Journal of Petroleum Science and Technology 13(2): 38, 2023, Pages 2-11
DOI:10.22078/jpst.2024.5209.1899

Journal of Petroleum Science and Technology

Research Paper

https://jpst.ripi.ir/

Thermal Maturity, Organic Petrography, Bulk and Compositional Kinetic of Hydrocarbon Generation in Cretaceous-Paleogene Source Rocks from Western Dezful Embayment, SW Iran

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Abstract

In this study, in order to know the effective petroleum system in charging reservoirs in oilfields located in the west of Dezful Embayment, the cutting shales from Pabdeh, Kazhdumi, and Garau formations (Cretaceous-Paleogene Source Rocks) were selected for Rock-Eval Pyrolysis, Organic Petrography, Bulk, and Compositional kinetic. Furthermore, the Pabdeh shale samples are described as a mixture of kerogen types II and III with lower thermal maturity. The Kazhdumi shale samples show Type III and Type II/III kerogens and fall within the oil window zone. In addition, the Garau shale samples are determined to have Type III and Type II/III kerogens with high thermal maturity in the zone of the oil window. The bulk and compositional kinetic parameters reveal that the organic facies of the Kazhdumi and Garau formations indicate thermally mature kerogens able to generate and expel mature oils, but the Pabdeh Formation does not have enough maturity for oil generation. The composition kinetic model demonstrates that the Pabdeh and Kazhdumi formations are very similar in pyrolysate composition to the Garau Formation (due to the high sulfur in the kerogen of the Garau Formation). Finally, the Garau Formation is the main source rock, and the Kazhdumi Formation is the second one for filling hydrocarbon reservoirs in the studied area.

Keywords: Source Rock Evaluation, Kerogen Type, Bulk and Compositional Kinetic, Petroleum Generation, Dezful Embayment.

Introduction

The Dezful Embayment was formed in the foreland of the collision between the Arabian and Eurasian Plates after the Late Cretaceous [1]. It is located in southwest Iran, and thick sedimentary sequences were formed in this region belonging to the Mesozoic and Cenozoic periods. The Location of studied wells in Dezful Embayment is shown in Fig. 1. Due to effective source rocks in this area, numerous petroleum systems have formed in the Dezful Embayment [2]. Garau and Gadvan (Neocomian-Aptian), Kazhdumi (Albian), Gurpi (Santonian-Maastrichtian), and Pabdeh (Paleocene-Oligocene) formations are considered source rocks of unequal importance in the Dezful Embayment which has gone through different stages of maturation, oil generation expulsion and migration [3, 4]. The main reservoir rocks filled with hydrocarbon in the Dezful Embayment are the Asmari (Early Miocene) and Sarvak (Cenomanian) formations. The Asmari and Sarvak reservoirs are connected by fractures and faults in most of the oilfields in the Dezful Embayment [5]. One of the main parameters for kerogen decomposition is kinetic parameters to determine the quantity of hydrocarbons generated by source rocks [6], which is described by the Arrhenius equation:

$$k = A \exp(-E/RT) \tag{1}$$

where K is the reaction rate, A is the pre-exponential frequency factor (s^{-1}), E is activation energy (J/mol), R is the molar gas constant (j/mol/K), and T is the absolute temperature (K) [7]. The main goals of this study are the geochemical assessment of nature, quality, thermal maturity (%Ro and TAI values), and kerogen types of the candidate source rocks.

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Received 2023-08-28, Received in revised form 2023-12-30, Accepted 2024-01-14, Available online 2024-02-12

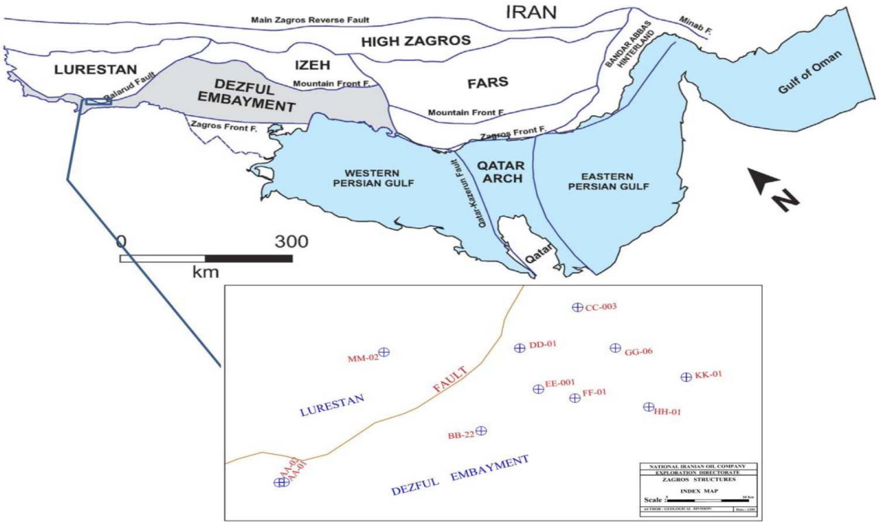

Fig. 1 The Location map of the studied area in the Dezful Embayment, Zagros fold and thrust belt, SW of Iran (modified from [8]).

Geological Settings

The studied source rocks in the Dezful Embayment have been deposited in the marine environment. The Pabdeh Formation, which has good potential as a source rock, was deposited in the last anoxic episode throughout the Zagros during the Middle to Late Eocene [2]. Throughout the Dezful Embayment, a gentle depression developed during the Albian time, and strongly anoxic paleoenvironmental conditions prevailed. These factors caused the Kazhdumi Formation to be recognized as the best rock source in the studied area. In the Aptian-Neocomian, an intrashelf basin developed the Garau source rock sequence, where reducing conditions dominated and led to preserving organic matter [9]. In this manuscript, three main candidate source rocks of Pabdeh, Kazhdumi, and Garau in the studied area have been focused by the authors (as seen in Fig. 2).

