The Effect of Nickel, Vanadium, Asphaltene, NSO and Sulfur on Crude Oil Quality

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Abstract
The Mishrif reservoir (Cenomanian - Turonian) in the Z, H, B and N oilfields in southern Iraq was investigated to clarify how nickel, vanadium, asphaltene, NSO and sulfur content affect the crude oil quality. The GC-Mass and ICP-MS analyses were used to provide fruitful hydrocarbon results. Classification of crude oil based on API gravity broadly indicates the oil's density and general properties. Typically, lighter crude oils are easier to refine, yield higher percentages of valuable products such as gasoline and diesel, and have a higher market value. Heavier crude oils require more processing and may yield more residual products, such as heavy fuel oil and asphalt. The Mishrif crude oil was classified as a medium sour crude oil containing high sulfur content (%) in Z oilfield (5.22), H oilfield (5.1), and B (5.12); more significant than those in N crude oil, which is classified a sweet based on less than 5% sulfur. The content of asphaltene, nickel, NSO, and vanadium affects the quality of crude oil and the market price because of its negative impact on refining processes, susceptibility to corrosion, and environmental damage later after fuel consumption and burning.

Keywords: Mishrif reservoir; Oilfield; Nickel; Vanadium; Sulfur content; Crude oil quality

1. Introduction

Oil quality can vary depending on factors such as its chemical composition, physical properties, and impurities or contaminants (Petersen, 2000). Oil quality is crucial as it can impact its suitability for refining, transportation, and various end uses (Anitescu and Bruno, 2012). Nickel (Ni) and Vanadium (V) are trace elements that can be found in some oil reservoirs, including the Mishrif reservoir (Awadh et al., 2018; Al-Mimar et al., 2018). However, the concentration of these elements can vary significantly depending on the reservoir's specific geology and depositional environment (Awadh et al., 2019). Nickel and V are often associated with heavy crude oils, and their presence can affect the refining and processing of the oil. They are known to contribute to the formation of metal deposits and can impact the refining process by increasing corrosion and fouling risks (Al-Dahham and Al-Bayati, 2015). To fully evaluate the quality of a specific crude oil, a comprehensive analysis that considers multiple parameters is necessary, such as sulfur content, viscosity, and chemical composition, which play crucial roles in the quality of crude oil (Al-Mimar and Awadh, 2019a; Alkhafaji et al., 2022). The American Petroleum Institute (API) gravity measures oil density relative to water. The sulfur content in oil can
vary, and it is typically expressed as a percentage. The specific composition of hydrocarbons in the oil, including paraffin, aromatics, and other compounds, can impact its quality (Awadh et al., 2021; Erhan and Asadauskas, 2000). The presence of impurities, such as water, sediment, and heavy metals, can also affect the quality. Viscosity refers to the resistance of oil to flow. It is an important property involving pumping, transportation, and processing. Low-viscosity oils are easier to handle, while high-viscosity oils require additional treatment for effective production and transportation (Beloglazov et al., 2021). The pour point is the lowest temperature at which oil can flow and is a critical property, particularly for oils that need to be transported or stored in cold climates. Oils with lower pour points are more desirable as they remain fluid at lower temperatures (Erhan and Asadauskas, 2000). Oil quality can be affected by contaminants such as water, sediment, organic matter, and various impurities.

Additionally, the stability of the oil, including its resistance to oxidation and degradation, is crucial for maintaining its quality over time (Paul et al., 1997; Al-Mimar and Awadh, 2019b). It is important to note that oil quality can vary significantly between oil fields and reservoirs. The specific quality parameters and their acceptable ranges may also depend on regulatory requirements and the intended use of the oil. The study aims to determine the crude oil quality of the Mishrif reservoir in the studied fields and demonstrate how S, Ni, and V affect oil quality.

