Chemical Composition and Geochemical Applications of Waxes Isolated from Pakistani Crude Oil

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(Received 30th November, 2005, revised 20th February, 2006)

Summary: Almost all crude oils even condensates contain some amount of high molecular weight hydrocarbons (HMWHCs) which include waxes and asphaltenes. These compounds are mainly associated with wax deposition problems during production which reduce the recovery rate and ultimately enhance the cost of drilling program. In this study, an attempt has been made to investigate hydrocarbon composition of wax isolated from Rajian field oil and to determine source rock depositional environment. Alumina adsorption sequential soxhlet extraction method was used to isolate wax and asphaltene from crude oil. Wax hydrocarbons were fractionated into *n*-alkanes and branched and cyclic (B/C) alkanes by liquid chromatography using molecular sieves (*Silicalite S115)* and analyzed by high temperature gas chromatography (HTGC).

HTGC of wax branched and cyclic alkanes has shown an odd predominance of *n*-alkylcyclohexanes in HMW region (C_{39} to C_{45}), which is characteristic of marine depositional environment, therefore source rock paleoenvironment of Rajian oil is marine. HTGC provide an inexpensive and very effective analytical tool to establish geochemistry of geological samples.

Introduction

Wax deposition during production is a problem of considerable economic interest, which reduces the production rate and enhances the operational and remedial expenditures. Production and recovery of waxy oils in low temperature geographical regions usually requires application of pour point depressant or heating systems to well bores and pipelines to keep oil flowing, otherwise waxes can deposit in well-bores and other production equipments as the temperature and pressure drops, and may precipitate in reservoirs, thus reducing the ultimate recovery. Microcrystalline waxes are believed to have most significant impact on wax deposition [1].

There had been reports on occurrence of high molecular weight alkanes in petroleum several decades back [2], however study has been hindered due to analytical limitations for identification of compounds > C_{40}. High temperature gas chromatography (HTGC) has provided a useful means for the analysis and quantifying these compounds.

An understanding of the composition of high wax crude oils is directly linked with the production and exploration cost, economic value, field development, reservoir management and refinery operations. For example, high wax oils could be desirable refinery feed stock, not only for the production of wax based products, but also because they are usually low in sulphur & other heteroatoms and metals harmful for process catalysts. However, waxes can cause problems in lubricant formulations, destroying lubricant's low temperature performance as waxes crystallizes.

As regards the exploration, HTGC profile in high molecular region can provide a useful mean to distinguish oils derived from different sources and paleoenvironments. For example, OEP in nC_{23}- nC_{38} alkane range are typically diagnostic of higher plants input to sedimentary organic matter [3]. Carlson *et al.* [4] distinguished lacustrine sourced oil from marine-sourced oil by variations in the distribution of long chain, branched and alkylyclohexanes. Thanh *et al.* [5] extended this work and used odd even predominance (OEP) to distinguish saline-lacustrine and fresh water-lacustrine samples.

Most of the thermodynamic models consider the wax to be comprised entirely of *n*-alkanes, which

is not correct- rather in some cases more than 50% of wax is very complex mixture of branched and cyclic compounds comprising of more than 10 homologous series of hydrocarbons in different proportions all of which need to be considered for modeling properties of the oils. Burger *et al.* [6] characterized an oil sample comprised of 14% wax, of which 58% included hydrocarbons in the C_{46+} range. Barker [7] determined that microcrystalline waxes (*i.e.*, alkanes with melting points > 60°C) in a refined petroleum sample were composed of 20-40% *n*-alkanes, 15-40% *iso*-alkanes, and ~35% cycloalkanes. Dong *et al.* [8] have recognized long chain alkylcyclohexanes and alkylbenzenes as significant component (5.7% of the wax) of coal bed wax sample from Salt Lake City, Utah.

In this study, a crude oil sample from Rajian field has been analyzed for wax hydrocarbons and to determine paleoenvironment of the source during sedimentation.

Results and Discussion

HTGC and Wax Content

The geological and geochemical data of the sample is shown in Table-1. Crude oil was separated into maltene and wax free asphaltene fractions; and maltene was further fractionated into wax and non-wax components according to the method developed by Thanh *et al.*, [5] and Burger *et al.*, [6]. The wax content was calculated on weight percent basis. The HTGC profiles of maltene, wax and non-wax fractions are shown in Figure 1. Major peaks in wax chromatogram correspond to *n*-paraffins in the region of C_{20}-C_{35} (macrocrystalline waxes), which constitute > 90% of the wax; then, a decreasing amounts of microcrystalline wax in C_{35+} region is present. The chromatogram shows unimodal distribution of *n*-alkanes extending up to C_{50} with maxima at C_{24}. No significant odd or even predominance of *n*-alkanes has been observed. The carbon number extends to C_{40}-C_{60} region in the expanded section of chromatogram, although these compounds seem to be absent in maltene chromatogram. The wax content of crude oil (4%) is low, however, its asphaltene content is quite high (> 9%).