Materials and Methods

The main analytical program of the study consists of Total Organic Carbon (TOC) determination, Rock-Eval pyrolysis, organic petrography, Thermal Alteration Index (TAI) determination, vitrinite reflectance (Ro %) measurement, and bulk and compositional kinetic parameters determination.

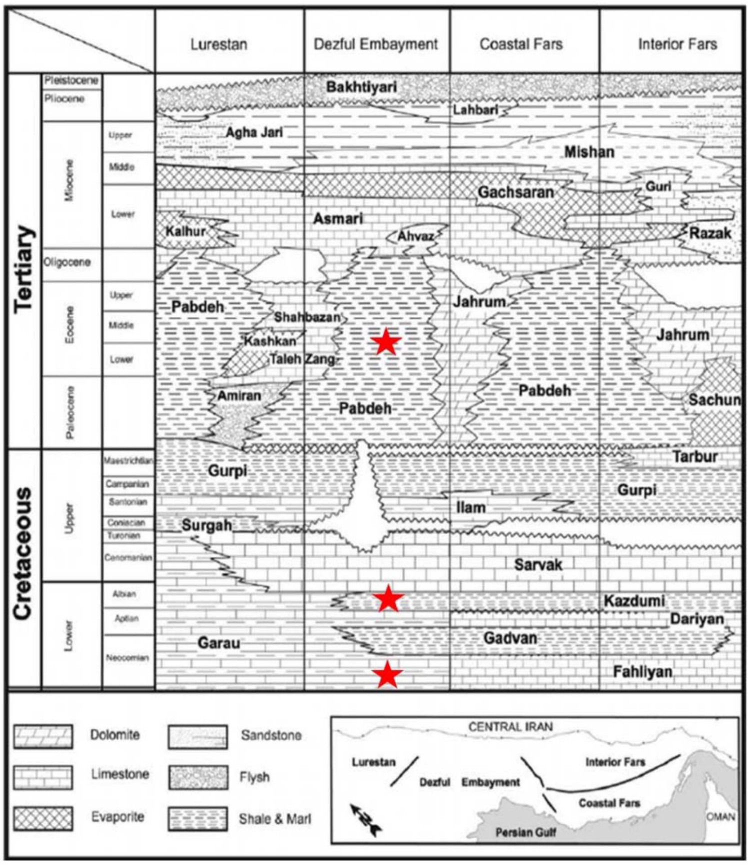

Fig. 2 The Stratigraphy correlation chart (Mesozoic – Cenozoic) in parts of the Iranian Zagros basin. The studied formations are shown in Figure (modified from [10]).

Based on a TOC cut-off of 0.5%, 149 samples from 10 wells were pyrolyzed by Rock-Eval. In this process, the cutting samples were washed with solvent before analysis to eliminate the effect of non-indigenous hydrocarbons (mud additives). A subset of 6 cutting samples was selected for visual kerogen microscopy analysis to evaluate the study area's thermal maturity and organic composition. Finally, 3 samples were selected for kinetic analysis. All the samples selected for thermal maturity assessment went through the kerogen separation before being submitted to kerogen microscopy analysis, which included kerogen typing, vitrinite reflectance (Ro) measurement, and Thermal Alteration Index (TAI) determination from spore coloration. The calculated vitrinite reflectance values were recorded on the best-quality indigenous vitrinite fragments without recycled, caved, or contaminated materials. The Rock-Eval analyses and Kinetic Bulk measurements were conducted at the Petroleum Laboratory of RIPI (Research Institute of Petroleum Industry) in Tehran. The Organic Petrography and Compositional Kinetic measurement have been carried out at StratoChem Services in Cairo, Egypt.

Rock-Eval pyrolysis and bulk kinetic parameters

Rock-eval pyrolysis is the first method for screening the quantity, quality, and thermal maturity of organic matter in source rocks [10]. The Rock-Eval 6 is used for Rock-Eval Pyrolysis on studied samples. Rock-Eval parameters are as follows: S_1 (mgHC/g rock), S_2 (mgHC/g rock), S_3 (mgCO_2/g rock), Tmax (°C), and TOC (wt. %), which were measured for the Pabdeh (74 samples), Kazhdumi (39 samples) and Garau (36 samples) formations in the studied area. The location map of selected wells is illustrated in Figure 1. More information about the analytical method and related parameters is described by [11, 12].

The activation energy distribution (Ea) and frequency factor (A) of the Pabdeh, Kazhdumi, and Garau source rocks were estimated using Kinetics 05, which was installed on the Rock-Eval apparatus [13].

Organic Petrography

Six samples were selected for the organic petrography and vitrinite reflectance studies based on the richness of total organic matter values. The prepared sample is placed on the sample stage in the Zeiss Axioplan II microscope (with 100 × magnification and wavelength of 546 nm) and focused on. This technique is based on [14]. The results of microscopic studies are shown in Table 1.

Table 1 Summary of microscopic analysis data for selected samples.

