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Using special additives for decreasing the asphaltene content of missan crude oil

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ABSTRACT

In crude oil, asphaltene is one of the fractions that may be dissolved in aromatics like benzene or toluene but cannot be dissolved in alkanes like n-heptane, n-pentane, or petroleum ether (a mixture of alkane compounds). A typical difficulty in oil recovery and refinery processes is asphaltene precipitation, which happens when the oil stream's pressure, composition, or temperature change. So, the stability of asphaltene in crude oil needs to be looked at to find out how likely it is to form asphaltene so that it can be stopped and high treatment costs can be reduced. In the present study, saturate, aromatic, resin and asphaltene (SARA) analysis of Missan heavy crude oil from the (Omar River Field) was performed. Three additives were used to show their effect on asphaltene at different concentrations and temperatures. The additives included nanoparticles (nano ferric oxide red, nano silica oxide, and a mixture of nano silica and ferric oxide red) and the polymer fiberglass. The concentrations of the additives of the nanoparticles were (200 ppm, 3533 ppm, 8667 ppm), (1667 ppm, 6667 ppm, 10000 ppm, and 16667 ppm) and (24000 ppm, 40000 ppm, and 48000 ppm) of nano-silica, ferric oxide red, and a mixture of nano silica and ferric oxide red, respectively, while fiberglasses, 3733 ppm, 7066 ppm, 10400 ppm, and 13733 ppm) and measured at temperatures (5, 25, and 45°C) The best result I got was when it was used. 4.249% from origin to 6.375% after treating the percentage of asphaltene with 48000 ppm of ferric oxide red and nano-silica.

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1. Introduction

Among crude oil components, asphaltene is the most polydisperse, heavy, and polarizable one. According to Boussignault, in 1837, it was first characterized as the substance that precipitates out of petroleum once petroleum ether is added [1], n-Pentane and n-Heptane, as well as petroleum ether, can precipitate these crude oil fractions, but they

are still soluble in aromatic solvents like toluene and benzene, [2]. Aggregates with 2–6 molecules each are also considered asphaltene. Molecules and small colloidal particles make up the aggregates. A precipitation-induced deposit is caused by the accumulation of aggregates into clusters, which are then added together as shown in Fig. 1 (Hoepfner, 2013). Asphaltene precipitation can be modeled in a variety of ways. Asphaltenes create micelles' centers and

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resins that surround and disperse the oil in the colloidal model, which is based on this idea.

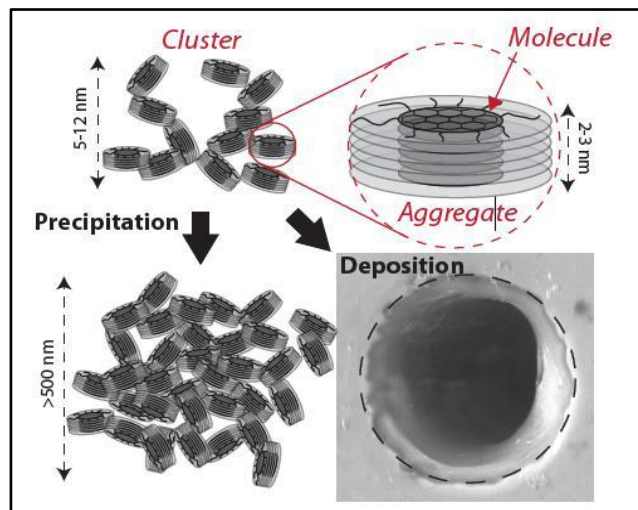


Figure 1. Asphaltene formation, precipitation, and deposition process, (Hoepfner, 2013)

When the resins are separated from the colloid, aggregation and phase separation will occur, resulting in precipitation, [3]. For dispersion to be stable, a delicate balance must be struck between attracting and repulsive forces: when particles meet, if the attraction forces are stronger, they agglomerate and the dispersion may become unstable. As long as the system is dominated by repulsive forces, it will remain scattered, [4]. In order to reestablish thermodynamic equilibrium, resin molecules tend to desorb from asphaltene by adding standard alkane liquids such as n-pentane or n-heptane or by adding petroleum ether to crude oil. Agglomeration is induced by peptizing resin desorption, and with sufficient alkane titration (n-alkane titration), the asphaltene molecules aggregate sufficiently to overcome the Brownian forces of suspension, leading to precipitation of the asphaltene molecules, [5]. Many researchers, including those listed below, have investigated the stability of asphaltene:

Analyzed SARA analysis by liquid chromatography and applied the CII (Oil with higher than 0.9 CII is unstable, and oil with lower than 0.7 CII is stable) and the Oliensis Spot Test (Oil with 9 or fewer spot test numbers has been known to be unstable) as an index of asphaltene stability. These three, Based on HPLC technology, RI and SARA fractions were correlated and depended on the difference between RI of the oil and alkane mixture at the asphaltene start point to reveal the crude oil's stability. Asphaltene precipitation was found to occur when the oil's RI was less than 0.05 and greater than 0.06; however, this was not the case for the oil's RI that was greater than 0.06. [6].

To better understand the stability of asphaltene, SARA and RI were compared to Fan et al's correlation. It was discovered that the oil from Alaska was unstable, [7].

Sulaimon et al. [8], showed that Fan [9] the correlation given is reliable in estimating the refractive index of crude oil with a maximum absolute deviation of 2.0%.

Rogel, [10] showed that the composition of crude oil as well as the chemical and structural characterization of asphaltenes, resins, and their relation to asphaltene stability were examined. They discovered

connections between crude oil flocculation onsets and asphaltene structural characteristics

2. Experimental work

2.1 Materials

To conduct SARA analysis, the Heavy crude oil sample is used. The experimental tests were conducted with Heavy crude oil samples from Missan fields depicted in Table 1.

Table 1. Heavy crude oil sample

Test	Crude oil from Omar River Field
Viscosity (c.p) at °5	124.8
Viscosity (c.p) at °15	84.6
Viscosity (c.p) at °25	54.3
Viscosity (c.p) at °35	39.6
Viscosity (c.p) at °45	32.7
API at 60 °F	23.13
Density 60 °F (gm/cm ³)	0.915
Asphalting content wt.%	4.928

2.2 Additives nanoparticles

The Additives include (nanoparticles and polymer) were nano silica oxide, nano ferric oxide red, and polymer fibereglass *silica*:

Experimental Nano silica was obtained from the following sources: (US research nanomaterials, Inc). The Nanoparticles element analysis as shown in Tables 2 and Table 3 were of this analysis was provided by the manufacturing company. Figure 2 shows the Nanosilica used in experimental work.

Table 2. Nanoparticles of Silicon Oxide with Specific Characteristics

property	value
purity	99.5(%)
Average particles size distribution	50 (nm)
Surface Area	180_600 (m ² /g)
color	white
Bulk density	<0.1 (g/cm ³)
Ture density	2.4 (g/cm ³)

Table 3. Examination of nanoparticles of silicon oxide

SiO ₂	Ti	Ca	Na	Fe
99.5%	120 ppm	70ppm	30ppm	20ppm

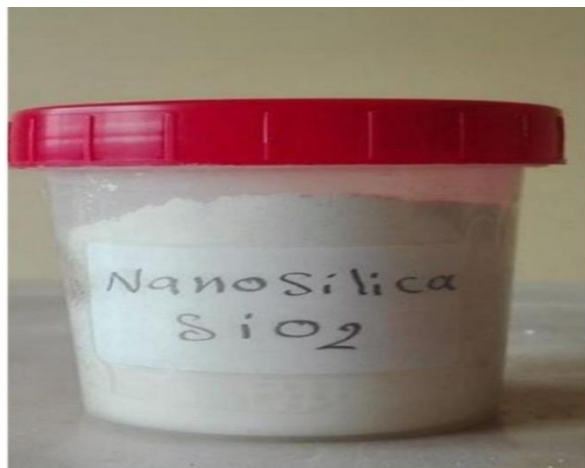


Figure 2. Nanosilica is used in experimental work.



Figure 3. Nanoferric oxide is used in experimental work.

