming (1998) and Pawlevich (1989), respectively, or to 66-70°C if considering regional geothermal gradients of about 3.3-3.5°C/100 m suggested by Carter et al. (1998). Wax deposits were not observed at the deepest level rods, suggesting that the oil cloud point is

at a temperature lower than the reservoir temperature and in the interval 40 to 68°C based on the above considerations.

Methods

Asphaltene / Maltene separation. Whole oils (~100 mg) were dissolved in a small amount of methylene chloride and the asphaltenes precipitated with an excess of n-pentane (50:1 v/v) after allowing to stand at 5°C overnight. The n-pentane insoluble fraction (asphaltenes) was separated from the n-pentane soluble fraction (maltenes) by centrifugation and subsequent decanting of the pentane. The asphaltene fraction was recovered in methylene chloride, and the solvent evaporated under nitrogen flow.

Wax precipitation was performed following the procedure described in Burger et al. (1981). The wax material was precipitated from the oil using a petroleum ether:acetone (1:3 v/v) mixture at -20°C, followed by filtration and recovery of wax fractions using toluene.

Wax deposition with a cold finger apparatus. The cold finger and 500 ml glass bottles used in the presented study were donated by Shell Chemical Co. to the Petroleum and Geological Engineering Department (PGE) at the University of Oklahoma, where the experiments were performed. The cold finger represents a modification of the cold finger described in Kruka et al. (1995) in that it consists of one cold surface instead of three. The cold finger modification used in the present study allowed the formation of larger amount wax deposits that can be collected and used in the subsequent HTGC analysis.

The settings of the equipment are as described in Kruka et al. (1995), and the procedure has been developed and tested by Shell E&P Technology (Kruka et al., 2000).

In brief, the apparatus consists of an insulated water bath container that is heated and stirred by a hot plate/ magnetic stirrer, a 500 ml (3.0 in. I.D.) bottle containing the oil, placed in water bath and independently stirred, and a cold finger placed within the oil bottle during the analysis. The water bath surface was covered with porous pieces ("pop-corn") to prevent evaporation and ensure stability in water and oil temperature. During analysis, the oil temperature was maintained to be 18-20°F above the set temperature of the cold finger in each experiment (Kruka et al., 1995). Temperatures of the water bath, oil and cold finger were recorded using thermocouples and data transferred to a computer every 60 sec during the analysis. The computer program for temperature data recording from all the thermocouples was written and installed by Professor C. Whitson. The achieved precision in detected temperatures was ± 0.5°F. A mixture of water and ethylene glycol (70:30 v/v) was used as a circulating coolant to control the cold finger temperature. Duration of each experiment was 17 hours. Cold finger was removed from the oil after test completion, allowed to drip dry and rinsed with methyl-ethyl ketone (MEK) by submerging the finger and deposited material several times in MEK. The MEK is supposed to remove the residual oil deposited with the wax on the cold surface (Kruka et al., 1995). After a rotary evaporation of the solvent, the collected material was referred to as "MEK recovery". If there was a film visual under a magnifying glass or an accumulation of wax, the finger was placed in another bottle with approximately 400 ml toluene and stirred at temperatures of 130-140°F for about three hours, which was considered a sufficient amount of time for all of the wax material to be dissolved in the toluene. The toluene was removed by rotary evaporation. The wax material was further transferred using toluene in a 20 or 50 ml vial (depending on the amount of deposited

wax), and the solvent completely evaporated under nitrogen flow in a water heating bath. Thus collected material was called "toluene recovery" and is considered to contain the wax material deposited at the pre-set temperature of the cold finger (Kruka et al., 1995). A new aliquot of the original oil was used in each experiment. The finger surface was polished with an emery cloth (1200 size) before each experiment to ensure the smoothness of the finger. The cloud point (temperature of initiation of wax deposition) was determined to be in the narrowest temperature interval where presence and absence of wax deposits is observed by a series of experiments at different set temperatures of the cold finger. The temperature difference between consecutive experiments could be narrowed down to 5°F.

