

## THE PRESENCE OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) IN OIL OBTAINED AT PYROLYSIS OF JORDAN OIL SHALE

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*The presence of polycyclic aromatic hydrocarbons (PAH) in the oil obtained at pyrolysis of Jordan oil shale in a fluidised-bed reactor in the atmosphere of nitrogen and nitrogen/steam has been investigated. The final pyrolysis temperature was 520 °C, at which the maximum oil yield was established. The derived oils were fractionated into chemical classes using mini-column liquid chromatography followed by analysis using capillary column gas chromatography with mass spectrometry (GC/MS) for identification and quantification of PAH. The derived oils were found to contain significant amounts of PAH, mainly naphthalene, fluorene and phenanthrene and their alkylated derivatives, and lower amounts of fluoranthrene, pyrene and chrysene. Some of the PAH found in the derived oils are known to be carcinogenic and/or mutagenic, and consequently the oils may represent a significant environmental and health hazard. The PAH have probably formed via Diels-Alder type reactions or via gas-phase cracking of aliphatic compounds.*

### Introduction

The challenge facing the oil shale industry today is the development of reliable, simple, efficient and low-cost oil-shale processes. This will require a clear understanding of chemical and physical processes that occur during oil shale utilisation. All the requirements for successful utilisation of oil shale as a source of liquid and gaseous fuels involve pyrolysis or distillation of oil shale in a retort to which heat can be supplied to thermally degrade the solid organic material (kerogen) present in oil shale. Kerogen decomposes or pyrolysis rapidly at about 510 °C evolving oil vapours and gas and leaving behind a solid char (spent shale). The heat can be supplied either directly

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through combustion within the retort or indirectly by outside combustion and contacting hot gases or solids with the oil shale feed.

As for slow pyrolysis of oil shale, Ekstrom et al. [1] reported a combined alkane, alkene and aromatic content of shale oil produced at a heating rate of  $3.0\text{ }^{\circ}\text{C min}^{-1}$ . Yanik et al. [2] reported the content of aliphatic and aromatic hydrocarbons in shale oil produced at a pyrolysis heating rate of  $5\text{ }^{\circ}\text{C min}^{-1}$ . However, fluidised-bed pyrolysis of oil shales (flash pyrolysis at high heating rates) produces oils which contain more aromatics and less aliphatics. Carter and Taulbee [3] have also shown that fluidised-bed pyrolysis of oil shales yields more aromatics than the Fischer assay.

### **Polycyclic aromatic hydrocarbons (PAH)**

All PAH, with exception of a few hydrogenated derivatives, are solids at ambient temperatures and are the least volatile of the hydrocarbons. Boiling points of PAH are therefore markedly higher than those of the *n*-alkanes of the same carbon number. Nevertheless, losses of PAH during sampling can occur unless stringent precautions are taken [4]. The non-polar nature and high molecular weight of PAH compounds make them very insoluble in water, with linearly fused PAH being more insoluble than their angular isomers [5]. This markedly increases solubility of PAH, particularly if emulsions are formed. Moreover, sorption of PAH on suspended particles such as minerals matter, sediments, and soil in natural waters may also lead to higher apparent concentrations [6, 7]. Chemically PAH are classed as rather inert compounds [8]. However, when PAH do react, they tend to retain their conjugated ring systems by forming derivatives by electrophilic substitution rather than by addition; PAH chemistry has been reviewed at length more recently by Clar [9]. Polycyclic aromatic hydrocarbons can be formed from both natural and anthropogenic sources. Naturally the degradation of isomer biological material is probably the most interesting method for production of PAH. Fossil fuels (petroleum, coal and shale oil) contain extremely complex mixtures of these compounds. Various sediments and fossils have been shown to contain PAH that most likely result from biological material. Anthropogenically it is believed that two distinct reaction steps are involved: pyrolysis and pyro-synthesis. At high temperature, organic compounds are probably cracked to smaller, unstable molecules (pyrolysis). These fragments, mostly radicals, recombine to yield larger, relatively stable aromatic hydrocarbons (pyro-synthesis) [5]. PAH have been linked with chemical carcinogenesis for over two centuries. In 1775, Sir Percival Pott observed that the high incidence of scrotal cancer in chimney sweeps is probably caused by some agent in the coal soot (now known to be rich in PAH) [10]. As a result of Pott's discovery, a number of biological studies of coal tar were carried out with little success. However, in 1918, Yamagiwa and Ichikawa [11] successfully indicated tumours on rabbits' ears by repeated skin application of a coal extract. This marked the

