Predicting the Temperature of Hydrocarbon Expulsion from Oil Asphaltene Kinetics and Oil Source Correlation: A Case Study of South Cambay Basin, India*

By

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Abstract

The oil asphaltene has structural similarity with parent kerogen. The kinetic data based on actual data from the reservoir oil is found to be a better method in reducing the risks associated with oil exploration and assessing the petroleum generation characteristics. An attempt has been made to assess the petroleum expulsion temperature/timing for predicting the kitchen in South Cambay Basin using oil asphaltene kinetics.

The Gandhar field covers an area of about 800 km^2 and is located on the rising northwestern flank of the Broach depression in the Jambusar-Broach block. The Olpad Formation was deposited during the Paleocene. The Eocene Cambay Shale, unconformably overlying the Olpad Formation, has excellent source rock characteristics. The Hazad Member of south Cambay Basin is a major hydrocarbon reservoir, and it consists of 12-individual sand units from GS-XII-GS-I.

The oil asphaltene kinetic/expulsion temperature studies have been carried out on Rock Eval-6 instrument having Optikin and GENEX-1D software. The saturate/aromatic biomarkers data and fatty acid studies are also integrated with the present study. The Gandhar oils are placed into three groups. The group C oils (GS-XII & GS-XI) indicate that the temperature of expulsion from asphaltene kinetics (Tasph 90-112^oC) corresponds to isothermal sequence of source rock from 2500 to 800m). Group B (GS- IX-IV) oils indicate that Tasph (119-132^oC) corresponds to isothermal sequence of 2900 to 3200m, whereas Group A oils (GS-III-I) indicate that expulsion temperature (141-142^oC) corresponds to the 3600-3800m sedimentary sequence. Asphaltene expulsion temperature data has shown positive correlation with biomarker maturity data and fatty acid distribution pattern and good matching with actual identified source rock units. The expulsion temperature determined by light hydrocarbons has no correlation with asphaltene expulsion temperature. This study will be very useful in fine-tuning the existing petroleum system where source rock data is not available.

Introduction

The timing of hydrocarbon expulsion, as well as the quantity and quality of expelled hydrocarbons, is controlled by the type of sedimentary organic matter, lithology of source rock, tectonic stress, and burial history, as well as the related temperature and pressure. Asphaltene represents the macromolecular fraction of reservoir oil as well as in sedimentary bitumen (Behr and Pelet, 1984). Pyrolysis experiments have shown that kerogen and asphaltene generally show similar structural characteristics (Horsfield, 1989; Horsfield, 1997; Eglinton and Larter, 1991). Therefore, asphaltene is thought to be moieties of kerogen generated during its early thermal evolution and to contain maturity-related information from the kerogen that generated it.

Di Primo and Horsfield (2000) applied kinetic concept to oil asphaltene for identification of specific source-rock facies charging the reservoir in the Sonda de Cache area (Mexico) and Snorre field (Norway). They did not share the same formation window as that modeled for source-rock samples. In this context, Dieckmann et al. (2001) linked asphaltene kinetics with characteristics of light hydrocarbons. The expulsion history can be reconstructed utilizing characteristics of both the ends of hydrocarbons. Fatty acids have been reported to be used as biological markers for migration and maturation (Surdan et al., 1984, Kawamura and Kaplan, 1987). The distribution of fatty acids in oil is of considerable importance in understanding the migration and filling mechanism of reservoirs.

In the present paper, we focused on expulsion temperature ranges derived from asphaltene kinetics and lighter hydrocarbons. Fatty acids distribution pattern and routine biomarkers are also included to under stand the effect of maturity on these parameters. The study area, Gandhar field, is located in the rising northwestern flank of the Broach depression in the Jambusar-Broach block. The generalized stratigraphy of the southern part of Cambay Basin is shown in Figures 1 and 2. The Olpad Formation, deposited during the Paleocene as nonmarine sedimentary sediments, has poor source-rock characteristics. The Cambay Shale unconformably overlies the Olpad Formation and was deposited during early Eocene to middle Eocene. This sequence has excellent source-rock character. Cambay shale represents the marine transgressive episode in Cambay Basin. The Hazad Member, a sandstone deposit, represents the major hydrocarbon reservoir in Gandhar field; it consists of 12 individual sand units.