High-temperature gas chromatography (HTGC) analysis was performed on a Hewlett Packard 5890 gas chromatograph with an on-column injector system and a flame ionization detector (FID). The HTGC analysis of waxes was performed using a 30 m x 0.32 mm i.d. DB-1 HT column with 0.1 µm film thickness and a temperature program from 80°C to 350° at 4°C/min with a final hold time of 51 min. For selected high molecular weight wax samples, HTGC analysis was performed on a gas chromatograph GC 8000 Top series, equipped with a 25 m x 0.32 mm i.d. HT5 column bonded with non-polar (5% phenyl equiv. polysiloxane-carborane) phase and film thickness of 0.1 µm. Temperature programs were from 60°C to 400°C at 6°C/min. or from 40°C to 370°C at 4°C /min. with a final hold time of 37 min. Wax samples were commonly dissolved in hot p-xylene prior to injection. Detector temperature was set at 10°C higher than the programmed maximum column temperature to prevent condensation effects. Quantitation of components was performed by using deuterated C_{36} alkane as an internal standard. The

standard compound elutes between $n-C_{35}$ and $n-C_{36}$ without interference from other compounds. The standard solution was prepared by diluting 0.5 mg of $n-C_{36}D_{74}$ in 10 ml p-xylene. The wax solutions were prepared at concentrations of 1 mg to 4 mg per ml p-xylene based on considerations either not to overload the column or to achieve representative chromatograms. Wax and standard solutions were mixed in proportion 100 μl : 25 μl, and 1 μl of heated solution injected in the gas chromatograph. Peak integration was commonly performed on baseline subtracted chromatograms in order to adjust for the baseline increase above 300°C due to column bleed using Nelson 3000 series chromatography data system software. Best results were obtained with noise threshold, area threshold and minimum peak width settings of 20. The baseline from which peak areas (or heights) are calculated was drawn on a cluster-by-cluster basis, i.e., from the start of the first peak in each cluster to the end of the last peak. The automatic peak integration was checked for each sample and manual corrections made if necessary.

Results and discussion

Oil, wax and asphaltene characterization

Prior to initiation of the cold-finger experiments, wax and asphaltene precipitates were obtained from the whole oil by acetone and n-pentane precipitation, respectively. The HTGC chromatograms of the whole oil, wax and asphaltene fractions are shown in **Figure 1**. The n-alkane distribution in the whole oil extends to about nC_{50}, but the higher molecular weight components are hardly distinguishable on the chromatogram (**Figure 1a**). The concentration of all the n-alkanes detected above nC_{18} represents 7.7% of the oil. Definitions of high-wax oils based on GC analysis, namely total nC_{20} to nC_{35} alkane

content higher than 10 wt.%, have been presented in several studies (Martin et al., 1963; Saikia and Dutta, 1980). Related to these definitions, the studied Gulf of Mexico oil can be characterized as a low-wax oil with nC_{18+} alkane content less than 10 wt.%.

Total wax precipitate represents 12.2 wt.% of the oil and is characterized by an n-alkane distribution maximizing at nC_{24}-nC_{26} (**Figure 1b, 2**). The higher amount of wax precipitate (12.2 wt.% of the oil) compared to the total nC_{18+} alkanes (7.7 wt.% of the oil) could be related to the fact that the wax precipitate does not represent a pure n-alkane mixture as demonstrated by Musser and Kilpatrick (1998). Total amount of nC_{18+} alkanes represents 26 wt.% of the wax precipitate, with macrocrystalline (total nC_{20}-C_{35} alkanes) and microcrystalline (total nC_{35+} alkanes) type waxes representing 21% and 5% of the total wax precipitate, respectively. Thus, the wax fraction can be characterized as an intermediate type wax, consisting of macrocrystalline (nC_{20}-nC_{35}) and microcrystalline ($>nC_{35}$) type waxes in ratio 4:1.

Total asphaltene fraction represents 0.5 wt.% of the oil. The HTGC chromatogram of the asphaltene fraction demonstrates a significant abundance of HMW ($>C_{40}$) n-alkanes with a distribution maximizing in the range nC_{44}-nC_{50} (**Figure 1c, 2**). The possibility of co-precipitation of HMWHC with the asphaltenes for some oils was first discussed by del Rio et al. (1992), and later on confirmed in the studies of Chouparova and Philp (1998) and Than et al. (1999). For the case of presently studied oil, total sum of n-alkanes above C_{18} and C_{35} represents 39 wt.% and 35 wt% of the asphaltene fraction, respectively.

In summary, studied Gulf of Mexico oil can be characterized as a low-wax, low-asphaltene oil. The hydrocarbon composition of the wax fraction is dominated (80%) by a macrocrystalline type wax (nC_{20}-C_{35} alkanes) with 20% contribution from microcrystalline type wax (HMW nC_{35+} alkanes).

