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High Molecular Weight Paraffins (>C₄₀) in Crude Oils and Source Rocks

High molecular weight hydrocarbons (HMWHC) in crude oils and source rock extracts have received relatively little attention in recent years compared to lower molecular weight hydrocarbons (< C₄₀). However many reservoir and production problems are associated with these compounds which also contain significant amounts of information useful for correlation purposes, characterization of depositional environments, and other properties of crude oils. For several years we have investigated the origin and distribution of these HMW compounds and developed methods for efficient separation of HMWHCs from the asphaltenes. This paper will review some of the results from this work and describe the identification of several homologous series of HMW branched hydrocarbons present in crude oils. The significance of these compounds in relation to the properties of the crude oils will also be discussed. Studies such as ours will not prevent the occurrence of paraffin deposits in pipelines or production facilities but will provide a better understanding of where we might anticipate the occurrence of significant quantities of HMWHCs and their carbon number distribution. In summary, although long overlooked, HMWHCs are ubiquitous in crude oils and can play an important role in a wide variety of exploration and production studies.

Introduction

High molecular weight hydrocarbons (HMWHCs) in crude oils have had an undistinguished history over the years, apart from a few landmark papers such as the classic paper by Hedberg (1968) who proposed that waxes in crude oils reflected terrigenous organic source material. Furthermore it was proposed that the oils were typically restricted to non-marine stratigraphic sequences deposited during the Devonian to Pliocene periods. Improvements in analytical technology, such as high temperature gas chromatography (HTGC) and methods to isolate and concentrate HMWHCs have resulted in observations dispelling earlier beliefs that HMWHCs are restricted to higher plant derived organic matter (Hedberg, 1968; Kinghorn, 1983). A multitude of evidence is now available which demonstrates the ubiquity of HMWHCs in crude oils and source rocks originating from terrigenous, marine, and lacustrine source materials, varying in age and maturity (Moldowan *et al.*, 1985; Tegelaar *et al.*, 1989; Carlson *et al.*, 1993; Heath *et al.*, 1995; Philp *et al.*, 1995; Hsieh, 1999; Hsieh and Philp, 2001). Routine analyses of waxy crude oils by HTGC have subsequently revealed that the HMWHC fractions are composed of complex mixtures of alkyl-cycloalkanes, methylbranched alkanes, and alkyl-aromatic hydrocarbons, and may represent a significant fraction of the whole oil (Hsieh and Philp, 2001).

Experimental

Isolation of the HMWHC fraction is typically undertaken using the method Than *et al.*, (1999) which was subsequently modified by Hsieh *et al.*, (2000). The method involves adsorption of the crude oil on alumina, followed by extraction of the alumina to remove the maltenes,

including the HMWHCs, leaving the asphaltenes adsorbed to the alumina. The maltenes were subsequently separated into wax and non-wax fractions via acetone precipitation (Burger *et al.*, 1981) and the fractions analyzed by high temperature gas chromatography.

Discussion

Oklahoma, where many of our studies have been conducted, is a state with abundant oil wells, and wells with abundant wax or paraffin deposition problems despite the fact that most oil is produced from marine source rocks (in particular the Woodford Shale). In our early work several waxes responsible for blocking oil wells in various locations of the Oklahoma oilfields were examined by HTGC, and it was noted that the wax deposits were typically dominated by hydrocarbons maximizing around C₄₀-C₅₀ (del Rio and Philp, 1992). Carlson *et al.* (1993) noted variations in coeluting monocyclic/acyclic hydrocarbons with the nature of the depositional environment in which the original source material was deposited. The homologous series of compounds, subsequently tentatively identified as alkylcyclopentanes, was found to extend into the C₆₀ region of crude oils. Carlson *et al.* (1993) observed that in marine oils this series of compounds had a distinct odd/even predominance pattern (Fig. 1a), whereas oils from saline lacustrine environments demonstrate a high even/odd predominance pattern (Fig. 1b), and freshwater lacustrine oils were characterized by a low even/odd or no clear predominance (Fig. 1c). Carlson *et al.*, (1994) discussed the relationship between pour points of crude oils and their wax content and noted the isotopic compositions of the HMWHCs were found to be similar to those of the LMWHCs, suggesting that these hydrocarbons were probably derived from the same or similar sources (Carlson *et al.*, 1997). Recently Hsieh *et al.* (2000) noted the presence of alkylaromatic compounds in this fraction along with a wide variety of branched hydrocarbons, alkylcyclohexanes and alkylcyclopentanes. However, the need to completely document the identities of all the compounds cannot be over-emphasized. Physical properties of the branched hydrocarbons, particularly melting points, vary significantly with degree of branching. If the individual compounds can be identified it will greatly improve any modeling efforts designed to predict the anticipated extent of wax deposition and assist in predicting temperatures at which wax deposition may be expected to occur. Garcia *et al.* (2000) have also demonstrated that iso- and cyclo-alkane concentrations of greater than 40 wt % can hinder wax crystal arrangement and increase the cloud point of an oil. Most thermodynamic models consider the wax to be comprised entirely of n-alkanes, which is not correct. More than 50% of wax is a very complex mixture of branched and cyclic compounds comprising at least 7 to 8 homologous series of hydrocarbons in differing proportions, all of which need to be considered when modeling properties of the oils. A number of additional homologous series of branched hydrocarbons have been identified in the HMWHC fractions (Fig. 2) including monomethylalkanes, *n*-alkylcyclohexanes, methyl- *n*-alkylcyclohexanes, *n*-alkylcyclopentanes and *n*-alkylbenzenes, *n*-alkyltoluenes and *n*-alkylxylenes. Several homologous series of *n*-alkylmonoaromatic compounds including *n*-alkylbenzenes, *n*-alkyltoluenes and *n*-alkylxylenes have been tentatively identified in the HMW aromatic hydrocarbon fraction.