Well	Formation	Depth (m)	Min Ro%	Max Ro%	Ro (%)	TAI	Maceral*					Oil- prone(%)	Gas- prone(%)
							Alg.	Lip.	Amorph	Vit.	Iner.		
FF-1	Pabdeh	3450-3452	0.605	0.61	0.61	2.6	1	3	95	1	0	99	1
CC-3	Pabdeh	1772	0.421	0.50	0.45	2.4-2.5	0	95	0	4	1	95	5
DD-1	Pabdeh	2860-2862	0.484	0.56	0.51	2.5	0	90	5	5	0	95	5
EE-1	Pabdeh	4114-4116	0.512	0.76	0.58	2.6-2.7	1	4	90	5	0	95	5
DD-1	Kazhdumi	4211-4212	0.526	0.85	0.74	2.7	0	80	20	0	0	100	0
BB-22	Garau	5114-5116	0.549	1.22	0.81	2.8	0	0	99	1	0	99	1

MSSV Technique and Compositional Kinetic

A closed system pyrolysis-gas chromatography with a micro-scaled sealed vessel (MSSV) technique [15]. was used to provide a better insight into the artificial maturation efficacy of the samples. Three samples from potential source rocks (Pabdeh, Kazhdumi, and Garau formations) were selected, and 15-35 milligrams of each sample were sealed in glass capillaries and artificially matured at 0.7 K/min using a special MSSV prep-oven. The Phase Kinetics Method [16] makes it possible to relate the source rock organic facies to the generated hydrocarbon type. To carry out PVT modeling, 14 fluid compounds have been described. The gas fraction includes seven compounds (C1, C2, C3, i-C4, n-C4, i-C5, n-C5) derived from the MSSV analysis. The GOR-gas-wetness correlation from natural black oils is used to correct the gas composition [17]. The Liquid fraction consists of a pseudo-C6 (n-C5 to n-C6, excluding n-C5) and compound groups of C7-15, C16-25, C26-35, C36-45, C46-55 and C56-80. The corrected gas phase composition is used to measure physical properties. To assess the amount and molecular weight of the C7+ fraction, the estimation method suggested by [18] was used.

Results and Discussion

Source Rock Potential

The probable source rocks of Pabdeh, Kazhdumi, and Garau demonstrate variable organic matter content, ranging from 0.17% to 4.43%, 0.45% to 5.25%, and 0.16% to 3.43%, respectively. These values indicate the presence of good source rocks with high potential [12]. This variability in hydrocarbon generation potential can be attributed to different sedimentary environments and organic matter in the Zagros Basin [2]. The S2 versus TOC plots reveal that Pabdeh and Kazhdumi formations have fair to very good hydrocarbon generation potential, while the Garau Formation has poor to very good hydrocarbon generation potential (Fig. 3). The plotting of HI versus Tmax can be used to determine the kerogen type and maturity of source rocks. As shown in Fig. 4, most samples of the Pabdeh Formation have lower thermal maturity (immature and early mature zone) with an admixture of oil-prone (Type II) and gas-prone (Type III) organic matter. In contrast, most samples of Kazhdumi and Garau formations fall within the mature zone (oil window zone) of Type III and Type II/III kerogens.

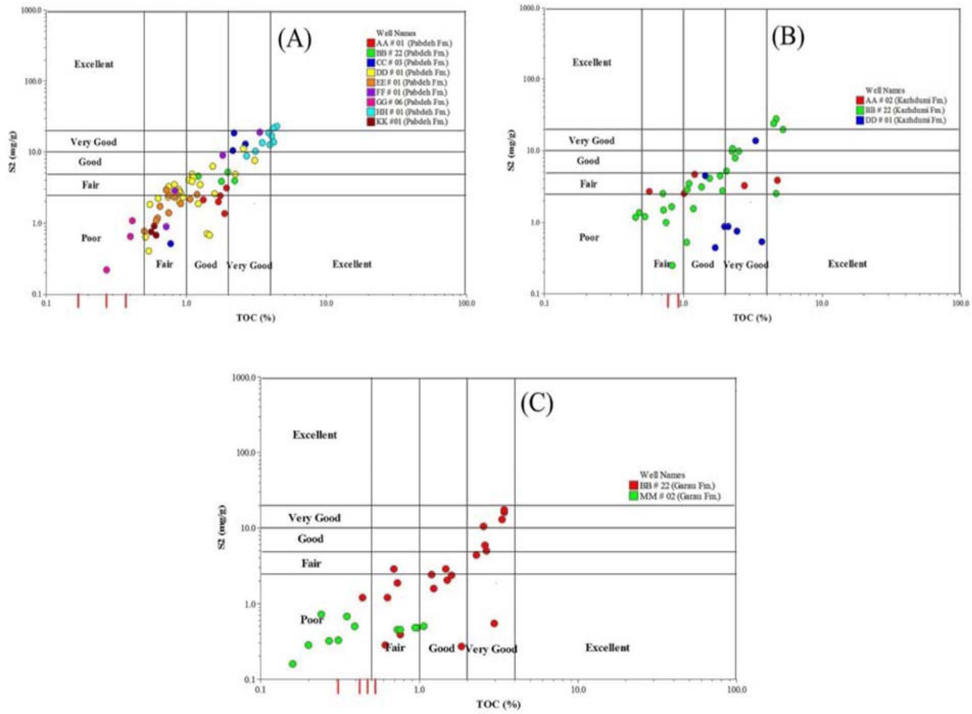

Fig. 3 TOC vs. S2 for Pabdeh (A), Kazhdumi (B), and Garau (C) formations in the studied area.

