



Crude oil fingerprint heterogeneity assessment by investigation of asphaltene subfractions: Implementation for reservoir continuity evaluation

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ABSTRACT

Asphaltenes are being a proxy of kerogen in the reservoir oil, which they have structural similarity. This characteristic provides an invaluable tool for obtaining oil fingerprints from the structural composition of asphaltenes. Since these compounds are classically defined as a solubility class, they constitute a large number of compound types with similar solubility features, instead of chemical characteristics. An effective strategy for the comprehensive characterization of these complex compounds is the fractionation of asphaltenes into several solubility subfractions. In this paper, asphaltenes were fractionated into three subfractions via adsorption of asphaltene onto CaCO_3 . The three obtained subfractions were entirely distinguishable, in which the FR-3 has the highest aromatic content, lowest aliphatic content, and the highest polarity among three subfractions. The FTIR spectroscopy was used for achieving structural composition information from each subfraction. Ninety peak ratios (10×9) based on ten characteristic bands were calculated for each subfraction, and a total of 270 peak ratios (90×3) were generated for each asphaltene sample. The modified moving window correlation coefficient technique was employed on generated peak ratios to obtain oil fingerprints for each sample and then the pairwise comparison between different samples. As exemplified, ten samples from the Asmari and Bangestan reservoirs in the Rag-e Sefid field were studied by the proposed procedure. The thresholds of MMWR and AMWR were determined as 0.9494 and 0.9894, respectively, in the Rag-e Sefid field. The similarity matrix was constructed based on a comparison of calculated MMWR and AMWR for all pairs of samples and thresholds to distinguish homogeneous and heterogeneous oil fingerprints. However, the Bangestan reservoir has fingerprint homogeneity, some heterogeneities were observed in the Asmari reservoir. The investigation of migration pathways revealed initial heterogeneity in the reservoir, in which these fingerprints dissimilarities were removed in connected wells during geological times. The examination of heterogeneities revealed three compartmentalized regions in the Asmari reservoir.

1. Introduction

As crude oils are charged and accumulated into the reservoir trap, impacts of different forces gradually begin to influence. These forces attempt to remove any disequilibrium in the oil column both laterally and vertically. In this regard, molecular diffusion and thermal convection are critical mass transport mechanisms within a reservoir. On the opposite side, thermal or gravitational segregations should be accounted for the forces to disturb the equilibrium. In the molecular diffusion process, random motions of molecular components cause removing potential chemical gradients in the reservoir. Hence, chemical

components will be redistributed, and horizontal concentration gradients are eliminated. However, vertical gradients due to gravitational or thermal segregations being established. Despite molecular diffusion, thermal convection occurs on exceptional conditions in the reservoir and causes heat transfer by the movement of fluids. This mechanism leads to completely homogenizing fluids in the reservoir in which gravitational and thermally induced gradients are eliminated (England et al., 1995, 1987). Fig. 1 schematically illustrates how molecular diffusion and thermal convection mechanisms are acted in the reservoir to equilibrate chemical composition. Thermodynamic equilibrium will occur within the oil column of individual wells by diffusion during

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geological times (Fig. 1b). After sufficient time, molecular diffusion causes the homogenization of fluid composition in different wells. But the vertical compositional gradients due to gravitational and thermal segregations have remained (Fig. 1c). However, the thermal convection mechanism causes completely vertical and horizontal homogenization of fluid composition across the reservoir in different wells (Fig. 1d; England et al., 1987).

Above mentioned mechanisms have an effective role when the reservoir is laterally connective, and the presence of barriers impedes lateral fluid composition homogenization (England, 2007). Hence, one of the critical approaches to investigate reservoir compartmentalization is the assessment of fluid composition heterogeneity. It is well established that methods rely on fluid composition outdoes other techniques based on reservoir engineering data (e.g., pressure, GOR, PVT (pressure-volume-temperature relationships), etc.) to revealing compartmentalized regions. This preference is due to the higher time required for composition equilibrium than for pressure equilibrium. There are numerous studies in the literature which the pressure data failed to disclose reservoir compartmentalization (Westrich et al., 1999; Brown, 2003; Milkov et al., 2007; Pfeiffer et al., 2011; Dong et al., 2012; Zuo et al., 2012; Chen, 2013). It is noteworthy to mention that other phenomena can also be responsible for fluid composition heterogeneity besides reservoir compartmentalization. Generally, these phenomena can be classified into in-filling and post-filling processes. Different source rocks, various source rock facies, gradual maturation of source rock, and different filling directions are regarded as an in-filling fluid composition heterogeneity process. The post-filling processes are evaporative fractionation, water washing, biodegradation, charge history, and so on (Larter and Aplin, 1995; Westrich et al., 1999; Rein and Schulz, 2007). Furthermore, insufficient time in slow mixing reservoirs causes fluid composition heterogeneity in the reservoir (England, 2007).

Asphaltenes are macromolecular structures. These compounds mostly consist of polynuclear aromatic compounds with normal alkane side chains, cyclic alkanes, and heteroatoms (Tharanivasan, 2012). But these polar compounds are classically defined based on solubility, instead of structure. Asphaltenes are insoluble in light normal alkane solvents (e.g., *n*-pentane, *n*-hexane, *n*-heptane, etc.) and soluble in aromatic solvents (e.g., benzene, toluene, etc.) (Orangi et al., 2006; Gray et al., 2011; Hemmati-Sarapardeh et al., 2019). Furthermore, asphaltenes are regarded as a proxy for kerogen in the reservoir oil. This feature is due to the structural similarity between these compounds and precursor kerogen (Rubinstein et al., 1979; Behar et al., 1984; Behar and Pelet, 1984, 1985; Pelet et al., 1986; Lehne et al., 2009). The structural similarity of asphaltene with kerogen has created scientific interest.

These compounds are routinely employed in different disciplines of geochemistry studies such as oil-oil correlation, reservoir compartmentalization, obtaining oil fingerprints, get information about source rocks, thermal maturity determination, and so on (Behar et al., 1984; Behar and Pelet, 1984, 1985; Christy et al., 1989, 1991; Nali et al., 2000; Pan et al., 2002; Pomerantz et al., 2010a, 2010b; Asemani and Rabbani, 2016; Asemani et al., 2020). Detailed characterization of asphaltenes is a crucial parameter in geochemistry studies. Not only asphaltenes are not a pure component, but they also include an incredibly large number of species that have similar solubility characteristics (e.g., insoluble in light normal alkanes and soluble in aromatic solvents). These species might have different chemical structures, shapes, and sizes (Tharanivasan, 2012; Rogel et al., 2015). This feature makes a thorough chemical characterization of asphaltenes with problems. Fractionation of asphaltenes into several solubility subfractions is an effective strategy to reduce the complexity of these compounds and providing a distribution for each given properties instead of average values (Rogel et al., 2015). In other words, the fractionation procedure furnishes detailed and thorough structural information about asphaltenes. Several procedures have been employed in the literature to separate asphaltenes into different subfractions. Some of these procedures are exemplified in the following: Trejo et al. (2004); washed asphaltenes with three different volume ratios of toluene/heptane (i.e., 35/65, 25/75, and 18/82) in the soxhlet to obtain different subfractions from these compounds. Rogel et al. (2015); prepared asphaltene solution with methylene chloride (DCM) and mixed with 60 mesh non-porous PTFE particles. After the evaporation of solvents, the PTFE-supported sample was washed successively with different binary solvents, including 15/85 CH_2Cl_2 /*n*-heptane, 30/70 CH_2Cl_2 /*n*-heptane, 100% CH_2Cl_2 , and 90/10 CH_2Cl_2 /methanol, respectively, and several subfractions were recovered. Subramanian et al. (2016, 2017; Ruwoldt et al. (2018); obtained three subfractions from the absorption of asphaltenes onto calcium carbonate powder. Subramanian et al. (2017); Ruwoldt et al. (2018); added different amounts of *n*-hexane to crude oil (e.g., 3.5v, 6v, 40v) to stepwise precipitation of asphaltenes and obtaining three subfractions. Taheri-Shakib et al. (2018); employed a procedure similar to Subramanian et al. (2017, 2016; Ruwoldt et al. (2018); but they used from three different minerals including calcite, dolomite, and sandstone, and three subfractions were yielded from each mineral.