Cold finger experiments

Cloud point determination

Laboratory simulation of wax deposition using a cold finger submerged in hot oil has been described in a number of studies (e.g., Hunt, 1962; Kolesnik et al., 1971; Bern et al., 1980; Woo et al., 1984; Weingarten and Euchner, 1986; Kruka et al., 1995). In the present study, one purpose of the cold finger experiments was to determine the cloud point of a black oil, which consists of locating two close temperatures where the first wax deposit is observed (Kruka et al., 1995). The cloud point is defined to be within this temperature interval. Cold finger experimental results with the oil used in this study are presented in **Table 1**. No wax was deposited at 54.4°C and the first visible wax deposit was observed to form at 51.7°C. Thus, the cloud point of the oil was determined to be 53.1 ± 1.4°C. The first significant wax deposit formation occurred at 40.5°C, which is more than ten degrees below the cloud point. The wax deposits formed between 51.7°C and 43.3°C appeared as very tiny films of wax covering the cold finger, mixed with oil. The HTGC analysis of the wax deposits (toluene recovery) complemented these observations and suggested that the waxes consist mainly of HMW ($>C_{40}$) n-alkanes with the trapped oil consisting of LMWHC (**Figure 4**). It should be noted that the cloud point was determined on thermally pre-treated oil, which may have reduced the

concentration of lower molecular weight n-alkanes and may have changed the cloud point of the oil (Brownawell and Hollyday, 1962).

A plot of the amount of trapped oil (MEK recovery) in wax deposits formed at different temperatures (**Figure 3, Table 1**) demonstrates a linear trend increasing with decreasing temperature. It should be noted that MEK does not remove all of the trapped oil, as evidenced by the distribution of LMW n-alkanes on HTGC chromatograms of the deposits (**Figure 4**), and apparently contributes to the variation of 10% in the MEK recovery amounts (**Figure 3**). A plot of the amount of wax (toluene recovery) deposited on the cold finger at different temperatures below the cloud point is presented in **Figure 3**. Based on these results, several stages of wax deposition can be distinguished to occur at different temperature intervals. The deposits formed in the range from 51.7°C to 37.8°C are characterized by small amounts of wax (53 mg to 340 mg), with large portions of trapped oil (**Table 1, Figure 3**). A rapid increase (10 to 70 times) in amount of wax deposits (1300 mg to 3600 mg) occurs in the temperature range 35°C to 4.4°C. And a further increase in wax deposit amount of more than ten times (>24,000 mg), compared to the preceding temperature interval, is observed at -13°C. The observed trend in deposit amounts at different temperatures shows similarities with the nuclear magnetic resonance (NMR) results presented by Pedersen et al. (1991) and cold finger measurements by Kolesnik et al. (1971). In both studies, an intermediate temperature interval exists, where the amount of deposited wax increases rapidly. This temperature range for the oils studied by Pedersen et al. (1991) was 20°C to -15°C and for the oils studied by Kolesnik et al. (1971) was 20°C to 5°C and 10°C to -5°C. For the oil in the present study, this range encompasses relatively high temperatures, extending from 35°C

to 4.4°C, which could be related to the specifics of studied oil and/or to the applied thermal pre-treatment at the beginning of analysis. The temperature interval with a rapid increase in amount of deposited wax can be regarded as corresponding to a region of decreased solubility of the most abundant wax components in the oil, and therefore as oil specific.

A second increase in deposited wax amount was observed at the lowest temperature (-13°C; **Figure 3**) and can be related to solidification of the whole oil while approaching the pour point of the oil. The pour point is the temperature at which a part of the oil matrix, which can not crystallize, transforms into a frozen solid, which drastically reduces molecular mobility and increases the oil viscosity. At the end of experiment (-13°C), the wax deposit was more than 2.0 inches thick and most of the oil had a high viscosity, suggesting a pour point very close to -13°C for this oil.

Distribution of n-alkanes in wax deposits formed at different temperatures

Another purpose of the cold finger experiments was to study the composition of wax deposits formed at different temperatures using HTGC analysis (**Figure 4**). The chromatograms demonstrate a considerable increase in HMW ($>nC_{30}$) n-alkane distributions in temperature deposition range from 40.5°C to 15.6°C, corresponding to the temperature interval with a rapid wax deposit formation. Additionally, the maximum of HMW n-alkane distributions in this temperature interval demonstrates a subsequent shift towards lower molecular weight n-alkanes at lower temperatures (**Figure 5**). For example, the maximum of n-alkane distribution at 37.8°C is at nC_{50}, and it shifts to nC_{42} at 26.7°C and nC_{33} at 15.6°C. Shifts in maximum of n-alkane distributions towards LMW

components have been reported by other studies for petroleum distillate fractions of decreasing boiling range (Krishna et al., 1989), for waxes precipitated from the same oil at decreasing temperatures of precipitation (Rønningsen et al., 1991) as well as in a model n-alkane mixture consisting of nC_{18}-nC_{30} components in decane (Pauly et al., 1998). The nC_{35}- n-alkane distributions on the chromatograms (**Figures 4** and **Figure 1b**) can be regarded mainly as trapped oil, and at lower temperatures (15.6°C and 4.4°C) a progressive contribution of LMW macrocrystalline type wax could be observed.

