

Pyrolysis of petroleum asphaltenes from different geological origins and use of methyl-naphthalenes and methylphenanthrenes as maturity indicators for asphaltenes

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Abstract. Asphaltenes separated from two different crude oils from upper Assam, India, having different geological origins, viz. DK (eocene) and JN (oligocene–miocene) were pyrolysed at 600 °C and the products were analysed by gas chromatography–mass spectrometry (GC/MS) especially for the generated alkyl-naphthalenes and alkylphenanthrenes. Both the asphaltenes produce aliphatic as well as aromatic compound classes. Alkyl-naphthalenes and alkylphenanthrenes were identified by using reference chromatograms and literature data and the distributions used to assess thermal maturity of the asphaltenes. The ratios of β -substituted to α -substituted isomers of both alkyl-naphthalenes and alkylphenanthrenes revealed higher maturity of the JN asphaltenes than the DK asphaltenes. For both the asphaltenes, the abundance of 1-methylphenanthrene dominates over that of 9-methylphenanthrene showing the terrestrial nature of the organic matter.

Keywords. Maturity; methyl-naphthalenes; methylphenanthrenes; asphaltenes; pyrolysate; kerogen.

1. Introduction

The complexity of petroleum fractions increases with increase in boiling point owing to the exponential increase in the number of isomers for a given carbon number. Moreover, the presence of aromatic and heteroatom-containing compounds makes it very difficult to study the detailed composition of the heavier ends of petroleum. However, the rapid depletion in oil resources forces us to study and utilize every fraction throughout the refining processes (Neurock and Klein 1995). The heavy ends of petroleum, especially, asphaltenes represent an enigmatic yet important class of compounds (Bunger and Li 1984; Sheu and Mullins 1995; Mullins and Sheu 1998). They strongly influence the rheology of paving material (Sheu and Mullins 1995; Mullins and Sheu 1998) and impact on the production, transportation and refining of crude oils (Bunger and Li 1984; Sheu and Mullins 1995; Mullins and Sheu 1998). Asphaltenes are brown to black amorphous solids containing carbon, hydrogen, nitrogen, oxygen and sulphur. They are believed to be made up of condensed aromatic rings with short aliphatic chains and naphthenic ring structures, as well as being of high molecular weight (Nali *et al* 1995). The classical definition of asphaltenes is based on the solu-

tion properties. They are defined as the *n*-pentane insoluble and benzene soluble fractions of coal or petroleum. Later it was demonstrated that the elemental composition of asphaltene fractions precipitated by different solvents from various sources of petroleum varies considerably (Kawanalca *et al* 1989). Several authors considered them as the most labile part of the respective kerogen in oil reservoirs (Speight and Moschopedis 1981; Arefyev *et al* 1982). So, the study of asphaltenes brings important clues concerning the chemical reactions taking place during kerogen maturation. Pyrolysis (Py) followed by (GC/MS) has provided new insight into their structure, especially for side chains on polyaromatic nuclei. Several reaction pathways have been proposed for asphaltene pyrolysis (Rubinstein and Strausz 1979; Larter and Douglas 1982; Neurock *et al* 1990; Murata *et al* 1995; Yasar *et al* 2001). For example, the pyrolysis at 350–800 °C produces substantial amount of alkanes and polynuclear aromatic hydrocarbons. Py–GC has become a tool for correlation studies. Rubinstein and Strausz (1979) tried to correlate biodegraded oil with its “normal” oil. The study of asphaltenes is also important as there exist striking physical and chemical similarities between oil-forming kerogen and petroleum asphaltenes which in turn may provide better understanding of their role in petroleum generation, migration and maturation. Asphaltenes are emerging as frontier molecules in geochemical research as they provide important clues about nature and source of organics, maturation, migration and secondary alteration effects. They represent a major class of

