

Novel Environmentally Friendly Nanomaterials for Drag Reduction of the Emulsified Acid System

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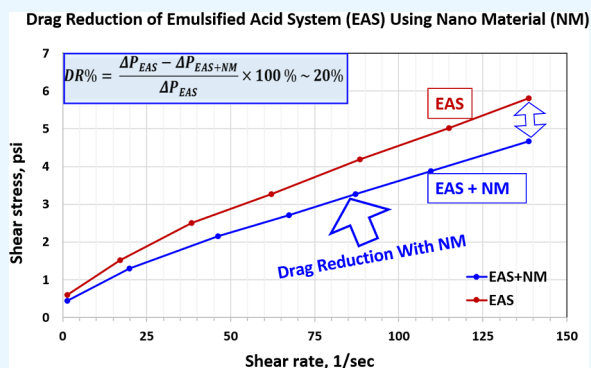
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ABSTRACT: Matrix acidizing is a technique that is widely used in the petroleum industry to remove scales and create channels in the rock. Removal of scales and creation of channels (wormhole) enhance productivity. Conventional acidizing fluids, such as hydrochloric acid (HCl) for carbonate and a mixture of hydrofluoric acid (HF) and HCl acid, are used for the matrix acidizing process. However, these fluids have some drawbacks, including strong acid strength, corrosion at high temperatures, and quick reactions with scale and particles. Emulsified acid systems (EASs) are used to address these drawbacks. EASs can create deeper and narrower wormholes by reducing the reaction rate of the acid due to the external oil phase. However, EASs have a much higher viscosity compared to conventional acidizing fluids. The high viscosity of EASs leads to a high drag that restricts pumping rates and consumes energy. This study aims to utilize environmentally friendly and widely available nanomaterials as drag-reducing agents (DRAs) of the EAS. The nanomaterials used in this study are carbon nanodots (CNDs). CNDs have unique properties and are used in diverse applications in different industries. The size of these CNDs is usually smaller than 10 nm. CNDs are characterized by their biocompatibility and chemical stability. This study investigates the use of CNDs as DRAs for EAS. Several experiments have been conducted to investigate the CNDs as a DRA for the EAS. The developed EAS was initially tested for conductivity and drop-test analysis to ensure the formation of an inverted emulsion. Thereafter, the thermal stability for the range of temperatures and the rheological properties of the EAS were evaluated to meet the criteria of field operation. Then flow experiments with EASs were conducted before and after adding the CNDs to investigate the efficacy of drag reduction of EASs. The results revealed that CNDs can be used as viscosity reducers for the EAS, where adding the CNDs to the EAS reduces the viscosity at two different HCl concentrations (15 and 20%). It reduces the viscosity of the EAS in the presence of corrosion inhibitors as well as other additives to the EAS, showing its compatibility with the field formulation. The drag reduction was observed at the range of temperatures investigated in the study. The conductivity, stability, and rheology experiments for the sample taken after the flow experiment are consistent, ensuring CNDs work as a DRA. The developed EAS with CNDs is robust in terms of field mixing procedures and thermally stable. The CNDs can be used as a DRA with EAS, which will reduce drag in pipes, increasing pumping rates and saving energy.



INTRODUCTION

Well stimulation is a process used to enhance and increase the productivity of oil and gas wells. It can be done by two different methods: matrix acidizing and hydraulic fracturing. Matrix acidizing is a process that uses acids to dissolve rock formations and create channels for oil and gas to flow through, and it is performed at a pressure lower than the fracture pressure of the reservoir. Hydraulic fracturing is a process that uses high-pressure fluids to create cracks in rock formations. These cracks allow oil and gas to flow more easily into the wellbore. Hydraulic fracturing is done at a pressure exceeding the reservoir's formation pressure.

HCl acid systems are used in the petroleum industry to improve the productivity of oil and gas wells by removing formation damage in carbonate reservoirs. However, there are challenges in delivering acid deep into the reservoir while minimizing rock face dissolution. Conventional acidizing fluids have limitations, such as strong acid strength, quick reaction

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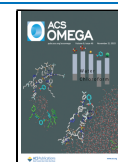


Table 1. Summary of the Development of EAS

authors	findings
De (1933) ²¹	Pioneering researchers first utilized acid-in-oil emulsion in well stimulation
Al-Anazi et al., (1998) ²²	Field application of emulsified acid in a carbonate reservoir
Hoefner et al., (1987) ²³	Role of acid diffusion in matrix acidizing
Mohamed et al., (1999) ²⁴	Acid stimulation of water injectors and saltwater disposal wells in a carbonate reservoir
Nasr-El-Din et al., (2000) ⁸	Stimulation of water-disposal wells using acid-in-diesel emulsions
Sayed and Nasr-El-Din (2011) ²⁵	Effect of emulsifier concentration and acid volume fraction on the elastic properties of emulsified acids
Pandya et al., (2012) ²⁶	Introduced a unique EAS formulation that combines three intensifiers for the stimulation of extremely high-temperature 163 °C (325 °F) carbonate reservoirs
Sabhapondit et al., (2012) ²⁷	Optimization of a 26% HCl-based EAS was performed for stimulating high-temperature carbonate reservoirs. Effects of two different corrosion inhibitors (CI) at various temperatures and time durations
Madyanova et al., (2012) ²⁸	Conducted a case study on matrix acidizing stimulation Sungai Kenawang (SKN) gas-condensate field. A combination of emulsified and viscoelastic surfactants led to significant stimulation throughout the targeted interval, resulting in a notably higher productivity index
Cairns et al., (2016) ²⁹	A systematic approach, exploring key parameters such as pore pressure, flow rate, acid-rock contact time, and fluid treatment composition. The results demonstrated the remarkable efficacy of the developed stabilized system, showcasing a 3-fold increase in core permeability improvement compared to conventional acid systems
Sidaoui and Sultan (2016) ⁵	Investigated thermal stability and rheology of the EAS. Varying the emulsifier concentration from 0.5 to 1.5 vol % did not significantly affect the stability of the EAS. The small droplet size of the emulsion contributed to its higher viscosity
Sidaoui et al. (2017 and 2016) ^{30,31}	Utilization of waste oil as the external phase of a 70:30 acid/oil ratio with 15% HCl in an EAS. The developed HCl-waste oil EAS demonstrated shear-thinning behavior, exhibiting favorable rheological properties
Sidaoui et al., (2018) ³²	Investigate adding iron control and chelating agents to EAS stability and its reaction with dolomite. The stable EAS was achieved without iron control and with the inclusion of a lower concentration of the chelating agents
Sayed et al., (2018) ³³	Introduced a novel low-viscosity retarded acid system, resulting in reduced drag. A 0.28 pore volume (PV) to achieve a breakthrough in a 12 in. core sample pumping
Aldakkan et al., (2018) ³⁴	Proposed acid system with a combination of a potent acid and a highly soluble organic compound. Achieved a remarkable 4-fold reduction in core weight loss due to the dissolution, compared to 15 weight percent HCl acid. The proposed acid system exhibited minimal corrosion effects and a delayed acid reaction with calcite
Ahmed et al., (2018) ³⁵	Replace surfactants with specific nanoparticles. The developed EAS with waste oil showed superiority at high injection rates. EAS stability is affected by acid-to-oil ratio, types of acid and oil, and chemical additives
Yousufi et al., (2019) ³⁶	Developed Jatropa oil-based EAS, which exhibited superior thermal stability, a more environmental alternative for acidizing
Sokhanvarian et al., (2019) ³⁷	Formulated a stable EAS for HPHT at 149 °C (300 °F) with a nonaromatic nonionic surfactant. Nonionic surfactants provide stable EAS and exhibit superior performance with low acid pore volume breakthrough (PVBT) at 149 °C (300 °F)
Jafarpour et al., (2019) ³⁸	Designed a novel multibatched acid system designed for heterogeneous carbonate reservoirs. The developed EAS is effective in stimulating complex carbonate reservoirs
Sayed et al., (2021) ³⁹	A low-viscosity, single-phase acid system for acid fracturing. The system consists of a pre-engineered blend of an alkyl sulfonic acid and a strong mineral acid and exhibited comparable performance to the 15 wt % HCl-EAS in terms of diffusion and reduced drag
Al-Sabea et al., (2022) ⁴⁰	Developed a low-viscosity, polymer-free acid-retarded system and a successful case study in the west Kuwait field. The acid system consists of a robust mineral acid, HCl, with a nondamaging retarding agent. Exhibited great promise compared to the EAS.
Zakaria et al., (2022) ⁴¹	Developed a polymer-free delayed HCl acid system with low viscosity. The HCl acid system required a reduced acid PVBT compared to standard HCl acid at all injection rates. The low-viscosity delayed HCl acid system enhanced acid penetration
AL-Dogail et al., (2023) ⁶	Investigated different types of organoclays (OC) as emulsifiers to develop Pickering EASs. Selected types of OCs can be used as emulsifiers to develop Pickering EAS with good thermal stability and low viscosity at high shear rates

with scale and fines, and corrosion of the tubing, casing, and downhole equipment at high temperatures.

EAS is one of the solutions to the limitations of conventional acid systems. The EAS is typically made of acid and oil (usually diesel), with diesel acting as a diffusion barrier between the acid in the EAS and the rock.^{1,2} The EAS is a type of water-in-oil (W/O) emulsion in which the acid phase is encapsulated by the diesel phase using an emulsifier.^{3–6} The EAS is a non-Newtonian shear-thinning fluid, meaning that its viscosity changes with the shear rate. EAS can be represented by the power-law model, in which the viscosity reduces as the shear increases.^{7,8}

Many researchers have studied the use of the EAS to stimulate carbonate reservoirs.^{6,9–17} However, EAS faces certain constraints in its application, including diminished stability at elevated temperatures, high viscosity that constrains the rate of pumping, the potential for causing formation damage, and the complexity of achieving uniform mixing on a

field-scale level. Additionally, the current EAS methodology restricts injection or pumping at low flow rates and limits the depth of acid penetration within the matrix and fractured systems. Mitigating this challenge remains a formidable task, with the current design primarily focused on delivering acid as rapidly and deeply as frictional forces permit. Consequently, a reduction in pipeline friction would facilitate higher pumping rates, enhance the efficiency of EAS treatments, and result in energy savings.

Carbon nanodots (CNDs) are a type of carbon nanoparticle with a size of fewer than 10 nm. They are composed of carbon atoms arranged in a disordered structure, and they are characterized by unique properties such as bright fluorescence, high electrical conductivity, and chemical stability. CNDs are considered a relatively new class of nanomaterials, and research on their properties and applications is ongoing in different industries. However, they have already shown great potential in

many fields and are likely to become increasingly important in the future.

This study aims to utilize environmentally friendly and chemically stable CNDs as drag-reducing agents (DRA) for the EAS. More specifically, this study investigates CNDs as viscosity reducers and DRAs for the EAS prepared to stimulate the carbonate reservoirs. The procedures of EAS preparation, thermal stability, rheological properties, and flow experiments have been presented in detail for the EAS before and after the addition of the CNDs.

Acidizing is a technique required in the oil and gas industry to stimulate wells and enhance the productivity of oil and gas wells. Conventional acidizing fluids that are used in the petroleum industry for well-stimulation of carbonate reservoirs are hydrochloric acid (HCl) or a combination of hydrofluoric acid (HF) and hydrochloric acid (HCl) acids. However, these liquids possess high acid strength, leading to fast reactions with scales and fines near the wellbore. Moreover, at high temperatures, they pose challenges for tubing, casing, gravel pack screens, and downhole pumps. In certain cases, using HCl acid above 93 °C (200 °F) is not recommended due to its potential to damage the formation.¹⁸

As a solution to these issues, alternative acid systems have been developed to operate at high temperatures without causing damage to the downhole equipment. Examples of such acid systems include a mixture of tricarboxylic acids, amino carboxylic acids, and dicarboxylic acids.¹⁸ By utilizing these innovative acid systems, the oil and gas industry can overcome some of the limitations of conventional acidizing fluids. However, these alternative acids are still limited to specific carbonate reservoir conditions, and these acids have complex formulations, compatibility issues, and corrosion problems that are still being less corrosive compared to the conventional acidizing fluids. A need for another acidizing liquid is required to overcome these limitations. The EAS has become widely used in the oil and gas industry as a solution to the limitations of conventional acid systems.