The main goal of this paper is to investigate oil fingerprint heterogeneities by a comprehensive study of asphaltene subfractions. To achieve this goal, firstly, asphaltene samples were separated into three different subfractions. Then, FTIR spectroscopy was used to investigate the structural composition of asphaltenes, and the modified moving

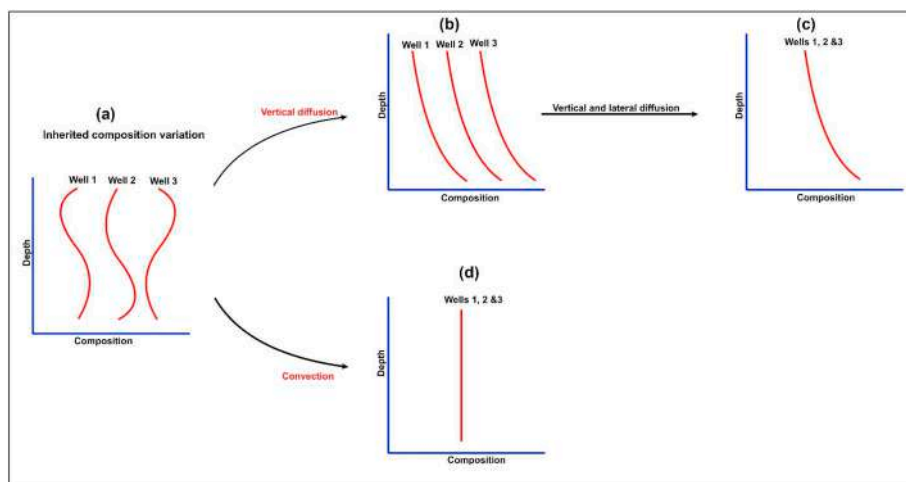


Fig. 1. Schematic of different mass transfer mechanisms impacts on fluid composition in a reservoir: a) inherited fluid composition due to the filling process, b) effect of vertical diffusion on the fluid composition, c) horizontal fluid composition homogenization due to sufficient time of acting molecular diffusion on vertical and horizontal scales, d) effect of thermal convection mechanism on vertical and lateral fluid composition homogenization (England et al., 1987).

window correlation coefficient technique was applied to reveal subtle differences between samples. Finally, the reasons for fingerprint heterogeneity or homogeneity were examined by considering different possible phenomena. As an example, ten oil samples from different wells across the Rag-e Sefid oil field located in the Dezful Embayment, SW Iran, were studied.

2. Geological setting

Zagros fold-thrust belt (ZFTB) is an important part of the Zagros orogeny in Iran from the point of hydrocarbon reserves. Although the ZFTB includes several regions such as Lurestan, Khuzestan, and Fars, the Khuzestan region is the most known due to the occurrence of Dezful Embayment in this region (Fig. 2a). A petroliferous depression region in the ZFTB is named as a Dezful Embayment, which covers 60,000 km², and Asmari Formation has not an outcrop in this area (Bordenave and Burwood, 1995). The presence of several rich source rocks, excellent reservoirs, and efficient cap rocks have been completed by the Neogene folding of the Zagros, which caused the forming of structural traps and providing migration pathways (Bordenave and Hegre, 2005). These factors lead to the formation of five petroleum systems in the ZFTB. The Middle Cretaceous to Early Miocene system contains two main source rocks (e.g., Kazhdumi and Pabdeh Formations) and two main reservoirs (e.g., Asmari and Bangestan reservoirs) (Fig. 3). The Asmari and Bangestan carbonates host about 8% of world reserve in the Dezful Embayment (Bordenave and Hegre, 2010). Most of the oils have been accumulated in the Asmari reservoir (ca. 75%), and another 23% have

been trapped in the Bangestan reservoir (Sarvak and Ilam Formations). The Gachsaran Formation with halite and anhydride lithology completely preserved the Asmari reservoir. Both of the Asmari and Bangestan reservoirs are fractured carbonate reservoirs. The Ahvaz member is a sandstone reservoir that is deposited in the basal of the Asmari Formation and can be traced mostly in the SW Khuzestan (Bordenave and Hegre, 2005). The Kazhdumi Formation is a rich source rock which deposited in an intrashelf silled depression (Bordenave and Burwood, 1995). These marls have a high gamma-ray and low density. The initial source rock potential index (SPI) of the Kazhdumi source rock in the deeper parts of the depression may have reached 25 to 30, which is considered among the highest values in the world. The kerogen type of this source rock is characterized as an IIS that has a high sulfur algal organic matter with hydrogen index (HI) 500–700 g HC/g TOC (Bordenave and Huc, 1995). The average TOC of this formation in the Dezful Embayment ranges from 3.1 to 12% with S₂ ranges from 17 to 40 mg HC/g rock (Bordenave and Burwood, 1990). The Pabdeh Formation is defined as type II kerogen, and its average TOC ranges from 1 to 12% (Bordenave and Burwood, 1990).

The Rag-e Sefid field is an important oil field located in the southern part of the Dezful Embayment. The structure of this field is a boomerang-shaped anticline, which has 55 km length and 5–7 km width (Fig. 2b). Similar to most of the oil fields in the Dezful Embayment, the Asmari and Bangestan are the main oil-producing reservoirs, and the Khami group is gas producing reservoir in this field. Most of the wells have been completed in the Asmari reservoir and few wells in the Bangestan.

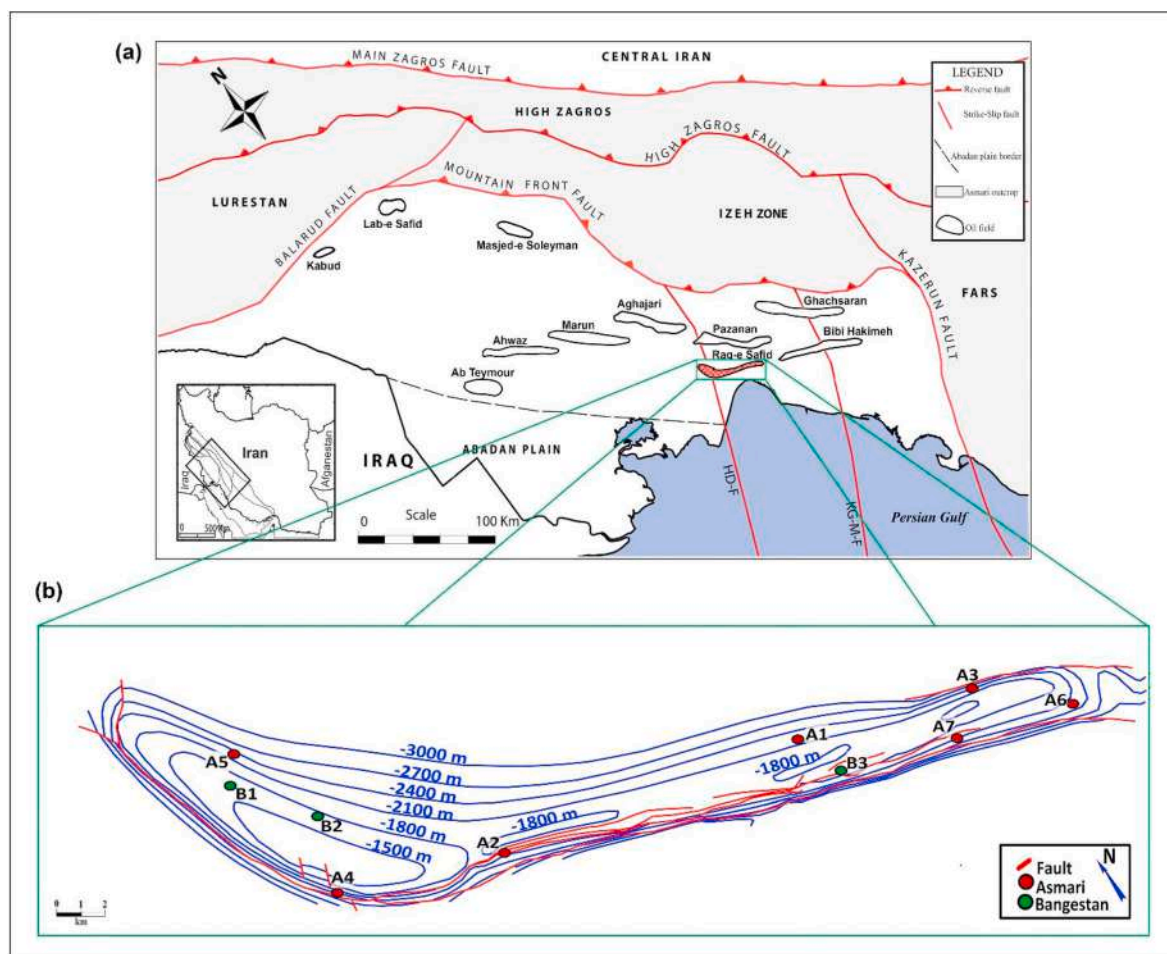


Fig. 2. a) Location map of Rag-e Sefid oil field in the Dezful Embayment, SW Iran (modified after Farahzadi et al., 2019). b) Contour map of the Rag-e Sefid field based on top of the Asmari Formation. The studied wells are pointed in the contour map.