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petroleum components that have no analogous counterpart in the biological systems. This suggests that they are secondary products formed after the deposition of the source material. They may be fragments of the original kerogen from which the petroleum is derived and may be expelled as part of it. In addition to their geological significance, they are indispensable in either demonstrated or proven applications in production and refining (International conference on petroleum geochemistry and exploration in Afro-Asian region, Nov 1985). The alkylnaphthalenes and alkylphenanthrenes have widely been used as thermal maturation indicators (Radke 1987; Stojanovic *et al* 2001; Shuichang *et al* 2005; Asif and Tahira 2007). In the present communication, asphaltenes from two crude oils of different sources were pyrolysed at 600 °C in a pyrolyser and the different alkylnaphthalenes and alkylphenanthrenes generated in the pyrolysates were used to assess the maturities of the two asphaltenes.

2. Experimental

Asphaltenes (ca. 2 mg) separated from the 300 °C+ fraction of DK and JN were introduced into a PY-2020iD double-shot pyrolyzer at 600 °C, which was directly connected to a GC/MS instrument comprising a thermo trace gas chromatograph and a thermo DSQ mass spectrometer. The GC column was DB-1 (30 m × 0.35 mm i.d., 0.32 μm film thickness) and the oven temperature programme was −35 °C (5 min) to 300 °C at 2 °C/min (holding time, 5 min). The chromatograph conditions were: split injector 300 °C; split flow 20 ml/min; split ratio 20:1; carrier gas He at constant flow; transfer line 300 °C. The MS operating conditions were: ion source 200 °C, full scan with mass range 50–500 amu, total time of analysis 105 min.

3. Results and discussion

The physical characteristics of the two crude oils, DK and JN, are presented in table 1. They were selected on the basis of their geological time scale. DK is from eocene and JN from oligocene–miocene origin. The distillation characteristics are presented in table 1. Petroleum asphaltenes have been a subject of pyrolytic studies for more than a decade (e.g. Moschopedies *et al* 1978; Gonzalez *et al* 2001); it provides an important quantitative information on identity, composition and structure. Here, the asphaltenes were pyrolysed at 600 °C and the products were analysed using GC/MS. Figures 1 and 2 show partial mass chromatograms for the methyl-naphthalenes and methylphenanthrenes in the pyrolysates of JN and DK asphaltenes, respectively. A general feature is, apart from the presence of a series of *n*-alkane/*n*-alkene doublets the abundance of aromatic biological markers such as alkylnaphthalenes and alkylphenanthrenes were identified through MS library, Wiley and comparison with other published data. Alkylnaphthalenes

Table 1. Physical characteristics of crude oil.

Physical properties	Oil	
	DK	JN
Origin	Eocene	Oligocene–miocene
Density	0.8843	0.856
API gravity	28.6	33.7
Pour point (°C)	30	24
Dist. characteristics IBP%	78	85
Vol.% at (°C)		
5	142	85
10	170	122
15	202	140
20	240	164
25	258	206
30	280	236
33	300	268
35		294
40		300
42		

and alkylphenanthrenes were the most abundant compound classes which are discussed in detail. The identified ones and their abundance in the pyrolysates are presented in table 2.

3.1 Origin and geochemical significance of alkylnaphthalenes

Alkylnaphthalenes are mainly derived from terrestrial sources (Radke and Willsch 1994) and several precursors are known: cyclic sesquiterpenoids derived from resinous constituents of conifers are potential precursors of alkylnaphthalenes (Pentegova *et al* 1968); thermal degradation of β -carotene led to the formation of 2,6-dimethylnaphthalene, 1- and 2-methylnaphthalene and naphthalene (Day and Erdman 1963; Achari *et al* 1993), 1,2,7-trimethylnaphthalene is suggested to originate from compounds like β -amyryn that are constituents of angiosperms (Strachan *et al* 1988); β -amyryn and monoaromatic seco-hopanes are among several potential precursors of 1,2,5-trimethylnaphthalene and 1,2,5,6-tetramethylnaphthalene (Püttmann and Villar 1987); 1,2,4-trimethylnaphthalene might originate from α -tocopherol present in recent marine sediments (Brassell *et al* 1985); 1,2,2',5-tetramethyltetralin and 1,2,2',5,6-pentamethyltetralin from microbial sources, might be precursors of 1,2,6-trimethylnaphthalene, 1,2,5,7- and 1,2,3,5-tetramethylnaphthalene (Alexander *et al* 1992).

