Study of Crude Oil types in the Mishrif Formation within Noor oil field, Missan Governorate South Iraq

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Abstract
Mishrif crude oil is characterized by low API° gravity, high sulfur content, and carbon isotope ratio of -27.59. The composition of Mishrif crude oil is mainly aromatic. The different relation between different biomarkers indicate that the source of Mishrif crude oil is an anoxic marine carbonate mature kerogen type II, with an age of Upper Jurassic – Lower Cretaceous. Accordingly, the most probable source for this crude oil may be the Sargelu and Sulaiy Formations. The studied crude oil is non- biodegraded evidenced from chromatograms and crude oil composition of ternary diagram.

Keywords: Crude oil, Biomarker, Bulk properties, Steranes, Terpanes, Carbon isotopes.

Introduction
Mishrif Formation is one of the most important formations in Iraq, both economically and geologically. It was deposited during the Cretaceous period in the secondary sedimentary cycle (Cenomanian – early Turonian). It is regarded as the principle carbonate reservoir in central and southern Iraq [1]. It represents a heterogeneous formation originally described as organic detrital limestone, with beds of algal, rudist, and coral- reef limestone, capped by limonitic fresh water limestones [2]. The lower contact of the formation is conformable. Where the Rumaila Formation is the underlying unit .The upper contact of the Mishrif Formation is marked by an unconformity of Khasib Formation [3].

Noor oilfield is located in the south of Iraq within Missan province. It is situated near the Iraq-Iran border, about 350 km southeast of Baghdad and 15 km northeast of Amara city. It is 20 km long and

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6.5 km wide. Figure 1. Noor oilfield was discovered in the late 1973. Where the Noor -1 well was drilled in 1977. Oil was discovered in good quantities in Mishrif and Nhar Umr Formations. There are eight producing wells in this field. Five wells are producing from Mishrif Formation [4].

Methodology

Five oil samples were taken from five oil producing wells from Noor oilfield. The crude oil sample are analyzed using gas chromatography/Mass spectrometry (GC/MS), in Geomark laboratories in Houston Texas to determine crude oil characterization and biomarker, as well as predicting age, environment, and lithology of source rock.

Source environment

The source affinity of Mishrif crude oil is determined by using and comparing different parameters. C31 / C30 hopane is used to distinguish between marine versus lacustrine source rock depositional environments. Oil from marine shale, carbonate, and marl source rocks generally show high C31 22R homohopane/ 30 hopane greater than 0.25 [6]. The C31/C30hopane value for Mishrif oil is ranging between 0.32 to 0.33, which indicate a marine source rock. 30-Norhopane/hopane could be used to distinguish anoxic carbonate or marl source rock from other environments, where high 30-Norhopane/hopane (> 1.0) indicate anoxic carbonate or marl environments [6]. 30-Norhopane/hopane values for Mishrif Formation are higher than 1.0 which refers to anoxic carbonate source.

C35 homohopane index is an indicate of redox potential in marine sediments during digenesis. High values indicate anoxia, but are also affected by thermal maturity. Most oil from marine carbonate
source rocks show high $C_{29}/C_{30}$ hopane (greater than 0.6) [6]. The values of C35 homohopane index for Mishrif crude oil samples are ranging from 0.98 to 1.08, indicates that these oil are generated from high reducing condition marine carbonate source rocks. The $C_{27}-C_{28}-C_{29}$ steranes ternary diagram [6], support the others parameters and referred to marine carbonate source for Mishrif Formation Crude oil as shown in figure-2.

The sulfur content can be used as a source indicator, as oil of marine origin has more than 0.5% sulfur content, the high sulfur content is derived from carbonate source rocks, on the other hand oil derived from clastic source rock are typically low in sulfur [7]. The sulfur content of Mishrif Formation in Noor oilfield characterized by high sulfur content ranging from 4.35% to 4.75%, so indicate marine depositional environment of the source. Acyclic isoprenoids are used as biomarker for the source. The most used parameters in this group are Pristane/Phytane ratios. According to [8], Pr/Ph<1 indicate anoxic source rock deposition particularly when accompanied with high sulfur content, while pr/ph>1 indicate oxic environment. The pr/ph in Mishrif Formation crude oil is ranging from 0.83 to 0.85; this indicates anoxic conditions of the source environment. [9] suggest that pr/ph<1 indicate hypersaline environments. However [6] suggests that high pr/ph values(>3.0) indicate terrigenous organic matter input under oxic conditions, while low values (<0.8) indicate typify anoxic, commonly hypersaline or carbonate environment, the values between 0.8 to 3.0 is influenced by environment conditions and other factors. In this case Mishrif crude oil derived from carbonate anoxic environment source.