With the identification of these additional homologous series of compounds in both the saturate and aromatic fractions, a number of wax concentrates isolated from oils sourced from different types of environments are currently being re-examined to obtain additional information on the variability of the methylalkanes with depositional environments. Paraffin deposits in pipelines and production facilities will also be re-examined to determine whether there is a trend in the deposition of one or more particular series of branched hydrocarbons relative to another. While

this work will not necessarily prevent paraffin deposition, a better understanding of the origin and occurrence of the HMW compounds in crude oils (structures, physical/chemical properties, and origin) could reduce clean-up and remedial expenses, lower operation costs and investigative/research expenses, and improve production (Tuttle, 1983; Escobedo and Mansoori, 1992; Leontaritis, 1996). It should also permit the more efficient development of wax inhibitors and solvent systems necessary to remove or reduce paraffin deposits. Delineation of the structure and distribution of the HMW branched alkanes (C_{40+}) will enable us to better understand the behavior of waxy oils, develop/implement more accurate models to predict wax precipitation, and develop preventative and remedial measures before precipitation and deposition become a major issue.

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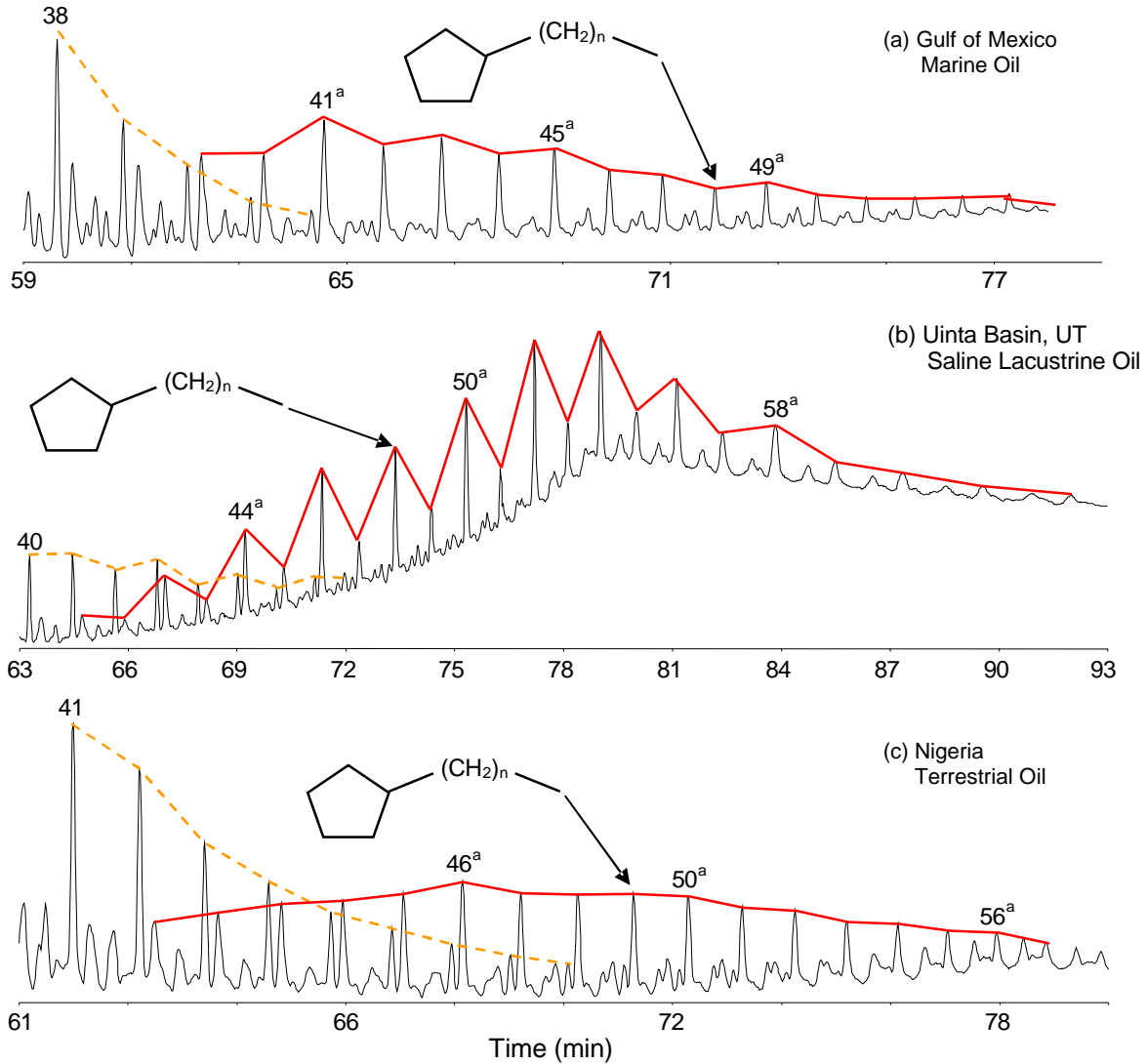