Some alkylnaphthalenes have various potential biological sources. Strachan *et al* (1988) found high proportions of 1,2,5- and 1,2,7-trimethylnaphthalene in sediments of cretaceous age and younger. The degradation of β -amyryn via 8,14-seco-triterpenoids is supposed to additionally yield in high proportions of 1,2,5,6-tetramethylnaphthalene

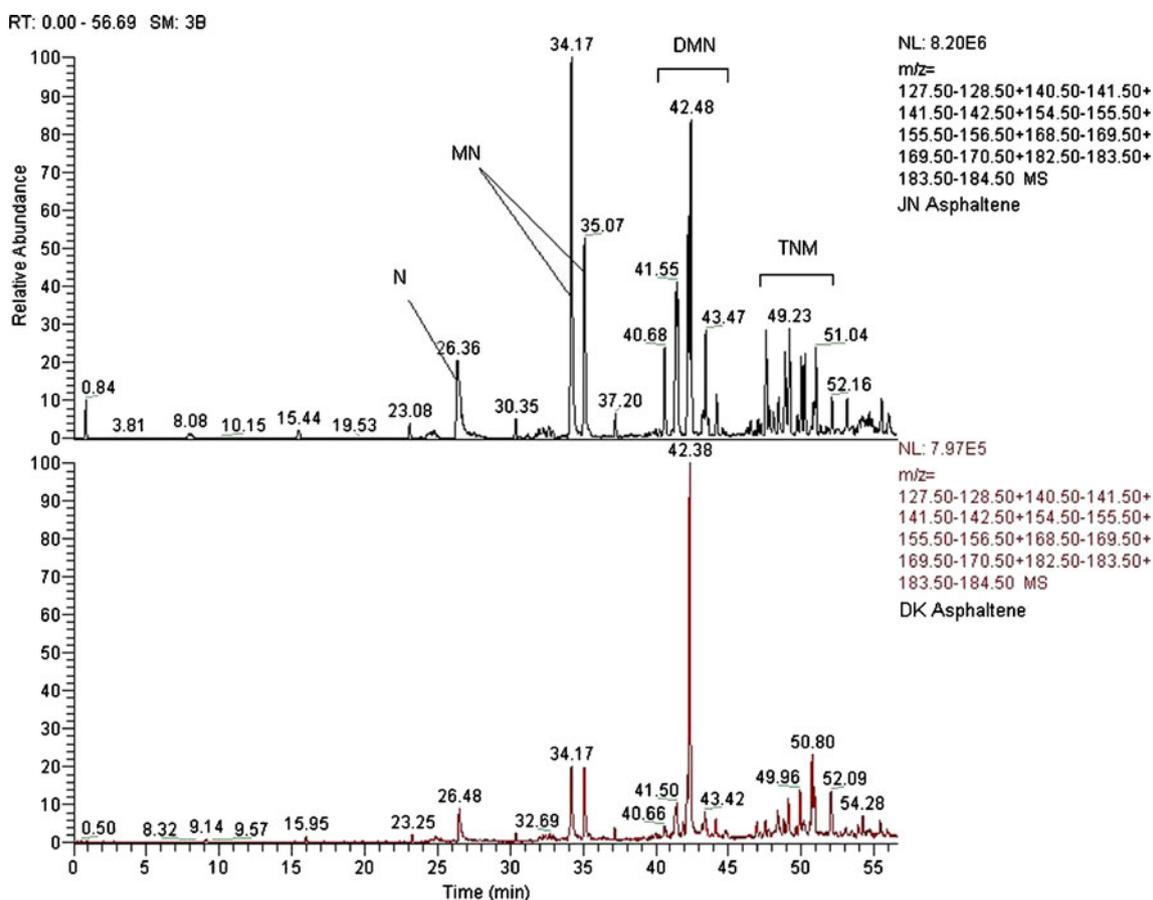


Figure 1. Partial summed mass chromatograms for alkylnaphthalenes in DK and JN asphaltene pyrolysates (N = naphthalene; MN = methylnaphthalene and DMN = dimethylnaphthalene).