In the case of EASs, the continuous phase or external phase is diesel, which surrounds the HCl acid droplets, resulting in an acid-in-diesel emulsion, which is a type of W/O emulsion. In the oil and gas industry, a concentrated HCl acid (typically ranging from 15 to 28%) is commonly used.^{19,20} The EAS is extensively used in fracturing and acidizing operations within carbonate reservoirs, aiming to improve formation permeability and increase oil and gas production. The presence of the oil's external (outer) phase in the EAS leads to reduced or retarded reaction rates, resulting in the formation of deeper and narrower wormholes. This characteristic allows for more effective well stimulation and enhanced reservoir performance.

An emulsifier is required for forming an EAS by combining the aqueous acid phase with the diesel phase and enhancing its stability at high temperatures. To achieve this stability, very small particles, such as colloidal clay particles and/or nanoparticles, are incorporated into the EAS.¹⁸ The stabilized EAS comprises at least one oil, an aqueous acid solution containing one or more acids, at least one emulsifier, and acid-insoluble nanoparticles with an average particle size of 1000 nanometers or smaller. Emulsified acids, where the acids are emulsified with oil (typically diesel), offer several advantages in oil and gas operations. They help minimize the corrosion of pumping and downhole equipment and reduce the rate of reactions with carbonate reservoirs, particularly at high temperatures. This enables the active acid to penetrate deeply

into the formation, enhancing stimulation and overall reservoir performance. The preparation methods of emulsified acids significantly affect their physical properties. Therefore, analyzing emulsified acids based on their droplet size distribution allows for a comprehensive understanding of their chemical composition and provides a specific and reproducible description of their properties.²⁰ This approach is crucial for achieving consistent and predictable results in emulsified acid treatments, ensuring their effective application in various oilfield scenarios.

Over the years, acid stimulation techniques in the oil and gas industry have seen significant advancements and innovations. Table 1 summarizes the studies of developments in the EAS.

These studies represent just a portion of the ongoing research aimed at improving acid stimulation techniques for enhanced efficiency and environmental considerations in the oil and gas industry. It demonstrates a wide range of advancements and innovations in acid stimulation techniques for the oil and gas industry, with a focus on improving efficiency, environmental sustainability, and performance in various reservoir conditions.

In summary, it can be seen that several studies have explored the formulation of an EAS to overcome the limitation of conventional acid fluid for stimulation. The EAS involves acids dispersed in an external oil phase, offering benefits such as reduced corrosion and controlled reaction rates. The EAS formulations required for well stimulation are stable in high-temperature carbonate reservoirs. Emulsion stability varies based on factors like pH, temperature, and droplet size distribution and needs to be addressed while developing the EAS.

Various researchers have explored novel EAS formulations for well stimulation in high-temperature carbonate reservoirs. These include macro- and microemulsions, low-viscosity systems, and formulations with alternative components such as nanoparticles or waste oil. Factors influencing EAS stability and performance include the emulsifier concentration, acid-to-oil ratio, and temperature. Researchers have proposed diverse solutions to optimize the EAS for deeper penetration, reduced core loss, and more efficient stimulation, especially in challenging reservoir conditions. Such innovations could enhance oil and gas production while addressing environmental and operational concerns.

However, limited studies on the drag reduction of the EAS are available in the literature. Some studies have addressed the drag reduction of the emulsion but not the emulsified acid system (EAS). It should be noted that the drag reduction of the emulsion cannot be translated to the drag reduction of the EAS. The nature of the EAS needs to be considered while addressing the drag reduction of the EAS. It includes the compatibility of the material with acid and ensuring the formation of an emulsion that is thermally stable and possesses the characteristics of an emulsion that is ready to use, considering operating and field conditions. This requires rigorous experiments and a laboratory setup for testing the EAS and its drag reduction.

This study provides a unique solution to reduce the drag of the EAS with a material that is compatible with acid and matches the field and operating conditions. The EAS is prepared in large volume (100 times larger in volume compared to rheometer testing) and tested with a flow loop capable of handling high-viscosity EASs, temperature, flow rates, and the acidic nature of the fluid. The results are

encouraging as they reduce the drag of EAS meeting field preparation and operation. The indigenous material is compatible with the acid system and is ready to be tested in the field.

METHODOLOGY

To achieve the objectives of this study, the EAS was prepared using a commercial formula; this is considered the base case, and then the necessary tests were conducted. The acid phase-to-diesel phase ratio for all prepared EASs was 70:30. The prepared base case EAS was investigated by different tests, and these tests include conductivity, pH, drop-test, rheology, and thermal stability tests. Many acid emulsions were prepared, where diesel was mixed with the emulsifier (surfactant) and the aqueous phase, which includes acid that was added while the mixing process was on. After that, CNDs were added to the base case EAS, and again, the necessary tests (conductivity, pH test, drop-test, rheology, and thermal stability) were performed. After that, and based on the rheology results, the best CND was selected for the flow and drag reduction experiment.

In the flow experiment, first the base case EAS was prepared in large amounts (30–40 L), and the flow rates of the EAS flowing through the flow loop were recorded against the pressure drop readings. Then, CND was added to the base case EAS, and the solution was pumped again through the drag reduction unit to see the effect of CND on the drag; again, the flow rates were recorded against the pressure drop readings. Samples of the EAS base case and the EAS base case with CNDs were taken from the flow loop after flow experiments, and the conductivity, pH test, drop test, and thermal stability at ambient temperature were investigated again. The methodology and procedures are presented in this section in detail.

Materials and Equipment. Materials utilized in this study include lab-grade hydrochloric acid (HCl) with a 37 wt % concentration, industrial-grade hydrochloric acid (HCl) with a 26 wt % concentration, deionized (DI) water, commercial diesel from a gas station, the EAS formula including one CI, one inhibitor intensifier, two iron controls, and one emulsifier (surfactant). Equipment required to perform this study includes a high-shear mixer/homogenizer (IKA T 25 digital ULTRA-TURRAX homogenizer with an acid-resistant titanium shaft and a speed range of 3000–25000 rpm), a magnetic stirrer, a rheometer (Anton-Paar MCR-702 rheometer), a see-through oven, test tubes, conductivity and pH meters (Thermo Scientific-Orion StarA215 pH/Conductivity Benchtop Multi-parameter Meter), a high-speed mixer/homogenizer (TAIS-TESMART JRJ-300SH-220 V high-speed homogenizer lab disperser emulsifier capacity 40 L 200–11,000 rpm 510 W digital display blender), and a drag reduction unit (flow loop).

EAS Preparation. The EAS was prepared based on the commercial formula with the 70:30 acid-to-diesel ratio, where 70% is the ratio of the aqueous phase or acid phase (dispersed phase), while 30% is the ratio of the diesel phase, representing the continuous or external phase. The concentrations of HCl in the EAS were 15 and 20%. First, the emulsifier (surfactant) was added with a specific concentration according to the formula to the diesel, and they were mixed using the homogenizer at 6000 rpm for 2–3 min, while the 37% lab-grade HCl acid was titrated with DI water in a separate beaker to the required concentrations of 15 and 20% using a magnetic stirrer for 1–2 min. Then, the CI was added at a specific concentration to the aqueous phase during mixing by the

magnetic stirrer; similarly, the inhibitor intensifier and iron controls were added to the aqueous phase at a specific concentration during mixing by the magnetic stirrer. After that, the aqueous phase (acid phase) was added to the oil phase (diesel phase) progressively while being mixed at 6000 rpm.

Conductivity/pH and Drop Test. The electrical conductivity was measured for the prepared EAS to ensure that the prepared EAS is a W/O emulsion (the external phase is diesel) if the electrical conductivity reading is close to zero, thus suggesting that it is a W/O emulsion. Also, a drop-test was performed to confirm that it is a W/O emulsion. The drop test was performed by putting 1 mL of the prepared EAS in 20 mL of water and 20 mL of diesel in two separate beakers. The emulsion is an O/W emulsion if the dispersion takes place in a beaker containing water, while the emulsion is a W/O emulsion if it takes place in a beaker containing diesel. To confirm the acidity of the prepared EAS, the pH was measured.

Thermal Stability. Thermal stability is essential to guaranteeing that the prepared EAS reaches formation in its original form. The thermal stability was explored at three different temperatures (25, 80, and 120 °C) using high-temperature graduated glass tubes and a see-through oven. By visually observing the EAS separation every 10 min for the first 30 min, then every hour after the first 30 min for the next 2–3 h, and finally after 24 h, thermal stability was carried out simply and easily. The EAS separation volume was plotted against the time, and photographs of the graduated glass tubes were taken before and after heating in the oven.

Rheology. The rheological properties were assessed using the Anton Paar rheometer MCR-702, which has an acid-resistant bob/cup setup. 15.9 mL of the prepared EAS is needed for the setup being used. All rheology measurements were performed at 65 °C. Every test took 2 h, while the shear rate ranged from 0.1 to 1000 1/s.

Flow Experiment. The EAS was prepared based on the commercial formula as the base case, with large amounts (30–40 L) for one flow experiment. After that, the prepared EAS was pumped through the flow loop (drag reduction unit), and this flow loop consisted of a gear pump with a variable frequency drive (VFD), a tank, a pressure transducer, and a flow meter. The flow loop is equipped with a heating system to heat and control the desired temperature of the fluid throughout the experiment. Once a set of experiments at various flow rates at a fixed temperature is completed, the temperature is changed, and another set of experiments is generated covering the range of temperatures investigated in this study. Once the fluid attains the desired temperature, the flow rate of the system is adjusted using the VFD, and the reading of pressure drop against flow rates is recorded. This procedure is followed, covering the range of flow rates starting from low to high and then high to low to check the hysteresis. Similarly, the flow experiment was again repeated after adding CND. The flow experiments were done for two different HCl concentrations of the EAS (15 and 20%) before and after adding CNDs.