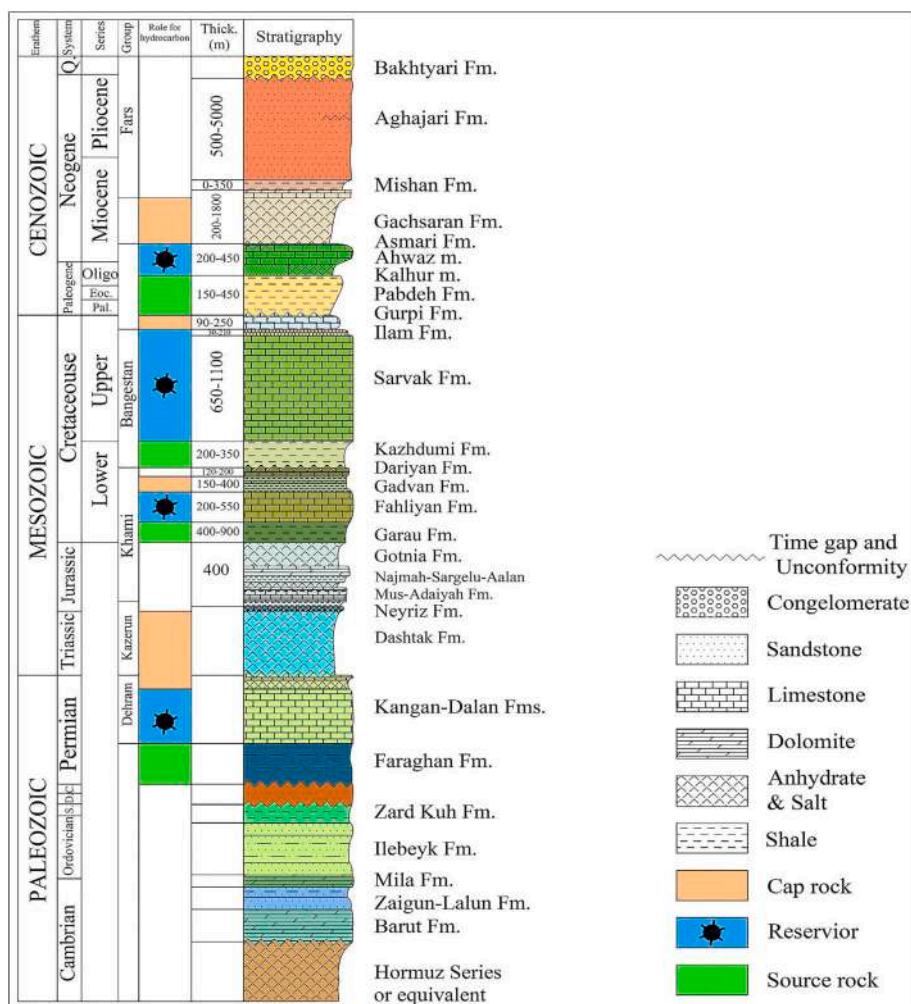


Fig. 3. Stratigraphic column in the Dezful Embayment showing characteristics of different formations (modified after Derikvand et al., 2018).

3. Material and methods

3.1. Samples

Ten oil samples were collected from producing wells in the Asmari and Bangestan reservoirs at atmospheric conditions. Because limited wells are producing from the Bangestan reservoir, only three samples were collected from this reservoir, and others were sampled from the Asmari reservoir. The collected wells have been producing for more than fifteen years. The workover and well treatments were not performed one month before sampling. The collected samples are listed in Table 1, and their locations are represented in Fig. 2b.

Table 1

SARA analysis results for the studied samples from the Rag-e Sefid field.

NO	Samples	Reservoir	Saturate (wt%)	Aromatic (wt%)	Resin (wt%)	Asphaltene (wt%)
1	RS-A1	Asmari	42.90	30.65	21.45	5.00
2	RS-A2	Asmari	34.01	33.58	20.67	11.74
3	RS-A3	Asmari	39.85	32.47	21.15	6.54
4	RS-A4	Asmari	40.09	30.98	21.41	7.51
5	RS-A5	Asmari	42.12	33.70	18.38	5.80
6	RS-A6	Asmari	37.95	33.90	21.25	6.91
7	RS-A7	Asmari	39.10	34.21	20.04	6.65
8	RS-B1	Bangestan	41.84	33.85	20.22	4.09
9	RS-B2	Bangestan	43.74	32.08	20.41	3.76
10	RS-B3	Bangestan	39.07	32.06	22.04	6.83

3.2. SARA analysis

Firstly, asphaltenes were extracted from crude oils according to ASTM D6560 standard method with *n*-hexane as a precipitant solvent (D6560, 2017). *N*-hexane was mixed with crude oil at the ratio of 30:1 (ml: g) and refluxed for 1 h. This process causes fresh *n*-hexane continuously added to crude oil, and most of the asphaltenes are precipitated. After overnight storage in a dark place, the mixture was filtrated. As the precipitated asphaltene contains impurities such as wax, resins, etc., these impurities should be removed. So, the filter paper consists of impure asphaltenes washed under reflux by *n*-hexane until the eluting solvent becomes colorless. Then, the pure asphaltene was obtained by washing with toluene. Solvents evaporated, and pure asphaltene was heated at 100 °C before weighting and subsequent analysis. The soluble part of crude oil in *n*-hexane (maltene) was further fractionated into saturate, aromatic, and resin with column chromatography. *N*-hexane, toluene, and toluene/methanol (90/10) solvents were employed to elute saturate, aromatic, and resin from the silica gel packed column, respectively.

3.3. Fractionation of asphaltenes

The fractionation of asphaltenes was performed as a procedure described by Subramanian et al. (2016), 2017; Ruwoldt et al. (2018); with some modifications. Briefly, 1 g of asphaltene was dissolved in the 250 ml toluene to obtain a 4 g/l solution. The solution firstly stirred for 30 min and then sonicated for 30 min to assure complete dissolution of

asphaltenes. Subsequently, the pure calcium carbonate (CaCO_3 , 30 g) was added to the mixture and stirred for 24 h. After this time, the solution was left to evaporate excess solvents. The adsorbed asphaltene onto calcium carbonate was washed with different solvents to obtain various subfractions. To avoid contamination of each subfraction with calcium carbonate, a round aluminum tube similar to Fig. 4 (4.2 cm outer diameter, 3.8 cm inner diameter, 6 cm height) was designed. A small amount of cotton (cotton was prewashed by DCM) was placed at the bottom of the tube and pressed to the height of about 1 cm. Two layers of filter paper placed on the top of the cotton, and then the prepared calcium carbonate powder was added to the tube. Another two layers filter paper and 1 cm cotton were placed on the top of the powder (Fig. 4). The prepared tube was washed by the Buchi extraction system (B-811) with different solvents. The first subfraction of asphaltene, named FR-1, obtained by washing with *n*-hexane: toluene (50:50, v: v), and the second subfraction of asphaltene, named FR-2, was obtained by toluene: DCM (50:50, v: v). Washing was continued for 48 h to assure complete washing for each subfraction. After washing of each subfraction, about 200–300 mg of calcium carbonate powder was taken for pyrolysis analysis and determining remaining asphaltenes absorbed onto calcium carbonate. The remaining part of asphaltenes is strongly and irreversibly adsorbed to calcium carbonate. This subfraction (FR-3) was extracted by removing calcium carbonate with HCl acid. For this, 350 ml of 4 N HCl and 350 ml mixture of DCM: methanol (90:10) was added to the flask containing calcium carbonate. The mixture was stirred about 4 h, and the organic and water phases separated by separating funnel. Distilled water was added several times to the organic phase to remove HCl acid from the asphaltenes surface completely. The organic phase allowed to evaporate, and the obtained asphaltenes named FR-3.

3.4. FTIR spectroscopy

A 13 mm KBr pellet was prepared by pressing of grounded asphaltene and KBr powder mixture (1 wt: 100 wt) under high pressure. FTIR spectra from different subfractions of asphaltene samples were obtained on the KBr pellets via Bruker-Tensor 27 with 40 scans and 4 cm^{-1} resolution in the range of $4000\text{--}400\text{ cm}^{-1}$.

3.5. Open system pyrolysis

The yield of different asphaltene subfractions was determined by the open system pyrolysis method. About 50 mg of calcium carbonate powder was loaded in the crucible and analyzed by Rock-Eval 6. The detail of this analysis is mentioned elsewhere (Behar et al., 2001). This technique heats the sample in the pyrolysis oven from 300 to 650°C . In this step, the pyrolysable organic carbons of the sample are determined. Then the sample is transferred to the oxidant oven, and the sample is heated from 300 to 850°C to determine residual carbon in the sample. The amount of pyrolysable carbon and residual carbons are used to

measure total organic carbon (TOC). In this paper, this parameter was used to calculate the yield of different subfractions. The TOC for prepared calcium carbonate before fractionation and after each step of fractionation was measured. The amount of different subfractions is calculated from the following equations:

$$(AS_{\text{remain}})_i = \frac{TOC_i^* (AS_{\text{remain}})_{i-1}}{TOC_{i-1}}, \quad i = 1, 2, 3 \quad (1)$$

$$AS_{\text{FR}i} = (AS_{\text{remain}})_i - (AS_{\text{remain}})_{i+1}, \quad i = 1, 2, 3 \quad (2)$$

$(AS_{\text{remain}})_i$ is amounts of asphaltene remained in calcium carbonate after subfraction i (g). TOC_i is the measured TOC value for calcium carbonate after subfraction i . TOC_0 and TOC_1 are equal and are related to the TOC value for calcium carbonate before fractionation. The amount of $(AS_{\text{remain}})_0$ and $(AS_{\text{remain}})_1$ is equal, which is determined from the amount of used asphaltene to mix with calcium carbonate. The TOC value of calcium carbonate without asphaltene was measured three times. The calcium carbonate produces CO_2 in the oxidant oven at higher temperatures. The average of these three analyses was subtracted from the measured value of TOC for the mixture of asphaltenes and calcium carbonate.