beginning of the search for identification of active carcinogenic substances in soot, which culminated in the isolation of dibenzo(a,k)anthracene by Kennaway [12] in 1930 and benzo(a)pyrene by Cook et al. in 1933 [13]. During the next quarter century the major emphasis was on the synthesis of PAH compounds and assessment of their *in vivo* carcinogenic potential in a variety of rodents and primates [14]. Generally, PAH were found to act locally and induce tumourgenesis at the site of administration of the compound. Although the development of tumours could be initiated by a single administration of a carcinogen, repeated doses were generally considered to be more efficient. Carcinogenic PAH were also shown to act transplacentarily causing the induction of tumours in progeny [5].

PAH are very lipophilic [5], and therefore they need bio-transformation to water-soluble derivatives so they can be effectively extracted from the body. This is achieved by enzymes, some of these enzymes convert the PAH into epoxide derivatives, which then undergo further enzymic reaction to convert finally to the tetrahydro-epoxy compound [5]. Zedeck [15] has shown the structure of this compound to be far the most active mutagen in the range of possible benzo(a)pyrene metabolites. Studies into the metabolism of benzo(z)anthracene have also been reported by Marquardt et al. [16]. Variations can occur in the metabolism scheme, according to species type, gender, and within specific organs [15, 17]. These observations help to clarify why the carcinogenic activity of a particular compound is very dependent upon its structure, shape size, substituent and steric factors all seeming to be important. Isomeric PAH may differ markedly in their activities; activity of benzo(a)pyrene is significantly greater than that of benzo(e)pyrene. Variations in carcinogenic activity of nitrogen PAH heterocycles have been reported by Zajdela et al. [18]. Substitution of nitro or amino-group in a ring also causes a marked increase in carcinogenicity and/or mutagenicity compared to the parent compound. This also has the effect of converting the molecule from an indirect to a direct carcinogen/mutagen. Several nitro-PAH compounds have recently been found in diesel exhaust and other environmental samples, and the compounds are currently undergoing extensive bioassay procedures to assess their full toxicities [19].

Oesche [17] demonstrated that PAH can act as co-carcinogens by applying mixtures of carcinogen and non-carcinogen, as a mixture always increases the expected tumour incidence. Other organic compounds such as solvent and certain inorganic metals have also been implicated as co-factors in PAH carcinogenesis.

## Experimental

### Shale sample

The oil shale sample (about 50 kg) was taken from the Sultani deposit in the south of Jordan and stored in a closed container avoiding any adsorption of

**Table 1. General characteristics of Sultani oil shale sample, wt. %**

Moisture	2.6
Organic carbon	12.5
Total carbon	79.8
Hydrogen	11.1
Nitrogen	0.85
Oxygen	0.90
Sulfur	6.5
Calorific value, kJ kg <sup>-1</sup>	6400

water or loss of volatiles. The sample was crushed by a jaw crusher, well mixed and sieved to four grain sizes 0.25–0.65 mm, 0.65–1.20 mm, 1.20–3.33 mm, and 3.33–5.6 mm. The fraction 1.2–3.33 mm was used in this study, and the other parts will be used in further tests on the effect of grain size on the presence of PAH in the derived oil. The proximate and elemental properties of the sample used are shown in Table 1.

### Pyrolysis reactor

This work concerns the presence of PAH in the oil obtained at pyrolysis of Jordan oil shale under the atmosphere of nitrogen and nitrogen/steam. In this work fluidised-bed pyrolysis reactor was used (Fig. 1).