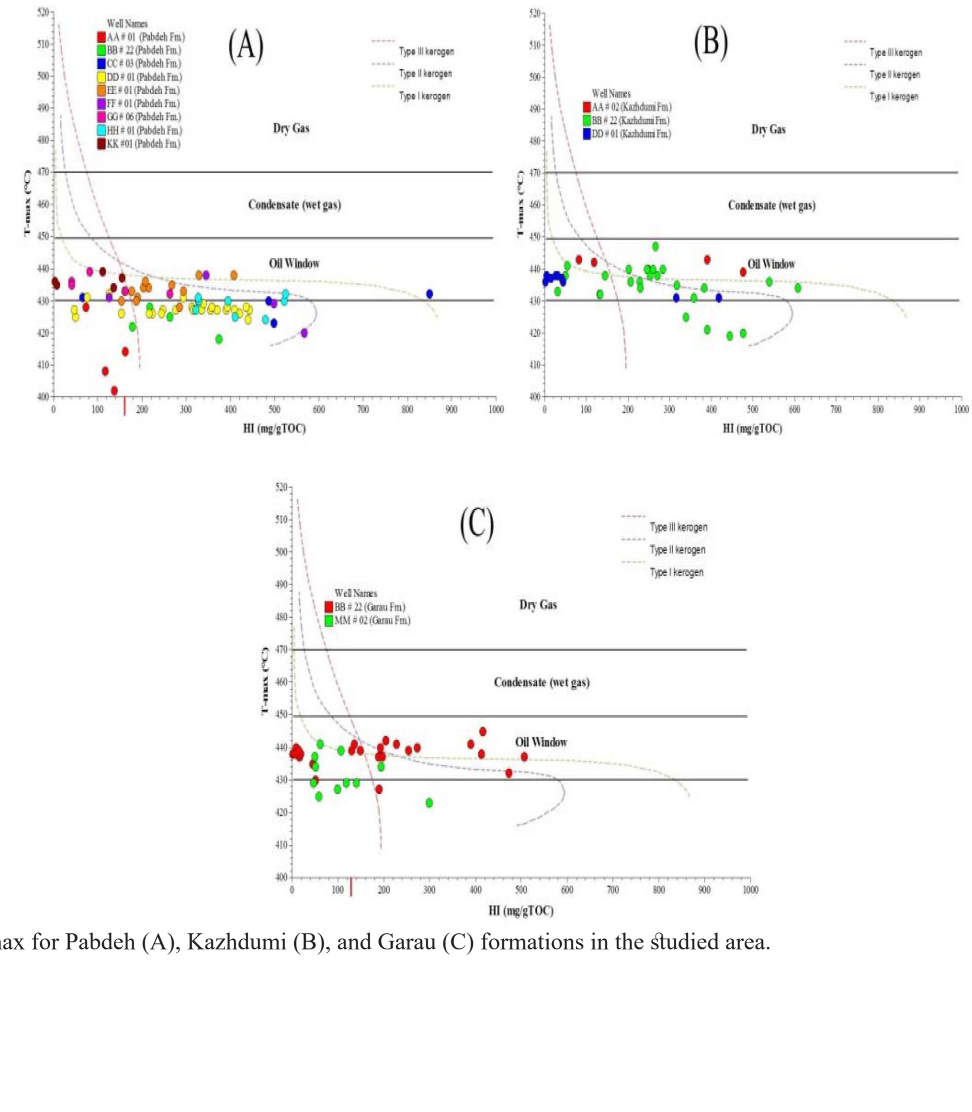

Fig. 4 HI vs. Tmax for Pabdeh (A), Kazhdumi (B), and Garau (C) formations in the studied area.

Vitrinite reflectance measurements can confirm the maturity assessment as the other parameter. Vitrinite reflectance values (Table 1) range from 0.42–0.76% for Pabdeh, 0.52–0.85% for Kazhdumi, and 0.54-1.22% for Garau Formations, suggesting that Pabdeh Formation is immature or entered the oil window but Kazhdumi and Garau formations are mature or entered the mid oil window. The vitrinite reflectance results confirm Tmax values from the Rock-Eval pyrolysis for the studied samples.

Organic Petrography

A total of 4 samples from the Pabdeh Formation were selected for organic petrography analysis in this study. Generally, the organic matter in the Pabdeh samples (wells of FF-1, CC-03, DD-01, and EE-01) mainly consist of massive amounts of well-preserved amorphous associated with a rare amount of terrestrial fragments (non-opaque phytoclasts), Pediastrum and dinoflagellate cysts (Fig. 5a and b). The good fluorescence properties, comparable with a measured average Ro of 0.53%, suggest a TAI value of about 2.55 (Chevron scale). All these data reveal that the organic matter in this sample has just reached maturity. The Kazhdumi Formation in the well DD-01 sample consists mainly of massive amounts of well-preserved non-opaque phytoclasts and cuticles associated with moderate amorphous organic matter (Fig. 5c and d). The yellow-orange color of the cuticles and their good fluorescence properties suggest a TAI value of about 2.7 (Chevron scale) for the sample. These data show that the organic matter in the sample has reached maturity. The Garau Formation organic matter in the well BB-22 sample consists mainly of massive amounts of well-preserved amorphous organic matter with traces of humic debris. The measurement of the better-preserved vitrinite particles shows that the average Ro is 0.81%. The good fluorescence properties of the sample indicate a TAI value of about 2.8 (Chevron scale). All the data demonstrate that the organic matter in this sample has reached the maturity phase level (Fig. 5e and f). The summary result of the microscopic analysis for the studied samples is shown in Table 1.

The Microscopic studies reveal that liptinitic and amorphous organic matter are common in the Pabdeh, Kazhdumi, and Garau formations (AOM). The presence of alginite maceral with the amorphous organic matter demonstrates oil-prone potential. This maceral could be originated from the algal or other phytoplanktonic [19].