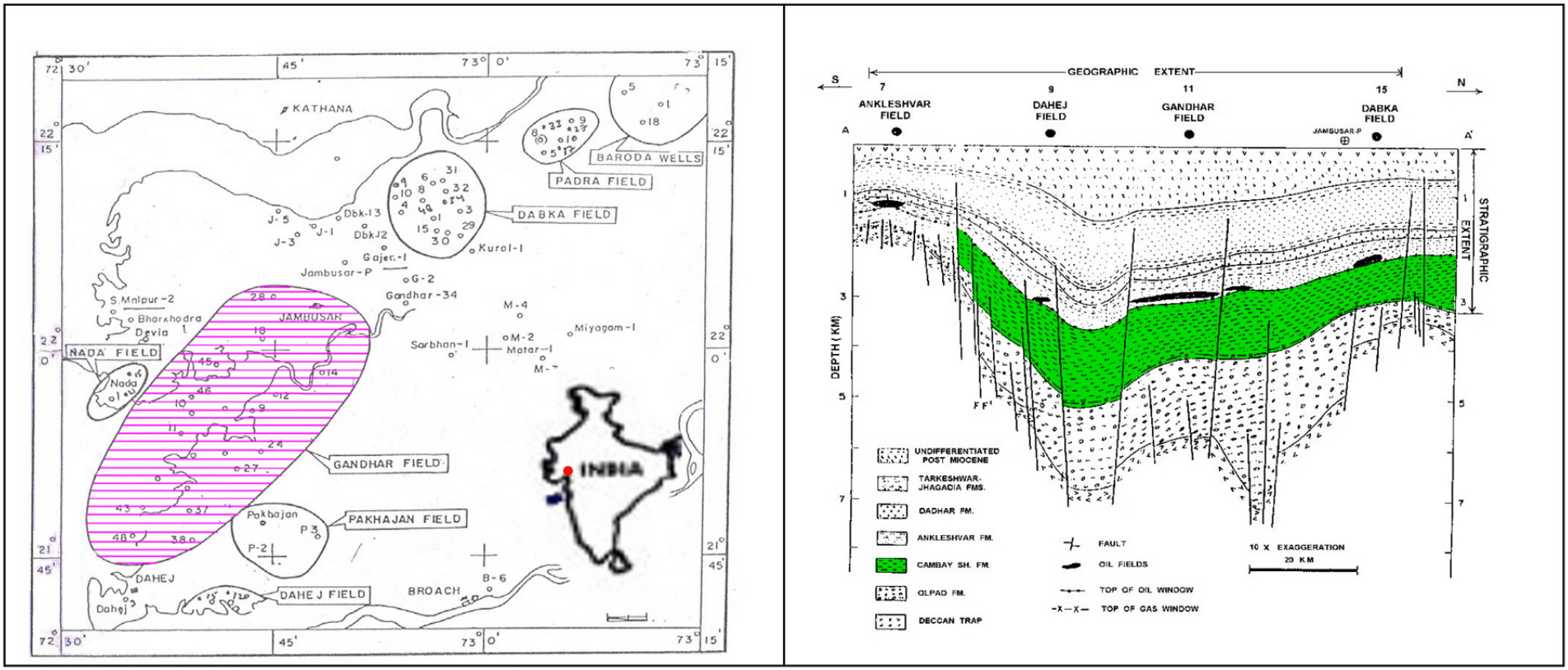


Figure 1. Location map and cross section of Cambay Hazad (!) petroleum system.

Sample Selection and Study Area

The oil samples were selected from 12 individual sand units of the Hazad Member, the main reservoir of Gandhar field, for asphaltene kinetics studies, light hydrocarbons, fatty acids, and molecular level analysis based on GC and GC-MS. Source-rock data of the study area is integrated with kinetic and maturity data.