RESULTS AND DISCUSSION

EAS Preparation. The EAS was prepared with a 70:30 acid-to-diesel ratio based on the commercial formula as the base case, where the HCl acid concentration in the EAS was 15%. The emulsifier (surfactant) was added to the diesel, and they mixed using the homogenizer at 6000 rpm for 2–3 min, while the 37% lab-grade HCl acid was titrated with DI water in

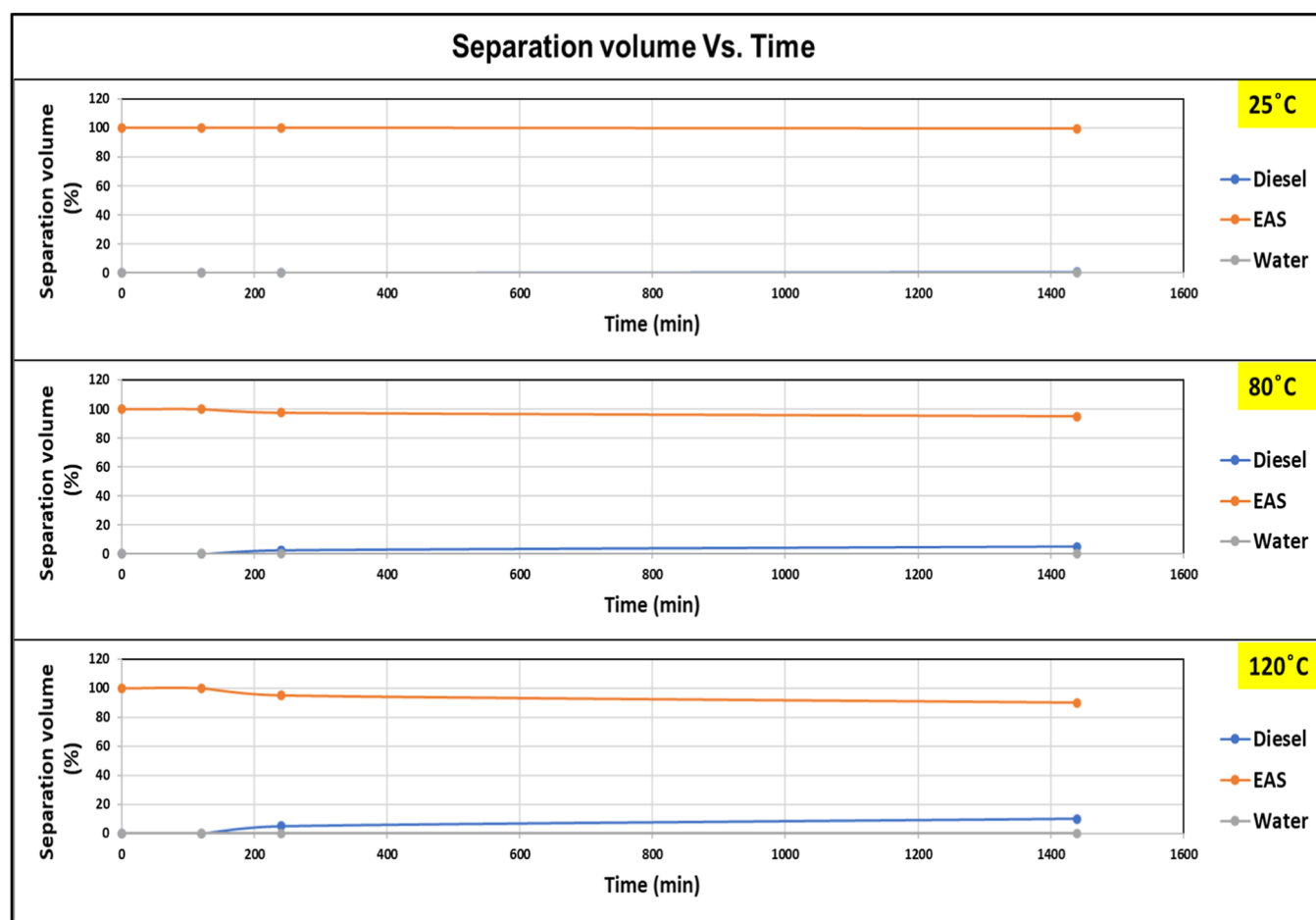


Figure 1. Separation volume of the EAS at three different temperatures (EAS + 0.4% NM as an example).

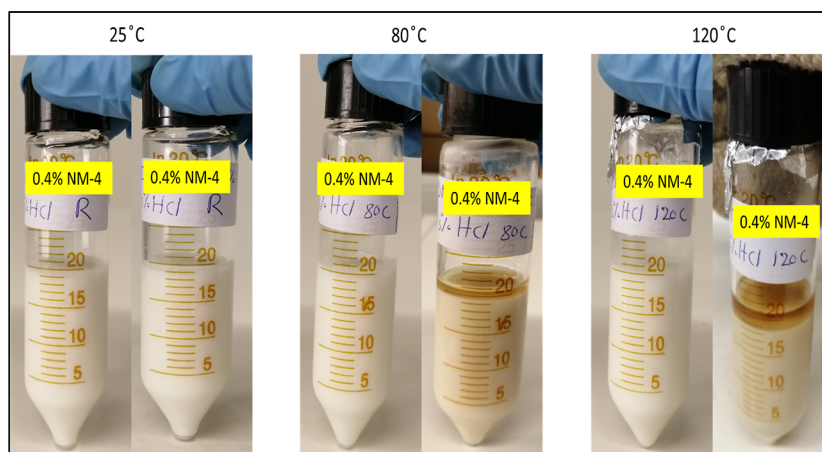


Figure 2. Photo of the EAS at three different temperatures before and after oven (EAS + 0.4% NM as an example).

a separate beaker to the required concentration of 15% using a magnetic stirrer for 1–2 min. Then, the CI was added at a specific concentration according to the formula to the aqueous phase during mixing by the magnetic stirrer; similarly, the inhibitor intensifier and iron controls were added to the aqueous phase during mixing by the magnetic stirrer with a specific concentration according to the formula. After that, the aqueous phase (acid phase) was added to the oil phase (diesel phase) progressively while being mixed at 6000 rpm. Then, the prepared EAS was tested for thermal stability at different

temperatures (25, 80, and 120 °C). The same preparation procedures were followed for the EAS with a 20% HCl acid concentration.

Conductivity/pH, and Drop-Test. The conductivity/pH meter was used to measure the electrical conductivity and the acidity of the prepared EAS. In addition, a drop-test was carried out to ensure that the EAS is a W/O emulsion. The electrical conductivity results show values close to zero, which means the external phase is diesel and the prepared EAS is a W/O emulsion. According to pH measurements, the EAS is an

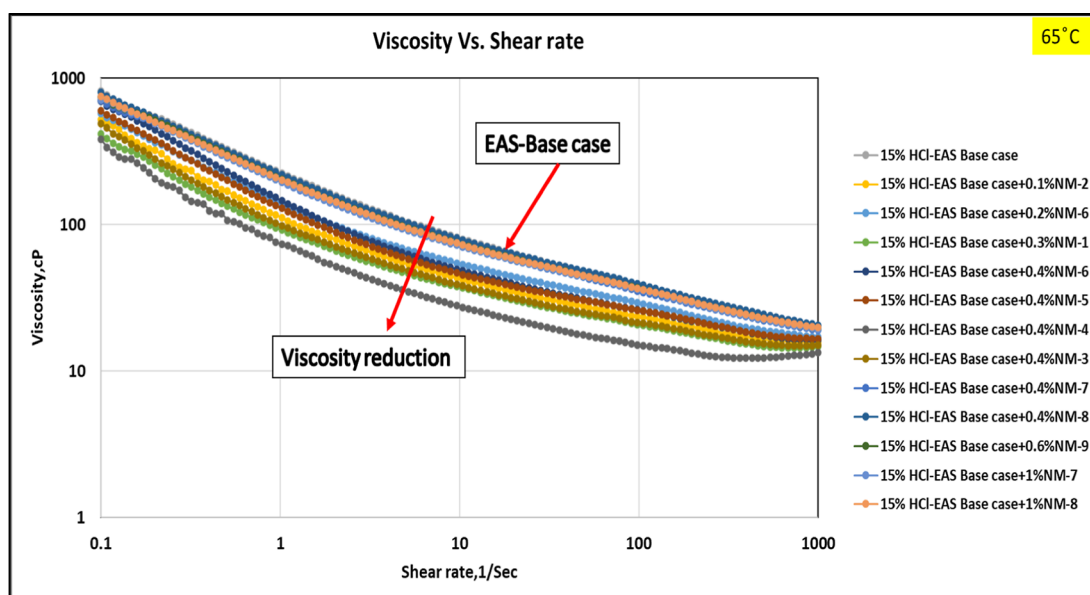


Figure 3. 15% HCl EAS viscosity (cP) vs shear rate (1/s) at 65 °C.

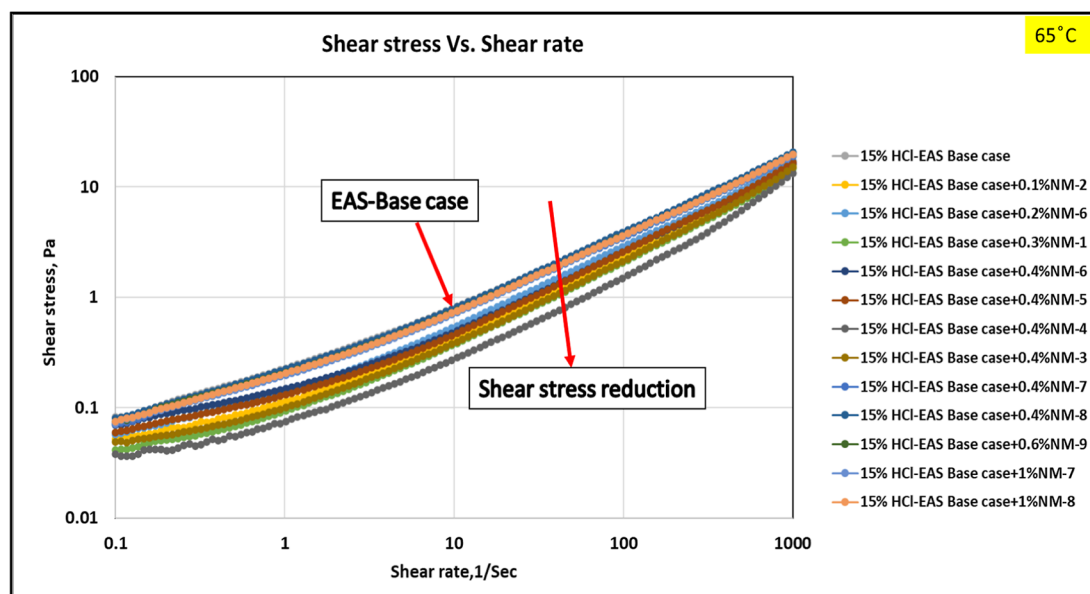


Figure 4. 15% HCl EAS shear stress (Pa) vs shear rate (1/s) at 65 °C.

extremely acidic solution. The drop-test results show that the EAS is a W/O emulsion since it is dispersed in diesel and not in water.

Thermal Stability. High-temperature graduated glass tubes were utilized to explore the thermal stability at three different temperatures (25, 80, and 120 °C), and a see-through oven was used to measure the thermal stability at 80 and 120 °C. The outcomes demonstrated that even at high temperatures, the created EAS is thermally stable. Figure 1 shows the separation volume as a function of time for the EAS at the three different temperatures (25, 80, and 120 °C), while Figure 2 shows photographs of the EAS in the test tubes before and after being taken from the oven after 24 h.

Rheology. Rheological properties were explored for the prepared EAS. First, the viscosity was measured at different shear rates, which ranged from 0.1 to 10001/s at 65 °C for all prepared EAS with and without nanomaterials (CNDs) at 15%

HCl acid concentrations, as shown in Figure 3. Adding CNDs to the EAS reduces the viscosity, as shown in Figure 3, while adding CNDs has a negligible effect on the EAS pH, conductivity, and thermal stability. After screening and optimizing different nanomaterials, the best nanomaterial was selected with the optimum concentration, which is 0.4 volume % (vol %) of NM-4. After that, more investigation was conducted on this nanomaterial (NM-4). Figure 4 shows the shear stress as a function of the shear rate for the prepared EAS with CNDs.