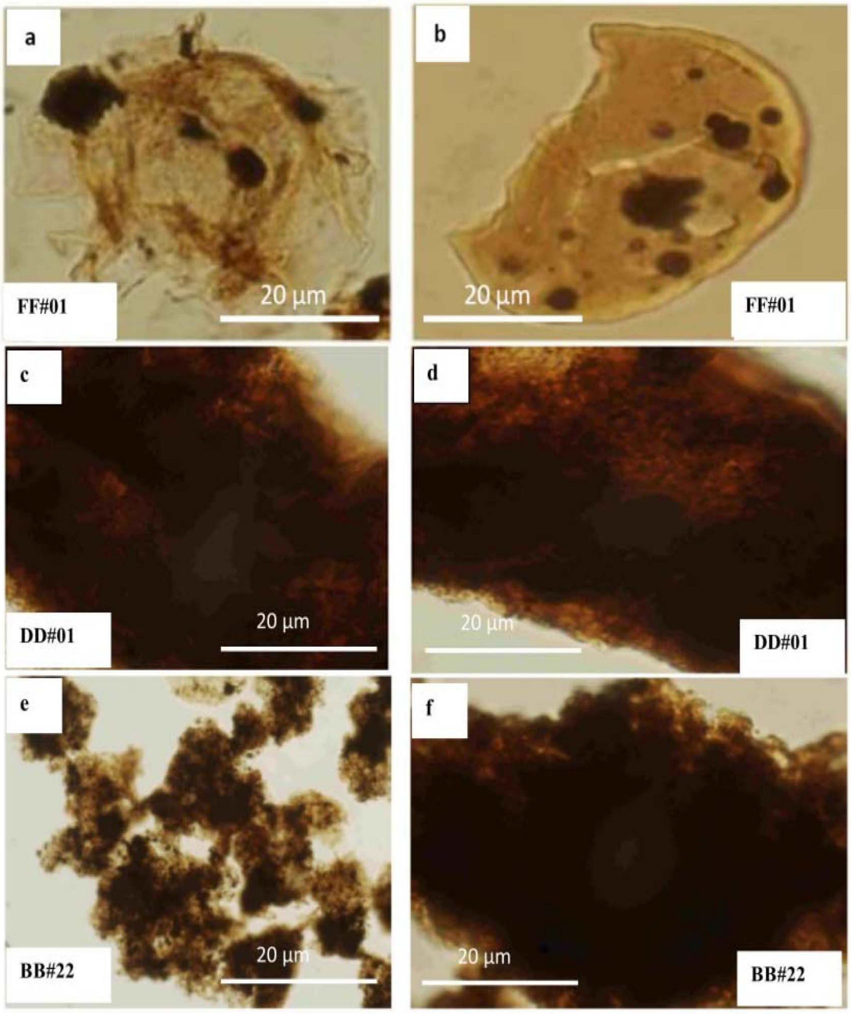

Fig. 5 (a, b) Photomicrographs of kerogen in the Pabdeh Formation showing dinoflagellate cyst and the orange trilete spore in well FF-01, (c, d) Photomicrographs of kerogen in the Kazhdumi Formation (well DD-01) showing amorphous organic matter and cuticles with brown and yellow color under the fluorescence light (e, f) Photomicrographs of kerogen (AOM) in the Garau Formation (well BB-22) demonstrating amorphous organic matter with brown color under the fluorescence light.

Bulk Kinetic Parameters

The chemical kinetics in terms of activation energy and frequency factor are used to characterize the petroleum generated from organic matter. For the conversion of kerogen to petroleum, more activation energy is required, which it causes the particles to move faster, and the frequency factor is increased [20]. Three samples were selected for Bulk kinetic analysis as candidates for the studied source rocks (Fig. 6). The measured activation energy distributions and frequency factors are shown in Table 2. Three samples have peak activation energies between 53–55 kcal/mol. The frequency factor is equal to 1.00 E+14/sec. The type of organic matter can cause differences in frequency factors and activation energy [21]. Due to the heterogeneity of the kerogen in three formations, a fairly wide distribution of activation energies was observed (Fig. 6). Generally, the activation energies vary from 39 to 63 kcal/mol.

The kinetic parameters are used to calculate the temperature and timing of bulk hydrocarbon generation through a linear geological heating rate of 3.3°C/my. It is the mean of the geological heating rate in most sedimentary basins [22]. Fig. 7 represents the transformation ratio against final temperature diagrams for the organic facies of the Pabdeh, Kazhdumi, and Garau formations. Also, the onset (10% TR) and peak generation (geological Tmax) temperature data are shown in Table 3.

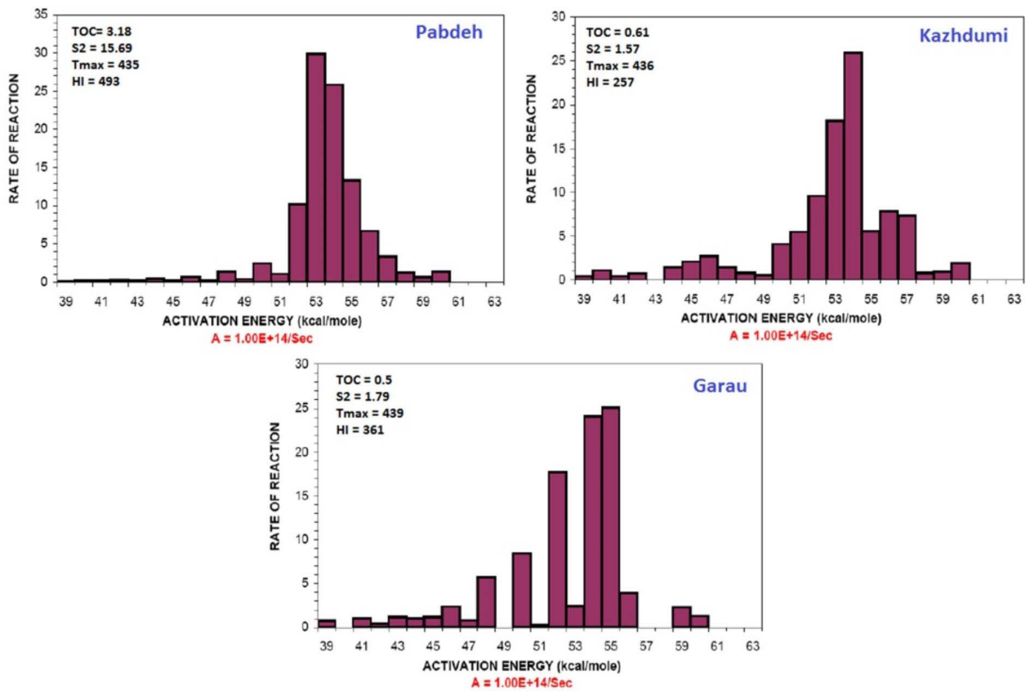

Fig. 6 Activation energy (Ea) distributions and frequency factors (A) for 3 selected samples.