(Püttmann and Villar 1987). High proportions of 1,2,7-trimethylnaphthalene have been attributed to the contribution of angiosperms to sediments. In contrast, 1,2,5-trimethyl- and 1,2,5,6-tetramethyl naphthalene may also derive from other natural precursors. They may be formed via degradation of monoaromatics seco-hopanoids (Hussler *et al* 1984). Additionally, both 1,2,5-trimethyl- and 1,2,5,6-tetramethyl naphthalene were detected as major constituents in the fluorinate filling of needles from *Abietites linkii*, a gymnosperm (Heppenheimer *et al* 1992); 1,2,5-trimethylnaphthalene may also originate from the dehydrogenation of biological precursors like agathic acid, communic acid and manool (Thomas 1970; Carman and Craig 1971). The latter compounds are constituents of gymnosperms (Karrer 1976; Thomas 1970).

To recognize source effects, Strachan *et al* (1988) compared the relative amounts of 1,2,7- to 1,3,7-trimethylnaphthalene and those of 1,2,5- to 1,3,6-trimethylnaphthalene. While 1,2,7- and 1,2,5-trimethylnaphthalene are supposed to have direct biogenic precursors, 1,3,7- and 1,3,6-trimethylnaphthalene are suggested to originate from the isomerization of these two potential biomarkers. Although the two ratios depend on the maturity of the samples, source effects are assumed to be recognizable from establishing a logarithmic plot (Strachan *et al* 1988).

3.2 Origin and geochemical significance of alkylnaphthalenes

Diterpenoids, with an abietane and pimarane skeleton are likely biological precursors of alkylnaphthalenes (Simoneit *et al* 1986). These compounds are constituents of ambers and resins (Thomas 1970; Simoneit *et al* 1986) in vascular plants. The most prominent alkylnaphthalene, directly attributed to diterpenoids of the abietane type is 1-methyl-7-isopropylphenanthrene (retene). 1,7-dimethylphenanthrene (premanthrene) probably originates from diterpenoids of the premarane type but is also a potential decomposition product of retene (Simoneit *et al* 1986). Additionally, phenanthrene and alkylnaphthalenes may originate from pentacyclic triterpenoids or steroids (Streibl and Herout 1969; Greiner *et al* 1976). A detailed study of the distribution of alkylnaphthalenes regarding their potential biological origin and dependence on maturity has been carried out by Budzinski *et al* (1995). The authors compared the distributions of methyl, dimethyl and trimethylphenanthrenes in samples originating from terrestrial and marine sources. High proportions of 1-methylphenanthrene were preferentially found in the organic matter of terrestrial source rocks, whereas 9-methylphenanthrene was relatively enriched in organic matter from marine shales. Additionally, a