Source Rock Development Status

The effective source rock for commercial viable hydrocarbons in south Cambay Basin is the lower-middle Eocene Cambay Shale (Figure 2) which extends across the entire south Cambay Basin including Gulf of Cambay. The amount and type of organic matter and its level of thermal maturity indicate that the Cambay Shale is a good oil- and gas-prone source rock (TOC: 2.6%). The plot of HI against oxygen index (OI) indicates that the bulk of organic matter is of type III with some contribution from type II. Vitrinite reflectance, Tmax, and TTI data indicate that entire Cambay Shale is in the catagenetic stage.

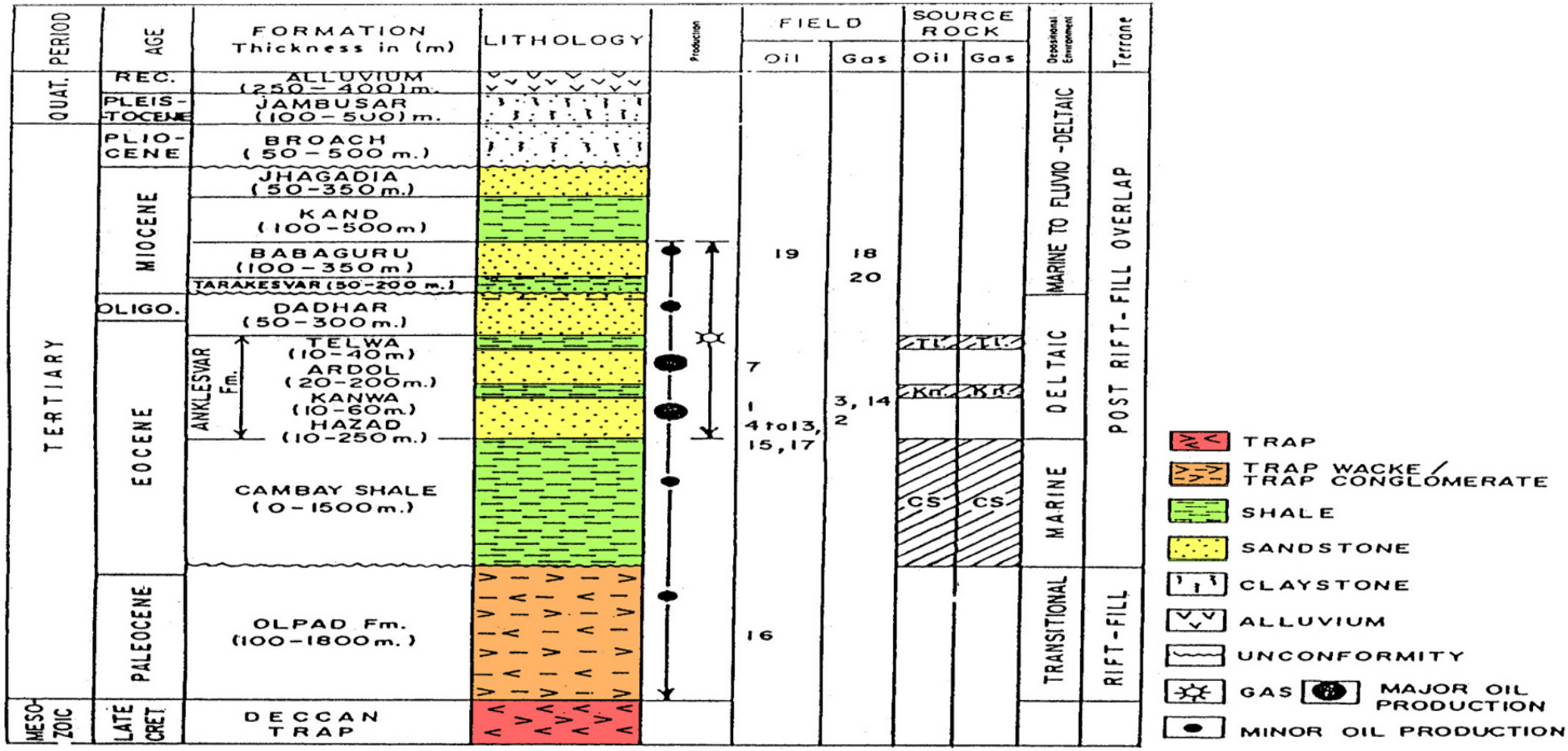


Figure 2. Generalized stratigraphic column of the South Cambay Basin

Methodology:

The kinetic analysis was performed on about 3 mg of isolated asphaltene mixed with inert substance to make up 100 mg sample on Rock Eval-6 at four different heating rates of 5, 10, 15 and 25^{o}C from 180 to 650^{o}C, using Optkin software. The light hydrocarbons were analyzed on a whole oil sample diluted 1:1 with dichloromethane. .The GC temperature programmed was started at 35^{o}C, held for 5 min., and then Ramp to 120^{o}C at 1.1^{o}C.The expulsion temperatures based on light hydrocarbon were calculated, using formula proposed by Mango (1997):

$$Ctemp\ (^{o}C) = 140 + 15\{\ln (2.4\text{-}DMP/2.3\text{-}DMP)\}$$

For fatty acid isolation, 20g of crude oil was refluxed with 50 ml mixture of KOH and methanol (6%). The aqueous phase was washed 2-3 times with petroleum ether to remove non-acidic components. The aqueous phase was acidified with 6N HCl to make the solution acidic (pH 2-3). The acidic solution was extracted with petroleum ether to extract fatty acids. Extracted fatty acids from oils were methylated with 14% BF_3-methanol mixture. Esterified fatty acids were resolved at GC-MS along with standards for identification. GC and GC-MS studies were conducted on saturate and aromatic fractions of oil for routine biomarker and MPI.

Results and Discussion

The bottom hole temperature (BHT) recorded in studied wells varies between 110^{o}C and 120^{o}C. The API gravity of studied oils was in the range of 38-43^{o}. The n-alkane profile indicates that these oils are normal oils, and there is no sign of biodegradation.

The objective of the study was to determine temperature of expulsion of hydrocarbons based on lighter and heavier ends. The asphaltene kinetic parameters with minimum error function (0.06-0.10) were considered for the study. The lighter hydrocarbons were analyzed with the help of 2.3-DMP and 2.4- DMP standards. The results of asphaltene kinetics evaluation in terms of activation energy distribution and prediction of asphaltene transformation ratio/temperature for the oils reservoired from GS-I to GS-XII sands are shown in Figure 3. The activation energy distribution observed is typical for oil generated by terrestrial organic matter and type III source rocks. The activation energy are in the range of 6.2E-10 and 1.4E-15 common for low and high mature type III/type II source rocks (Schaefer et al., 1990).

In order to compare the effects of the calculated kinetics on the asphaltene degradation behavior, the geological extrapolations were made using a constant heating rate of 3^{o}K per My. The fractions of reacted asphaltene were normalized to 100 and are plotted as a function of geological temperature using a constant heating rate. The wide variation in the asphaltene degradation behaviour indicates the difference of organic matter richness and their types. The asphaltene degradation of GS-I, GS-II, GSXI and GS-XII are smooth, indicating homogenous distribution of organic matter while GS-VIII shows wide range of temperature variation. The expulsion temperatures defined by these curves correspond to the temperatures at which the asphaltene starts to be transformed to volatile hydrocarbons. In order to avoid the possible impact of contamination (volatile entrants in asphaltene), the asphaltene temperatures were determined at a value of 10% of asphaltene transformation.

Based on biomarker, fatty acid, and asphaltene temperature ranges, Gandhar oils can be classified into three distinct groups . The asphaltene expulsion temperature of the studied oils from GS-I to GS-III is in the range of 141 to 142^{o}C under geological conditions and can be classified as Group A (Table 1; Figure 4). Further GS-IV and GS-IX show asphaltene expulsion temperature of 119 to 132^{o}C; these oils can be classified as Group B, indicating contribution from mixed source input and variability in organic facies at different maturity levels. The asphaltene temperatures are in the range of 90 to 112^{o}C for GS-XI and GS-XII and can be classified as Group C.