3.6. GC-MS analysis

GC-MS analysis was performed on the saturate fraction to determine maturity parameters. The Shimadzu QP2010SE gas chromatograph-mass spectrometer in the selected ion monitoring mode (SIM) was used. The capillary column was DB-1 (60 m $\times$ 0.1 mm and 0.25 mm film), and helium was used as a carrier gas. The heating program of the GC oven was from 80 to 150°C with a rate of $20^\circ\text{C}/\text{min}$ and then increased to 310°C with a rate of $2^\circ\text{C}/\text{min}$ and held for 60 min.

3.7. Modified moving widow correlation coefficient technique

Asemani et al. (2020); employed the modified moving window correlation coefficient technique, for the first time, to evaluate oil fingerprint similarity between different samples. They applied this technique on the FTIR data of asphaltenes and showed that this technique has similar results with the well-known technique of GC fingerprinting. These authors suggest the modified moving window correlation coefficient as a reliable alternative method to assess oil fingerprint similarity. The general scheme of this technique is illustrated in Fig. 5. Peak ratios calculated from second derivative FTIR spectra are considered as an input data series. Unlike the traditional correlation coefficient, which calculates one correlation coefficient for two studied data series, a series of correlation coefficients is calculated in this technique. The number of the calculated correlation coefficients is equal to the number of moving windows. If W and N were the width of the moving window and the number of data points in the input data series, respectively, the number of the calculated correlation coefficients is $N-(W-1)$. Hence this technique discloses subtle differences between samples that are likely to obscure in the traditional method. In this paper, a combination of asphaltene fractionation and modified moving window correlation coefficient technique was applied to obtain detailed information about oil fingerprints similarities and dissimilarities in the studied samples. The workflow of the proposed procedure is shown in Fig. 6. After asphaltene fractionation with adsorption onto calcium carbonate, ten bands from the second derivative spectra of each subfraction were selected, and 90 (10×9) peak ratios were calculated by dividing each band to others. Generally, 270 peaks ratios (90×3) calculated for each sample were considered as an input data series in the modified moving window correlation coefficient technique. The optimum width of the moving window is determined from the replicates of one sample. Two replicates with the highest differences are selected, and correlation coefficients with different window sizes (e.g., 5 to 17 points with two intervals) are calculated. The identification thresholds are used to decide about

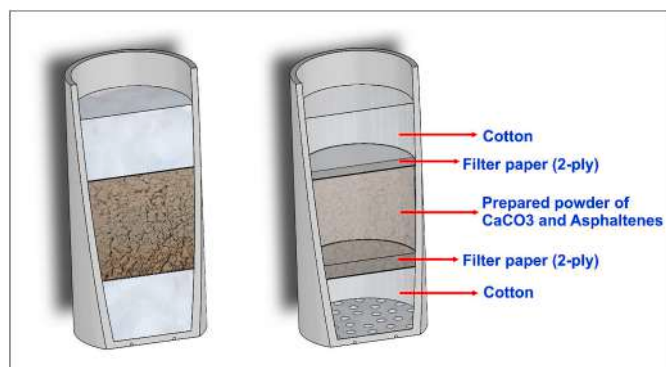


Fig. 4. Schematic of the prepared tube for fractionation of asphaltenes.

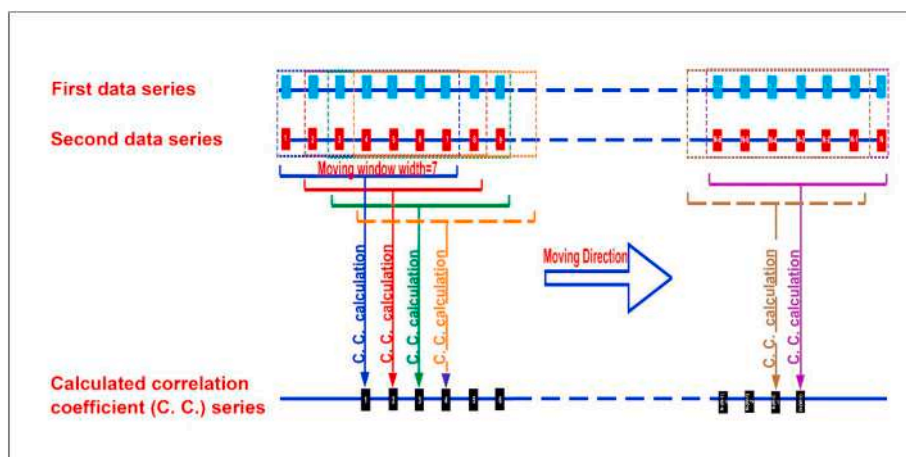


Fig. 5. General concept of the modified moving window correlation coefficient technique with seven points moving window width (Asemani et al., 2020).

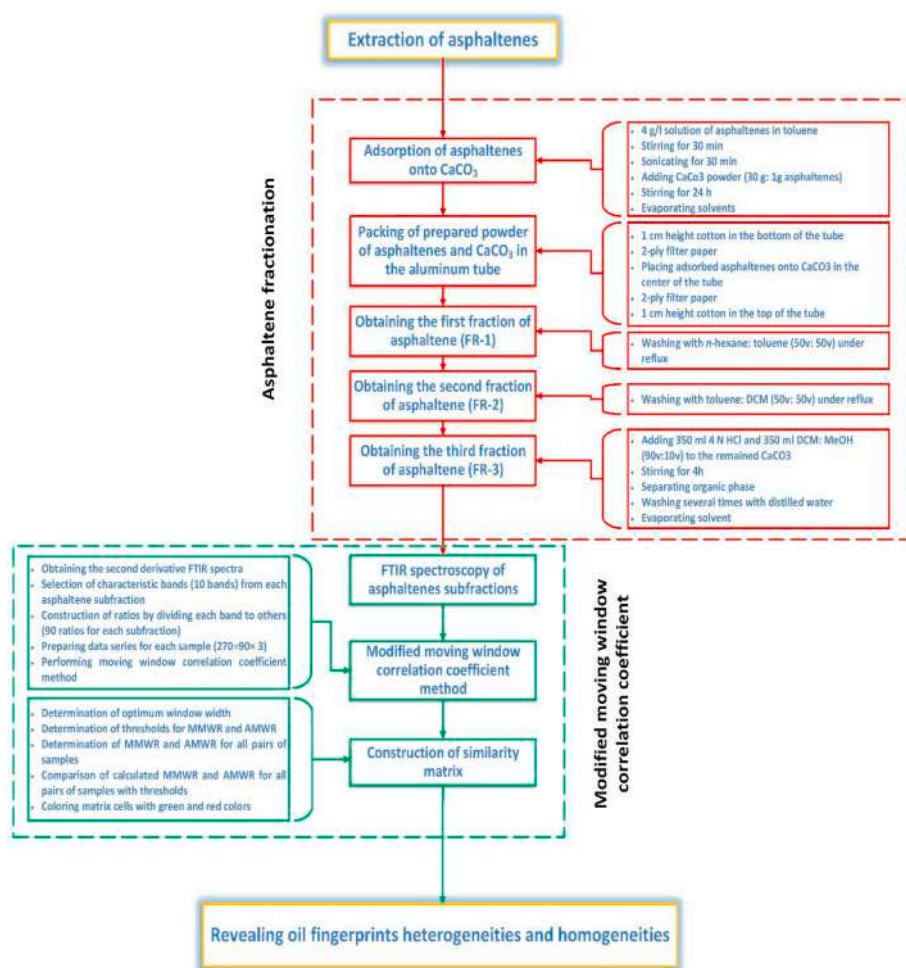


Fig. 6. The proposed procedure to obtain detailed information about oil fingerprints in the studied samples.

similarity or dissimilarity between studied samples. The lowest value of the minimum correlation coefficient in all moving windows (MMWR) and the lowest value for an average of correlation coefficients in all moving windows (AMWR) for six replicates of one sample are assigned as thresholds. Results of the obtained MMWR and AMWR for all pairs of samples are summarized in a similarity matrix, and matrix cells are colored based on comparison with thresholds (Asemani et al., 2020).

4. Results and discussion

4.1. Oil bulk properties

SARA analysis results are reported in Table 1, and the location of studied samples is shown in Fig. 2b. Saturate fraction has the highest amount among different fractions of crude oil. This fraction ranges from 34.01% (RS-A2) to 43.74% (RS-B2), and its average is 39.43% and

41.55% for samples from the Asmari and Bangestan reservoirs, respectively. The average value of aromatic, resin and asphaltenes is 32.78%, 20.62%, and 7.16% for the Asmari reservoir, respectively, and 32.66%, 20.89%, and 4.89% for the Bangestan reservoir, respectively. The amount of SARA analysis fractions shows a descending trend from saturate, aromatic, resin, and asphaltene for both of the Asmari and Bangestan reservoirs. The lowest and highest amount of asphaltenes are related to RS-B2 (3.76%) and RS-A2 (11.74%), respectively. Generally, the samples from the Bangestan reservoir has higher saturate and lower asphaltene content than the Asmari reservoir.