The results described above suggest that wax deposits formed under higher temperatures of a reservoir, well equipment and/or pipeline, will be dominated by HMWHCs, and at lower temperatures the n-alkane composition will change towards distributions dominated by more of the lower molecular weight homologues. These distributions can be related to variations in melting points and solubilities of the HMW hydrocarbons. In offshore pipelines, for example, the composition of wax deposits would be expected to change from a broader carbon number n-alkane distribution (both LMW and HMW ranges) in the cooler offshore part of the pipeline to a narrower, predominantly HMW n-alkane distribution in the onshore part of the pipeline, located at relatively higher temperatures. The narrow, HMW dominated n-alkane solid mixtures are much more stable and less soluble compared to the broad carbon number range n-alkane mixtures (Clavell-Grunbaum et al., 1997; Tchouparova, 1999). Chemical remediation of such a profile of wax deposits formed in the same pipeline, for example, using one solvent or solvent blend is not likely to efficiently dissolve the variety of n-alkane mixtures deposited at different temperatures. Oil type (paraffinic, naphthenic, aromatic) and relative proportions of non-hydrocarbons (resins and asphaltenes) in the deposits

could require further modifications to the solvent choice for most efficient treatment (as discussed in Tchouparova, 1999; Chouparova and Philp, 2000, this volume). In the case of wax deposits formed in producing oil wells at moderate climates where the lower temperature limit will be determined by surface temperature conditions (e.g., 15-20°C), the results suggest that wax deposits will be dominated mainly by HMW n-alkane distributions. The profile of wax deposits from the reservoir to the surface could be expected still to show a variability in composition and shifts towards relatively LMW components at lower temperatures, but the whole range of n-alkanes in the wax deposits is likely to be in the HMW range (above nC_{35}).

Recognition that wax deposits vary in their composition with respect to n-alkane carbon number distributions as a function of temperature is particularly important for the development of thermodynamic models with better predictive capabilities. Many currently available models (Won et al., 1986; Hansen et al., 1988; Pedersen et al., 1991; Ungerer et al., 1995), directed to predict the phase behavior of reservoir fluids, are based on the assumption that all wax components (heavier and lighter) precipitate at the cloud point temperature as discussed in Pauly et al. (1998). Considering the experimental results in the present study, such an assumption would model a wax deposit with the composition formed at 4.4°C to be considered as formed at 51.7°C, for example (**Figure 4**). In addition, it is not well understood from a geochemical point of view how the other classes hydrocarbon and non-hydrocarbon compounds that comprise the complex mixture of wax deposits behave as a function of temperature. Apparently, a detailed compositional characterization of different classes compounds in wax deposits and oils

and their close integration with modeling is necessary in order to improve the predictions

for wax deposition occurring in production equipment and reservoirs.

Field wax deposits – rod waxes and pipeline waxes

Cold finger experimental results discussed above demonstrated that significant

compositional changes and variability can be expected in wax deposits formed at

different temperatures along the same well or pipeline. To further test if the experimental

results would show a consistency with field samples, naturally formed wax deposits

collected at different locations along the same oil producing well and a pipeline were

analyzed.

HTGC results for rod wax deposits formed at two different depths (**Figure 6a**)

demonstrate that the deposit formed at the shallower depth (lower temperature) is

characterized by an n-alkane distribution maximizing at lower carbon number (nC_{35})

compared to the deposit formed at the deeper (higher temperature) location (nC_{51}). The n-

alkane distributions in both samples are relatively narrow, encompassing approximately

23 and 26 carbon number ranges of n-alkanes for the shallower and deeper samples,

respectively (**Figure 6b**). The significant shift (16 carbon number n-alkanes) in n-alkane

distributions in the rod waxes is consistent with the observed changes in composition of

wax deposits using the cold finger apparatus. The consistency of these results suggests

temperature to be a main factor controlling wax deposition in the rods of studied well. In

addition, the consistency of these results suggests that the compositional information

revealed by a geochemical study of wax deposits could be used to predict the relative temperature of wax deposition