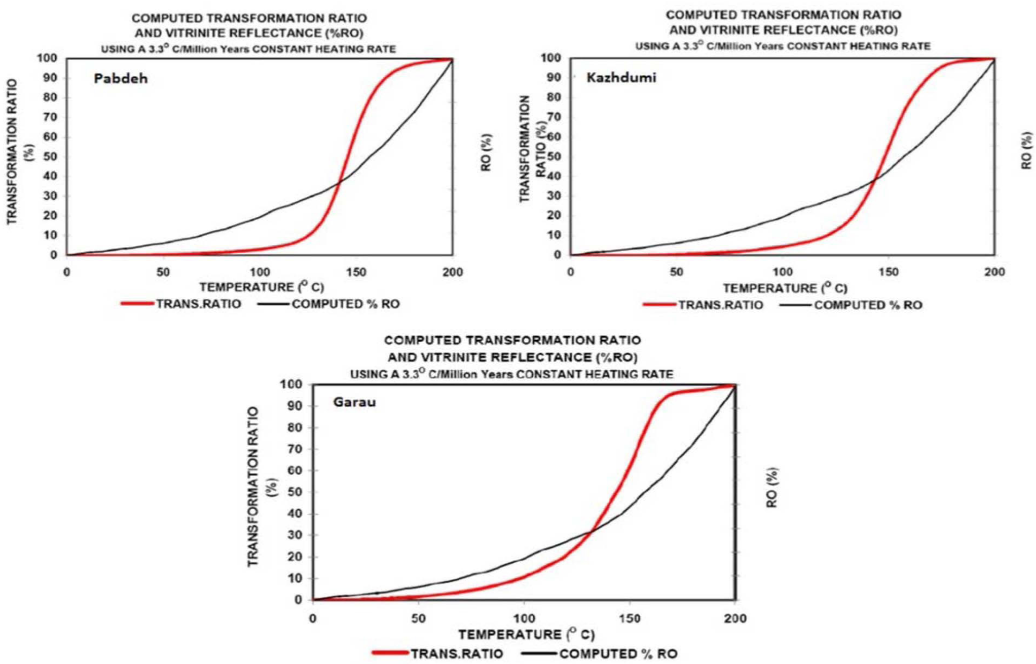

Fig. 7 Transformation ratio evolutions of 3 samples assuming a heating rate of 3.3 °C/Ma.

Table 2 Kinetic parameters activation energy (Ea), distribution and frequency factors (A) for 3 source rock samples.

Pabdeh Formation			Kazhdumi Formation			Garau Formation		
Discrete Model, Fixed A (1.00E+14) Results			Discrete Model, Fixed A (1.00E+14) Results			Discrete Model, Fixed A (1.00E+14) Results		
Ea Kcal/mole	Rate Reaction	Normalized Reaction	Ea Kcal/mole	Rate Reaction	Normalized Reaction	Ea Kcal/mole	Rate Reaction	Normalized Reaction
39	0.07	0.07	39	0.25	0.43	39	0.76	0.78
40	0.11	0.11	40	0.65	1.12	40	0.00	0.00
41	0.16	0.16	41	0.25	0.43	41	0.98	1.00
42	0.29	0.29	42	0.45	0.77	42	0.42	0.43
43	0.22	0.22	43	0.00	0.00	43	1.13	1.16
44	0.43	0.44	44	0.87	1.50	44	0.98	1.00
45	0.21	0.21	45	1.23	2.12	45	1.14	1.17
46	0.68	0.69	46	1.58	2.72	46	2.31	2.36
47	0.19	0.19	47	0.87	1.50	47	0.78	0.80
48	1.34	1.36	48	0.49	0.84	48	5.60	5.73
49	0.34	0.34	49	0.34	0.59	49	0.00	0.00
50	2.35	2.38	50	2.39	4.11	50	8.23	8.42
51	1.07	1.09	51	3.21	5.52	51	0.31	0.32
52	10.02	10.16	52	5.58	9.60	52	17.33	17.72
53	29.47	29.89	53	10.58	18.21	53	2.35	2.40
54	25.49	25.85	54	15.08	25.95	54	23.56	24.09
55	13.15	13.34	55	3.25	5.59	55	24.63	25.09
56	6.58	6.67	56	4.57	7.86	56	3.84	3.93
57	3.29	3.34	57	4.28	7.37	57	0.00	0.00
58	1.17	1.19	58	0.49	0.84	58	0.00	0.00
59	0.63	0.64	59	0.56	0.96	59	2.25	2.30
60	1.34	1.36	60	1.14	1.96	60	1.28	1.31
61	0.00	0.00	61	0.00	0.00	61	0.00	0.00
62	0.00	0.00	62	0.00	0.00	62	0.00	0.00
63	0.00	0.00	63	0.00	0.00	63	0.00	0.00

The beginning of bulk petroleum generation from Pabdeh, Kazhdumi, and Garau samples is estimated to happen at temperatures of 125, 126, and 100 °C and equivalent to 0.7, 0.75, and 0.6% vitrinite reflectance, respectively. The peak generation temperatures (geological Tmax) from the Pabdeh, Kazhdumi, and Garau formations are 145, 147, and 140 °C, and the vitrinite reflectance equivalent for these three formations are 0.9, 0.95, and 0.85% respectively (Table 3). The peak generation temperature values indicate that the Kazhdumi and Garau kerogens reach a significant transformation ratio (approximately 50% transformation). In contrast, according to vitrinite reflectance measurements, the Pabdeh Formation does not reach the peak oil generation. Therefore, the higher thermal maturity in Kazhdumi and Garau organic facies could have generated and expelled mature oils. This finding reveals that Kazhdumi and Garau source rocks are geochemically similar (e.g., in potential and oil generation).