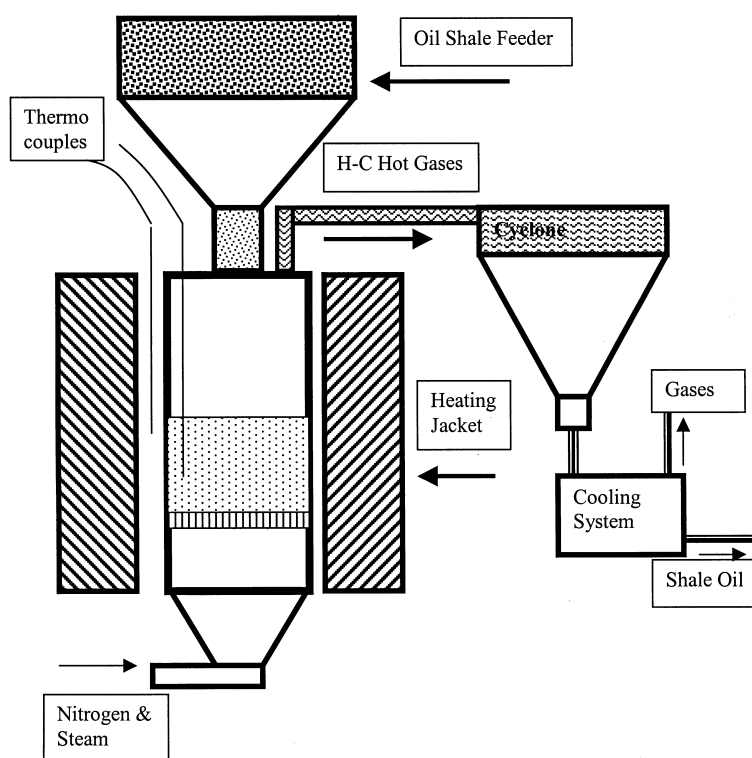


Fig. 1. Schematic diagram of the fluidized bed reactor.

## Oil separation

The oil obtained at pyrolysis of oil shale is known as an extremely complex mixture. Complexity of oil's nature makes the direct analysis using capillary column gas chromatographic techniques to produce very poor separation and resolution of oil components. In addition significant deterioration of the capillary column could also occur due to the non-volatile nature of the oil. This would lead to further loss of resolution and reduce the life of the column [2]. Therefore a preliminary separation of the oil was necessary to divide the oil into fractions (chemical classes).

The oils obtained consisted of an aqueous phase and an oil phase. The oil was separated from the aqueous phase by centrifugation, decantation and removal of the aqueous phase by pipette. Asphaltenes were precipitated with *n*-pentane. The pentane-soluble fraction was separated into chemical class fractions by liquid chromatography which consisted of 10 cm × 1.0 cm glass column packed with silica, Bondesil sorbent, pre-treated at 105 °C for two hours prior to use. The formation of solid phase was prevented by mixing the oil with Chromosorb G/AW/DMCS 60-80 support and packed in the column above the analytical phase. The column was then sequentially eluted under vacuum with pentane, benzene, ethyl acetate and methanol to produce aliphatics, aromatics, ester and polar fractions, respectively. To investigate the overall composition of the oil, each fraction was analysed by capillary column gas chromatography/ mass spectrometry (GC/MS) for the presence of polycyclic aromatic compounds (PAC) in the fraction of aromatics.

## Results and discussion

### Chemical class fractionation of shale oil

Table 2 shows the chemical class fractionation of shale oil generated by fluidised-bed pyrolysis at the temperature of 520 °C under nitrogen and nitrogen/steam fluidisation pyrolysis, respectively. The pentane (1 and 2), benzene, ethyl acetate, and methanol eluents represent the fractions containing aliphatics, aromatics, hetero-atom containing (ester), and polar compounds, respectively.

The aliphatic material represented by the pentane fractions 1 and 2 showed a decrease from 18.15 wt.% to 10.80 wt.% for nitrogen and nitrogen/steam fluidisation pyrolysis, respectively. The benzene fraction showed a corresponding increase from 27.06 to 31.42 wt.% for nitrogen and nitrogen/steam fluidisation pyrolysis, respectively, as well as the ethyl acetate fraction with an increase from 30.60 to 37.5 wt.% respectively, as shown in Table 2. The methanol fraction showed very little change in concentration occurring in the average of  $5.5 \pm 0.3$  wt.% for both nitrogen and nitrogen/steam pyrolysis.

**Table 2. Chemical fractionation of the oil obtained at pyrolysis of oil shale in fluidized-bed reactor under the nitrogen and nitrogen/steam atmosphere. The results are in terms of the oil composition**

Fraction yield (wt.%)		Pyrolysis Atmosphere	
		Nitrogen	Nitrogen/steam
Pentane-1+2	(aliphatics)	18.15	10.80
Benzene	(aromatics)	27.06	31.42
Ethylacetate	(ester)	30.60	37.50
Methanol	(polars)	4.92	5.15
<i>Total</i>		80.73	84.87
Asphaltene	(by difference)	19.27	15.13

The addition of steam caused some of the organic material that remained in shale during retorting in a nitrogen atmosphere as heavy material by the aromatisation of the oil to produce oils which contain more aromatics and less aliphatics.

### PAH in oil

The fractions separated from the shale oil were examined by capillary gas chromatography. The pentane and benzene fractions were examined firstly for PAH. To examine the retention time and the scan range, a standard mixture of naphthalene, anthracene, fluoranthrene, and chrysene was injected as shown in Fig. 2, the peak identities being established by library sample spectra matching as shown in Fig. 3.