Pipeline wax deposits formed at two different locations of the same pipeline were used as another field sample example. Sample # 10 was collected at a location with relatively higher temperature compared to sample # 9. In this case, the chromatograms of the samples did not show a drastic shift in n-alkane distributions as it was previously observed for the rod wax deposits (**Figure 7a**). A slight shift, however, in the maximum of n-alkane distribution towards HMW components was observed to occur from wax deposit # 9 (nC_{50}) to wax deposit # 10 (nC_{54}-nC_{57}). Quantitative HTGC results further demonstrated that the HMW n-alkane concentration in wax # 9 is more than twice that for wax # 10 (**Figure 7b**), and could be suggestive for higher proportions of non-hydrocarbons that are not detected by HTGC. These characteristics suggested that sample # 10 was likely to have been deposited at a higher temperature than sample # 9, and were consistent with the calculated temperatures of sample locations. Changes in the composition of wax deposits formed at different locations of the same pipeline apparently relate to differences in temperature conditions. However, specifics in pumping rates, fluid dynamics and pressure induced changes in oil composition could be some of the other factors that may influence the composition of field wax deposits, and their effect is not accounted for in the present study.

Conclusions

(1) Cold finger experiments demonstrated two temperature regions of rapid increase in the amount of wax deposit that could be regarded as being determined by processes of a different nature. The first interval of a rapid deposit growth (35°C to 4.4°C), occurred ca. 20°C below the cloud point of the oil, and could be related to a subsequent crystallization of the most abundant HMW and LMW n-alkanes, respectively, in the oil. Therefore, this temperature interval can be regarded as oil specific. The second stage (-13°C and possibly lower) of rapid deposit growth relates to solidification of the oil matrix in approaching the pour point, and is not influenced by the wax content of the oil.

(2) The carbon number distribution of n-alkane mixtures in wax deposits changes with the temperature (depth) of deposition as demonstrated by both laboratory and field formed wax deposits, and demonstrates a significant compositional variability in deposits formed along the same well/pipeline. The carbon number distribution of n-alkane mixtures in wax deposits formed within the same production tubing/pipeline increases in molecular weight, and possibly becomes narrower, with the increase in temperature, and the proportions of hydrocarbon/non-hydrocarbons in formed deposits may change. Compositional variability of wax deposits formed in the same well/pipeline closely relates to variability in physical properties (e.g., solubility, hardness) of deposits and suggests that an efficient chemical wax remediation should account for this variability in the deposits.

(3) The results presented in this study demonstrate that compositional characterization of wax deposits by geochemical methods could predict correctly the relative temperature conditions of wax deposition. Further integration of detailed geochemical characterization of different classes compounds in oils and wax deposits formed at different temperatures with thermodynamic modeling is a must in development of better predictive models of wax deposition, its prevention and remediation.

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Figure Captions:

Figure 1. HTGC chromatograms of whole oil (a), acetone wax precipitate (b), and asphaltene n-pentane precipitate (c) of Gulf of Mexico oil used in cold finger experiments. HTGC temperature program 40-400°C at 6°C/min.

Figure 2. Quantitative HTGC results for n-alkane distributions recovered in wax and asphaltene precipitates in comparison to the concentration of n-alkanes in the whole oil. The inset presents a portion of the diagram with an extended vertical scale up to 3 mg/g oil.

Figure 3. Amount of (a) trapped oil recovered by methyl ethyl ketone (MEK) and (b) wax recovered by toluene in wax deposits formed during cold finger experiments at different temperatures of deposition.

Figure 4. HTGC chromatograms of wax deposits (toluene recovery) formed at different temperatures of deposition by cold finger experiments.

Figure 5. Partial HTGC chromatograms of wax deposits formed during cold finger experiments at different temperatures. Note the shift in maximum of n-alkane distributions towards lower carbon number components with decreasing temperature of deposition.

Figure 6. HTGC chromatograms (a) and quantitative results (b) for two rod wax deposit samples collected at different depths of Mosteller 1-21 well, eastern Anadarko Basin, Oklahoma. Note the significant shift in maximum carbon number distribution towards higher molecular weight n-alkanes in deeper deposit.

Figure 7. HTGC chromatograms and quantitative results (inset) for wax deposits formed in the same pipeline at two different locations. Oven temperature program 40-400°C at 6°C/min.