2. Methods and Data Collection

Nickel and V contents measurements in crude oil are typically performed through laboratory analysis using specialized techniques. Two standard methods are used for measuring them in crude oil. First, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) is widely used for determining V and Ni in crude oil. The method involves vaporizing the oil sample and introducing it into an ICP source. The resulting emissions from V and Ni are then measured to quantify their concentrations in the oil. Second, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is also used for trace element analysis in crude oil, including V and Ni, where the ions generated from the sample are analyzed using a mass spectrometer, providing susceptible and precise results. Techniques (ICP-OES and ICP-MS) offer reliable and accurate measurements of V and Ni in crude oil. The results obtained from these analyses can provide valuable information for evaluating the quality and potential refining challenges associated with crude oil. Necessary detailed geochemical analyses of the produced oil samples were done. The Asphaltene, SNO, S%, and API were measured using the Gas Chromatography-Mass Spectrometry technique (GC-MS) using the GC-Mass analyses in Houston, Texas, Geomark Research, Ltd. Some little data were collected from publications to compare with the research results.

3. Results and Discussion

3.1 Nickel, V, Asphaltene, SNO and Sulfur Content

Nickel and V are typically found in the organic matter of source rocks and can be transferred to crude oil during maturation and migration processes (Ventura et al., 2015). The concentrations of Ni and V in the oil reservoir can influence the quality of the produced crude oil. The sulfur content, nitrogen, sulfur, and oxygen (NSO) compounds, resinous, asphaltene, and organometallic compounds are dominant compounds associated with crude oil. The chemistry of the Mishrif crude oil is presented in Table 1. High sulfur, Ni, and V content with relatively low API gravity values varied from 19.0 to 27.2 were reported in the Mishrif Reservoir by Al-Khafaji et al. (Al-Khafaji et al., 2018). Crude oil is divided into sweet and sour categories based on sulfur content. Sulfur content in sweet crude oil is typically less than 0.5% by weight, whereas it is higher in sour crude oil and frequently exceeds 0.5%. The sulfur content influences the refining process's complexity and how much of an impact it has on the
environment. High-sulfur oil is called sour, while low-sulfur oil is described as sweet. Low-sulfur oil is preferred because it is simpler to refine and emits fewer pollutants when burned. The Mishrif crude oil is sour because it has high sulfur content. Additional classification considers the amount of asphaltenes, Ni, V and certain chemical properties. These are frequently employed for specialized tasks, such as evaluating the suitability of crude oil for particular refining procedures or determining its susceptibility to corrosion or fouling. Crude oils are also classified according to their paraffin content, the proportion of long-chain hydrocarbons in the oil. Paraffinic crudes have a higher concentration of straight-chain hydrocarbons, whereas naphthenic crudes have a higher concentration of cyclic hydrocarbons. The paraffin content of the oil can affect its viscosity, stability, and processing requirements.

Unfortunately, the paraffin results are not available in this research. Fig.1 illustrates sulfur%, SNO%, Asphaltenes%, and API gravity with Ni and V (ppm) in the Mishrif crude oil. The Crude oil quality is inversely proportional to API and directly proportional to S, NOS, Asph, Ni, and V. The highest content of sulfur and NSO were found in the Z oilfield, while the asphalt recorded the highest value in H. The N field was characterized by high Ni and V. The direct relationship between the API and the quality of the crude oil indicates that the Mishrif crude oil is of the medium grade ranging between 23.6 and 29.1.

Table 1. Chemistry of the Mishrif Crude oil in different oilfield

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Oilfield</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>H</td>
</tr>
<tr>
<td>S</td>
<td>%</td>
<td>5.22</td>
<td>5.1</td>
</tr>
<tr>
<td>NSO</td>
<td>%</td>
<td>17.23</td>
<td>14.2</td>
</tr>
<tr>
<td>Asph</td>
<td>%</td>
<td>7.2</td>
<td>17.2</td>
</tr>
<tr>
<td>API</td>
<td>°</td>
<td>26.87</td>
<td>29.21</td>
</tr>
<tr>
<td>Ni</td>
<td>Ppm</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>V</td>
<td>Ppm</td>
<td>---</td>
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</tr>
</tbody>
</table>

*Al-Ameri and Al-Zaidi, 2014

Fig.1. Parameters (%), Ni and V (ppm) affecting the Mishrif Crude oil in different oilfields (Z, H, B, and N).
The NSO is the mixture of high-molecular-weight resins and asphaltenes found in crude oil. Asphaltenes are the less soluble component, and resins are the more soluble component. NSO can change crude oil's density, viscosity, and stability, impacting its quality. The high NSO content can be problematic during refining because it can increase fouling, form coke, and reduce the yield of valuable products.