Ferric oxide:

Researchers have been fascinated by the unusually strong magnetic properties of iron oxide (Fe_2O_3) for a long time. Magnetic storage, catalysis, sensors, and ultra-sensitive magnetic resonance imaging are among its most common applications (MRI). Researchers are looking into using it instead of the more harmful copper oxychloride for therapeutic purposes because iron oxide is nontoxic. Many of the most important Fe_2O_3 nanoparticle properties are listed in the following Table 4. Figure 3 depicts the nano ferric oxide that was used in the experimentation.

Table 4: The properties of iron III oxide nanopowders

Chemical Formula	Fe_2O_3
Molecular weight	159.69g/mole
Appearance (color)	Red-brown to brown
Appearance (form)	powder
Average particle size	<50nm
Surface Area	(40_60)m ² /g

Table 5: Properties of Fiberglass.

Type of Glass	E
Filament Diameter , μm	13
Chop Length, mm	3, 6, 12
Sizing code	562A

Fiberglass:

The Fiberglass element analysis, as shown in Table 5, was provided by the manufacturing company. Figure (4) shows the Fiberglass used in experimental work.



Figure 4. Fiberglass used in experimental work.

2.3 Instruments and Devices

1. The hydrometer for measuring the density and then calculating the API gravity of the crude oil sample.
2. The BROOKFIELD DV Viscometer (HB) for measuring the dynamic viscosity (μ) crude oil sample dynamic viscosity (μ)em to extract the asphaltene fraction of the crude oil.

2.4 Asphaltene content wt. %

According to the French Institute of Petroleum, SARA fractionation involves the addition of excess liquid hydrocarbons like n-pentane, n-heptane, or petroleum ether to the crude oil with a 40-ml-to-1-g oil ratio, which separates asphaltenes from the crude oil (IP 143).

In this study, half the amount was used (20 ml of n-heptane added to 0.5 gm of crude oil), and leaving the mixture for one day by shaking three times during the day to homogenize the mixture and also covering the beaker well with aluminum foil to prevent volatilization of the solvent (n-heptane) [11].



Figure 5. Show Calculating the percentage of asphaltene.



Figure 8. Shows the membrane after filtration.



Figure 6. Separation of asphaltenes from the crude oil.



Figure 9. Shows the membrane after filtration.



Figure 7. Shows the deposition of asphalt at the end of the tube.

2.5 Filtration process

Leave the mixture of topped crude oil and n-heptane for one day. Then, the mixture was filtrated through a filter membrane of 0.45 μm and left it until

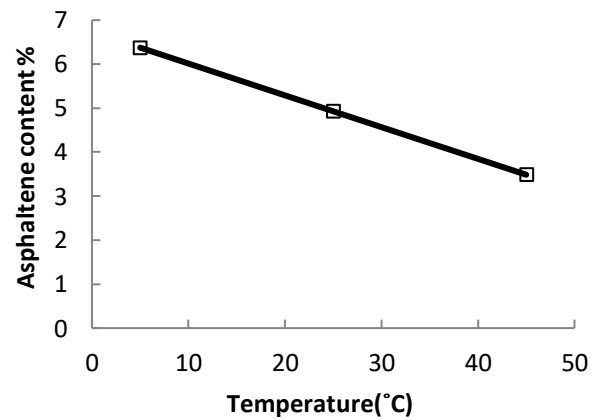


Figure 10. Asphaltene content at different temperatures

complete the filtration process was. This step was shown in Figure 8 and Figure 9. The weight percent of the precipitated asphaltene on the filter was calculated by Eq1. [12].

$$AR\% = (C_0 - C_E) / C_0 \tag{1.1}$$

3. Results and discussions

3.1 Effect of additives on asphaltene content

The impact of various additive types, concentrations, and temperatures on asphaltene content has been studied. A variety of solvents and temperatures are used to treat the feedstock. Reduced asphaltene content and the dispersion of asphaltene agglomerates by polar solvents were reduced by these solvents. Asphaltene content before addition at different temperatures is shown in Figure 10.