Examination of the GC/MS chromatograms of the pentane-1 and pentane-2 fractions showed that none of those aromatic compounds and others are present. Detailed examination of the aliphatic fractions by GC/MS was not carried out. It was established that the components of this fraction were aliphatic hydrocarbons.

The benzene eluent from the column fractionation (the fraction containing aromatics) was examined by establishing the retention index from the literature and standards injection. The presence of substituted PAH was identified by Single Ion Monitoring (SIM) and confirmed by examination of the full mass fragment spectrum. The compounds were identified with confidence with retention index data in conjunction with the full mass fragment spectra library matches standards. By use of the standard material and retention index data, the matching of peaks from one chromatographic system to the other was done. The retention index for every compound identified was calculated.

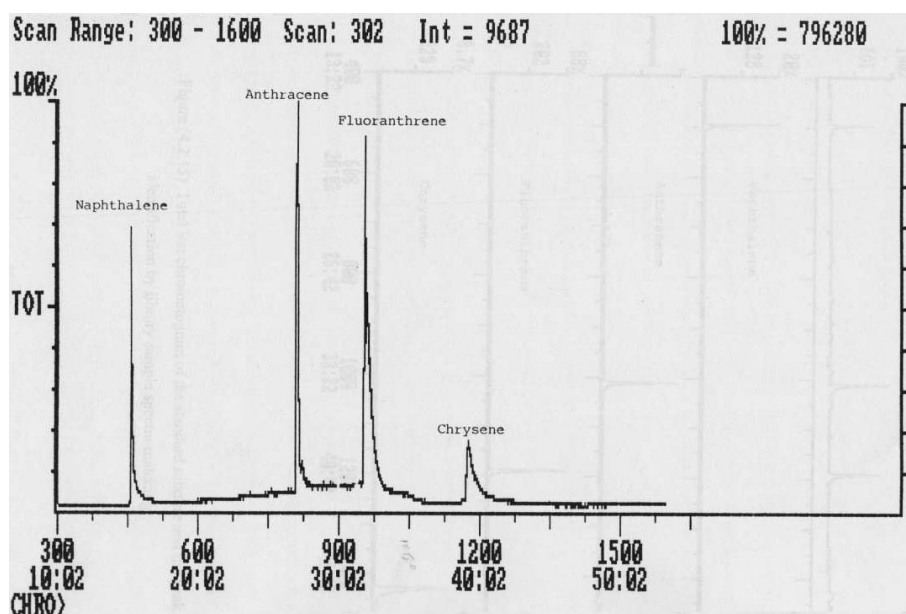


Fig. 2. Typical gas chromatogram of the STD mixture.

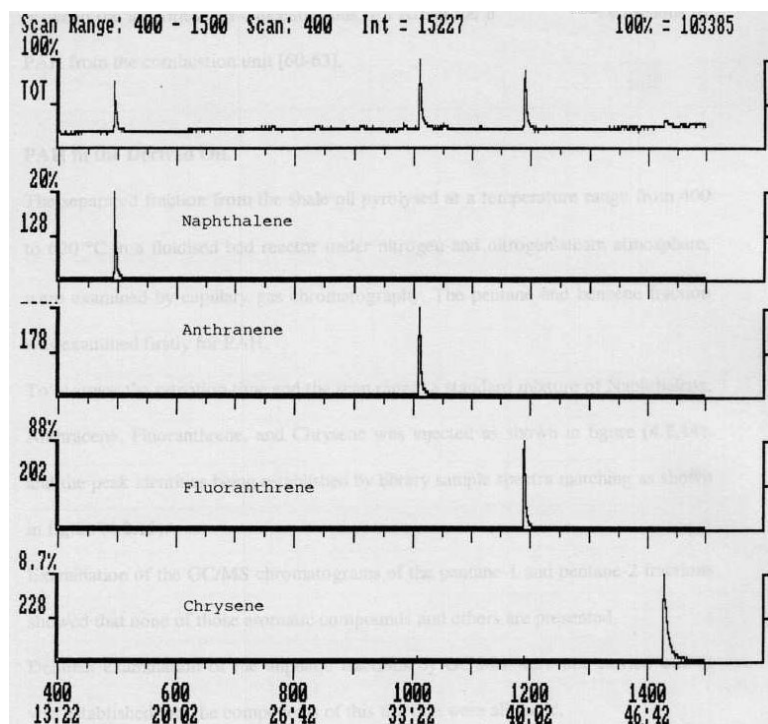


Fig. 3. Total ion chromatogram of the STD mixture and the peak identification by library spectra matching.