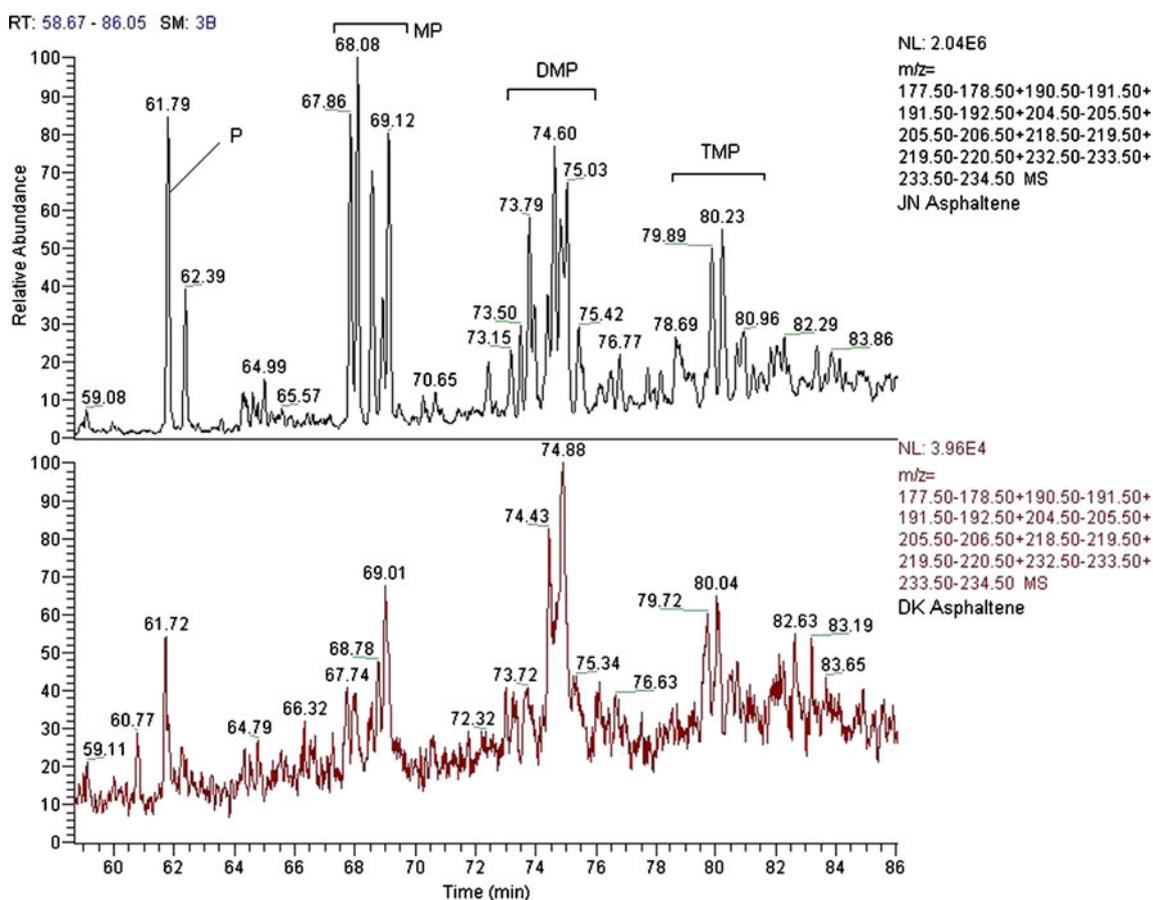


Figure 2. Partial summed mass chromatograms of alkylphenanthrenes in DK and JN asphaltene pyrolysates (P = phenanthrene; MP = methylphenanthrene; DMP = dimethylphenanthrene and TMP = trimethylphenanthrene).

predominance of pimanthrene and retene has been attributed to terrestrial organic matter. Among trimethylphenanthrenes, 1,2,8-isomer, was in general the most abundant isomer. While there is so much evidence for the biological origin of alkylnaphthalenes, investigation of them mainly addresses their common use as maturity parameters (Radke *et al* 1982b). In immature samples, 9-methylphenanthrene and 1-methylphenanthrene are often highly abundant, with 9-methylphenanthrene being predominant (Radke *et al* 1982a). With increasing maturity, 2-methylphenanthrene and 3-methylphenanthrene become more prominent, due to their enhanced thermal stability. Normally, 2-methylphenanthrene is present in higher proportions than 3-methylphenanthrene (Alexander *et al* 1992). Based on these observations, the methylphenanthrene ratio (MPI 1, table 3) was established, showing an excellent correlation with the vitrinite reflectance for organic material of type III kerogen (Radke *et al* 1982a). Therefore, the vitrinite reflectance (R_r) of terrestrial organic matter, with ratios of MPI1 ratio < 2.65 can be approximated by calculation (R_r , table 3). MPI 2 normally is little enhanced in comparison to MPI 1, due to the slight predominance of 2-methylphenanthrene.