First, all experiments (preparation, conductivity, drop-test, thermal stability, and rheology) were repeated three times (at 15% HCl) to ensure the repetition. Figure 5 and 6 show the viscosity and shear stress as a function of shear rate, respectively, for these prepared EASs. Then, the same nanomaterial (NM-4) was tested with 20% HCl EAS, and the viscosity and shear stress as a function of the shear rate are

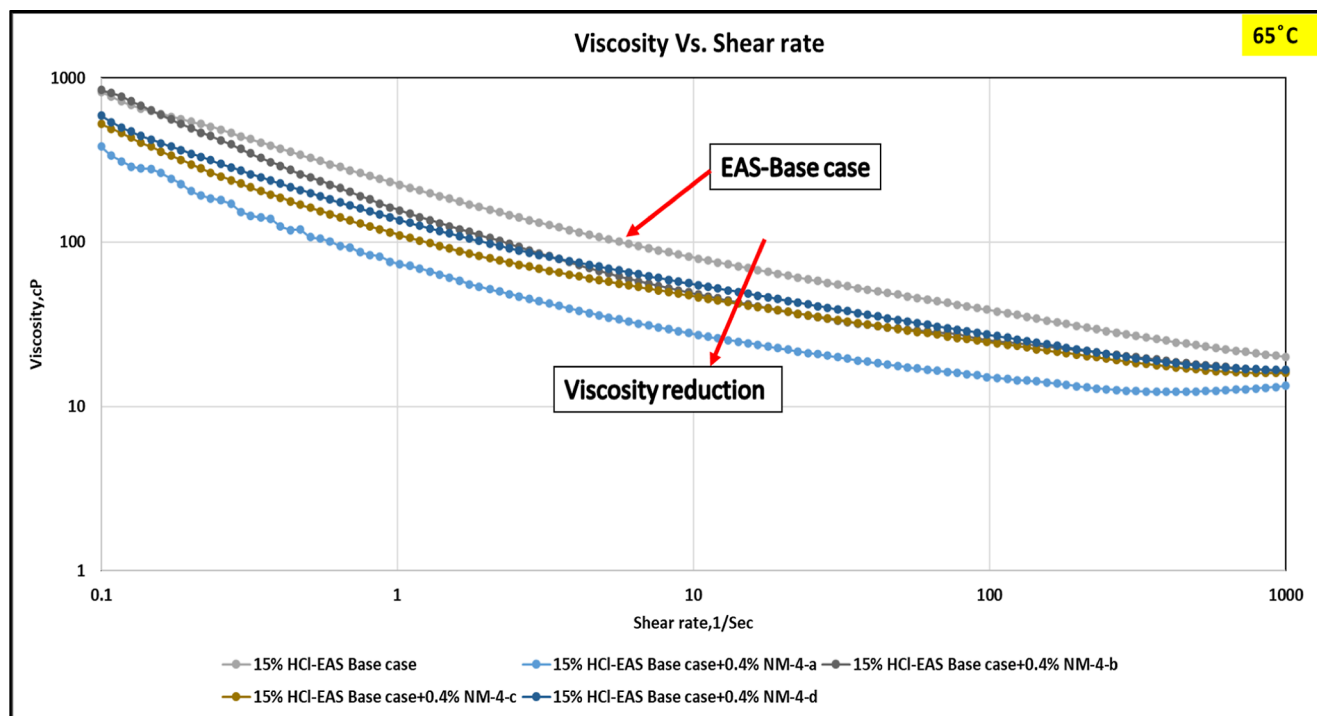


Figure 5. 15% HCl EAS viscosity (cP) vs shear rate (1/s) at 65 °C (repeated 3 times).

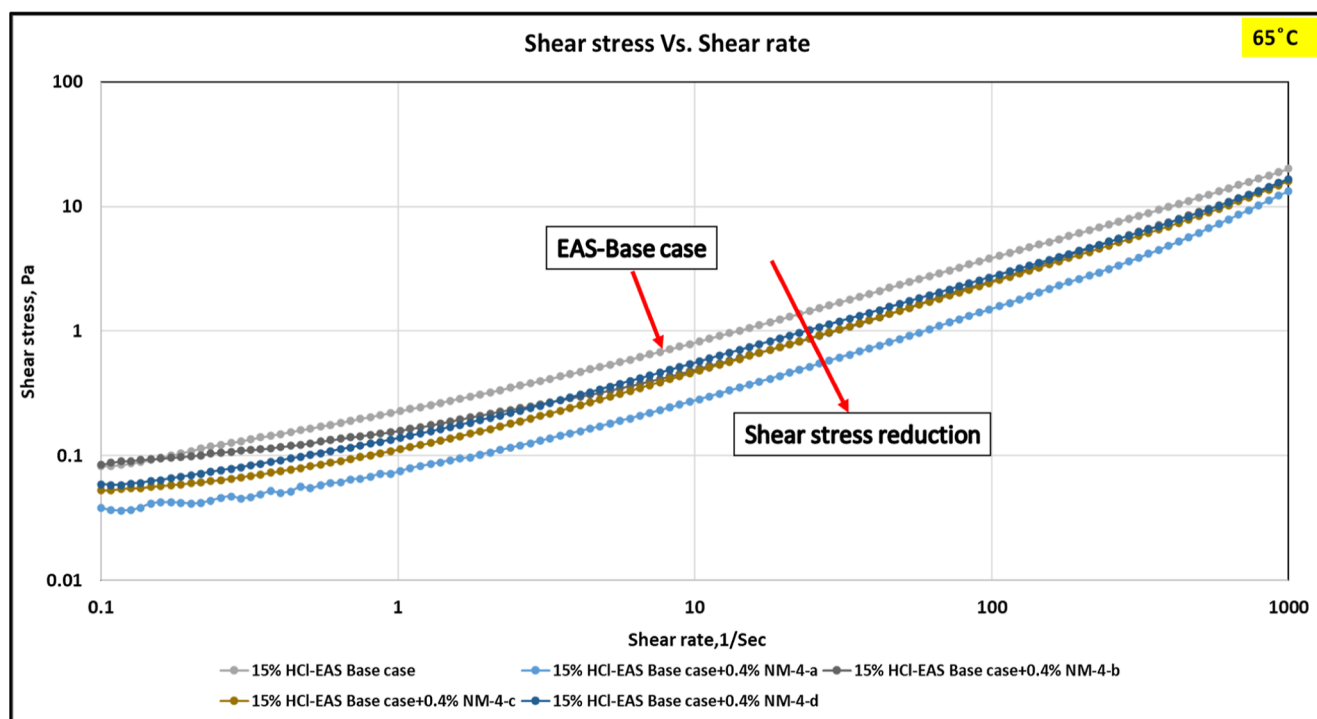


Figure 6. 15% HCl EAS shear stress (Pa) vs shear rate (1/s) at 65 °C (repeated 3 times).

shown in Figure 7 and 8. After that, the same nanomaterial (NM-4) was tested with another CI, and the viscosity and shear stress as a function of the shear rate are shown in Figure 9 and 10. Also, a sample was taken from the flow loop after the flow experiment of the EAS with the same nanomaterial (NM-4), and the viscosity was compared with the base case, as shown in Figure 11. Figure 12 shows the comparison of shear stress as a function of shear rate for the two samples, the base

case, and the sample that was taken from the flow loop after the flow experiment.

As shown in Figures 3, 5, 7, 9, and 11, adding nanomaterials (CNDs) reduces the viscosity of the EAS under different conditions, including different HCl acid concentrations, different CIs, and the sample of the EAS after the flow experiment. Furthermore, all experiments (preparation, conductivity, drop-test, thermal stability, and rheology) were

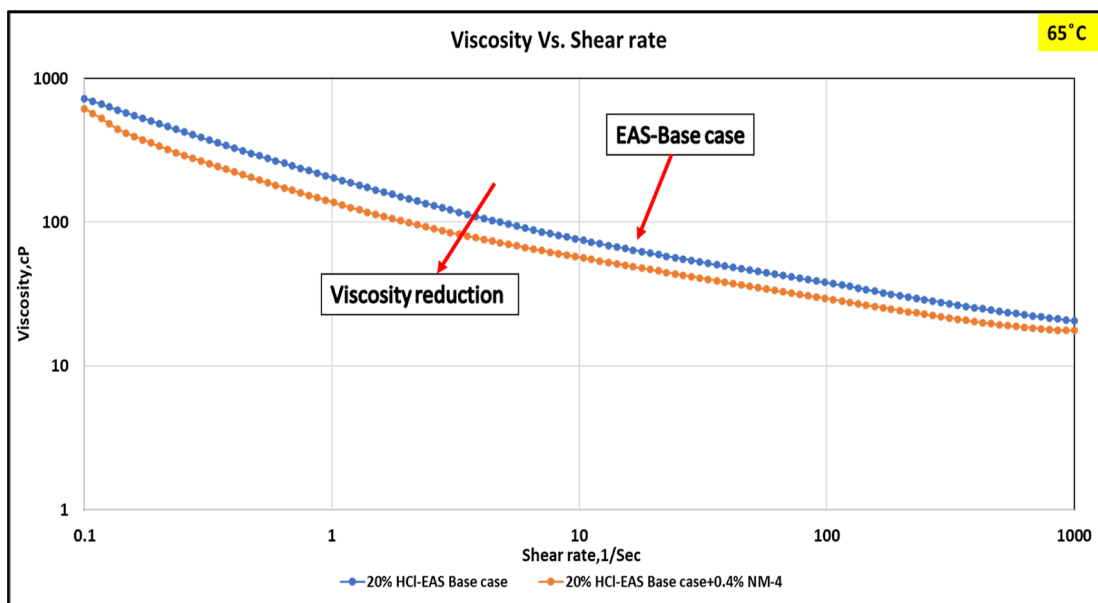


Figure 7. 20% HCl EAS viscosity (cP) vs shear rate (1/s) at 65 °C.

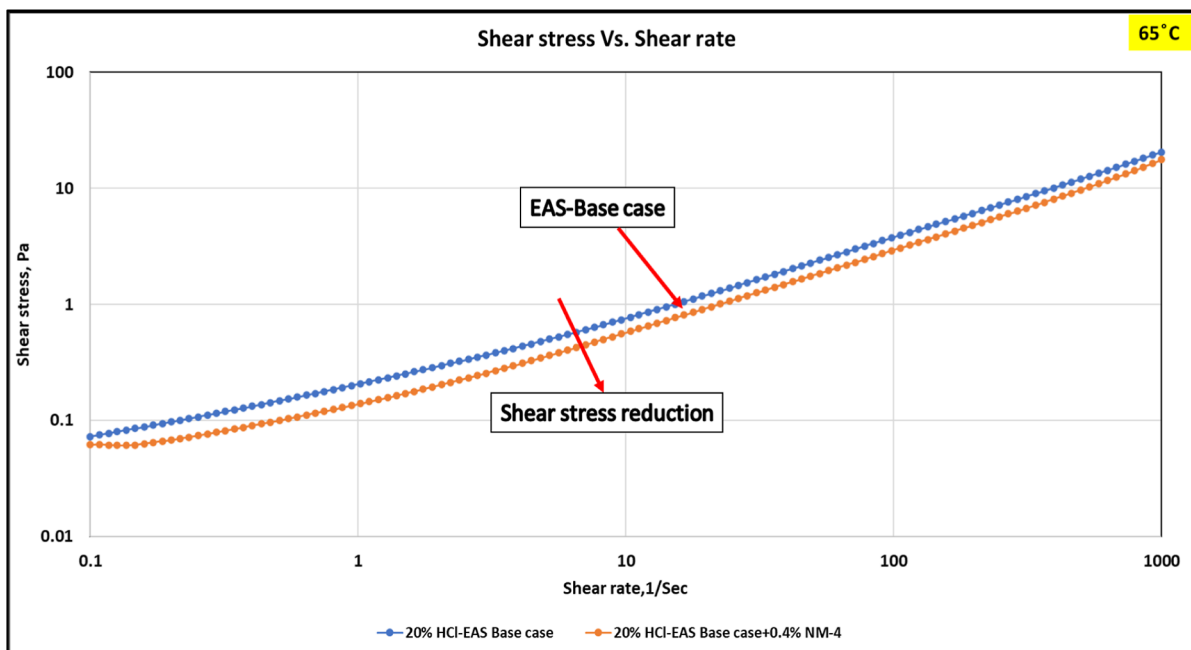


Figure 8. 20% HCl EAS shear stress (Pa) vs shear rate (1/s) at 65 °C.

repeated (at 15% HCl) with another batch of the same nanomaterial (NM-4) at the same concentration (0.4%). Figure 13 and 14 show the rheology results of the new batch of NM-4, which again shows that adding NMs reduces the viscosity of the EAS.