3.2 Effect of fiberglass on asphaltene content

The effect of fiberglass on the asphaltene content was studied at temperatures (5°C, 25°C, and 45°C) and concentrations (3733, 7066, 10400, 13733).

effect of fiberglass on the percentage of asphaltene is very high compared to nano-silica, where the highest percentage of reduction reached 2.593% when the concentration increased from 3733 ppm to 13733 ppm at a temperature of 45°C. and it is considered the second material in terms of its efficiency in reducing asphalt as shown in figure 11.

3.3 Effect of nanoparticles on asphaltene content

The effect of nanoparticles (nano silica and ferric oxide red) on the asphaltene content was studied at temperatures (5 C, 25 C, 45 C) and concentrations (200, 3533, 6867), (1667, 6667, 10000, 16667), respectively. Nanoparticles reduced asphaltene content by 2.194% and 2.427% weight percent, The content of asphaltene is obtained using 16667 ppm and 6867 ppm of each ferric oxide red and nano-silica at temperature 45°C, As shown in figure 12 and 13 respectively.

Where these concentrations were studied in three cases, In the first case when the concentration was 24000 ppm, which is equivalent to 6 g, 2 g of nano silica was mixed with 4 g of iron oxide, and the asphaltene content readings were recorded at this concentration, and at 40000 ppm, which is equivalent to 10 g, 4 g of nano silica was mixed with 6 g of iron oxide, and asphaltene content readings were also recorded. As for the last concentration, 48000 ppm, which is equivalent to 4 g of nano-silica with 8 g of iron oxide red, we notice when using the mixture at these concentrations, the asphaltene content by a very large percentage, as shown in the figures below.

The results were represented using the Minitab program and using a method as shown in the following figures:

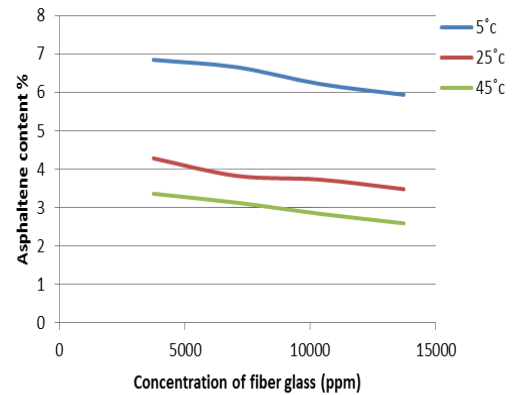


Figure 11. Effect fiber glass concentration on Asphaltene content

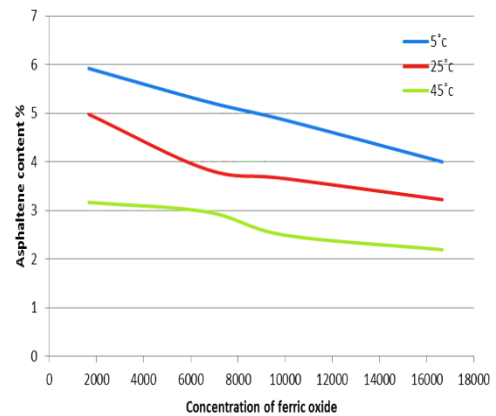


Figure 12. Effect ferric oxide concentration on Asphaltene content

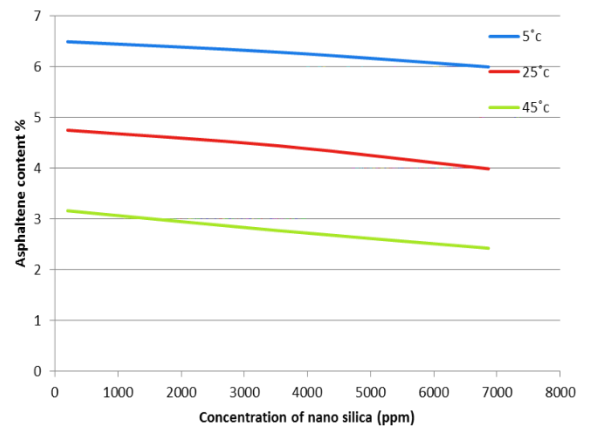


Figure 13. Effect nano silica concentration on Asphaltene content

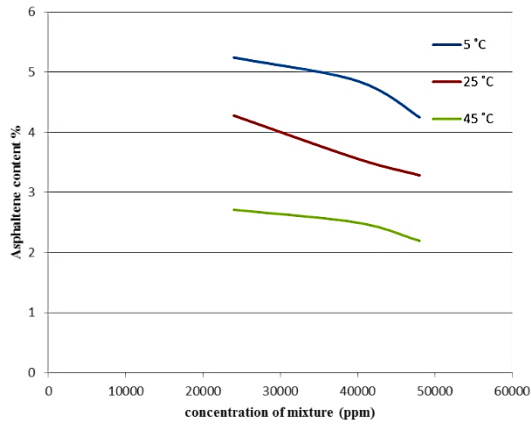


Figure 14. effect mixture of nanoparticles concentration on Asphaltene content (case 1).

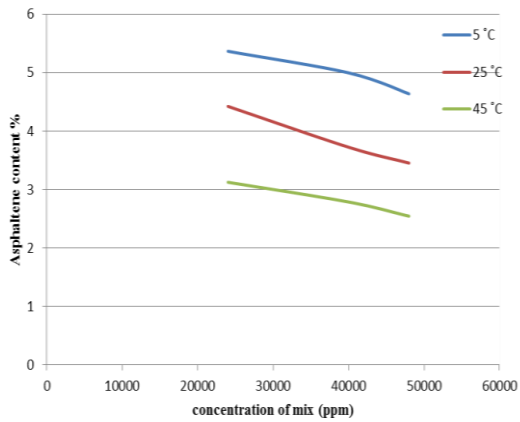


Figure 15. effect mixture of nanoparticles concentration on Asphaltene content (case 2).

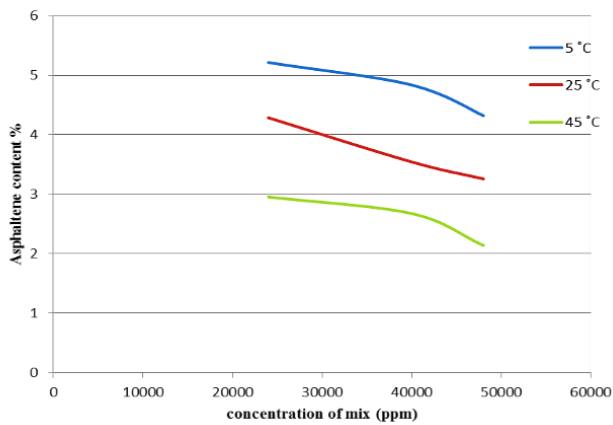


Figure 16. effect mixture of nanoparticles concentration on Asphaltene content (case 3).

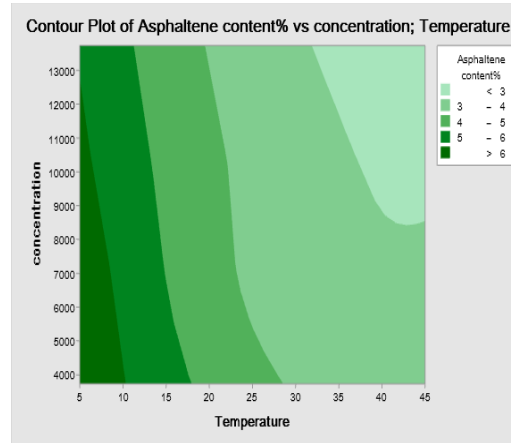


Figure 17. Contour plot of Asphaltene content after treatment by adding fiberglass

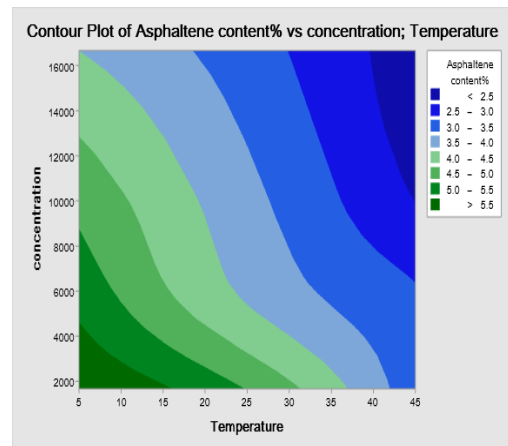


Figure 18. Contour plot Asphaltene content after treatment by adding nano ferric oxide