Table 3 shows the absolute content of PAH present in shale oil obtained at fluidised-bed pyrolysis of oil shale under the nitrogen and nitrogen/steam atmosphere. The data on the content of those PAH positively identified are used to illustrate the influence of the pyrolysis atmosphere on the formation of PAH in the fluidised-bed reactor. The PAH found consist mainly of naphthalene, biphenyl, fluorene, phenanthrene and their alkylated derivatives.

The total content of the 2-ring, 3-ring, and 4-ring PAH compounds of the shale oil formed under the nitrogen/steam pyrolysis atmosphere was higher than that in the oil formed under the nitrogen atmosphere.

The formation of aromatics and PAC *via* secondary reactions during pyrolysis has been attributed to Diels-Alder type reactions. A Diels-Alder type aromatisation reaction involving cyclisation of alkenes and subsequent formation of monoaromatic and polycyclic aromatic compounds is reported by Cypres [20], Fairburn et al. [21], Depeyre et al. [22], Williams and Taylor [23], Williams and Besler [24], and Williams and Nazzal [25], or *via* conversion of hydrogen-poor materials to coke, and cracking of aliphatic moieties to gas resulting in the selective concentration of aromatic compounds as reported by Burnham [26].

**Table 3. Content of polycyclic aromatic hydrocarbons (PAH), in ppm, in the oil obtained at pyrolysis of oil shale in fluidised-bed reactor under nitrogen and nitrogen/steam atmosphere**

Compounds	Pyrolysis atmosphere	
	Nitrogen	Nitrogen/steam
Naphthalene	400	1200
2-Methylnaphthalene	1510	3500
1-Methylnaphthalene	1200	3000
Biphenyl	180	440
Ethyl-naphthalene	660	1500
2,6 or 2,7 Dimethylnaphthalene	420	700
1,6 or 1,3 Dimethylnaphthalene	1200	2000
2,3 or 1,4 Dimethylnaphthalene	500	800
Acenaphthalene	800	1350
Methylbiphenyl	1100	1200
Acenaphthene	40	90
Trimethylnaphthalene	250	710
Fluorene	400	870
1-Methylfluorene	15	70
Phenanthrene	500	500
Anthracene	100	150
1-Methylphenanthrene	180	200
Fluoranthene	110	100
Pyrene	110	200
1-Methylpyrene	20	50
Chrysene	110	100



It is not possible (according to the available knowledge) to eliminate the formation of PAH in the obtained oil without elimination or decreasing the aromatization processes *via* secondary reactions through either a Diels-Alder type reaction or selective cracking of aliphatic compounds resulting in selective concentration of aromatic compounds.

It is possible to think about a non-thermal process of oil extraction, but it needs a lot of research and cooperation between all the people who are interested in utilization of oil shale.

## Conclusions

- Oil shale has been pyrolysed under both nitrogen and nitrogen/steam atmosphere at the pyrolysis temperature of 520 °C.
- Chemical class fractionation of the obtained shale oil using solid phase extraction on silica gel was particularly useful for separation of the oil into aliphatic, aromatic, ester and polar hydrocarbons.
- The content of aliphatic material represented by the fractions pentane-1 and pentane-2 is lower in the oil obtained at pyrolysis under the nitrogen/steam atmosphere.
- A relatively high content of aromatic compounds in the oil obtained under the nitrogen/steam atmosphere could be caused by aromatisation of the oil.
- The ethyl acetate fraction represents oxygenated compounds which showed only a small increase in the nitrogen atmosphere. In the presence of steam a significant increase was observed.
- The methanol fraction represents polar compounds with very little changes in their amount in both nitrogen and nitrogen/steam atmosphere.
- The formation of aromatics *via* secondary reactions during pyrolysis has been attributed to Diels-Alder type reactions or to gas-phase cracking of aliphatic compounds resulting in selective concentration of aromatic compounds.
- The oil obtained at fluidised-bed pyrolysis under nitrogen and nitrogen/steam was found to contain a significant amount of PAH, mainly naphthalene, flourene, and phenanthrene and their alkylated homologes, and lower amounts of fluoranthrene, pyrene and chrysene. The amount of PAH in the oil obtained under the nitrogen/steam atmosphere was higher than that in the oil obtained under the nitrogen atmosphere. This could be a result of the steam reactions which could have caused an increase in the aliphatics degradation (cracking).

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