Drag Reduction. The drag reduction unit (flow loop) was used to conduct the drag reduction experiments. First, the drag reduction unit was calibrated with diesel, as shown in Figure 15; then the EAS was prepared in large quantities (30–40 L), as shown in Figure 16. After that, the prepared EAS was pumped through the flow loop, and the pressure drop was recorded using a pressure transducer at different flow rates.

Two different HCl concentrations of the EAS were investigated in the flow experiments (15 and 20%). The pressure drop of the base case of the 15% HCl–EAS was

plotted against the flow rates at ambient temperature (25 °C), as shown in Figure 17. Figure 17 shows that the pressure drop increases with an increase in the flow rate. However, the increase in pressure drop with flow rate is nonlinear, hence the EAS can be classified as a non-Newtonian fluid. Further, there is evidence that the pressure drop (shear stress) and flow rate (shear rate) show the shear-thinning behavior of EASs. The shear stress decreases with an increase in shear rate, attributable to the shear thinning behavior.

The effect of the temperature on the flow behavior of the EAS is shown in Figure 18 (15% HCl–EAS (base case)). Figure 18 shows that the increase in temperature causes a reduction in pressure drop. The changes in the viscosity at high temperatures are minimal. For a constant rate of 10 L/min, the pressure gradient is 12.5 psi/ft (1 psi ~6895 Pa) at 25 °C, 9

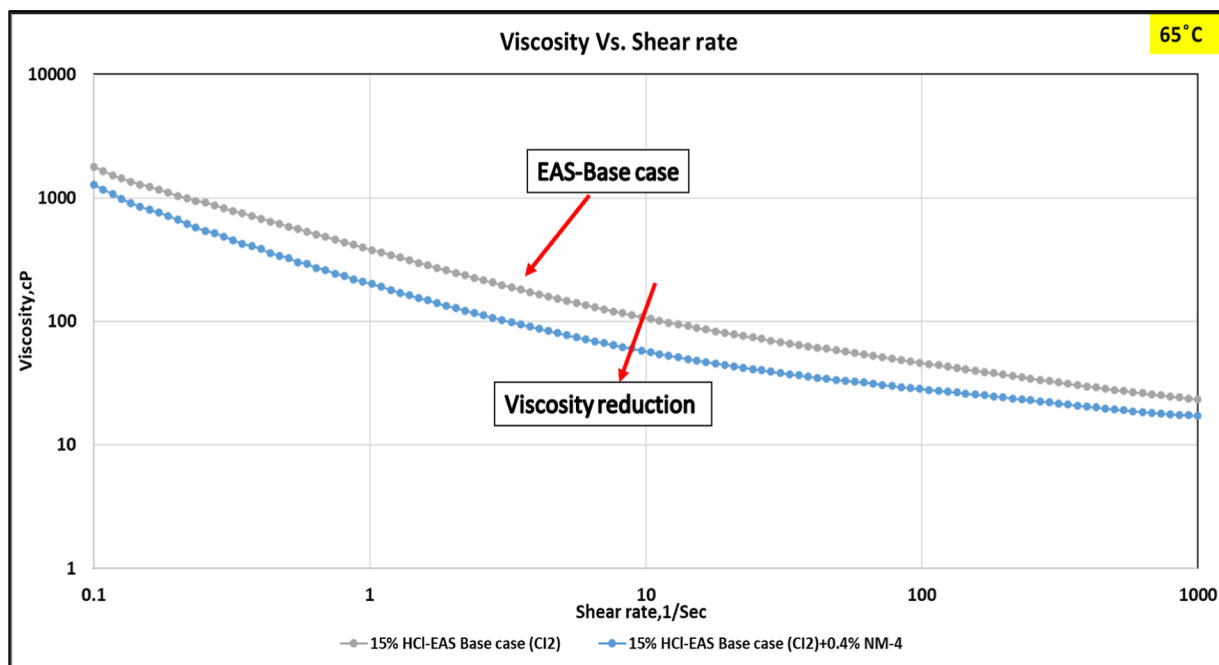


Figure 9. 15% HCl EAS viscosity (cP) vs shear rate (1/s) at 65 °C (tested with another CI).

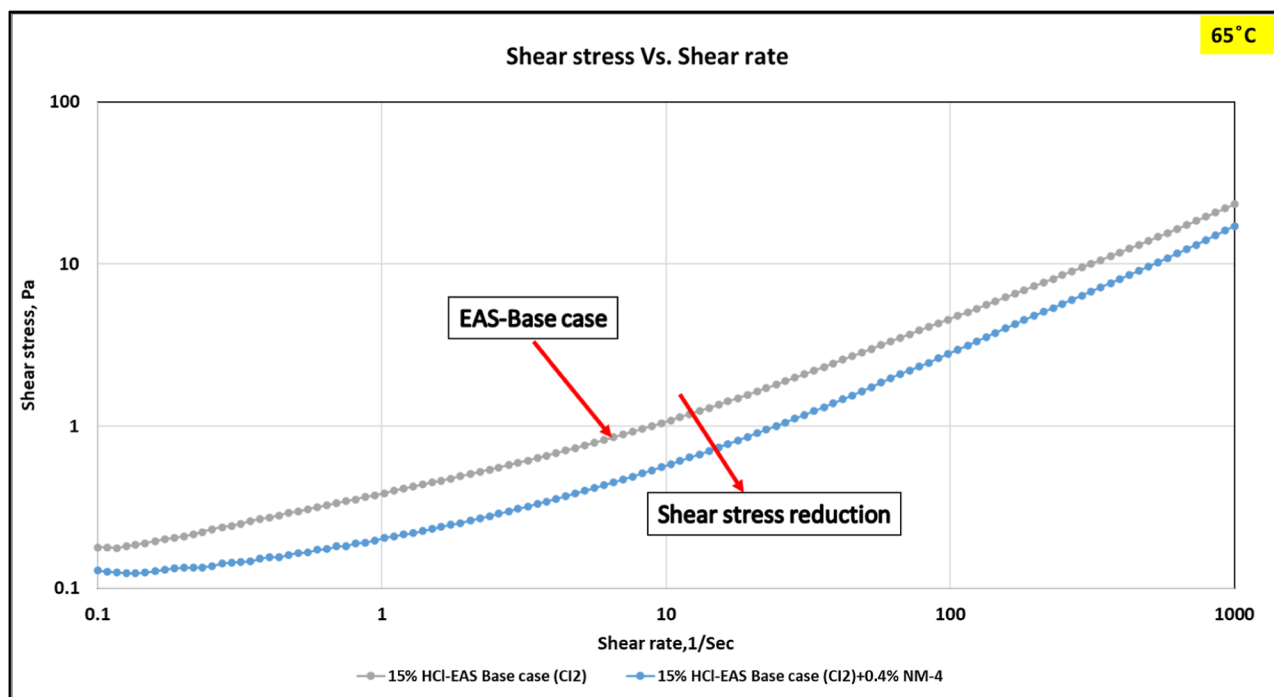


Figure 10. 15% HCl EAS shear stress (Pa) vs shear rate (1/s) at 65 °C (tested with another CI).

psi/ft (1 psi \sim 6895 Pa) at 40 °C, and 7.5 psi/ft (1 psi \sim 6895 Pa) at 50 °C. It indicates that the changes in the viscosity of the EAS are insignificant at high temperatures. These results are consistent with the results from rheology experiments, where a reduction in the viscosity of the EAS was observed with an increase in temperature.

Figure 19 shows the drag reduction of the EAS with the aid of the NM (CND). Figure 19 shows that the reduction of drag occurs for the EAS for the base case at 25 °C for both forward and backward flow rates, where symbol (a) in Figure 19 represents the forward flow rates, while symbol (b) represents

the backward flow rates. Initially, the experiment for the base case was performed for the range of flow rates and temperatures considered in this study. Then, NM (CND) was added to the solution of the base case of 15% HCl–EAS, the solution was pumped again through the drag reduction flow loop, and the pressure drop of the solution was recorded at different flow rates. The set of flow experiments was performed to cover a range of flow rates and temperatures.

It is evident from Figure 19 that the drag reduction can be achieved by adding NM (CND) to the EAS. The magnitude of drag reduction appears to be significant at higher flow rates

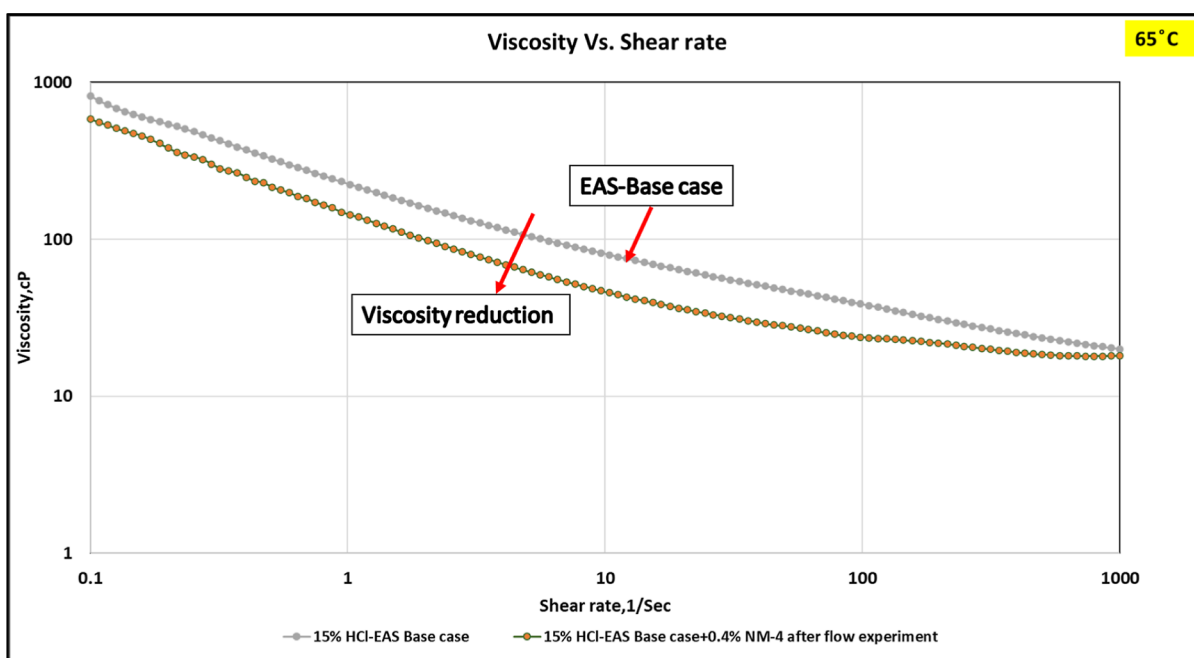


Figure 11. 15% HCl EAS viscosity (cP) vs shear rate (1/s) at 65 °C (sample after flow experiment).

