

KEROGENIZATION OF ASPHALTENES BY AIR OXYGEN: THE HEIMAR (B OLD PETROLEUM SEEPAGE) SANDSTONE FROM THE DEAD SEA BASIN (ISRAEL)

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Kerogen-like material was generated during a laboratory heating experiment with asphaltenes in the presence of air oxygen. Asphaltenes were extracted from a Heimar (A recent seep) and IPRG sandstones (Dead Sea Basin, Israel) impregnated by heavy/asphaltic crudes and heated at 50–200°C for 1–12 days. These results suggest the possible occurrence of low temperature ($\leq 100^\circ\text{C}$) kerogenization by air oxygen of the Dead Sea (DS) asphaltenes as (B old petroleum seepage location) impregnated with a heavy crude.

Key words: kerogenization; asphalt; oxygen

INTRODUCTION

Recent work by Premović et al. [1] on the asphaltene fraction extracted from Dead Sea (DS) asphalts indicated that amorphous kerogen-like material can be isolated from this asphaltene material when heated at 100–200°C in air. For this reason, asphaltenes were extracted from the Heimar (A recent seep) and IPRG sandstones and heated up to

200°C in air. The objective of the present communications was to carry out the oxygenic kerogenization of the Heimar A and IPRG asphaltic crudes and to evaluate the probability that kerogen within the Heimar B (old seep) is derived for special heating of the asphalt in air atmosphere.

EXPERIMENTAL

Samples

Petroleums of various forms have been found in a small area around the DS. Extraheavy crudes (asphalts) occur in the DS area on the surface as well as in the depth (up to 3600 m) [2]. Its occurrences on the surface (<80 m below) are found in association with Quaternary sands: the Heimar A/B and IPRG materials. Occasionally, large asphalt blocks (up to several tons) have been found floating in the DS. The organic geochemistry of the DS as-

phalt suggests two alternate mechanisms of formation [3]. The first pathway is through degradation of mature crudes. The second is by early diagenetic alternation of organic material in carbonate source rocks [4]. The Heimar A/B materials probably belongs to the first group and to second. On the other hand, organic geochemical data imply a genetic relationship between these two bituminous materials [1]. A detailed description of the samples and their locations are given elsewhere [1]. Geological map (the various samples considered are marked) is presented in Fig. 1.

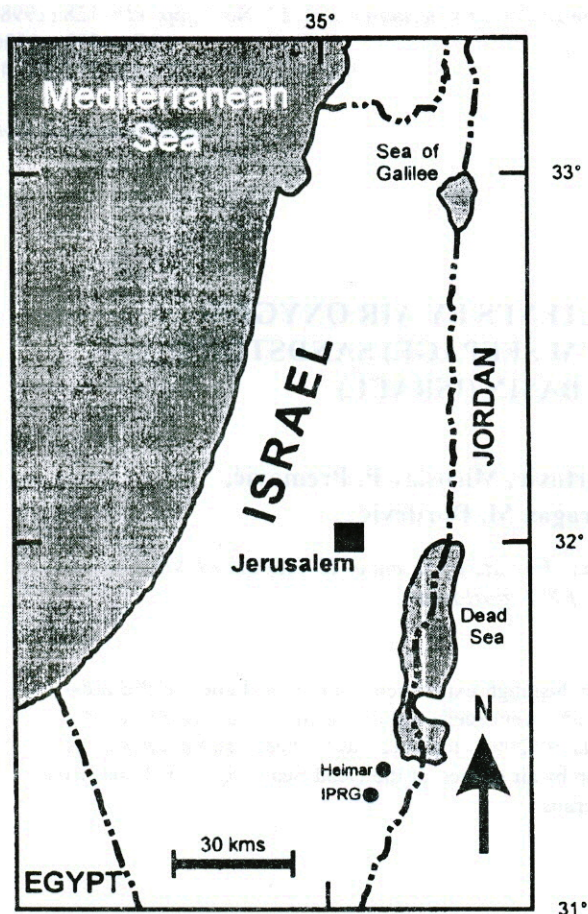


Fig. 1. Geological map indicating sample locations (after Bentor et al. [12])

Extraction and separation

The isolation procedures of the various fractions (kerogen, asphaltenes, maltene, resin and methanol) of the studied bituminous sandstones are given in Premović et al. [1].

Heating experiments

Heating experiments of extracted Heimar A asphaltene (HAA) and IPRG asphaltene (IA) were

conducted as follows. Sets of 50–100 mg of asphaltenes were put into glass tubes (4 mm i.d., 15 cm long) at room temperature. Each tube was heated in an electric furnace at temperatures ranging from 50 to 200°C, for 1 to 30 days. After heating, the reaction products were separated into a soluble part in a benzene: methanol (3:1 v/v) mixture (asphaltenes) and insoluble part (kerogen). The amount of soluble material was determined by the weight difference by solvent extraction, and the amount of kerogen was determined by weighing the residue obtained after solvent extraction.