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`pr/nC_{17}` values is ranged between 0.20 to 0.22, `ph/nC_{18}` values is ranged between 0.29 to 0.31, when these two ratios are cross plotted [7] as in Figure 3, it will give an indicator of kerogene type which is marine algal kerogene type II for Mishrif oil. All these parameters and biomarkers give a direct or indirect indicator for Mishrif crude oil source environment to be considered as anoxic marine carbonate.

Figure 2- Ternary diagram showing the relative abundances of C27, C28, and C29 regular steranes of Mishrif crude oil
Source Age

Determinations of source age give a good indication of the source of the reservoir Mishrif oil. The average carbon-13 isotope is -27.59 when cross plotted with pr/ph, it will put Mishrif oil in Mesozoic carbonate oil as shown in figure-4. The average stable carbon isotopic ratios for C_{15}+ saturated fractions for Mishrif oil of ~27.56, shows that the crude oil of Noor oilfield are related to Upper Jurassic- Lower Cretaceous as shown in Figure 5. No abundance of Oleanane index in all oil samples which indicates that these oil are from Cretaceous or older rocks. In [6] observed that C_{28}/ C_{29} steranes is less than 0.5 for Lower Paleozoic and older oil, 0.4 to 0.7 for Upper Paleozoic to Lower Jurassic oil, and greater than approximately 0.7 for Upper Jurassic to Miocene oil. The values of C_{28}/C_{29}steranes ratio between (0.59-0.65) for Mishrif crude oil indicate to age of Upper Paleozoic – Lower Jurassic. All oil samples of Mishrif Formation in Noor oilfield are from Upper Jurassic – Lower Cretaceous source rocks. Hence the most probable sources for this crude oil may be Sargelu and Sulaiy Formations.
Figure 4- Relationship between pristane/phytane and Carbon isotopic ratio of oil (%) for crude oil samples of Noor oilfield to predicate source rock environment and age.

Figure 5- Average stable carbon isotopic ratios for C15+ saturated fractions oil versus age for crude oil samples of Noor oilfield.
Source maturation
Ratios of certain n-alkanes can be used to identify changes in the relative amounts of terrigenous versus aquatic hydrocarbons in sediments or rock extracts, one of these ratios is the carbon preference index (CPI) which is the relative abundance of odd and even carbon numbered, this ratio is affected by source input, maturation and biodegradation, but it is mainly used to estimate thermal maturity of petroleum [6]. CPI values significantly above 1.0 indicate low maturity and land plant input, while values below 1.0 indicate low thermal maturity and marine organic input, values of 1.0 or ~1.0 suggest that the oil is thermally mature [6]. The CPI of the Mishrif crude oil is ranging from 0.992 to1.061, so it indicates mature oil, and the slightly shifting from 1.0 may be due other parameters as this ratio is affected by source input. The cross plot between pr/nC17 and ph/nC19 shows high maturity.

Biodegradation
The ternary plot between aromatic HC, saturated HC, and NSO compound figure-6, shows that Mishrif oil is normal oil and non-biodegraded. Also from noticing the distribution of normal alkans in the whole crude chromatograms, it gives an indicator that the oil is non-biodegraded as shown in figure-7.

**Figure 6**- Ternary diagram showing the gross composition: saturated hydrocarbons, aromatic hydrocarbons, and resins plus asphaltenes for crude oil samples of Noor oilfield

**Figure 7**- Whole crude chromatograms for No-1 oil sample
Conclusions
1- The gas chromatograms of the whole crude oil for all samples show same n-alkans distribution, close pr/ph ratios and CPI.
2- The different relation between different biomarkers that is related to environment indicates that Mishrif crude oil is derived from anoxic marine carbonate kerogen type II, where the pr/ph<1, Pr/nC17 is between 0.20 to 0.22, ph/nC18 is 0.29 to 0.31; all value ranges of terpanes and similar compounds includes C31/C30 hopane, 30-Norhopane / hopane, C35 homohopane, and the regular steranes ratios is 36.4% for C27%, 24.5% for C28 %, 39.1% for C29%.
3- Biomarkers related to age indicates that Mishrif source age is Upper Jurassic – Lower Cretaceous. That is obvious from the value of carbon isotope, Oleanane index, and the values of C28/C29 steranes ratio between 0.59 to 0.65.
4- All indicators of maturation show that Mishrif oil is derived from mature Kerogene type II.
5- The ternary plot between aromatic HC, saturated HC, and NSO compound show that Mishrif oil is normal oil and non-biodegraded.
6- All these biomarkers and characterization of crude oil may give an indication that the Mishrif oil is derived from Upper Jurassic – Lower Cretaceous anoxic marine carbonate rocks. Hence the most probable source for this crude oil may be Sargelu and Sulaiy Formations.

References