Fig. 1a. Oils derived from marine source rocks are characterized by a distinct odd/even predominance pattern for the alkylcyclopentanes, oils from saline lacustrine environments have a high even/odd predominance pattern (Fig. 1b), and freshwater lacustrine oils a low even/odd or no clear predominance pattern (Fig. 1c).

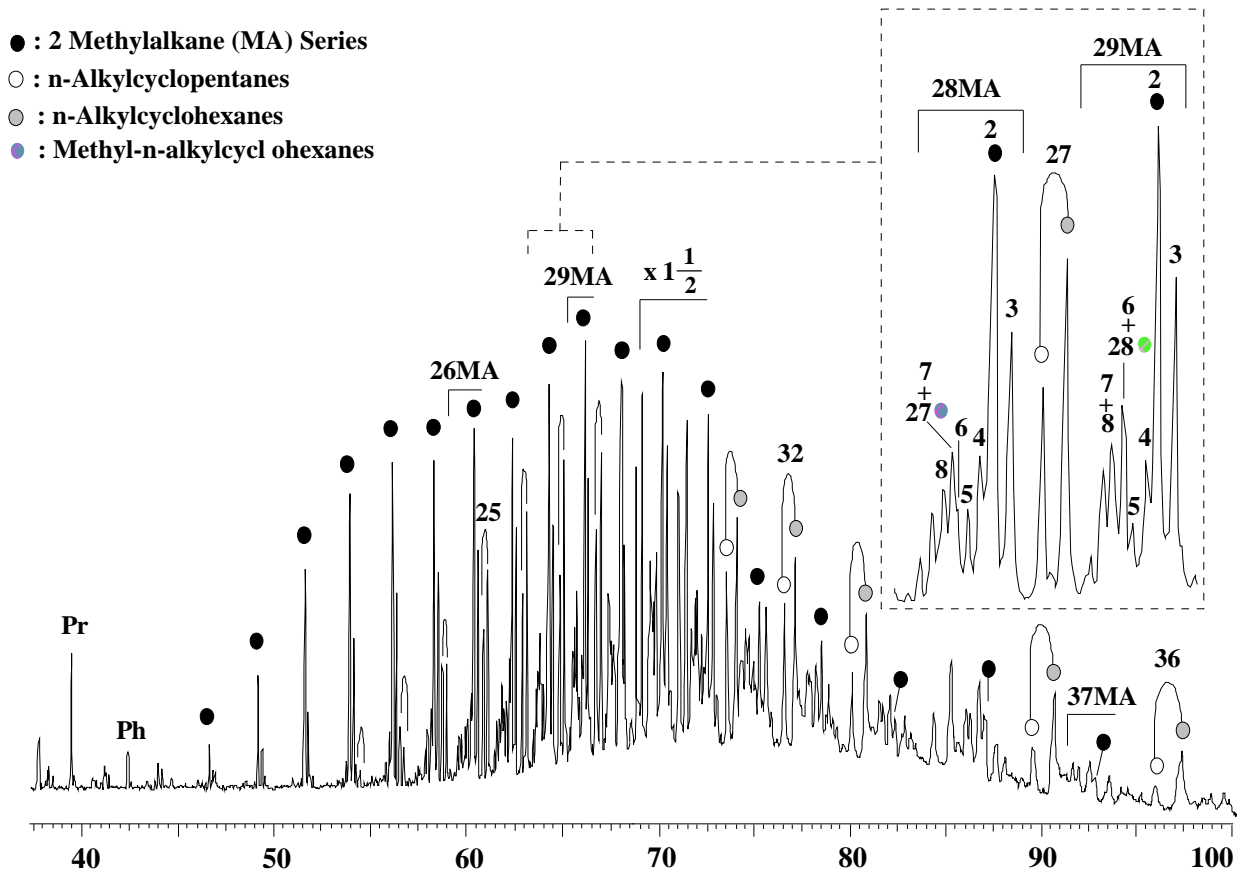


Fig. 2. The complexity of the fraction branched/cyclic HMWHC fraction is illustrated in this total ion current chromatogram. On the expanded parts of the chromatogram, the 28 and 29 refer to the carbon number of the hydrocarbon and the numbers 2 to 8 refer to the position of the methyl branching point in the chain.