The maturity of the asphaltenes was determined on the basis of maturity ratios of alkylnaphthalenes and alkylphenanthrenes (table 3). Several ratios based on the

distribution of alkylnaphthalenes therefore compare the amounts of more stable to less stable isomers. The more stable isomers are substituted at positions 2, 3, 6 and 7 of the naphthalene skeleton. Radke *et al* (1982b) found that samples of enhanced ($>0.9\%$ R_r) show elevated proportions of 2-methylphenanthrene vs 1-methylphenanthrene. This also accounts for the ratio of 2-methylphenanthrene to 1-methylphenanthrene (table 3). Instead of peak areas, peak heights of the compounds were taken for calculation of maturity ratios due to the poor resolution of some peaks. The relative abundances are presented in table 2. The naphthalene concentration in DK-asphaltene pyrolysates is much higher than JN-asphaltene pyrolysates. MNR increases with increasing maturity. It reveals from table 3 that MNR for JN is almost double that for DK, i.e. the more stable β -isomer (2-methylnaphthalene) predominates over less stable α -isomer (1-methylnaphthalene) in JN. For DK, both isomers have equal concentrations. Like MNR, the ratios of dimethylnaphthalenes (DNR) and trimethylnaphthalenes (TNR 1 and TNR 2) also increase with increasing maturity (table 3). Amongst dimethylnaphthalenes, 1,6-DMN has the highest and 1,5-DMN has the lowest concentration for DK whereas in JN the highest concentration was observed for 1,2-DMN and the lowest for 1,4-DMN+2,3-DMN. Both 1,4-DMN and 2,3-DMN elute at the same retention time

and appears as a single peak. The DNR ratio for DK is 1.77 and for JN 2.79. This means that the more stable β, β' -isomers (2,6- and 2,7-dimethylnaphthalenes) predominate

Table 2. Relative abundance of alkylnaphthalenes and alkylphenanthrenes of DK- and JN-asphaltene pyrolysates.

Compounds	Abundance %	
	DK	JN
Naphthalene	3.67	0.01
2-methylnaphthalene	0.29	0.97
1-methylnaphthalene	0.30	0.53
2,6-dimethylnaphthalene	0.09	0.35
2,7-dimethylnaphthalene	0.10	0.38
1,3-DMN+1,7-DMN	0.29	0.58
1,6-DMN	1.33	0.80
1,4-DMN+2,3-DMN	1.16	0.06
1,2-DMN	0.64	0.97
1,5-DMN	0.05	0.14
1,3,7-TMN	0.10	0.24
1,3,6-TMN	0.25	0.76
1,3,5-TMN+1,4,6-TMN	0.16	0.20
2,3,6-TMN	0.03	0.21
1,2,7-TMN	0.10	0.03
1,6,7-TMN	0.28	0.12
1,2,6-TMN	0.15	0.22
1,2,4-TMN	0	0.03
1,2,5-TMN	0.15	0.09
Phenanthrene	0.06	0.28
3MP	0.06	0.25
2MP	0.04	0.27
9MP	0.05	0.15
1MP	0.15	0.22

MN = methylnaphthalene; DMN = dimethylnaphthalene; TMN = trimethylnaphthalene and MP = methylphenanthrene.

more over the α, α -isomer (1,5-dimethylnaphthalene) for JN than DK. The distribution of alkylnaphthalenes is supposed to be mainly influenced by the thermal history. Increasing maturity results, for example, in the progressive conversion of 1,2,5-trimethylnaphthalene to the 1,3,6-trimethylnaphthalene and other isomers (Strachan *et al* 1988). This results from isomerization reactions, leading to the predominance of more stable isomers with increasing maturity. The TNNr and TrMN ratios reveal that the conversion of 1,2,5-trimethylnaphthalene to the more stable 1,3,6-trimethylnaphthalene appears to be greater for JN asphaltene than DK asphaltene. Amongst the trimethylnaphthalenes, the 1,3,6- and 1,6,7-isomers are present in significant quantities for DK whereas for JN, the 1,2,6-, 2,3,6-, 1,3,5 + 1,4,6- and, in particular, 1,3,6-trimethylnaphthalenes are present in significant quantity. TNR 1 and TNR 2 for DK and JN are 0.1, 1.05 and 0.32, 0.47, respectively. The comparison of all the methylnaphthalene ratios indicates that all the ratio values are greater for JN than DK asphaltene pyrolysates (figures 3 and 4). This proves that JN is more mature than DK.