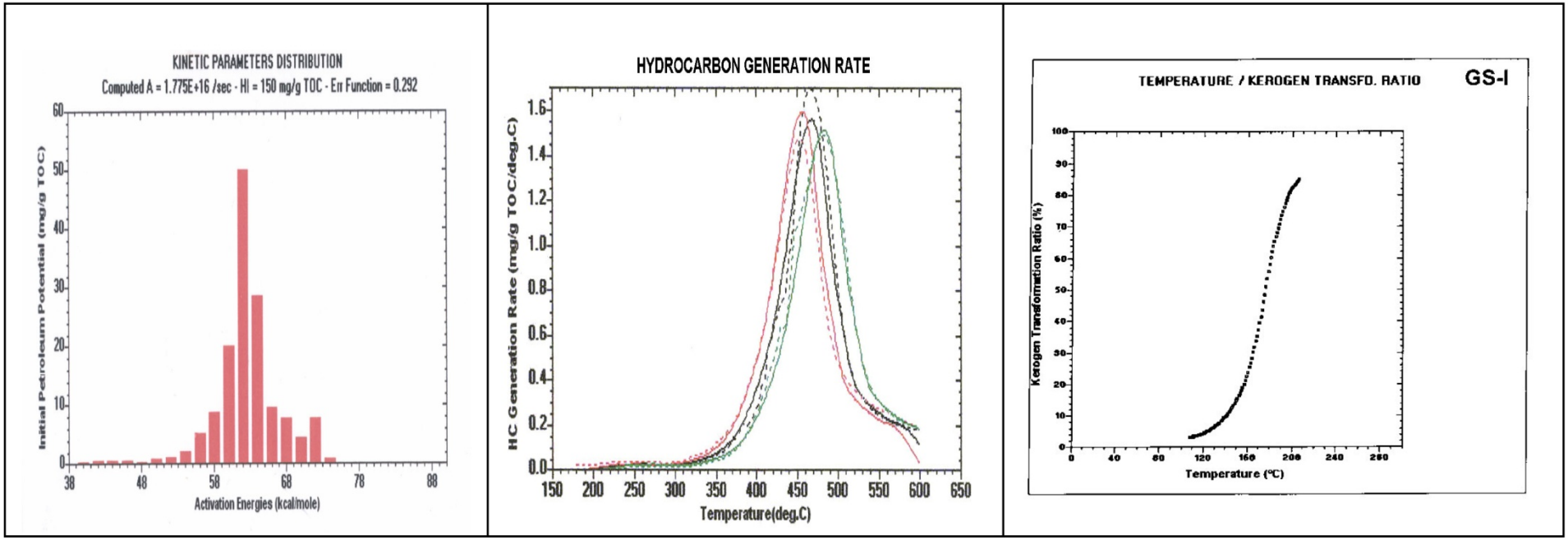
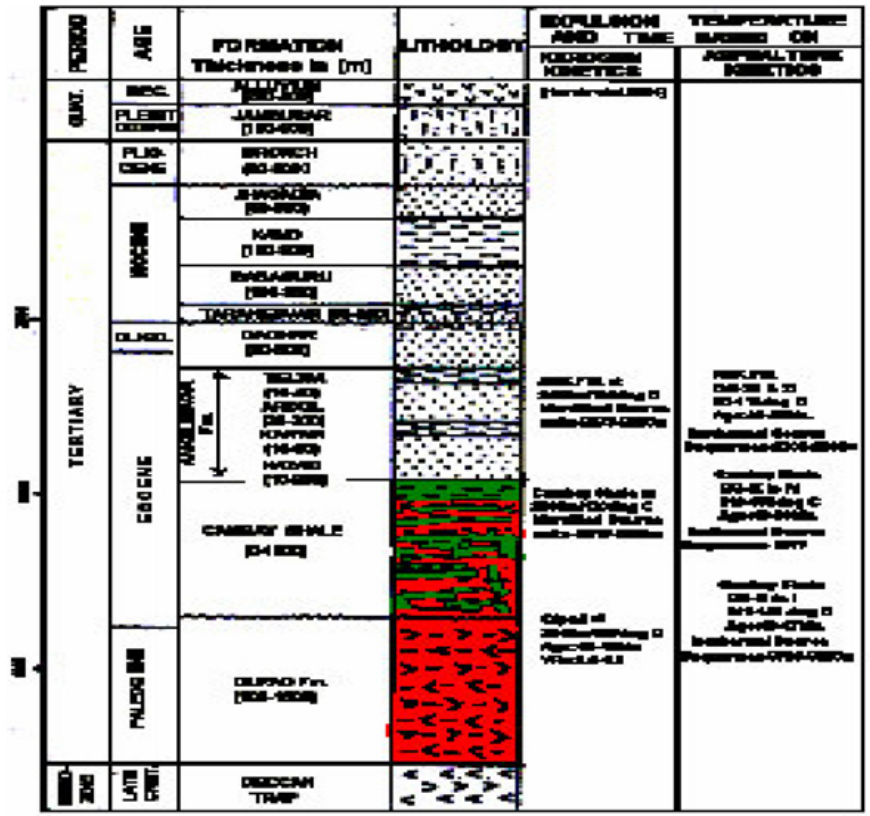