Elemental analysis

The samples were subjected to microanalysis in a Perkin-Elmer Model 240 elemental analyzer. In Table I the elemental analysis data for the organic components of the sediments studied are presented.

Table I

a) Organic fractions (%) of asphaltic crudes

Sediment	F r a c t i o n			
	Methanol soluble	Resin	Asphaltene	Kerogen
Heimar	64	13	22	< 1
IPRG	10	25	65	–

b) Elemental analysis (wt%) of asphaltic crudes

Sample	E l e m e n t s						
	C	H	N	S	O	H/C	O/C
Heimar	76.0	8.0	2.0	9.0	5.0	1.3	0.05
IPRG	78.0	9.0	1.0	8.0	4.0	1.4	0.04

RESULTS AND DISCUSSION

Fig. 2 shows the asphaltene (soluble part) percentage of HAA during the laboratory heating ($t = 1$ to 12 days) in air at 50, 100, 150 and 200°C ($[HAA] = 100$ when heating time $t = 0$). Since both HAA and IA are solid at room temperature and behave as semisolid/viscous liquids at ca. 70 °C, no insoluble kerogen-like products occur (to any measurable ex-

tent) at 50 °C in the accessible period of time. At temperatures of 100–200 °C insoluble kerogen-like materials did occur. In fact for the kerogen-like materials in question the atomic H/C and O/C ratios (Fig. 3a and b) are typical for kerogen as defined in [5]. Similar results were obtained for the IA. Hereafter, kerogen produced from heat-treated asphaltene-

nes (up to 200 °C) in the presence of air will be referred to as "asphaltene-derived kerogen" (AK). We shall use throughout this paper the term "kerogenization" for thermal conversion of HAA/IA asphaltenes (or similar asphaltenes) into kerogen-like material.

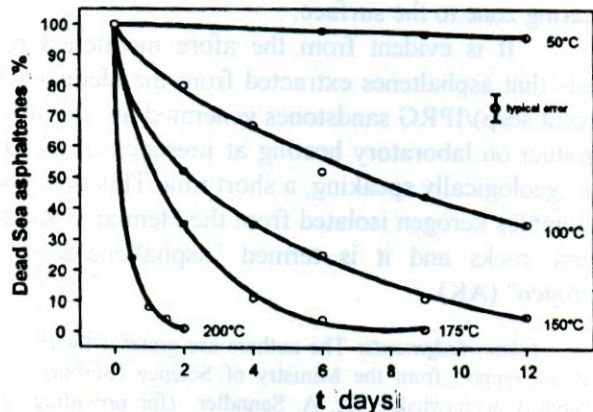


Fig. 2. The amount of HAA ([HAA]) on heating at 100, 150 175 and 200 °C for 1 to 12 days in presence of the air atmosphere

To estimate the rate of kerogenization of HAA, we model this process by a first order reaction. In this case we have the following equation:

$$-\ln(\text{HAA}) = kt - \ln 100$$

where k is a rate constant [1]. Applying this approach the (pseudo- i.e. the energy of the overall reaction pertaining to the intense generation of AK) activation energy (E_a) is calculated to be ca. 10 kcal mol⁻¹. Therefore, half-life $t_{1/2}$ (that is, the time of conversion of 50% of HAA onto AK) is estimated to be ca 2000 days (0 °C); 700 days (15 °C); 400 days

CONCLUDING REMARKS

It is an exception rather than a rule to find petroleum either at/near the surface (less than ca. 100 m) in initial conditions. The instability of its constituents make it especially prone to various alteration processes. They are rapidly accelerated by ready access of air O₂/oxygenic water. One of the earliest changes is the further enhancement in asphaltic components which converts petroleum into heavy/asphaltic crude [6]. Asphaltic crudes (such as the Heimar A/B and IPRG asphaltic crudes) often encountered in outcropping reservoirs of the DS Basin in which severe biodegradation/devolatilization coupled with photoxidation and oxidation by atmospheric O₂ contribute significantly to inspissation [7]. Alteration (especially surficial) may obliterate even

(25 °C); 150 days (35 °C); 100 days (50 °C) and 7 days (100 °C).