Compositional Kinetic Parameters

Compositional kinetic parameters were calculated for 3 samples, which were analyzed using bulk kinetic models. The petroleum composition and physical properties were measured using a micro-scaled sealed vessel (MSSV). Fig. 8 represents the fourteen components resulting from compositional kinetic models. The Pabdeh and Kazhdumi formation samples demonstrate partial similarity in pyrolysate composition, but the Garau Formation indicates some differences in petroleum composition. These differences reflect that the kerogen types of the source rocks are not similar. The development of GORs with increasing kerogen conversion to petroleum in the source rocks is represented in Fig. 9.

Table 3 Data for the onset (10% TR) and peak generation (geological Tmax) temperatures of 3 samples.

Well	Formation	Onset generation temperature (°C)	Ro equivalent (%)	Peak generation temperature (°C)	Ro equivalent (%)	Ro mean measurement (%)
FF-01	Pabdeh	125	0.7	145	0.9	0.52
DD-01	Kazhdumi	126	0.72	147	0.95	0.74
BB-22	Garau	100	0.6	140	0.84	0.81

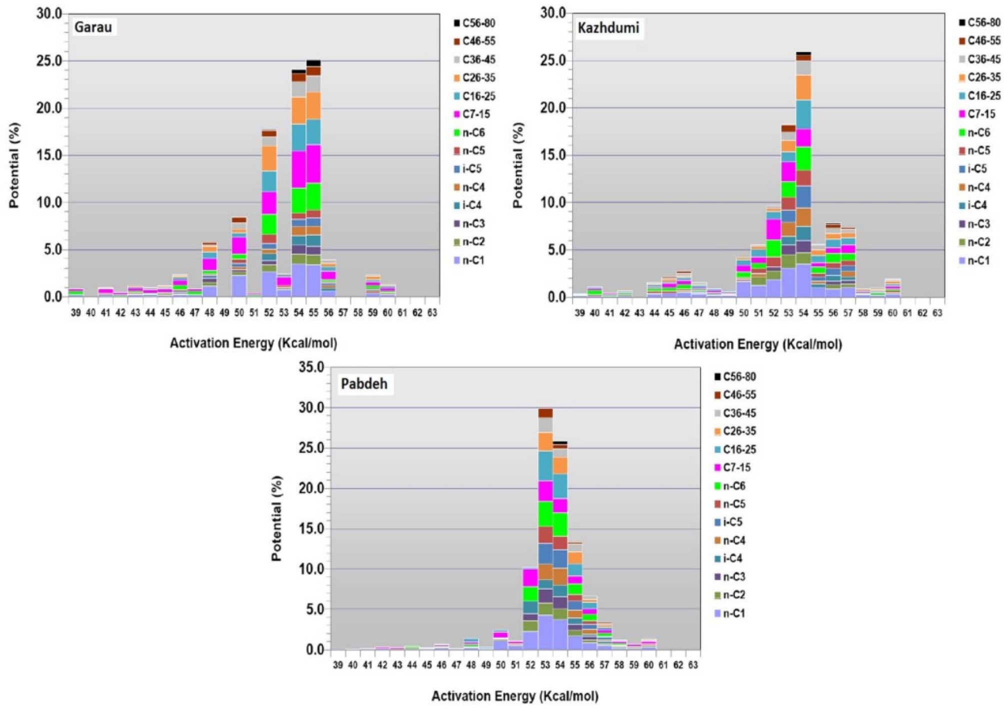

Fig. 8 Compositional kinetic models for 3 source rock samples from studied area.

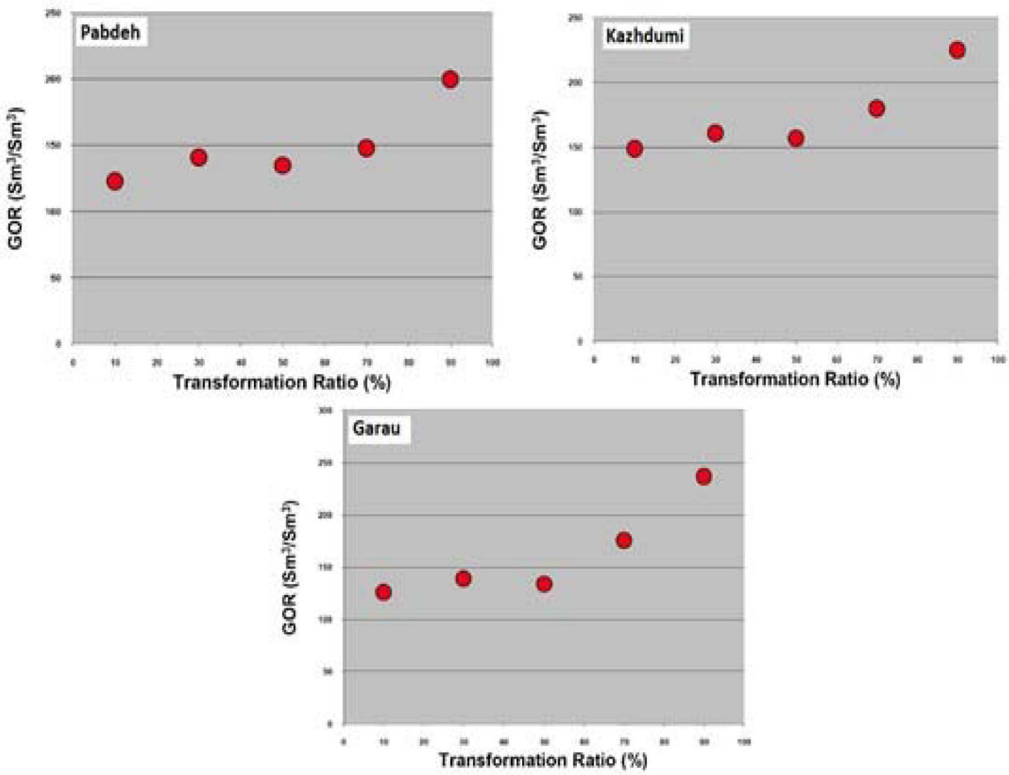

Fig. 9 The increase in transformation ratio with an increase in Gas/oil ratio during MSSV pyrolysis of 3 source rock samples.