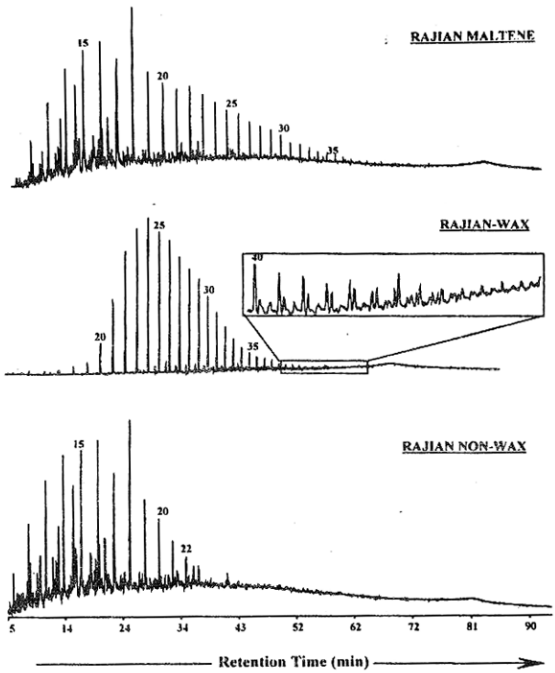

Fig. 1 HTGC showing distribution of hydrocarbon in wax and non-wax fractions isolated from Rajian maltene. Number on peaks denotes carbon number of *n*- alkanes.

Molecular Sieves Fractionation of Waxes

Branched and cyclic (B/C) fraction was isolated from the wax by liquid chromatography on silicalite S115 [9]. Figure 2 shows HTGC of wax and its B/C concentrate. Major peaks in lower chromatogram are HMW biomarkers, including mid-chain monomethylalkanes (MMAs) and long chain monocyclic alkanes. In contrast to the maltene or its wax, which shows traces of HMW biomarkers, a relatively high concentration of these compounds could be seen in B/C fraction. Molecular sieving, therefore, provides a very simple and useful mean to concentrate HMW biomarkers of crude oils which could be analyzed by HTGC. Molecular sieves excluded fraction contains some residual *n*-alkanes, which may help to indicate the elution order of B/C HMW saturated biomarkers relative to *n*-alkanes.

Table-1: Geological and geochemical data of Rajian crude oil.

Oil Field	Oil Formation*	Top* Depth (m)	Formation Temp*(°F)	Probable Geological Age*	Main Depositional Environment*	Maltene (%)	Asphaltene (%)	Wax (%)	API gravity
Rajian	Khewra	3495	160	E. Cambrian	Shallow Marine	74.1	9.24	4	20

* : Data from Oil and Gas Development Corporation (OGDC) Pakistan.

Odd Even Predominance and Depositional Environment

It has been noted previously that variations in distribution of a series of peaks eluting just after *n*-alkanes in HTGC can be correlated with depositional environment. This series has been named as "u-peaks" by Carlson *et al.* [4], whereas Hsieh and Philp [10] have named it "alkylcyclopentanes". In the present study, mass spectral data has shown that series of peaks eluting just after *n*-alkanes are *n*-alkylcyclopentanes followed by *n*-alkylcyclohexanes with one carbon number less than the preceeding *n*-alkane, i.e. pair of C_{35} *n*-alkylcyclopentanes/*n*-alkylcyclohexane elutes after C_{36} *n*-alkane.

In order to investigate that long chain B/C compounds carry signature of the source rock paleoenvironment, crude oil was examined for odd predominance of *n*-alkylcyclohexane which showed an odd predominance in C_{39} to C_{45} region, characteristic of marine oils (Figure 2). HTGC profile of Rajian oil is in agreement with the previous studies by Carlson *et al.* [4] and Hsieh and Philp [10]. HTGC, therefore, provides an inexpensive and a very effective means to establish geochemistry of geological samples which are lean in biomarkers.

Experimental

Sample

The petroleum sample belongs to Potwar Plateau of upper Indus basin. The location of Rajian oil field and geology of Potwar Plateau is provided in a study by Law *et al.* [11].