4.2. The yield of asphaltene subfractions

The yield of three subfractions for each sample are listed in Table 2. Open system pyrolysis technique (Rock-Eval) and gravimetric methods were employed for measurements. The total yield of asphaltene subfractions is better than 97.45%. Some differences are apparent in subfractions yields by two methods. Generally, the Rock-Eval method has slightly higher yields regarding the gravimetric method. There are some possible reasons for these differences. The total yield of asphaltene subfractions is considered 100% in the Rock-Eval method, according to eqs. (1) and (2), but the total yield in the gravimetric method is less than 100% (Table 2). Another possible reason is due to that in the fractionation process after washing of each subfraction, about 200–300 mg of calcium carbonate powder was taken for Rock-Eval analysis. So, the yield of each fraction by gravimetric is slightly decreased. These are the possible source of slight differences in the yield of subfractions by two methods. The latter reason seems to have more contribution to differences than the first reason because the yield of different subfractions in the Rock-Eval method is slightly higher than gravimetric. Thus, the Rock-Eval method has comparable results with the gravimetric method. This technique can be used as an alternative method to determine the yield of different subfractions and the amount of remained asphaltenes onto CaCO_3 . The yield of first subfraction (FR-1) ranges from 28.48 to 80.91%. The yield of FR-2 and FR-3 is ranged between 14.18 to 66.80% and 2.72–11.82%, respectively. The average of each subfraction is 59.49%, 34.94%, and 5.57% for FR-1, FR-2, and FR-3, respectively. Except for the RS-A2, RS-B2, and RS-B3 samples, the yield of FR-1 is higher than FR-2 in other samples.

4.3. FTIR spectroscopy assignment of asphaltene subfractions

Before the assignment of FTIR spectra for different subfractions, it should be assured that the treatment of HCl acid for extraction of FR-3 does not produce fake bands and if acid can modify the chemical structure of asphaltene. The RS-A4 sample used to simulate changes might occur during acid treatment. The FTIR spectra of this sample were recorded before acid treatment, after HCl acid treatment, and after the addition of CaCO_3 to HCl acid. The last item was used to investigate the

likely catalytic effect of CaCO_3 . The obtained FTIR spectra of the RS-A4 sample are shown in Fig. 7. This figure shows that acid treatment or presence of CaCO_3 has not any effect on the FTIR spectrum. This conclusion is similar to those mentioned in the literature (Subramanian et al., 2016). Furthermore, the FTIR spectra indicate that the washing process of the organic phase with distilled water was perfect for removing acid from the asphaltenes surface completely, and any remnant of HCl acid was not observed in FTIR spectra.

Fig. 8 illustrates the FTIR spectra of asphaltenes before fractionation and their subfractions (e.g., FR-1, FR-2, and FR-3) for two representative samples (e.g., RS-A2 and RS-B3) in the Rag-e Sefid field. Although the FTIR spectra of asphaltenes before fractionation and different subfractions show similar absorption bands, the value of bands is different, which indicates differences in the amount of specific functional groups in subfractions. The differences between FR-1 and FR-2 subfractions are slight, but the FR-3 has noticeable differences regarding other subfractions. A broad band in the $3600\text{--}3100\text{ cm}^{-1}$ region related to hydrogen-bonded O–H and N–H stretching vibrations. The prepared KBr pellet is highly moisture absorbent and causes the appearance of a band in the $3600\text{--}3100\text{ cm}^{-1}$ region. It is difficult, if not impossible, to attribute this band to functional groups in the structure of samples or absorbed moisture (Asemani and Rabbani, 2020). In this paper, the prepared samples were dried at 80°C overnight before recording FTIR spectra to reduce the amount of absorbed moisture. This time is sufficient for before fractionation, FR-1, and FR-2 samples, and the moistures are highly reduced. But, in the FR-3 sample higher amount of moisture is apparent relative to other subfractions. This moisture might have related to the remnant of distilled water used during acid treatment. A shoulder band at about 3050 cm^{-1} is attributed to C–H stretching in the polynuclear aromatic compounds (Asemani and Rabbani, 2020). A region of $3000\text{--}2750\text{ cm}^{-1}$ is related to the C–H stretching of aliphatic groups such as methyl, methylene, and methine (Pavia et al., 2008). Some bands are overlapped in this region, but in the curve fitting, five bands are observable (Asemani and Rabbani, 2020). The C=O stretching in the carboxylic acids and esters is appeared at about 1730 cm^{-1} (Smith, 1998). This band is so little in all fractions of asphaltenes and before fractionation asphaltenes. A band at about 1600 cm^{-1} is due to C=C stretching of aromatics and is called ring mode band (Pavia et al., 2008). The amount of this band indicates an ascending order of before fractionation, FR-1, FR-2, and FR-3 for both representative samples. This pattern shows the FR-3 subfraction has the highest amount of aromatic compounds. The bands at 1460 cm^{-1} and 1376 cm^{-1} are attributed to the C–H bending of aliphatics (e.g., methyl and methylene) (Smith, 1998). The amount of these bands shows a descending order of before fractionation, FR-1, FR-2, and FR-3 for both representative samples, which indicate the decreasing amount of aliphatic compounds. A stretching of sulfoxide groups gives rise a band near 1030 cm^{-1} (Lin-Vien et al., 1991). This band appears in different subfractions, and the FR-3 shows the highest amount. The bands in the region below the 900 cm^{-1} (e.g., three bands at about 862 , 809 , and 744 cm^{-1}) are due to C–H out of plane bending (wagging) in the aromatic rings. These bands are useful to obtain information about the different substitutions of aromatic rings (Yen et al., 1984). A small shoulder band in the 724 cm^{-1} is attributed to the rocking vibration of methylene in the straight-chain alkanes with more than four carbons (Asemani and Rabbani, 2020). Generally, samples show that the amount of aromatic compounds increases, and the amount of aliphatic compounds decreases in the order of FR-1, FR-2, and FR-3. Furthermore, the polarity of asphaltenes has an ascending order of FR-1, FR2, FR-3 due to increasing sulfoxide groups.

4.4. Investigation of oil fingerprint heterogeneity

Asphaltene as a proxy of kerogen in crude oil are valuable compounds to get information about the oil fingerprint of reservoir oil. These compounds have been already used for obtaining oil fingerprints (Riley et al., 2016; Asemani et al., 2020). Acquiring comprehensive

Table 2

Yield of asphaltene subfractions for studied samples in the Rag-e Sefid field.

Samples	Open system pyrolysis			Gravimetry			Total yield (wt%)
	FR-1 (wt%)	FR-2 (wt%)	FR-3 (wt%)	FR-1 (wt%)	FR-2 (wt%)	FR-3 (wt%)	
RS-A1	80.10	14.18	5.72	79.88	14.01	5.63	99.52
RS-A2	37.38	59.90	2.72	36.64	59.02	2.67	98.33
RS-A3	70.97	25.84	3.18	69.45	24.76	3.24	97.45
RS-A4	65.45	22.73	11.82	65.22	21.51	11.41	98.15
RS-A5	80.91	14.55	4.55	80.45	14.00	3.71	98.16
RS-A6	78.99	16.46	4.56	77.97	15.97	4.32	98.26
RS-A7	62.35	33.53	4.12	61.93	33.22	3.51	98.66
RS-B1	60.55	33.92	5.53	59.01	33.65	5.49	98.15
RS-B2	29.74	66.80	3.46	29.39	66.55	3.19	99.14
RS-B3	28.48	61.52	10.00	27.98	60.55	9.05	97.57

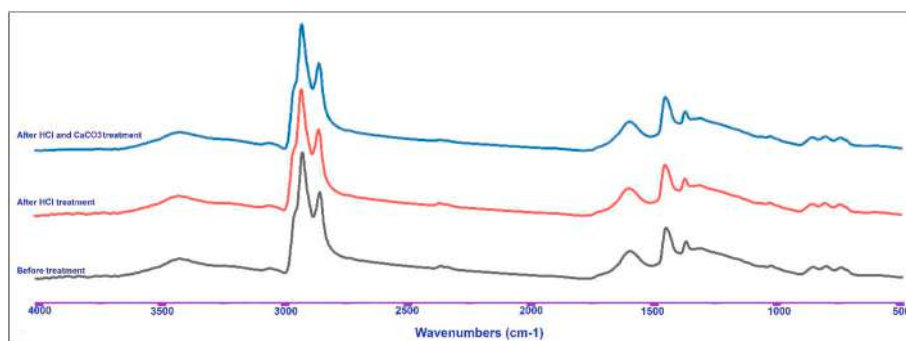


Fig. 7. FTIR spectra of RS-A4 sample to investigate the effect of HCl and combination of HCl and CaCO_3 treatment on the structural composition of asphaltene.