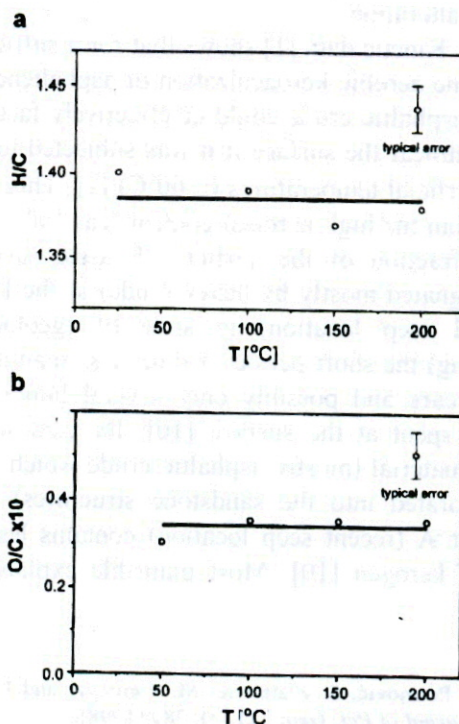


Fig. 3. The atomic H/C (a) and O/C (b) ratios of HAA/AK obtained on heating at various temperature for 1 to 12 days in the presence of air O₂

The most intriguing results of this study is that almost the entire HAA/IA is kerogenizable under suitable physicochemical conditions, i.e. it is possible to convert HAA/IA completely into artificial AK even during laboratory heating under relatively mild thermal conditions (e.g. 100°C, Fig. 2) in an air atmosphere.

primary organochemical "fingerprints" of preexisting petroleum and leave the origin of crude in doubt. Where alteration is not too profound, primary characteristics of petroleum may persist [6]. For this reason, we propose that some of the light/ mature petroleum found in the DS Basin may represent a relict of the primary (unaltered/mature) petroleum. In fact, it is suggested that heavy/asphaltic crudes (as predominant forms of petroleum in the DS area) are more likely alteration (mainly biodegradation/water washing) product derived from extrabasinal unaltered/mature (primary) petroleum [8]. An alternative conception is expressed [9] suggesting that primary petroleum was generated at a great depth somewhere in the DS area itself and that the

heavy/asphaltic crude shows represent an up-dip (intrabasinal) migration, possibly accompanied by partial alteration.

Kinetic data [1] shows that for a sufficiently long time aerobic kerogenization of asphaltenes in a heavy/asphaltic crude could be effectively fast especially at/near the surface if it was subjected to common surficial temperatures ($\leq 60^\circ\text{C}$) [2]. This is evident from the high kerogen content (ca. 19%) of organic fraction of the surficial Triassic sandstone (impregnated mostly by heavy crude) at the Heimar B (old seep location) in spite of (geologically speaking) the short period of time (less than a thousand years and possibly only several hundreds of years) spent at the surface [10]. By contrast organic material (mostly asphaltic crude which is also incorporated into the sandstone structures) of the Heimar A (recent seep location) contains less than 1% of kerogen [10]. Most plausible explanation is

that the aerobic kerogenization of HAA at the Heimar A site has advanced very little as this material has been exposed to the air at/near the surface for a very short period of time (less than ten years). According to Nissenbaum and Goldberg [11] both of these materials did migrate from a deep bitumen-bearing zone to the surface.

It is evident from the afore mentioned results that asphaltenes extracted from the Heimar (A recent seep)/IPRG sandstones generated an insoluble product on laboratory heating at presence of air O_2 for, geologically speaking, a short time. This material resembles kerogen isolated from the Heimar B sandstone rocks and it is termed "asphaltene-derived kerogen" (AK).

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Резиме

КЕРОГЕНИЗАЦИЈА НА АСФАЛТЕНИТЕ СО КИСЛОРОД ОД ВОЗДУХОТ: ПЕСОЧНАТА КАРПА НЕИМАР (СТАРО НАОГАЛИШТЕ НА НАФТА Б) ОД БАСЕНОТ НА МРТВОТО МОРЕ (ИЗРАЕЛ)

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Клучни зборови: керогенизација; асфалт; кислород

Со загревање на асфалтенот во воздушна атмосфера, во лабораториски услови, се добива материја слична на керогенот. Асфалтените се екстрахирани од песочни карпи импрегнирани со тешка нафта од Heimar (ново наоѓалиште А) и од IPRB (басен на Мртвото Море, Израел), со загревање на $100\text{--}200^\circ\text{C}$, во текот на 1–12 дена. Керогенизацијата на асфалтените со кислородот од воздухот ја следи кинетика од прв

ред, а пресметаното време на полуживот ($t_{1/2}$) за асфалтените од Мртвото Море изнесува 2000 до 3 дена на $0\text{--}100^\circ\text{C}$. Овие резултати сугерираат можност за нискотемпературна ($\leq 100^\circ\text{C}$) керогенизација на асфалтените од Мртвото Море, а со тоа и можност на тој начин да се формира материјал сличен на керогенот во песочните карпи во Heimar (старо наоѓалиште на нафта Б), импрегнирани со тешка нафта.