Figure 3. Prediction of asphaltene transformation ratio/temperature.

Comparison of temperatures calculated from asphaltene kinetics and those calculated from light hydrocarbons (Table 1) shows variation; namely in Group A oils, Ctemp<Tasph (124^{o}C vs. 142^{o}C), while Group B oils show both Ctemp<Tasph and Ctemp>Tasph and Group C oils show Ctemp>Tasph.

From the integration of light hydrocarbons, classical biomarkers ratios, and fatty acid distribution pattern it may be inferred that there were multiple source rocks and charging of the Hazad reservoirs. The hydrocarbons from deep source rock are getting mixed with low-maturity oils coming from shallower source rocks. The biomarkers data demonstrate that most of the biomarker maturity parameters have reached their equilibrium value so they may not show any trend with temperature variation data of Tasph.



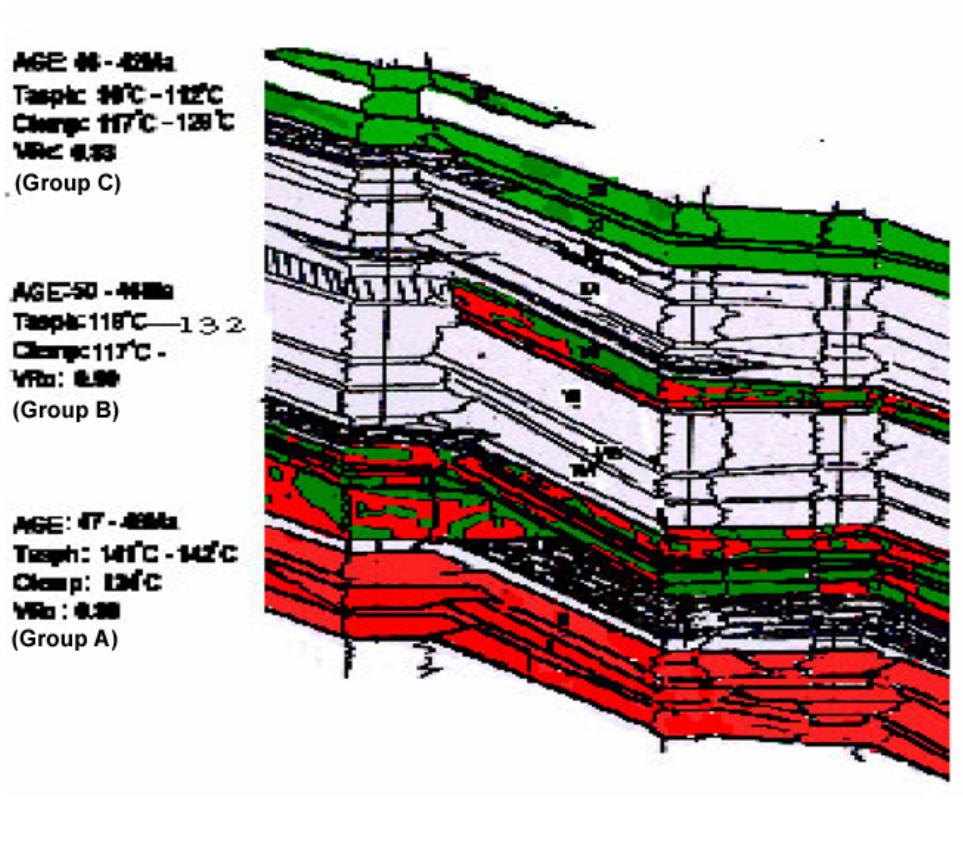


Figure 4. Temperature of hydrocarbon expulsion based on asphaltene kinetics.