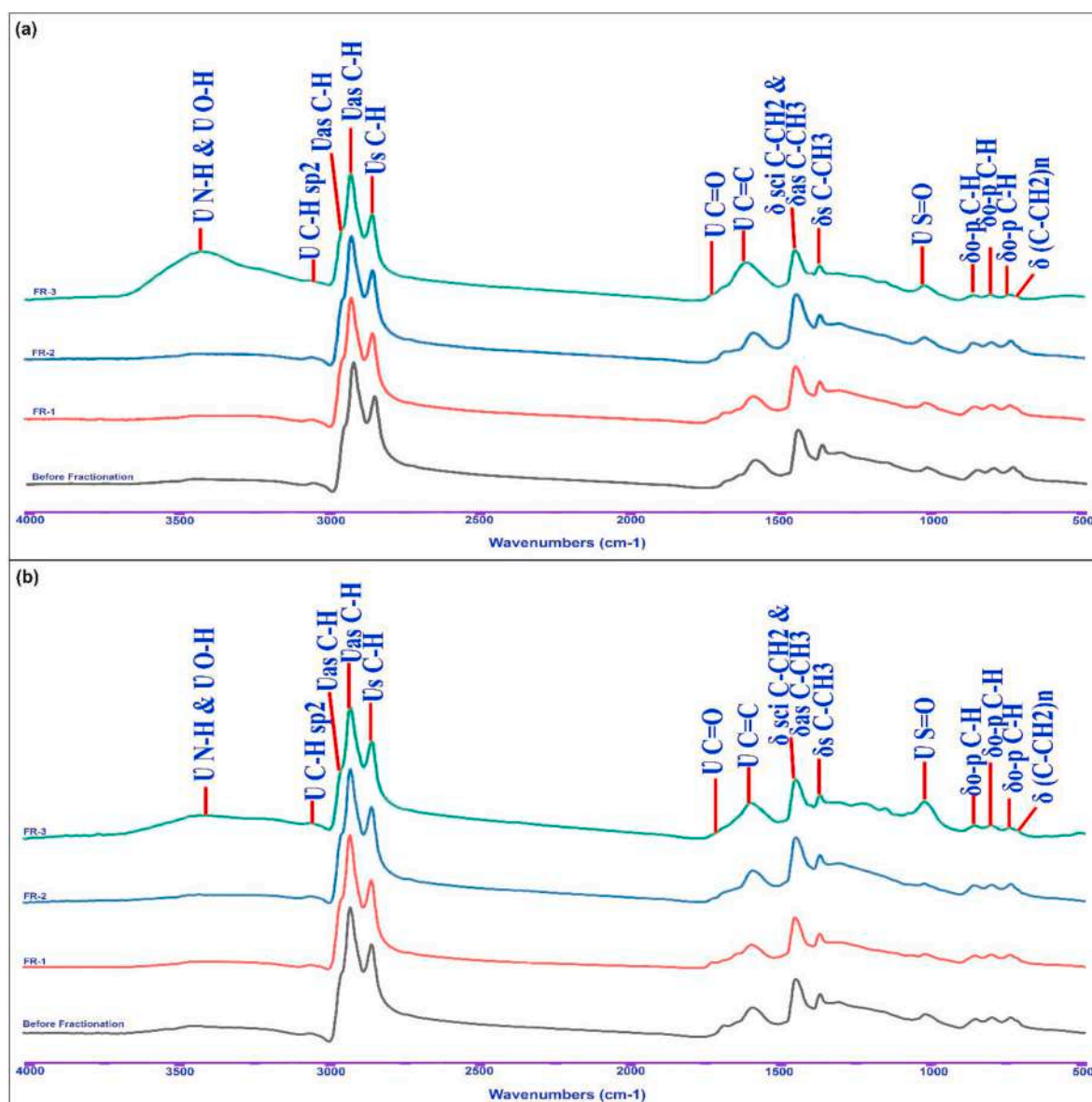


Fig. 8. FTIR spectra of asphaltene before fractionation and its three subfractions for two representative samples. a) RS-A2 sample, b) RS-B3 sample. V: stretching, δ : bending, o-p: out-of-plane, s: symmetric, as: asymmetric, sci: scissors.

information about the chemical structure and comparison of this structural information in different samples are the basic principles of oil fingerprinting by asphaltenes. The detailed structural information about asphaltenes can be achieved by FTIR spectroscopy of asphaltene

subfractions. Asemani et al. (2020); proposed the modified moving window correlation coefficient technique as a valuable method for comparison of structural information of asphaltenes. In this paper, this technique was employed on the asphaltene subfractions for the

comparison of asphaltenes composition across the Rag-e Sefid field. The height of ten characteristic bands was selected from the second derivative spectra of three different subfractions of asphaltenes (Fig. 9). These bands include 3052, 2958, 2923, 2850, 1600, 1460, 1375, 862, 808 and 746 cm^{-1} . The 90 peak ratios (10×9) was calculated for each sub-fraction by dividing the height of each band to other bands. Finally, the 270 (90×3) calculated peak ratios for each sample was used for pairwise comparison of different samples by modified moving window correlation coefficient technique. This procedure provides higher peaks ratios and structural information for a comprehensive comparison of asphaltenes and revealing indistinct differences.

One of the samples (RS-A2) was fractionated six times, and FTIR spectroscopy was performed (6×3) to determine the identification thresholds and the optimum size of the moving window. The correlation coefficient series for two replicates with the largest differences were calculated by different window widths ranges from 5 to 17 points with two intervals. Results showed that the correlation coefficient series calculated with 15 points has the highest values regarding lower and higher window widths. So, the optimum window width for this study is 15 points. The modified moving window correlation coefficient technique, with a window width of 15 points, was performed for pairwise comparison of the RS-A2 sample replicates to determine identification thresholds. The results of these comparisons are summarized in Table 3. The lowest value of the minimum correlation coefficient in all moving windows (MMWR) and the lowest value for an average of correlation coefficients in all moving windows (AMWR) for all replications is 0.9494 and 0.9894, respectively. These thresholds were employed to distinguish the homogeneity and heterogeneity of oil fingerprints in studied samples. The similarity matrix for the studied samples is shown in Fig. 10. This figure summarized the results of the pairwise comparison of different samples for the Asmari and Bangestan reservoirs in the Rag-e Sefid field. Green color signifies that both of the calculated MMWR and AMWR for two specific samples are higher than the thresholds. If both of the calculated MMWR and AMWR for two specific samples were lower than thresholds, the cell would become red color. The similarity matrix reveals that there are heterogeneities related to the RS-A4 and RS-A7 wells with other wells in the Asmari reservoir (Fig. 10a). The Bangestan reservoir shows a completely similar fingerprint across the reservoir (Fig. 10b).

Table 3

Pairwise comparison of the RS-A2 sample replicates with the modified moving window correlation coefficient technique to determine identification thresholds.

Sample	Duplicate Samples	Min correlation coefficient in all moving windows (MMWR)	Max correlation coefficient in all moving windows	Average of correlation coefficients in all moving windows (AMWR)
RS-A2	1&2	0.9562	0.99998	0.9900
	1&3	0.9997	1.00000	0.9999
	1&4	0.9995	1.00000	0.9998
	1&5	0.9539	0.99998	0.9898
	1&6	0.9623	0.99999	0.9925
	2&3	0.9518	0.99998	0.9898
	2&4	0.9619	0.99998	0.9896
	2&5	0.9990	1.00000	0.9997
	2&6	0.9948	1.00000	0.9992
	3&4	0.9991	1.00000	0.9996
	3&5	0.9494	0.99999	0.9894
	3&6	0.9583	1.00000	0.9922
	4&5	0.9597	0.99998	0.9897
	4&6	0.9676	0.99999	0.9922
	5&6	0.9946	1.00000	0.9991
Total	Min of each column	0.9494 ^a	1.0000	0.9894 ^b
	Max of each column	0.9997	1.0000	0.9999
	Average of each column	0.9738	1.0000	0.9942

^a Threshold of the minimum correlation coefficient in all moving windows (MMWR).

^b Threshold of the average of correlation coefficients in all moving windows (AMWR).

4.5. Scenarios for fingerprint heterogeneities and homogeneities in the Asmari and Bangestan reservoirs

The oil fingerprint heterogeneities were distinguished in the Asmari reservoir, but not in the Bangestan reservoir from the Rag-e Sefid field. There are two principal scenarios for interpretation of these heterogeneities and homogeneities in oil fingerprints: a) if there have never been any differences in oil fingerprints at the time of charging? b) if fluids have sufficient time for mixing? These scenarios are vital to answer before any interpretations about the reservoir discontinuity and

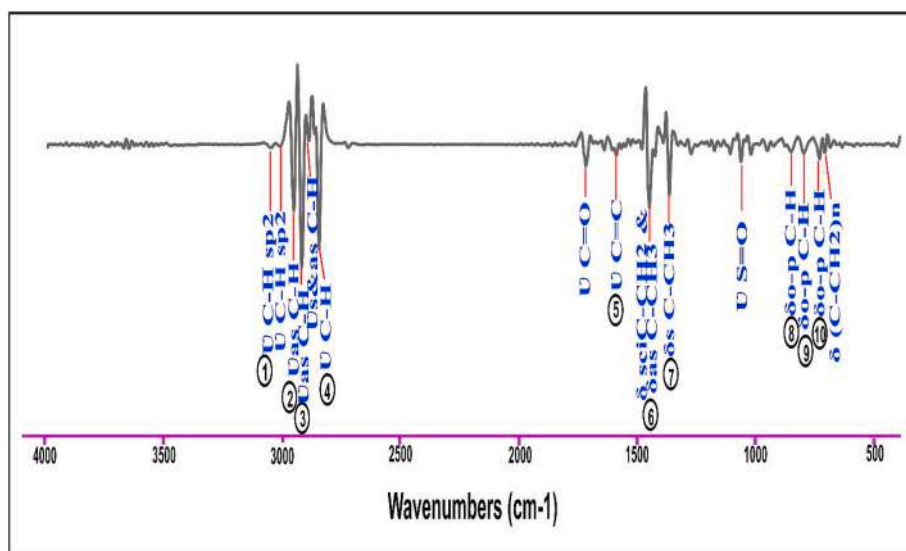


Fig. 9. Representative second derivative spectrum for FR-1 of the RS-A2 sample to show selected bands from each asphaltene subfraction for peak ratios calculation. V: stretching, δ : bending, o-p: out-of-plane, s: symmetric, as: asymmetric, sci: scissors.