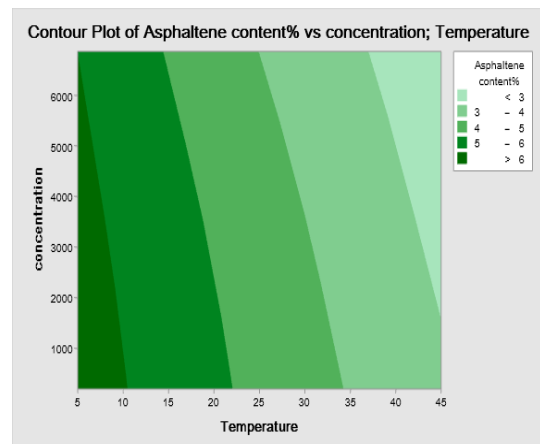


Figure 19. Contour plot Asphaltene content after treatment by adding nano-silica

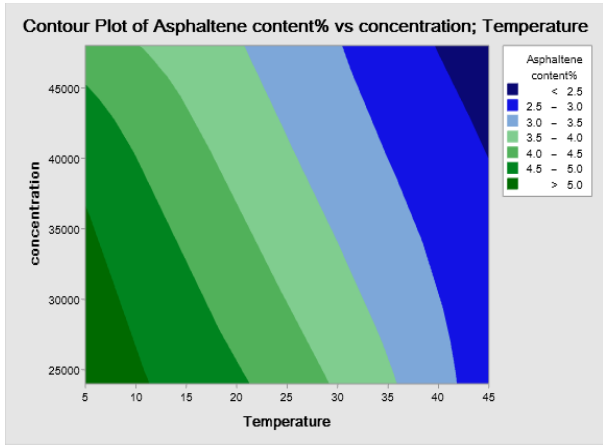
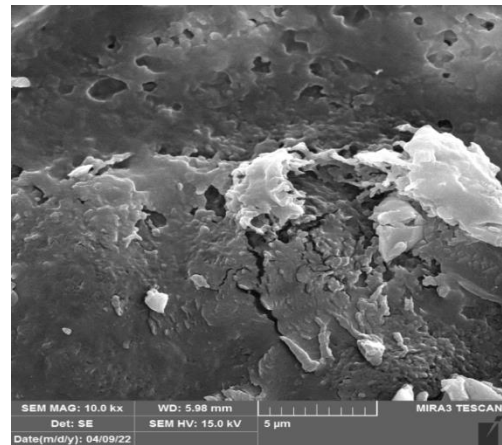


Figure 20. Contour plot Asphaltene content after treatment by adding a mixture of nanoparticles (case 1)



(a) 5μm zooming

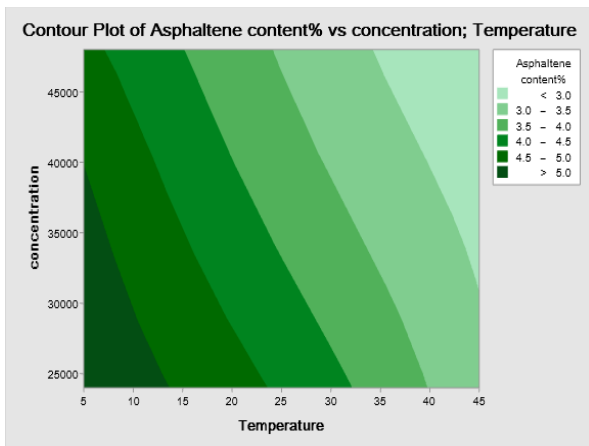
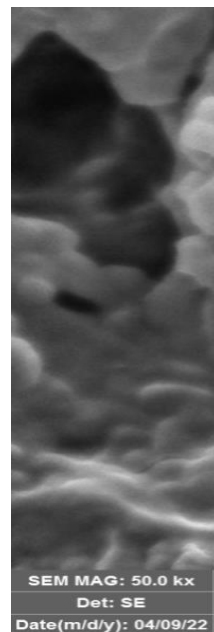
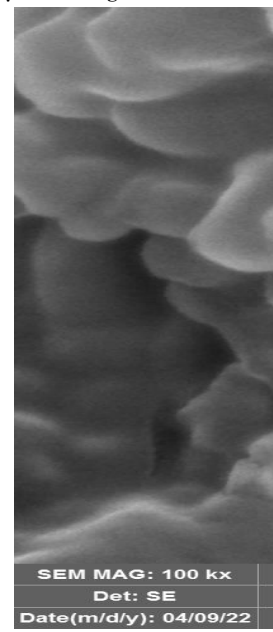