Different ratios of methylphenanthrenes have been used by petroleum geochemists as thermal maturity indices (Radke *et al* 1986). The maturity of DK and JN asphaltene was assessed by applying these ratios. Alkylphenanthrenes are the common constituents of sedimentary organic matter. They have been reported in shales (Radke *et al* 1982a; Fisher *et al* 1996; Borrego *et al* 1997), coal and crude oil (Fisher *et al* 1996; Borrego *et al* 1997). Methylphenanthrenes were commonly observed for both asphaltene. 2-methylphenanthrene and 3-methylphenanthrene being present to some extent in higher concentration than 1-methylphenanthrene and 9-methylphenanthrene for JN asphaltene. For DK asphaltene, the concentration of 1-methylphenanthrene was highest followed by 2-methylphenanthrene, 3-methylphenanthrene

Table 3. Methylnaphthalene and methylphenanthrene ratios for DK and JN asphaltene.

Name	Maturity ratio	Ref.	DK	JN
MNR	2MN/1MN	Radke <i>et al</i> (1982b)	0.97	1.83
DNR	2,6+2,7-DMN/1,5-DMN	Radke <i>et al</i> (1982b)	3.80	5.21
TNR 1	2,3,6-TMN/1,3,5+1,4,6-TMN	Alexander <i>et al</i> (1985)	0.19	1.05
TNR 2	1,3,7+2,3,6-TMN/1,3,5+1,3,6+1,4,6-TMN	Radke <i>et al</i> (1986)	0.32	0.47
TNNr	1,3,7-TMN/1,3,7+1,2,5-TMN	van Aarsen <i>et al</i> (2000)	0.40	0.73
TrMN	1,3,7+1,3,6+2,3,6-TMN/ \sum TMN	Kruege (2000)	0.31	0.64
MPI 1	1.5(2MP+3MP)/P+1MP+9MP	Radke <i>et al</i> (1982a)	0.58	1.2
MPI 2	3(2-MP)/P+1-MP+9-MP	Radke <i>et al</i> (1982a)	0.46	1.25
MPI 3	(2MP+3MP)/(1MP+9MP)	Radke <i>et al</i> (1987)	0.5	1.4
MPR	2-MP/1-MP	Radke <i>et al</i> (1982b)	0.27	1.23
Rc	0.60MPI 1+0.40 (for MPR < 2.65)	Radke <i>et al</i> (1986)	0.75	1.12
MPR 1	1-MP/P	Radke <i>et al</i> (1982a)	2.50	0.78
MPR 2	2-MP/P	Radke <i>et al</i> (1982a)	0.67	1.00
MPR 3	3-MP/P	Radke <i>et al</i> (1982a)	1.00	0.90
MPR 9	9-MP/P	Radke <i>et al</i> (1982a)	0.83	0.53

Rc = Calculated vitrinite reflectance.

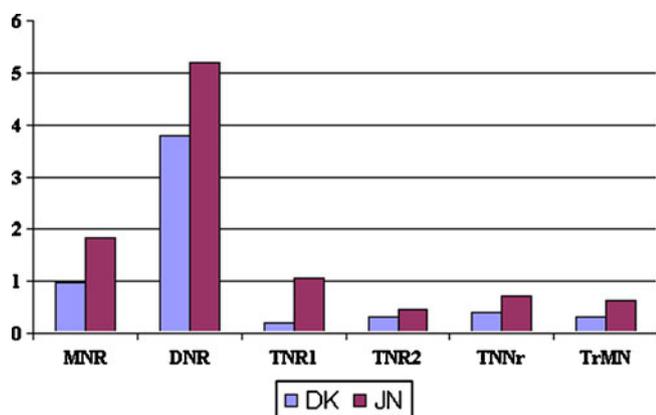


Figure 3. Comparison of methyl-naphthalene ratios of DK and JN asphaltene pyrolysates.