S. No	Sand	Group	Ts/ Ts+Tm	C30 H H+M	29H / 30H	OL/30 H× 100	C32S / S + R	ββ / ββ +αα	αααS/ S + R	C_{temp} (°C)	T_{asph} (°C)	VRc
1.	GS-I	A	0.36	0.88	0.47	4.04	0.60	0.36	0.58	123.0	141	0.88
3.	GS-I		0.37	0.89	0.53	4.35	0.61	0.31	0.58			0.88
4.	GS-II		0.40	0.88	0.41	4.32	0.56	0.31	0.59	124.68	142	0.88
5.	GS-IIIA		0.38	0.88	0.47	4.88	0.58	0.36	0.56	124	142	0.86
6.	GS-IV	B	0.38	0.86	0.58	8.49	0.58	0.36	0.56	117.96	132	0.89
7	GS-VC		0.42	0.87	0.51	15.19	0.58	0.43	0.52	123		0.90
8.	GS-VIII		0.41	0.86	0.46	16.13	0.56	0.34	0.48	124		0.86
9	GS-IX		0.44	0.87	0.48	13.21	0.59	0.43	0.53		119	0.88
10	GS-XI	C	0.47	0.85	0.58	8.86	0.58	0.34	0.46	117.35	112	0'83
11	GS-XI		0.49	0.85	0.57	10.13	0.57	0.30	0.52			0,83
12	GS-XII		0.50	0.85	0.52	9.12	0.57	0.24	0.57	129.06	90	0.83

Table 1. Biomarker.Tasph,Ctemp, and VRc data.

Generation Model Predicted Based on Asphaltene Kinetics

The hydrocarbon generation model based on expulsion temperatures of asphaltene kinetics and light hydrocarbon is shown in Figure 5. The subsidence and maturity history of source rock unit responsible for charging GS-1 to GS-3 are at the temperature of 142^{o}C with average Ctemp at 124^{o}C. The calculated temperature of sediments indicates that this temperature corresponds to the older Cambay Shale (OCS). Further, it is observed that the GS-V sands (Tasph 152^{o}C) have received hydrocarbons from a deeper source. Based on oil data it may be inferred that Group A oils of GS-I to GS-III have received oil from OCS, which corresponds to a depth of 3800m. The Group B oils (GS-IV to GS-VIII) have shown expulsion temperature Tasph of 119-152^{o}C; so the source rocks of different maturities from top of Olpad to top of Cambay Shale have charged the oil-producing sands of this Group. Group C oils (GS-XI to GS-XII), with Tasph 90-117^{o}C, correspond to the contribution from Ankleswar Formation Shale/younger Cambay Shale.