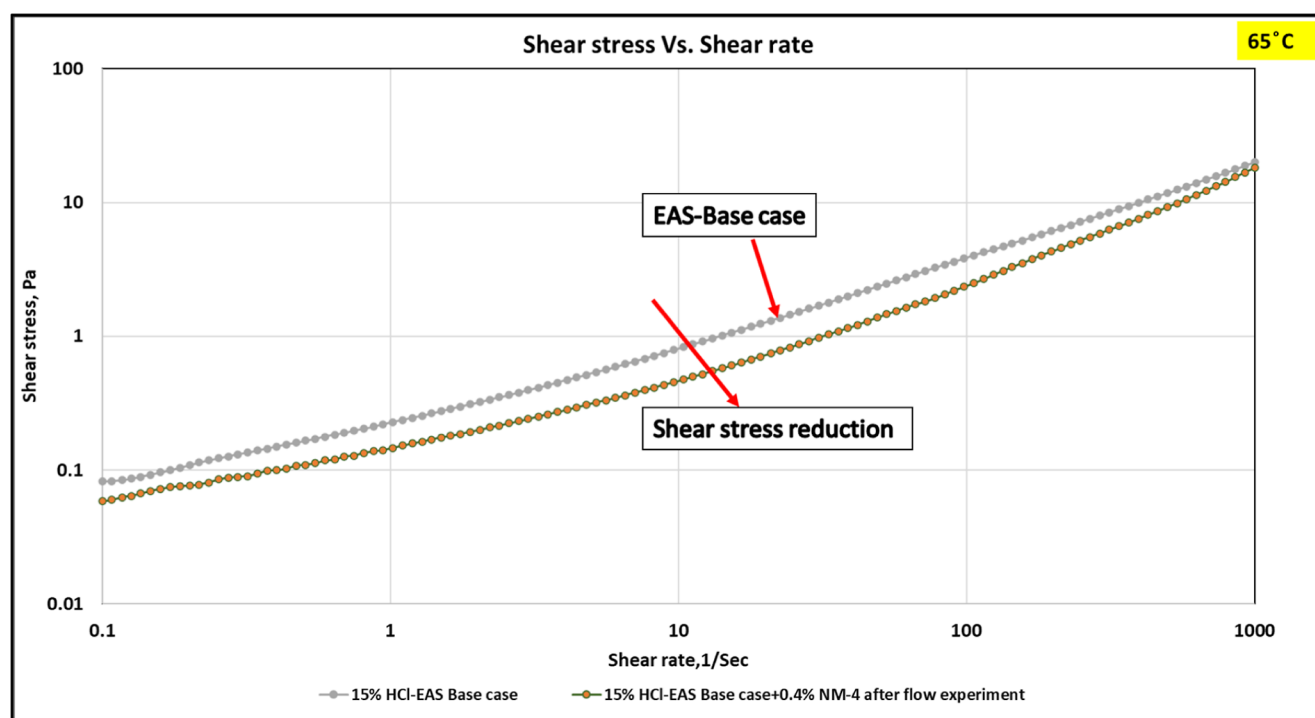


Figure 12. 15% HCl EAS shear stress (Pa) vs shear rate (1/s) at 65 °C (sample after flow experiment).

compared to lower flow rates. At the flow rate of 10 L/min, the drag reduction was ~ 2 psi (1 psi ~ 6895 Pa), while at 12 L/min, it was ~ 3 psi (1 psi ~ 6895 Pa). The reduction in drag due to the addition of the NM can be ascribed to hydrodynamic stabilization, turbulence suppression, and steric stabilization.^{42–44} CNs can form a layer on the surface of the fluid, which reduces the friction between the fluid molecules, and as a result, a reduction in the viscosity of the fluid occurs and the fluid can flow more easily.⁴⁵ This study does not reveal the exact mechanism of drag reduction. The main complexities associated with CN are its chemical nature and the

interaction of CN at the molecular level. Another challenge is the interaction of CN with the additives used for the preparation of the EAS.

Figure 20 shows the shear stress as a function of the shear rate for the 15% HCl–EAS flow experiment at 25 °C. It is similar to Figure 19, the only difference being the pressure drop and flow rate rates are presented in the form of shear stress and shear rates.

After that, the flow experiment of the 15% HCl–EAS + NM was conducted at higher temperatures (40 and 50 °C), as shown in Figure 21 and 22 respectively. It can be observed that

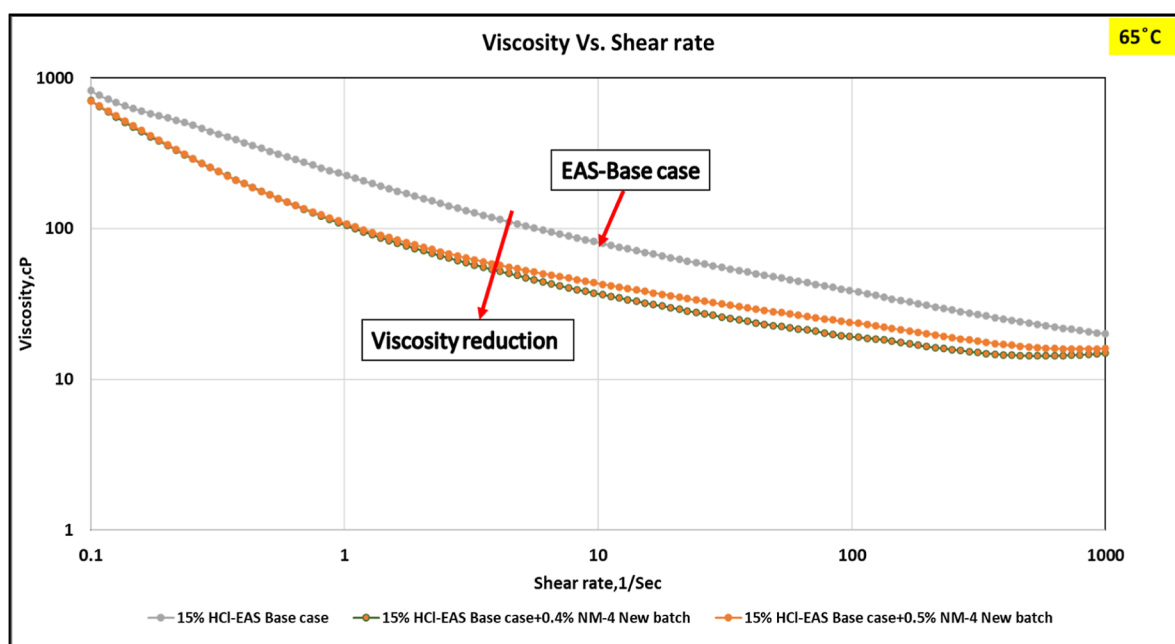


Figure 13. 15% HCl EAS viscosity (cP) vs shear rate (1/s) at 65 °C (new batch).

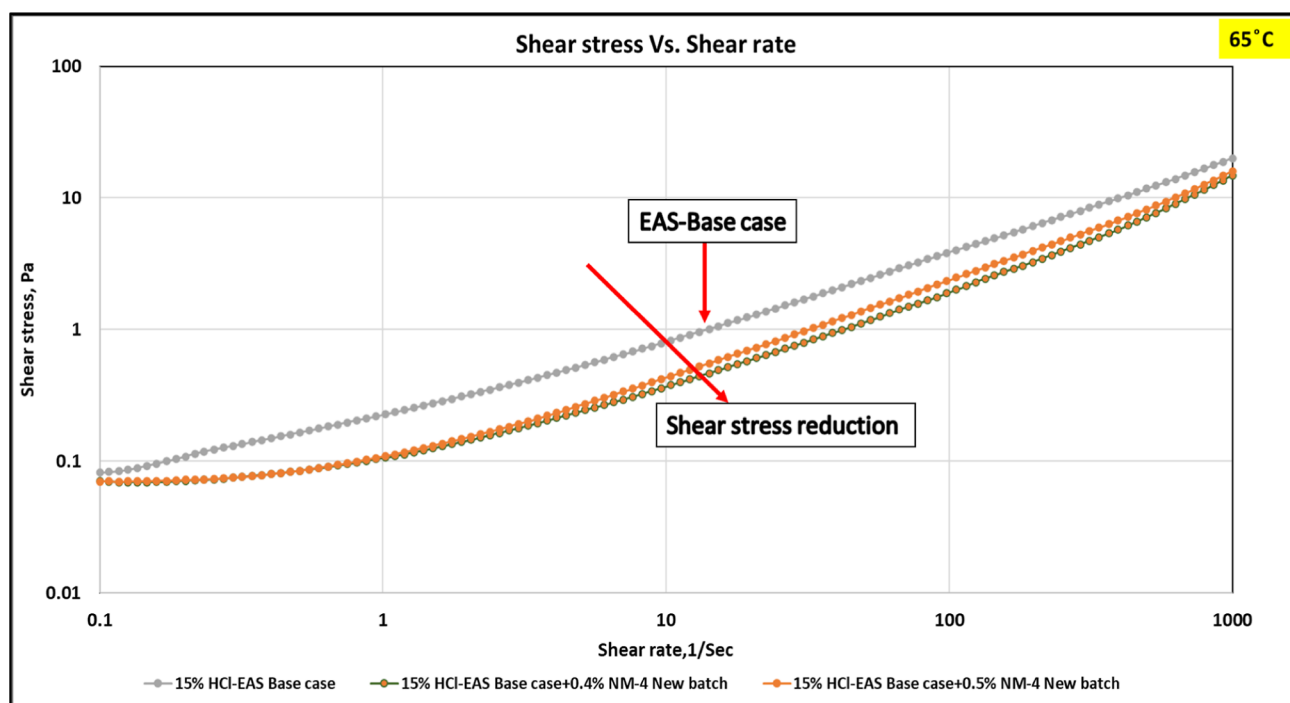


Figure 14. 15% HCl EAS shear stress (Pa) vs shear rate (1/s) at 65 °C (new batch).

the addition of NM even at high temperatures helps in drag reduction. The magnitude of the drag reduction decreased with an increase in temperature. Adding NM to the 15% HCl–EAS reduces the drag at 40 °C, while the drag reduction is small at 50 °C. It should be noted that at higher temperatures, the pressure drop/viscosity values of the EAS acid are lower compared to the base case; however, the trends show a higher drag reduction with an increase in flow rates, which is generally practiced in field operations.

In addition, the flow experiment for the 20% HCl–EAS before and after adding NM was conducted using the drag reduction flow loop, covering a range of flow rates and

temperatures comparable with the 15% HCl EAS. The effect of increasing the temperature on the flow experiment of the 20% HCl–EAS (base case) is shown in Figure 23. The results indicate that the increase in temperature causes a reduction in the pressure drop. The results of the 20% HCl EAS are similar to the 15% HCl EAS, there is a minor alteration in the pressure drop or drag reduction due to an increase in the concentration of HCl. After that, the NM (CND) was added to the base case of the 20% HCl–EAS, the solution was pumped again through the drag reduction flow loop, and the pressure drop of the solution was recorded at different flow rates covering the range of temperature.

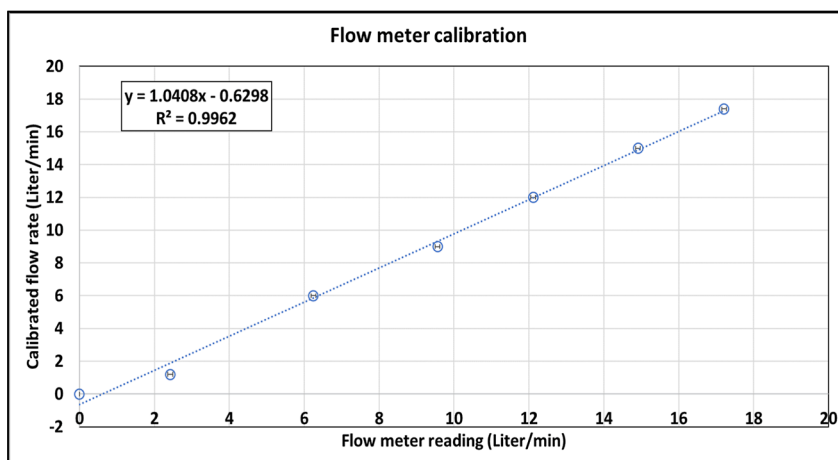


Figure 15. Drag reduction flow loop calibration with diesel.