3.2. API and Crude Oil Quality

The API gravity measures the density of crude oil relative to water (Pabón and de Souza Filho, 2019). The API gravity of crude oil is one of the factors used to assess its quality and suitability for different purposes. It alone does not provide a comprehensive picture of crude oil quality but offers valuable information about the oil's density and can indicate certain characteristics. Higher API gravity indicates lighter, less dense oil, while lower API gravity indicates heavier, more dense oil. Lighter oils are generally easier to produce, transport, and refine. The reservoirs studied in Z, H and B have a high sulfur content and low API gravity (Al Ibrahim et al., 2022). This study pointed out that the sulfur content is more than 5%, and API varies between 25.45 in B and 29.21 in H. The low to medium API and low to medium sulfur content were interpreted by Al-Khafaji (2015) as typically derived from low-oxidation shale and carbonate source rocks. The low API gravity, high S, Ni and V contents, and relatively low API gravity values ranged between 19.0 and 27.2 in the Mishrif within the Z oilfield may indicate an oil generated from early-mature source rocks (Al-Khafaji et al., 2018). It is important to note that crude oil is a complex mixture of hydrocarbons, and additional elements like S, Ni, Cr, and paraffin contents and other chemical properties affect its classification and market value. As a result, API gravity is frequently used with other classification criteria to give users a more thorough understanding of a particular crude oil's quality and suitability for different refining methods. For API gravity value is calculated at 60 degrees Fahrenheit using the equation below:

$$\text{API gravity} = \frac{141.5}{\text{Specific Gravity}} - 131.5$$  \hspace{1cm} (1)

The API gravity of crude oil is a significant factor used to categorize it as it expresses the most important issue for marketing value. The crude oil categories based on the API values can be summarized as follows:

- Light crude oil has an API greater than 31.1
- Medium crude oil has an API between 22.3 and 31.1
- Heavy crude oil has an API of less than 22.3
- Extra Heavy crude oil has an API of less than 10.0
Fig. 2. Crude oil classification based on API in different oilfields (Z, H, B, and N).

Light crude oils are typically easier to refine and yield a higher proportion of valuable products such as gasoline and diesel. Here are some general relationships between API gravity and crude oil quality:

- **Ease of Refining**: Lighter crude oils with higher API gravity are generally considered easier to refine. Lighter oils have a higher proportion of smaller, more desirable hydrocarbon molecules, such as those found in gasoline and diesel. Refineries can process lighter crude more efficiently, requiring less complex refining equipment and yielding higher-value products.

- **Refined Product Yields**: Crude oils with higher API gravity typically yield more valuable refined products like gasoline and distillates. Lighter oils have fewer heavy components, making refining more difficult and producing higher quantities of lower-value residual products such as fuel oil or asphalt.

- **Transportation**: Lighter crude oils with higher API gravity flow more readily and can be shipped or transported through pipelines more effectively. The higher viscosity of heavy oils with lower API gravity may necessitate specialized handling and transportation techniques.

- **Environmental Impact**: Lighter crude oils typically contain less sulfur and emit fewer emissions when burned. Because lighter crudes produce fewer pollutants and require less extensive processing to comply with environmental regulations, this may have a less negative impact on the environment.

- **Processing Costs**: Lighter crude oils might be processed more cheaply and with less energy. Heavy crude oils frequently require more time-consuming and expensive processing methods to produce the desired product yields and quality.