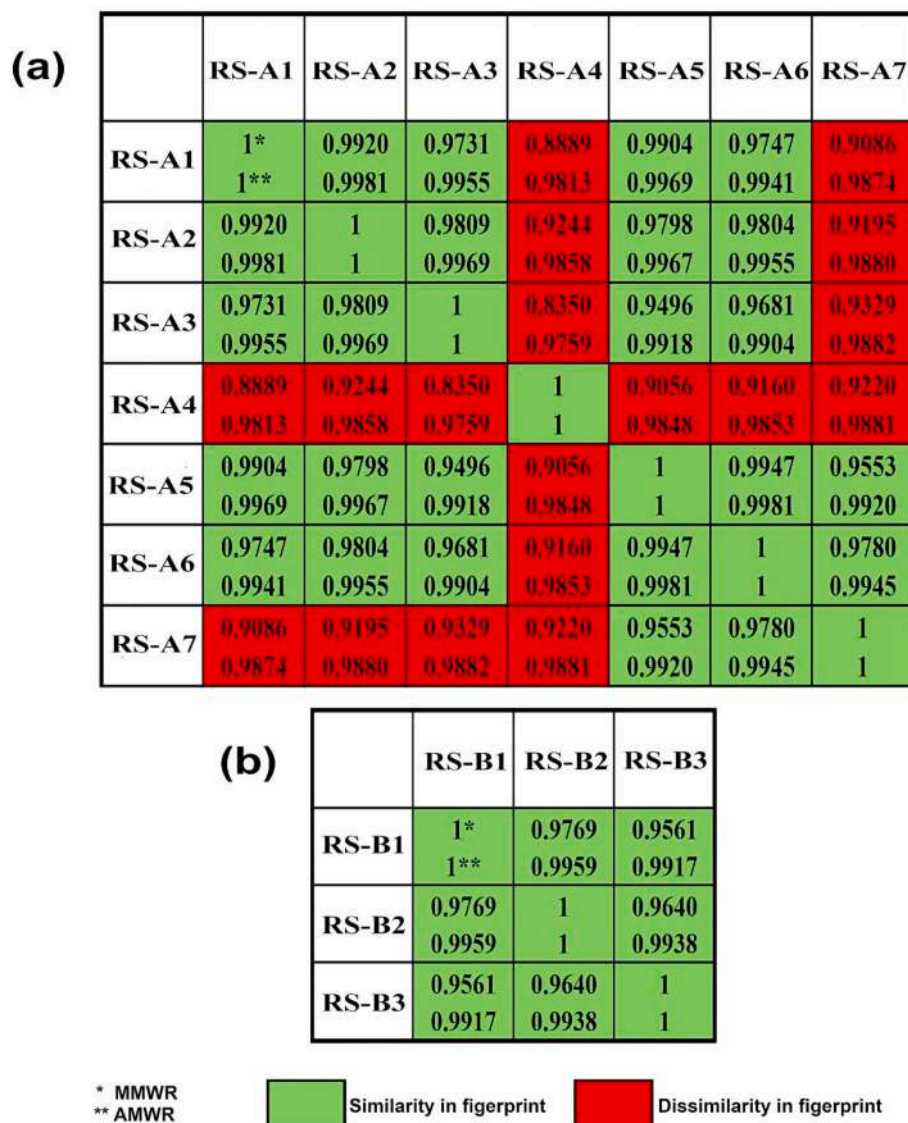


Fig. 10. Fingerprint similarity matrix for the: a) Asmari reservoir and b) Bangestan reservoir; in the Rag-e Sefid field.

continuity in the Asmari and Bangestan reservoirs from the Rag-e Sefid field, respectively. Determination of migration pathways is an efficient way to get information about the charging of the reservoir and initial homogeneity or heterogeneity of crude oil composition. England et al. (1987); proposed a mechanism for fluids movement in the reservoir and subsequent processes until achieving equilibrium. They suggested that some lateral heterogeneities in maturity parameters may be retained still after complete mixing. So, these parameters are a valuable tool for reconstruction of the reservoir filling history. According to their model, the late-filled oils in the reservoir has a higher maturity regarding early-filled oils. The higher maturity oil shows filling point(s) in the reservoir and is close to the source rock kitchen. Wang et al. (2004); suggested using different alkyldibenzothiophenes ratios such as 4-/1-MDBT, 2,4-/1,4- DMDBT, 4,6-/1,4- DMDBT instead of commonly used pyrrolic nitrogen compounds, to trace filling point(s) and migration pathways for the first time. Other maturity parameters have been successfully employed for tracing migration pathways in the literature (Li et al., 2008, 2014; Fang et al., 2016; Chen et al., 2017, 2018). Crude oils in the Rag-e Sefid field belong to the same oil family and sourced from the same source rock/kitchen (unpublished data). Thus, the distribution of maturity parameters controls by the geological chromatographic effect, and these parameters are suitable for the reconstruction

of migration history. In this paper, the migration pathways and filling point(s) were reconstructed by using the maturity parameters of saturate fraction. These parameters are including Ts/(Ts + Tm), C29 sterane $\alpha\beta/(\alpha\alpha+\alpha\beta)$, C29 sterane 20 S/(20 S + 20 R), and Dia/(Dia + Reg) C27 steranes (Table 4). Fig. 11a shows migration pathways based on the isopleth map of the Ts/(Ts + Tm). Crude oils have laterally charged into

Table 4

Maturity parameters for studied samples from the Asmari and Bangestan reservoirs in the Rag-e Sefid field.

Parameters Samples	Ts/(Ts + Tm)	C29 sterane $\alpha\beta/(\alpha\alpha+\alpha\beta)$	C29 sterane 20 S/(20 S + 20 R)	Dia/(Dia + Reg) C27 steranes
RS-A1	0.37	0.54	0.52	0.32
RS-A2	0.34	0.51	0.53	0.28
RS-A3	0.39	0.55	0.54	0.29
RS-A4	0.37	0.53	0.55	0.31
RS-A5	0.35	0.55	0.52	0.30
RS-A6	0.49	0.57	0.49	0.40
RS-A7	0.35	0.54	0.46	0.31
RS-B1	0.45	0.50	0.53	0.29
RS-B2	0.43	0.54	0.55	0.32
RS-B3	0.41	0.51	0.49	0.27

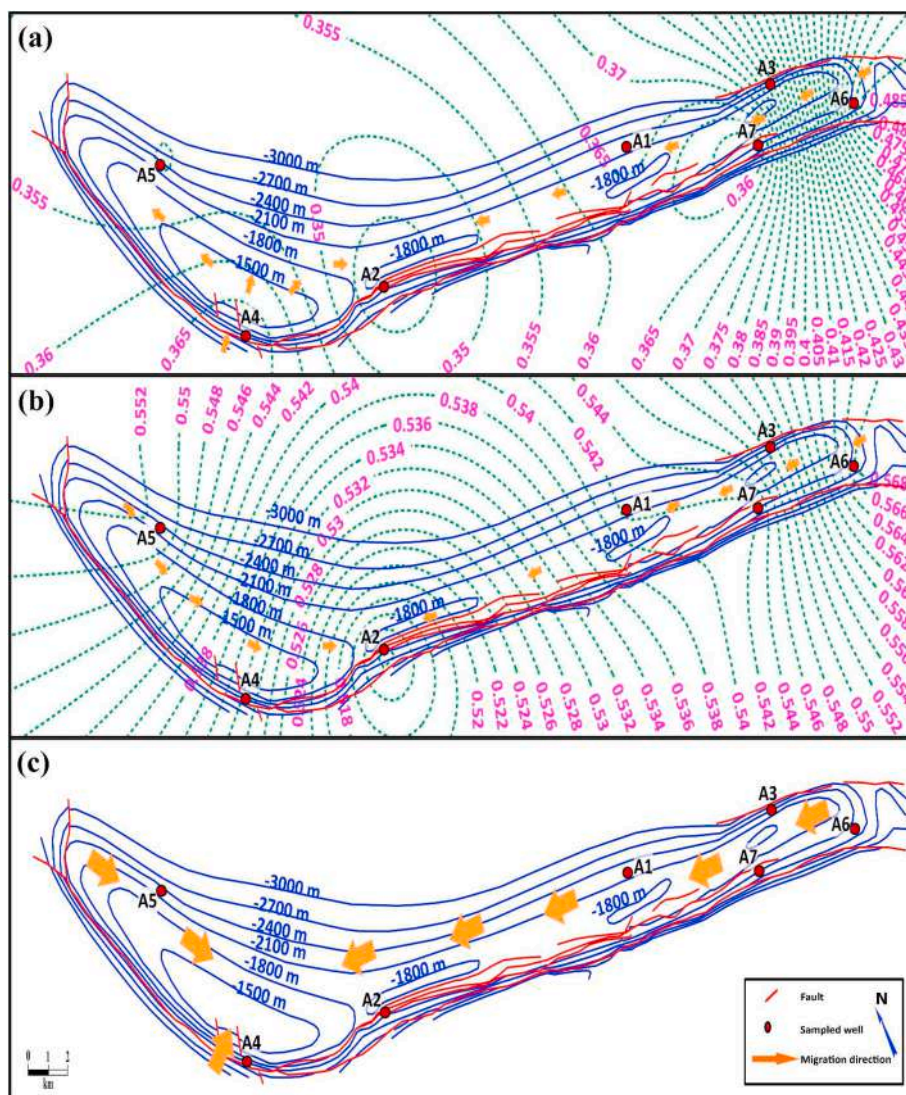


Fig. 11. Migration pathways and filling points in the Asmari reservoir. a) Isoleth map of $Ts/(Ts + Tm)$ parameter, b) isopleth map of C29 sterane $\alpha\beta/(\alpha\alpha\alpha + \alpha\beta\beta)$ parameter, c) general filling directions in the Asmari reservoir.