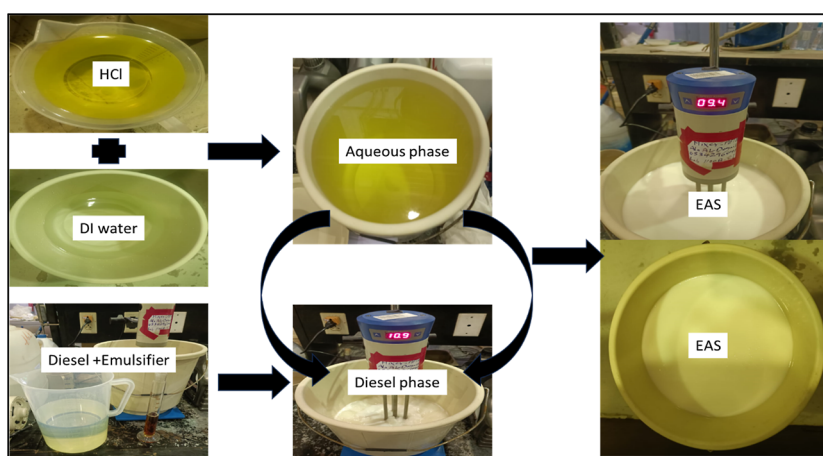


Figure 16. EAS preparation for the flow experiment.

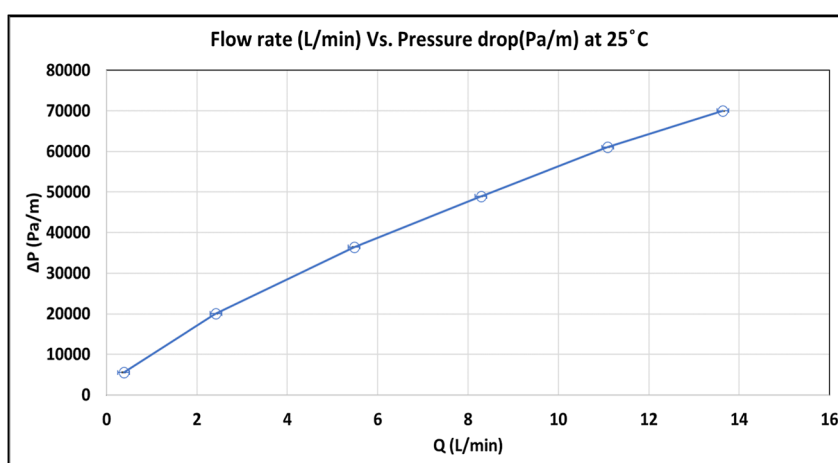


Figure 17. Flow experiment of the 15% HCl–EAS (base case) at 25 °C.

Figure 24 shows the comparison between the pressure drop of the 20% HCl–EAS before and after adding the NM at 25 °C. Adding NM to the EAS reduced the drag at ambient temperature (25 °C), and the drag reduction is very distinct at high flow rates.

After that, the flow experiment of the 20% HCl–EAS + NM was done at higher temperatures (40 and 50 °C), as shown in Figure 25 and 26, respectively. It is evident from the figures

that the addition of NM to the 20% HCl–EAS reduces the drag at 40 as well as at 50 °C. The trends in the drag reduction are similar to the base case of a 15% HCL emulsion, where the reduction in drag is significant at high flow rates. In addition, the effect of drag reduction is retained at high temperatures where the viscosities or pressure values are lower. It further strengthens the use of CNs NM for achieving the drag reduction of EASs, irrespective of viscosity and temperature.

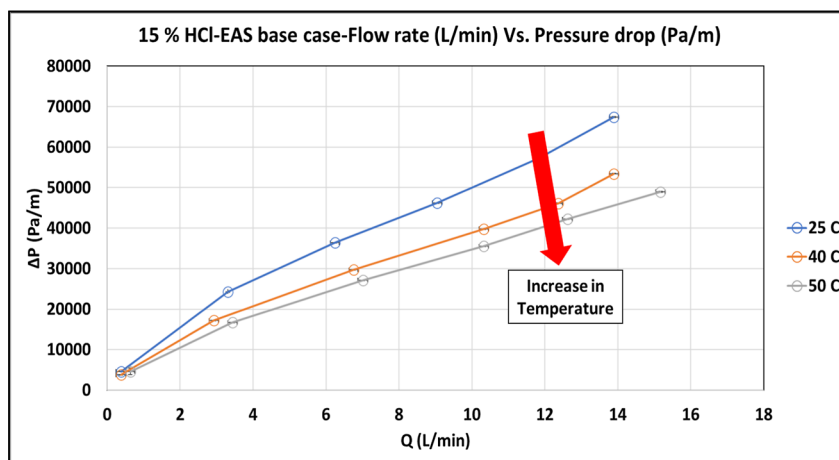


Figure 18. Effect of temperatures on the 15% HCl–EAS (base case) flow experiment.

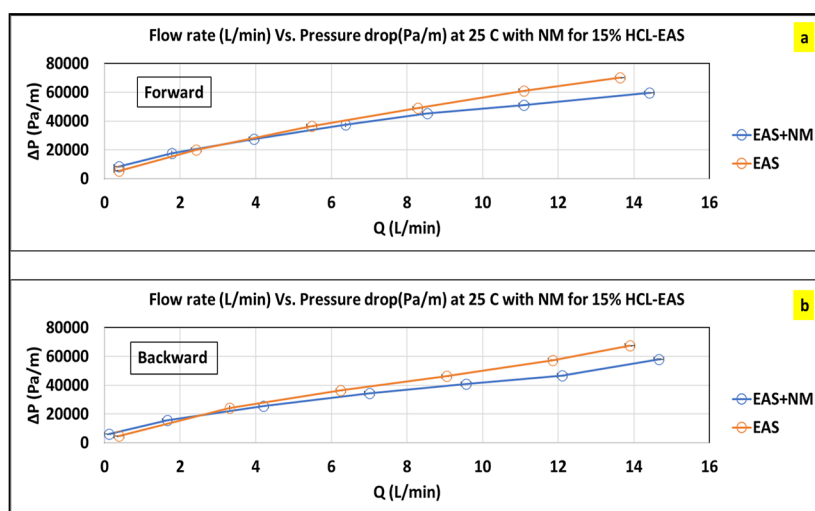


Figure 19. Effect of the addition of NM to the 15% HCl–EAS (base case) pressure drop at 25 °C.

Further, a sample of the 20% HCl–EAS (base case) as well as the 20% HCL at 40 and 50 °C was collected for analysis to ensure it retained the rheological behavior after the flow experiment.

The samples were analyzed for rheology by using a rheometer. Figure 27 shows the viscosity as a function of shear rates for the 20% HCl–EAS samples that were taken from the flow loop before and after the addition of NM. It is evident from Figure 27 that adding NM to the 20% HCl–EAS reduces the viscosity. In addition, the conductivity, pH, and drop test were measured for both samples that were taken from the flow loop to ensure the inverted emulsion and the acidity of the EAS. The stability of both samples that were taken from the flow loop was investigated at 25 °C (ambient temperature) for 24 h, as shown in Figure 28.

DISCUSSION

CNDs show potential to be used in the petroleum industry because they show promising results in different applications in the oil and gas industry.^{46–51} The unique properties and characterization of the CNDs make them attractive NMs for improving some processes and addressing some challenges in the petroleum industry. CNDs have a high surface area and tunable surface chemistry, so they can be utilized as catalysts

for many processes, such as hydrocracking and reforming, which improve refining operations efficiency. CNDs are promising surface-active agents for altering the wettability from strongly oil-wet to water-wet in carbonate reservoirs.⁵² CND can be used as nanofluids for heat transfer as well as a CI, where CNDs are dispersed in heat transfer fluids and they can create nanofluids that have better thermal conductivity compared to the conventional fluids. The incorporation of CNDs in the heat exchanger and cooling systems led to enhanced efficiency of heat transfer,⁵³ which is imperative for several processes in the oil and gas industry. CNDs can work as CIs due to their ability to form protective layers on metal surfaces.

CNDs can be used for enhanced oil recovery (EOR) due to their ability to change the reservoir fluids' properties and enhance the flow characteristics,⁴⁸ where CNDs can alter the interfacial tension (IFT), wettability, and viscosity, and as a result, enhance the oil displacement and increase the oil recovery.^{52,54–58} In addition, CNDs can be used as adsorbents for water remediation, and they can be used as smart fluids by introducing them into drilling fluids or completion fluids due to their ability to improve rheological properties, reduce friction, and improve wellbore stability.⁴² This paper explored

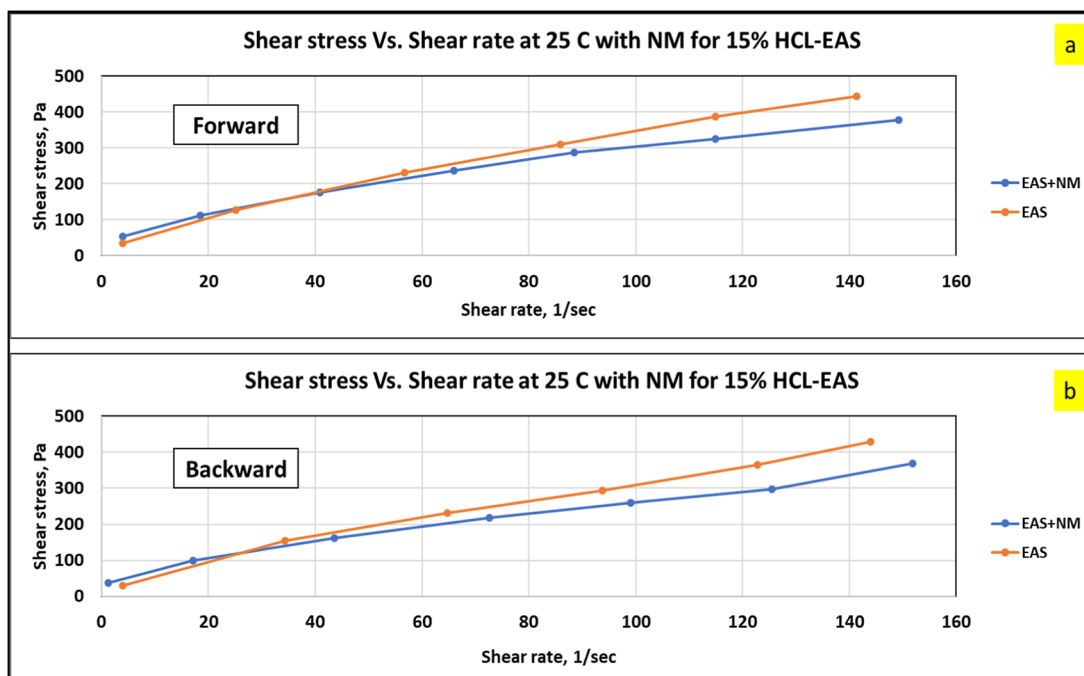


Figure 20. Effect of addition of NM to the 15% HCl–EAS (base case) shear stress at 25 °C.

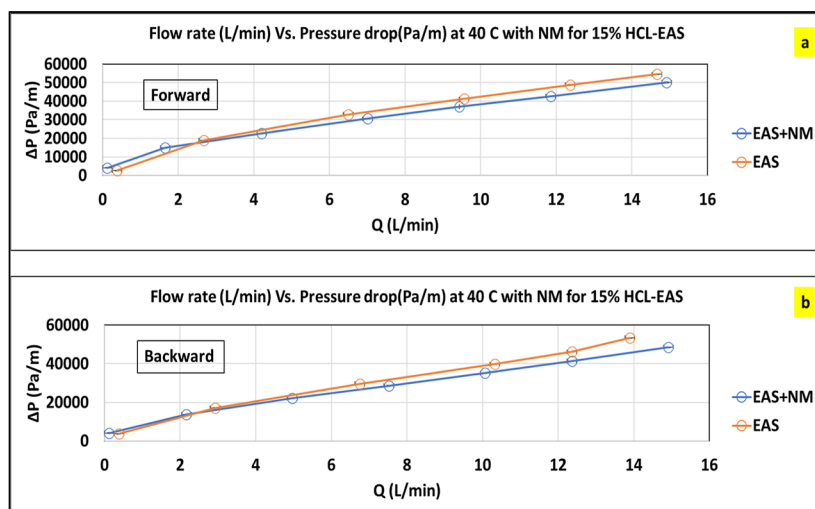


Figure 21. Effect of adding NM to the 15% HCl–EAS (base case) at 40 °C.

the utilization of CNDs as viscosity reducers for EAS, as well as DRAs for the EAS.