Deasphaltening of Crude Oil

Asphaltenes and maltenes were isolated from crude oils using the alumina adsorption sequential soxhlet extraction method described by Thanh *et al.*, [5]. Crude oil (1 g) was dissolved in hot iso-octane (~ 80°C; 10mL) and adsorbed on activated alumina (12g ; 250°C) packed in a glass column (40 cm x 1.5 cm i.d.). Maltenes were extracted from the alumina by soxhlet extraction (~ 48 hrs) using iso-octane as solvent. Wax-free asphaltenes were recovered during secondary extraction using chloroform : methanol (95:5 v/v) mixture (~ 6 hrs). The maltene and

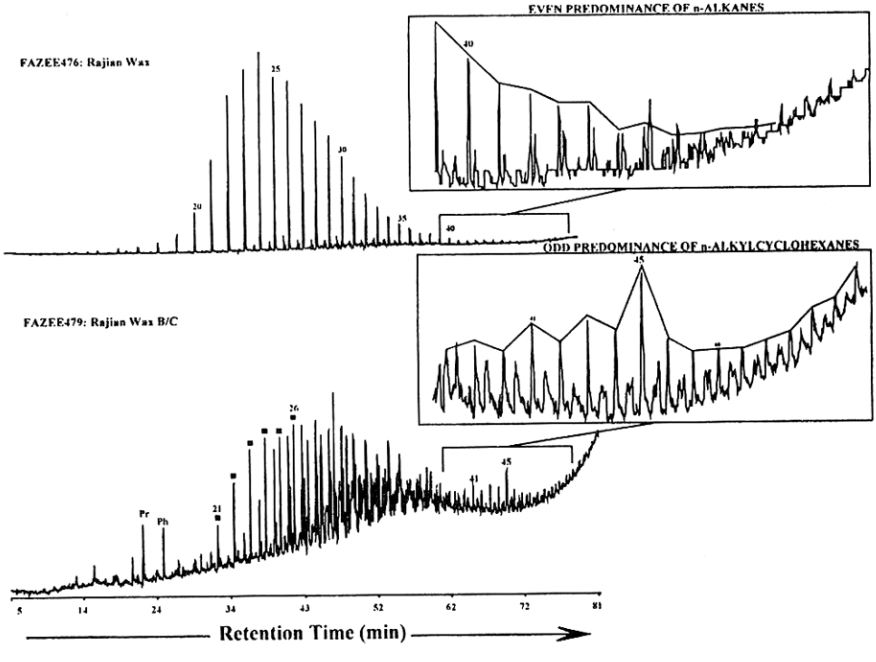

Fig. 2 Wax and its B/C fraction from Rajian crude oil. Even predominance of *n*-alkanes and odd predominance of *n*-alkylcyclohexanes charac-teristic of marine depositional environment is shown; ■ : *n*-alkanes.

asphaltene fractions were concentrated and weighed prior to wax separation or HTGC analysis.

Wax Precipitation

Waxes were precipitated from the maltene fraction according to the method of Burger *et al.* [6]. Maltene (1g) was dissolved in petroleum ether (~7mL) by heating and mixing in an Erlenmeyer flask (50mL). After cooling, acetone (~22mL) was added in small increments with continuous mixing. Once the addition of acetone has been completed, the sample was covered with aluminum foil and sonicated (~10min) and then placed in a freezer at –21°C for at least 2hrs.

The wax crystals were recovered by filtration through pre-cooled Buchner funnel and Whatmann No. 934 glass fiber filter, attached to a vacuum flask (100mL) while non-wax fraction remained in the filtrate. Wax crystals were rinsed 3-times with pre-chilled acetone : petroleum ether mixture (3:1 v/v). Both wax and non-wax samples were quantified in pre-weighed vials and analyzed by HTGC.

Separation of Branched and Cyclic (B/C) Fraction of Wax

Wax sample (20-30mg) dissolved in minimum amount of cyclohexane was sifted through a column packed with 2-2.5g of silicalite *S115* according to method of West *et al.* [9] and was eluted with three bed volumes of cyclohexane. Cyclohexane was used as solvent in all molecular sieve separations of waxes as HMWHCs including microcrystalline waxes are soluble in cyclohexane.

High-Temperature Gas Chromatography (HTGC)

Maltene, wax, non-wax and B/C fractions of wax were analyzed using a Carlo Erba GC8000 high temperature gas chromatograph, equipped with an on-column injector and a SGE HT-5 fused-silica capillary column (25 m×0.32 mm i.d.×0.1 μm film). The oven temperature was programmed from 40° to 370 °C at a rate of 4 °C/min, with flame ionization detector temperature set at 380 °C (total run-time of 120 min). Helium was used as the carrier gas at a flow rate of ~2 mL/min.

Conclusions

High temperature Gas Chromatography (HTGC) has provided a new, rapid and relatively inexpensive technique for the analysis of HMW biomarkers and to establish geochemistry of geological samples.

The variations in the composition of wax hydrocarbons reflects overall properties of crude oil. This information could assist in providing information on wax deposition problems and to plan remedial strategy.

An odd predominance of *n*-alkylcyclohexanes in the region C_{43} to C_{59} is characteristic of marine oil, therefore, source rock paleoenvironment of Rajian oil is marine.

The work described in this study will not only benefit academic community but will also improve efficiency with respect to production and exploration problems, field development, reservoir management and refinery operations and will have direct impact on the economy of the country.

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