Figure 21. Contour plot Asphaltene content after treatment by adding a mixture of nanoparticles (case 2).



(b) 1μm zooming



(c) 500nm zooming

Figure 23. Asphaltene content at 5°C SEM micrographs analysis showing grain microstructures

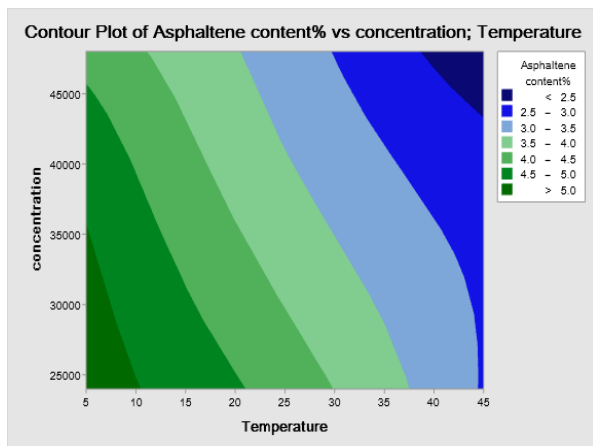


Figure 22. Contour plot Asphaltene content after treatment by adding a mixture of nanoparticles (case 3).

3.4 Scanning electron microscope (SEM) analysis

SEM analysis provides a micrograph of high resolution for flaws, contamination, and surface fractures. SEM analysis is an important investigative tool, where including the use of a focused beam of electrons to produce high magnification and complex images of a sample’s surface topography. As a result, the high magnification and high-resolution micrograph of SEM backed the particle size and shape determination [13].

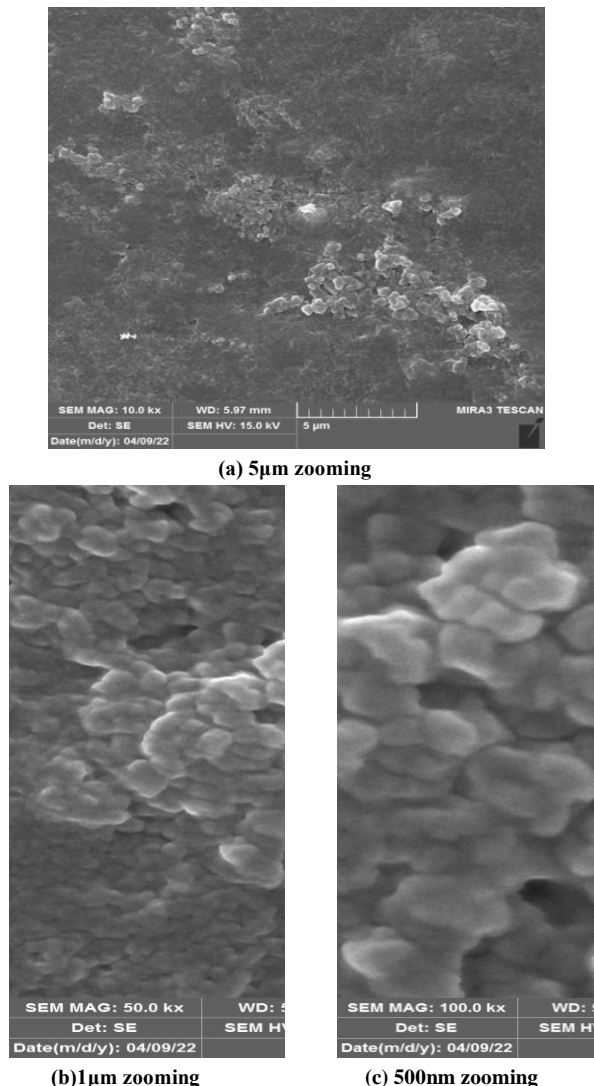


Figure 24. Asphaltene content at 25°C SEM micrographs analysis showing grain microstructures