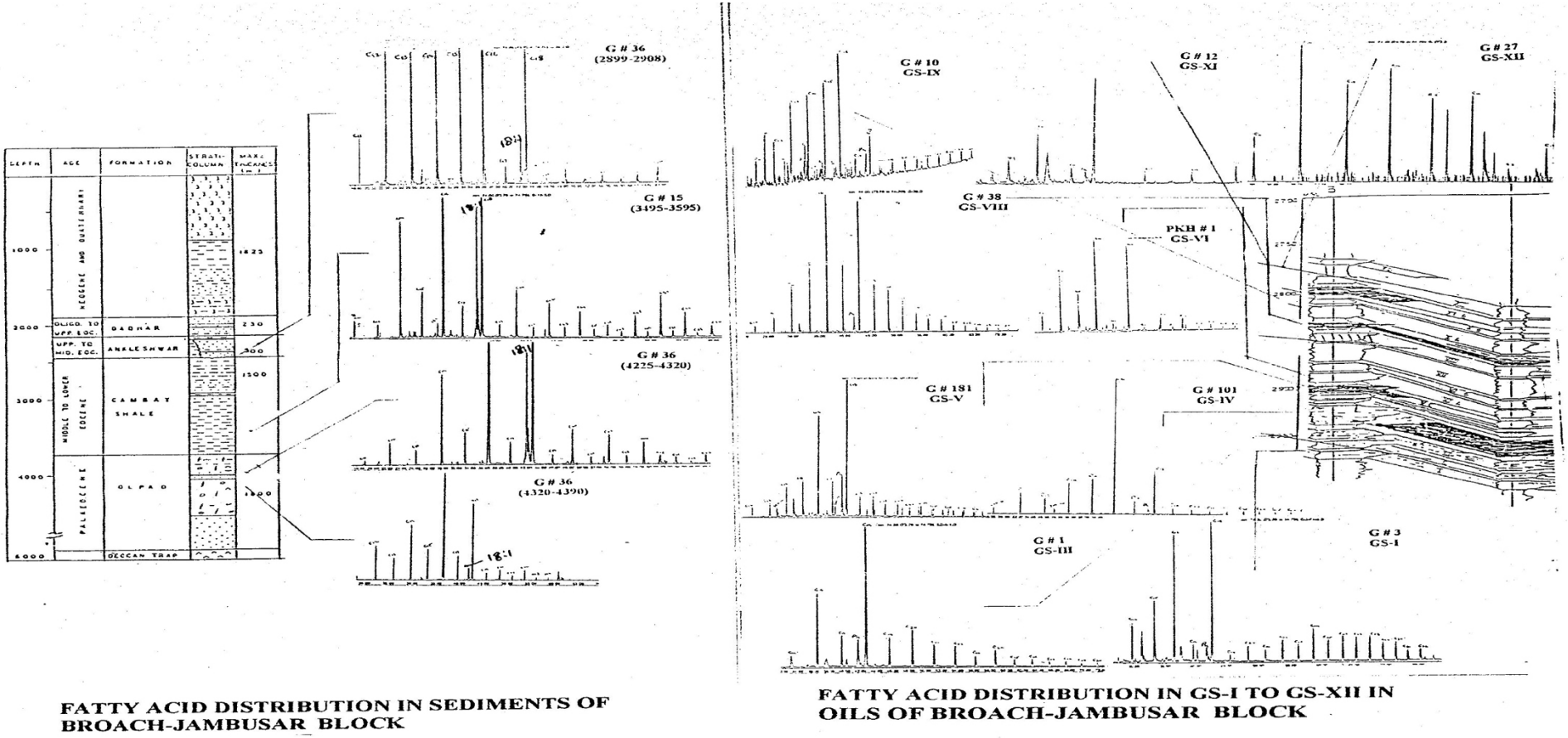


Figure 5. Fatty acid distribution in sediments of Broach-Jambusar block; fatty acid distribution in GS-I to GS-XII in oils of Broach-Jambusar block.

Conclusion

- Group-A oils (GS-III - GS-I), indicating Tasph of 141-142^{o}C, Ctemp-124^{o}C, and VRc-0.88, correspond to depth interval of 3780-3860m in Cambay Shale, 46-47 Ma in age. Tasph>Ctemp indicates good to fair source rock characteristics in this section.
- Group-B oils (GS-IX - GS-IV), which indicateTasph of 119-132^{o}C, L/H of 117-125^{o}C, and VRc 0.90-0.92, correspond to isothermal maturity sequence of Cambay Shale from 2975-4275m, 46-50 Ma in age. This data corresponds to available source rock units of Cambay Shale from 2910-3235m.
- Group- C oils (GS-XII - GS-XI) indicate Tasph of 90-112^{o}C, L/H of 117-129^{o}C, and VRc 0.83 and correspond to isothermal maturity sequence of Ankleshwar Formation (2200-2800m), 42-46Ma in age. Good source rocks are identified in Ankleshwar Formation between 2573-2880m. It may be inferred that this group has been charged from a source rock unit of Ankleshwar Formation.
- Biomarker and molecular level analyses indicate that oils are being produced from terrestrial organic matter deposited in suboxic to oxic environment of deposition. The biomarker maturity parameters indicate a maturity of more than VRc 0.8. Hence, the routine biomarkers which have attained equilibrium could not provide valuable information.

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