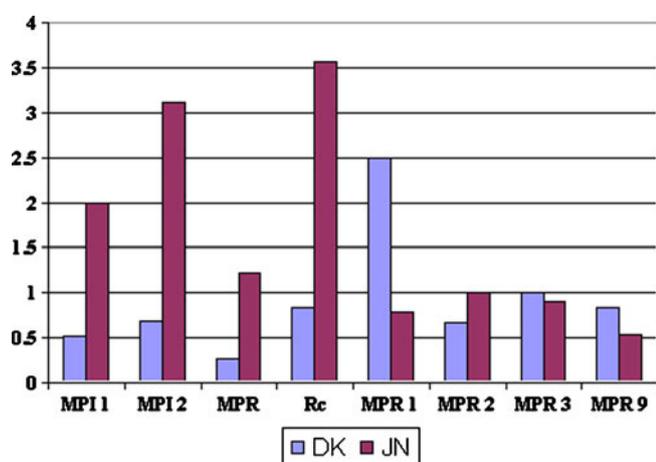


Figure 4. Comparison of methylphenanthrene ratios of DK and JN asphaltene pyrolysates.

and 9-methylphenanthrene. For both the asphaltenes, the concentration of 1-methylphenanthrene was higher than 9-methylphenanthrene. The 1-methylphenanthrene isomer is suggested to be produced from diterpenoid acids, specifically, dihydroabietic acid and podocarpic acid through reduction, followed by aromatization (Brassell 1985; Budzinski *et al* 1997), tentatively related 1-methylphenanthrene to a terrestrial origin and 9-methylphenanthrene to a marine origin. Both the asphaltenes thus appears to be of terrestrial origin. The methylphenanthrene ratio (MPR) for DK and JN is 0.27 and 1.23, respectively. $MPR > 1$ for JN reveals the predominance of more stable 2-methylphenanthrene over less stable 1-methylphenanthrene. The reverse is the case for DK. This indicates a higher level of thermal maturity of JN vs DK. MPI 1 is dependent on phenanthrene and methylphenanthrene homologues. With increasing maturity, α -methylphenanthrenes are gradually converted to the more stable β -methylphenanthrenes. The MPI 1 and MPI 2 values for JN is much greater than that of DK. The MPI 3 values for DK and JN are 0.5 and 1.4. This indicates that DK asphaltenes are immature ($MPI\ 3 < 0.8$, respectively).

Radke *et al* (1987) and JN asphaltenes are exceptionally mature ($MPI\ 3 > 1.0$, Radke 1987 and Stojanovic *et al* 2001). This indicates that JN asphaltenes have reached much higher level of thermal maturity than DK asphaltenes.

4. Conclusions

Pyrolysis of the two asphaltenes produced aliphatic as well as aromatic compound classes to varying extents. Some of the aromatic compound classes, like alkyl-naphthalenes and alkylphenanthrenes, which were previously been used to assess the maturity of crude oil, coal, etc. from their respective aromatic fractions can be utilized to assess the maturity of asphaltenes also. For both the asphaltenes, the concentration of 1-methylphenanthrene predominated over 9-methylphenanthrene revealing the terrestrial nature of organic matter in them. Alkyl-naphthalenes and alkylphenanthrenes ratios revealed that JN asphaltene is more matured than DK asphaltene. The aromatic biomarkers like methyl-naphthalenes and methylphenanthrenes produced from asphaltene pyrolysates can be used for maturity assessment for asphaltenes and the results can be combined with other maturity assessment techniques like, biomarker analysis of the saturated and aromatic fractions of crude oil to get a better understanding of their maturities as there exists striking physical and chemical similarities between oil forming kerogen and petroleum asphaltenes.

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