SEM analysis was used to characterize (asphaltene content at temperatures 5 °C and 25 °C) nanoparticles in the form of powder. By obtaining structural and micrograph images as shown in Figures 23 and 24 (a, b, and c), where micrographs of the particle shape, size, and surface metrology at zooming degrees about 5µm, 1µm, and 500nm respectively. As SEM analysis is used to determine particles size, the result unparticle Where is due to is this technology, s not enough to create statistical particle number results because it is measured only tens particle hundreds from a large number of particles [3].

4. Conclusions

1. The asphaltene weight percent in the crude oil was determined using the conventional solubility asphaltene detection test using heptane. It was found that the crude oil contained a relatively high concentration of asphaltene which is an indication of the oil being heavy oil since

asphaltene is one of the highest molecular weight components of the oil.

2. The highest percentage obtained in reducing the percentage of asphalt when it was used Mixture of Nanoparticles reduced asphaltene content by 2.195 weight percent, The content of asphaltene is obtained using 48000 ppm using ferric oxide re and nano silica.
3. The nano-silica weight percent in the crude oil was determined using the conventional solubility asphaltene detection test using heptane. It was found that the crude oil contained a relatively high concentration of asphaltene which is an indication of the oil being heavy oil since asphaltene is one of the highest molecular weight components of the oil.

REFERENCE

- [1] Ali, A. A., Al-JaReferenceS. a and Ali, A. A. (2019) "Asphaltene Stability of Some Iraqi Dead Crude oils", *Journal of Engineering*, 25(3), pp. 53–67. doi: 10.31026/j.eng.2019.03.05.
- [2] Chamkalani, A. (2012). Correlations between SARA fractions, density, and RI to investigate the stability of asphaltene. *International Scholarly Research Notices*, 2012.
- [3] Devendiran, D. K., & Amirtham, V. A. (2016). A review on preparation, characterization, properties, and applications of nanofluids, ds. *Renewable and Sustainable Energy Reviews*, 60, 21-40.
- [4] Fakher, S., Imqam, A., & Wanas, E. (2018). Investigating the viscosity reduction of ultra-heavy crude oil using hydrocarbon soluble low molecular weight compounds to improve oil production and transportation. SPE International Heavy Oil Conference and Exhibition.
- [5] Fan, T., Wang, J., & Buckley, J. S. (2002). Evaluating crude oils by SARA analysis. SPE/DOE improved oil recovery symposium.
- [6] Hthe oepfner, M. P. (2013). *Investigations into Asphaltene Deposition, Stability, and Structure*
- [7] Panuganti, S. (2013). *Asphaltene behavior in crude oil systems* Rice University].
- [8] Powers, D. P. (2014). Charact erization and asphaltene precipitation modeling of native and reacted crude oils.
- [9] Rogel, E., Leon, O., Espidel, Y., & Gonzalez, Y. (2001). Asphaltene stability in crude oils. *SPE Production & Facilities*, 16(02), 84-88.
- [10] Sulaimon, A., & Govindasamy, K. (2015). A new correlation for predicting a new asphaltene deposition. SPE/IATMI Asia Pacific Oil & Gas Conference and Exhibition.
- [11] Verdier, S. (2005). Experimental study and modeling of asphaltene modeling caused by gas injection. *Graduate Schools Yearbook 2005*, 179.
- [12] Yen, A., Yin, Y. R., & Asomaning, S. (2001). Evaluating asphaltene inhibitors: laboratory tests and field studies. SPE International Symposium on Oilfield Chemistry.
- [13] Zendejboudi, S., Shafiei, A., Bahadori, A., James, L. A., Elkamel, A., & Lohi, A. (2014). Asphaltene precipitation and deposition in oil reservoirs—Technical aspects, experimental and hybrid neural network predictive tools. *Chemical Engineering Research and Design*, 92(5), 857-875.