the Asmari reservoir, and the filling point is located in west near RS-A4 well. Fig. 11b illustrates filling directions based on the isopleth map of the C29 sterane $\alpha\beta/(\alpha\alpha\alpha + \alpha\beta\beta)$ parameter. This figure shows lateral charging, but the filling direction is different from the isopleth map of the $Ts/(Ts + Tm)$. The reservoir has been charged from the two directions are located in NW and E. The contradiction of migration pathways based on the $Ts/(Ts + Tm)$ and C29 sterane $\alpha\beta/(\alpha\alpha\alpha + \alpha\beta\beta)$ maturity parameters is likely due to several charging of reservoir and episodic charge histories. Another possible reason is related to $Ts/(Ts + Tm)$ parameter. Although this parameter is known as maturity parameters, some authors believe that both maturity and organic facies control this parameter. The first reason has more likely because C29 sterane 20 S/(20 S + 20 R) and Dia/(Dia + Reg) C27 steranes show similar migration pathways to $Ts/(Ts + Tm)$ parameter. Thus, general migration pathways in the Asmari reservoir is lateral migration from three directions located in NW, W, and E (Fig. 11c). The drawing of the isopleth map is not suitable for the Bangestan reservoir because three samples were collected from this reservoir. As mentioned above, the filling pathway is in the direction of high maturity samples (late-filled oils) to low maturity samples (early-filled oils). Fig. 12 shows a plot of different maturity parameters for three studied samples in the Bangestan reservoir. At first glance, various maturity parameters have different

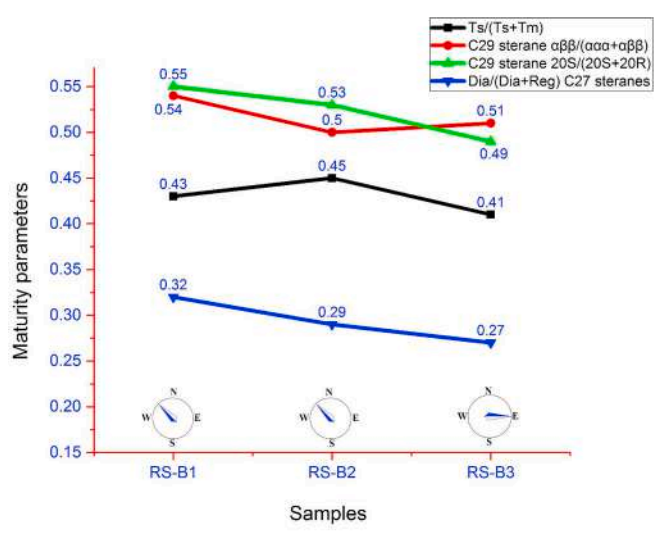


Fig. 12. Trend of different maturity parameters for studied samples in the Bangestan reservoir. The geographical location of samples is shown.

trends. The trend of maturity parameters indirectly shows migration pathways and filling points (the highest maturity samples) in the Bangestan reservoir. Similar to the Asmari reservoir, the differences in the trends displays episodic charge histories and several charging in the Bangestan reservoir. Furthermore, Bordenave and Hegre (2010) showed that most of the oil fields in the Dezful Embayment had been charged from different directions, and the episodic charge histories are characteristics of these fields.

The filling history reconstruction for the Rag-e Sefid field shows that this field was charged from several directions. So, both of the Asmari and Bangestan reservoirs had been compositionally heterogeneous at the time of filling.

Crude oils in the Asmari and Bangestan reservoirs of the Rag-e Sefid field have mainly originated from the Kazhdumi source rock (Bordenave and Burwood, 1990; Kamali et al., 2006; Bordenave and Hegre, 2010). This formation is one of the most known source rock in the world, and several geochemical studies have been performed on the Kazhdumi source rock. The burial history reconstruction and thermal modeling have shown that the initial generation phase of the Kazhdumi source rock in the Dezful Embayment has initiated in 15–13 Ma ago and the expulsion phase has occurred 10–9 Ma ago (Bordenave and Hegre, 2005; Rabbani and Bagheri Tirtashi, 2010; Alizadeh et al., 2012). Since the composition in the Bangestan reservoir has now homogenous, this implies that mixing was complete, and any barriers have not impeding the flow of crude oils across the field. Also, the time required for mixing was sufficient in the Bangestan. The time of filling in the Asmari reservoir may be later than the Bangestan reservoir because of lateral charging. The distance of RS-A4 and RS-A7 wells from near wells is about 5–6 km. The two farthest wells in the Asmari reservoir are RS-A5 and RS-A6 well with about 50 km distance. The time required for mixing in the 5–6 km distance is about one-tenth of the 50 km. Since two farthest wells (RS-A5 and RS-A6) have a similar fingerprint, the RS-A4 and RS-A7 have sufficient time for mixing.

4.6. Reasons for fingerprint heterogeneities in the RS-A4 and RS-A7 wells in the Asmari reservoir

It was proved that crude oils in the Asmari and Bangestan reservoirs were initially heterogeneous and then became homogeneous during geological times. Homogenization has been achieved entirely in the Bangestan reservoir. Except for the RS-A4 and RS-A7 wells, all wells in the Asmari reservoir has similar fingerprint due to complete mixing. The heterogeneity of the RS-A4 and RS-A7 wells implies that these wells have not or little communicated during geological times with surrounding wells. So, barriers or baffles restrict these wells from other wells in the Asmari reservoir, and mixing has not occurred, or little occurred. The restriction of these wells is a sign of segmentation in the Asmari reservoir. Hence, this reservoir constitutes three distinct compartmentalized regions which two of them located around the RS-A7 and RS-A7 wells, and the other comprises a major part of the Asmari reservoir. Several faults surround the RS-A7 well, and these faults are likely the main reason for reservoir compartmentalization in this part of the reservoir (Fig. 11). The heterogeneity reason for the RS-A4 well is complex, and several phenomena have contributed to the restriction of this well. One of the possible scenarios is related to different network fracture around the RS-A4 well. This scenario seems to be more reliable than other scenarios because the trend of faults around this well is NE-SW besides the general trend of faults in the Rag-e Sefid field. This pattern shows different compressional stress field in this part of the reservoir. In the naturally fractured reservoir (NFR) such as the Asmari reservoir, the distribution of network fracture is the main constituent of communication between different wells (Paredes et al., 2015).

5. Conclusions

In this paper, the evaluation of oil fingerprint similarity was

performed through the comprehensive and detailed study of asphaltene. The studied asphaltene samples were fractionated into three subfractions with different solubility characteristics. FTIR spectroscopy illustrates that FR-3 subfraction has higher aromatic compounds, lower aliphatic compounds, and higher polarity regarding two other subfractions. The 90 peak ratios based on ten selected characteristic bands in the second derivative FTIR spectra were calculated for each subfraction, and a total of 270 (90×3) peak ratios were generated for each studied sample. These 270 peak ratios were used as an input data series in the modified moving window correlation coefficient technique to disclose differences between samples. This procedure provides further details about the structural characteristics of asphaltene samples and is helpful in revealing subtle differences between studied samples. Ten samples from the Rag-e Sefid field were studied by the proposed technique. Results indicated that the Asmari reservoir includes fingerprint heterogeneities, but the Bangestan reservoir does not show. The investigation of migration pathways revealed that the Asmari reservoir had been charged laterally from three directions located in NW, W, and E of the field. The Bangestan reservoir has also been charged from different directions. Hence, both reservoirs had been heterogeneous at the time of charging, and homogeneities have been achieved during geological times. Both reservoirs have sufficient times for mixing, but the occurrence of barriers or baffles cause fingerprint heterogeneities and reservoir compartmentalization in the Asmari reservoir. The Asmari reservoir comprises three distinct compartmentalized regions. Two regions are located around the RS-A4 and RS-A7 wells, and the other covers a major part of the reservoir. The discontinuity of the RS-A7 is due to faults, and the RS-A4 is related to different network fracture nearby this well.

Credit author statement

Morteza Asemani: Methodology, performed experiments, Formal analysis, Writing - original draft, Writing - review & editing. **Ahmad Reza Rabbani:** Supervision, Methodology, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petrol.2020.107925>.

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