### 3.3. Effect of Ni and V on Crude Oil Quality

The presence of Ni and V in crude oil can impact both the API gravity and crude oil quality. Nickel and V do not directly affect the API gravity of crude oil. They do not significantly alter the density of the oil and, therefore, do not directly impact the API gravity. They can influence the crude oil quality and pose challenges during refining and processing. Here are some effects on oil quality:
Catalyst Deactivation: Nickel and V have the potential to poison catalysts during the refining process, leading to catalyst deactivation. The catalysts used in refining processes may become inactive or degrade, resulting in decreased efficiency and higher costs.

Corrosion and Fouling: Nickel and V have the potential to cause corrosion and fouling in refining equipment. These metals can combine with sulfur and other oil constituents to produce corrosive compounds that can harm machinery and shorten its useful life.

Environmental Issues: When burning crude oil, higher concentrations of Ni and V can cause higher emissions of pollutants like sulfur dioxide (SO₂). Regulations and the environment may be affected by this.

Upgrading Challenges: Crude oils with high levels of Ni and V may need extra processing steps or specialized upgrading methods to eliminate or reduce these metals to meet desired quality standards. It is significant to note that the specific effects of Ni and V on API gravity and oil quality can differ depending on their concentrations and the refining processes used. Additional impurities or contaminants in the crude oil may also have an impact.

3.4. Effect of S on Crude Oil Quality

The presence of S in crude oil can significantly impact the API gravity and oil quality. The API gravity of crude oil is not directly impacted by sulfur content. Crude oil's sulfur content significantly affects its quality, both in terms of the environment and during refinement. These effects on oil quality are listed below:

- **Environmental Impact:** When crude oil is burned, a high sulfur content causes increased sulfur compound emissions, including sulfur dioxide (SO₂). These emissions negatively affect the environment and people's health and add to air pollution. As a result, crude oils with lower sulfur content are frequently preferred from an environmental perspective.

- **Refining Challenges:** As organic sulfur compounds, sulfur can be found in crude oil. These sulfur compounds can create corrosive acids during the refining process, leading to the deactivation of catalysts, equipment corrosion, and a rise in maintenance needs. Additionally, sulfur compounds can have a negative impact on the performance and quality of refined goods like gasoline and diesel by contributing to problems like increased emissions and decreased product stability.

- **Regulatory Compliance:** Regulations and standards are in place in many regions and nations to restrict the amount of sulfur in refined products, particularly in fuels for transportation. To satisfy these regulatory requirements, crude oils with higher sulfur contents might need additional processing steps, like desulfurization.

- **Value and Marketability:** Lower sulfur crude oils are frequently considered more valuable and marketable because they adhere to environmental regulations, present fewer difficulties during the refining process, and produce refined products that burn cleaner and are of higher quality.

It is important to remember that crude oil's sulfur content can differ significantly, ranging from barely any (sweet or low-sulfur crude) to significantly more (sour or high-sulfur crude). API gravity and oil quality may be affected explicitly by sulfur concentration and the specific refining processes used to reduce sulfur content. The suitability of crude oil for processing and refining is typically assessed by considering several parameters, such as sulfur content, API gravity, metal content, and other impurities. Refiners use various methods, such as hydrodesulfurization (HDS), to lower sulfur levels and comply with regulations while enhancing product quality.

4. Conclusions

The concentration of Ni and V in an oil reservoir varies depending on the specific characteristics of the reservoir and the source rock from which the oil is generated. These trace elements are often
associated with heavy crude oils causing technical and environmental problems. Classification of crude oil based on API gravity broadly indicates the oil's density and general properties. Typically, lighter crude oils are easier to refine, yield higher percentages of valuable products such as gasoline and diesel, and have a higher market value. Heavier crude oils require more processing and may yield more residual products, such as heavy fuel oil and asphalt. The main factors (Ni, V, Asphaltene, SNO, API and S) affecting the quality of the oil determined the suitability of Mishrif crude oil for refining and processing. The Mishrif crude oil in Z, H, and B is sourly classified as medium crude oil.

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References


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