According to this Figure, GORs expected for the main oil window vary between 150 and 180 Sm^3/Sm^3. Still, with an increase in transformation ratios, the amount of GORs of the generated petroleum shows a progressive increase. At conversion ratios between 30 and 50% transformation, the GOR of these samples decreases. The composition of organic matter in the source rocks can cause this reduction. All three samples of source rocks show a slight increase in GOR at higher levels of transformation ratios. Generally, the slight increase in GORs at 90% transformation could be related to the continuous primary gas generation reactions, and secondary gas generation does not start in the experimental closed system pyrolysis [23]. These low GORs expected for these three source samples in laboratory conditions show that Cretaceous reservoirs contain crude oil in the studied area. This result corresponds to the vitrinite reflectance and organic petrographic results. The amount of sulfur compounds and normal alkanes in petroleum illustrates the organic sulfur, aromatic, and aliphatic compounds of the organic matter. The amount of generated thiophenes in pyrolysis of organic matter and the ratio of 2, 3-dimethylthiophene, ortho-xylene, and n-C9:1 can be used to determine differentiation between the major kerogen types in different source rocks [24]. The studied formations include a wide variety of kerogen types II and IIS. Although the Garau Formation contains sulfur-rich type IIS kerogen, the Pabdeh and Kazhdumi contain type II kerogen (Fig. 10a). It is used the alkyl chain length distribution (calculated by pyrolysis) in petroleum-generated source rock samples to predict the hydrocarbon fluid type produced under natural conditions [25]. The studied formations are plotted in the low wax PNA oil area (Fig. 10b). The low-wax PNA source rocks are generated from a restricted marine environment [25]. Most organic matter in the studied source rocks originated from marine organisms, with little contribution from terrestrial organic matter.

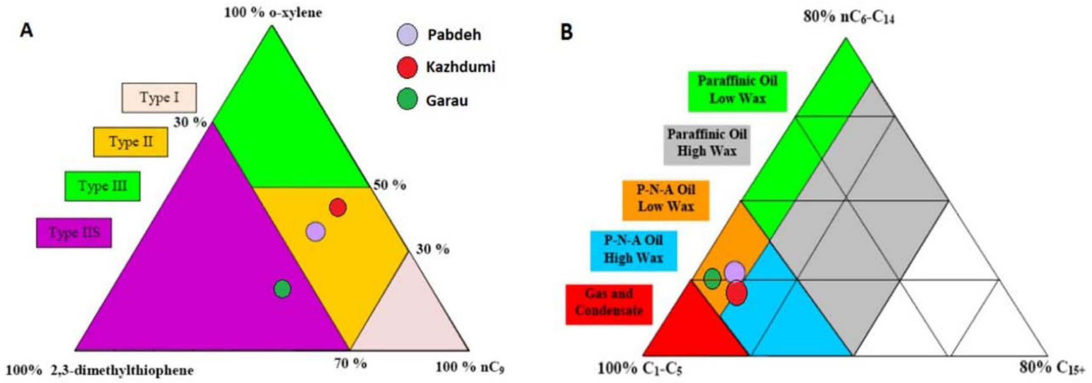

Fig. 10 Triangle plots: (A) the studied source rocks kerogen composition [25], (B) The type of the studied source rocks kerogen [24]. P–N–A =paraffinic–naphthenic–aromatic.

Conclusions

In this study, organic geochemistry, organic petrology, and kinetic parameters were used to evaluate the prediction of hydrocarbon generation types in Pabdeh, Kazhdumi, and Garau source rocks. The main objectives of the study are as follows:

(1) Rock-Eval parameters reveal that the Pabdeh, Kazhdumi, and Garau source rocks have fair to very good petroleum generation potential.

(2) The Pabdeh and Kazhdumi formations contain type II and II/III kerogen, mainly type II kerogen, while the Garau Formation contains type II-S kerogen. The liptinitic and amorphous macerals observed in the studied formations confirm this result.

(3) The Pabdeh, Kazhdumi, and Garau formations are immature (average Ro 0.55%), early mature (average Ro 0.74%), and mature (average Ro 0.81%), respectively.

(4) Bulk kinetic data indicate that most of the studied samples show a fairly broad range of activation energies, demonstrating the heterogeneity of kerogen type in source rocks. The samples have extremely broad activation energies of 39-63 kcal/mol.

(5) Temperatures as high as 145 oC (Ro 0.90%), 147 oC (average Ro 0.95%), and 140 oC (average Ro 0.84%) are required to extract petroleum from Pabdeh, Kazhdumi, and Garau formations, respectively, at more than 50% of kerogen transformation.

(6) Compositional kinetic data reveal that the studied source rocks contain marine kerogens, which can mainly generate low wax P-N-A oils. In addition, a slight increase in GOR at a higher level of TRs demonstrates the Cretaceous reservoirs in the studied area contain crude oil. This fact is confirmed by drilling results in Western Dezful Embayment oilfields.

(7) Based on Rock-Eval, organic petrography, and kinetic analysis, the efficient source rocks ranked in terms of charging hydrocarbon reservoirs are Garau and Kazhdumi formations, respectively.

Acknowledgments

The authors thank the National Iranian Oil Company-Exploration Directorate (NIOC-EXP) and Iranian Central Oil Fields Company (ICOFC) for providing the samples and data for this study. This project would have been impossible without the support of StratoChem Services in Cairo, Egypt.

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