CNDs can work as viscosity reducers and DRAs for fluids, and there are different mechanisms for CNDs to work as DRAs and viscosity reducers; these mechanisms include hydrodynamic stabilization, turbulence suppression, and steric stabilization.⁵⁹ CNDs can form a layer on the surface of the fluid, which reduces the friction between the fluid molecules, and as a result, a reduction in the viscosity of the fluid occurs and the fluid can flow more easily.⁴⁵ A similar mechanism was given for the nanomaterial for drag reduction in hydraulic fracturing fluid, horizontal pipe, and multiphase flow.^{43,44,60,61}

In addition, CNDs can suppress turbulence in the fluids due to the formed molecular layer on the fluid surface, which disrupts the formation of vortices. CNDs can work as steric stabilizers, preventing the fluid molecules from coming into close contact with each other, which helps reduce fluid

viscosity and improve flow.^{58,62} Adding CNDs to the fluid will create a hydrodynamic lift force that opposes the drag force on the fluid. CNDs can change the wettability of the fluid surface, which can affect the flow of fluid.^{52,54} CNDs can interfere with the formation of boundary layers, which are thin layers of fluid that form near solid surfaces. Boundary layers can cause drag; therefore, interfering with their formation can reduce the drag.

In general, the mechanism by which CNDs work as viscosity reducers and DRAs depends on different factors, including CNDs' type, CNDs' concentration, the fluid to which they are added, and the conditions under which they are used. Utilizing the CNDs as viscosity reducers, or DRAs, has some advantages, including an increased flow rate, enhanced fluid mixing, and reduced energy consumption required to pump fluids through the pipes and channels. The use of CNDs as viscosity reducers and DRAs is still in the early stages of development, but it has many advantages that help to reduce

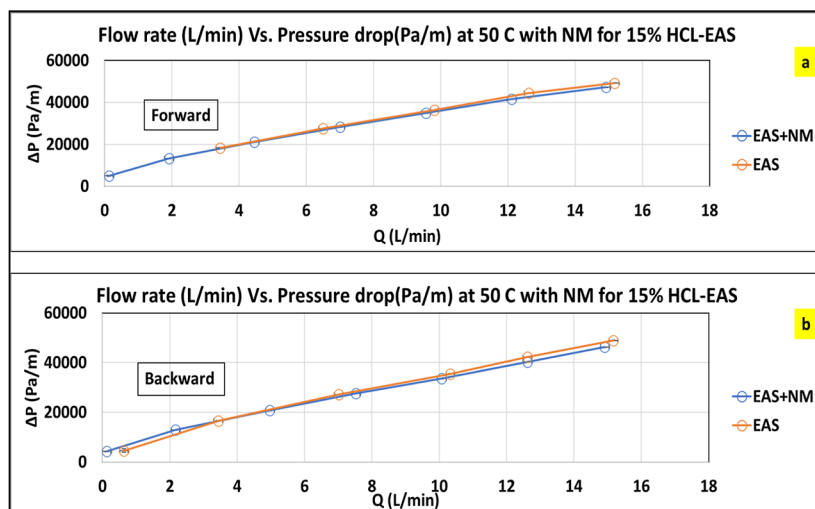


Figure 22. Effect of adding NM to the 15% HCl–EAS (base case) at 50 °C.

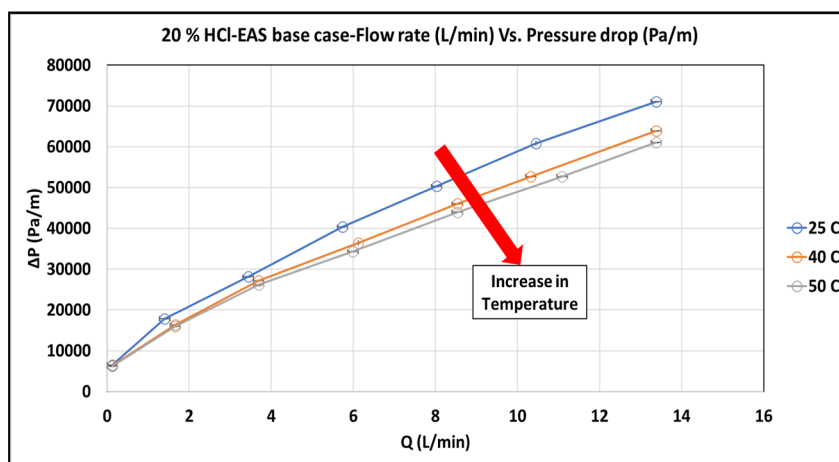


Figure 23. Effect of temperature on the 20% HCl–EAS flow experiment.

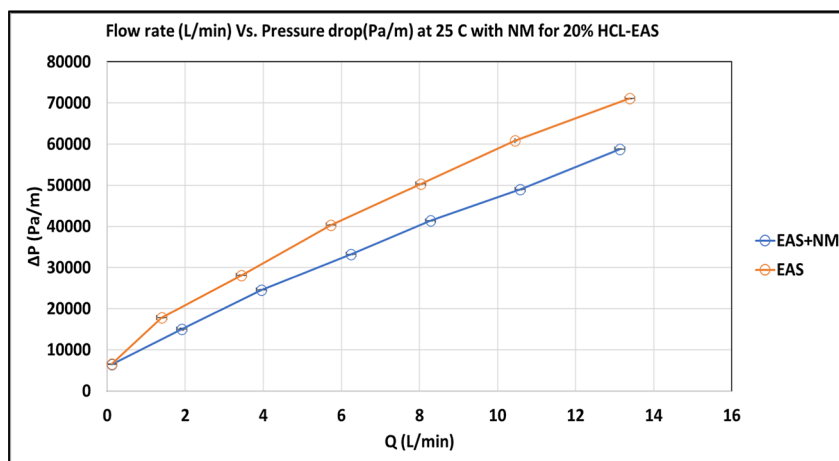


Figure 24. Effect of the addition of NM to the 20% HCl–EAS pressure drop at 25 °C.

the viscosity of the fluid and improve flow efficiency. CNDs can interact with the fluid at a microscopic level, particularly with the boundary layer of the fluid adjacent to the pipeline or conduit walls. This interaction can modify the behavior of the fluid molecules at the interface, reducing the resistance to flow and resulting in lower frictional forces. This microscale

modification can effectively improve the flow near the walls, and as a result, reduced viscosity and drag reduction occur.

In summary, CNDs are a type of carbon nanomaterial that typically has a diameter of less than 10 nm. CNDs are characterized by some unique properties, including high surface area, good dispersibility in water and other liquids,

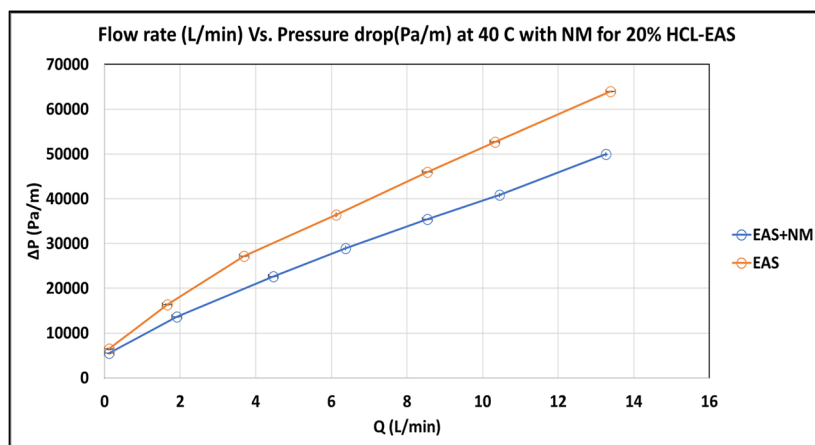


Figure 25. Effect of adding NM to the 20% HCl–EAS at 40 °C.

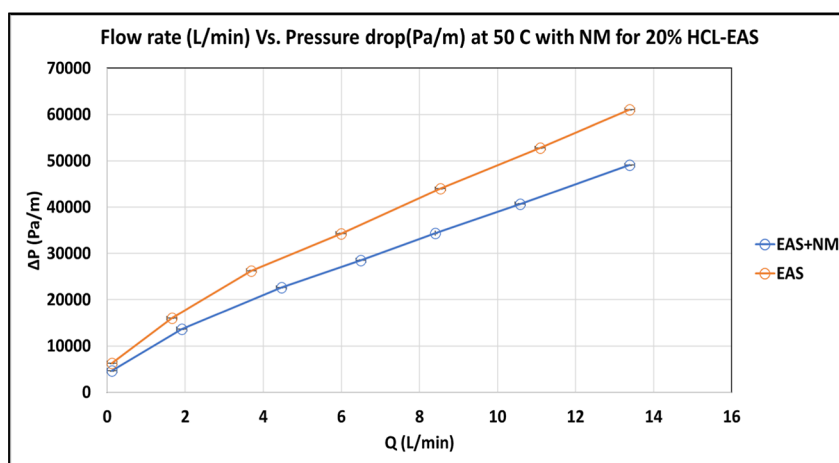


Figure 26. Effect of adding NM to the 20% HCl–EAS at 50 °C.

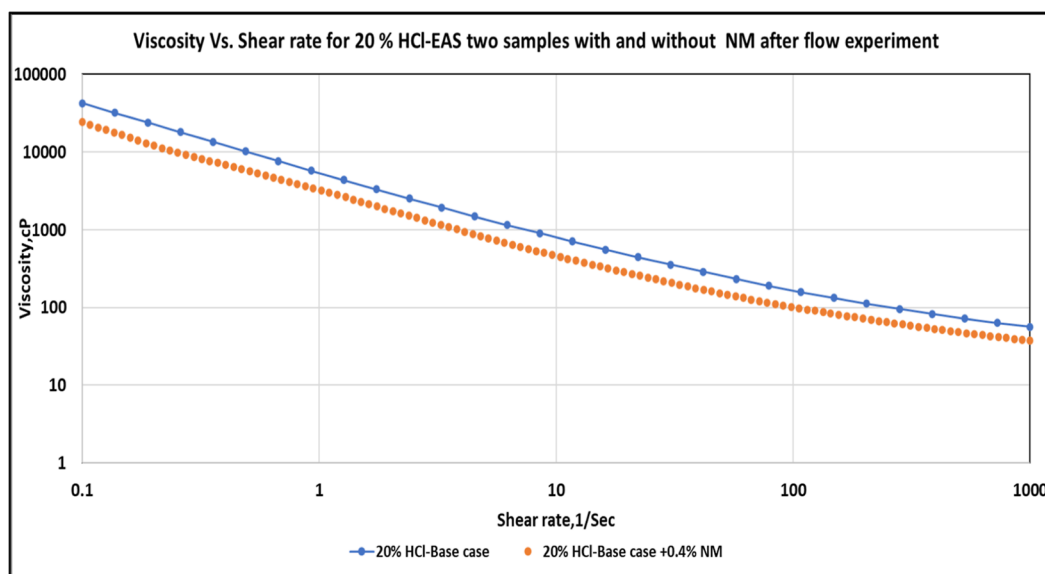


Figure 27. 20% HCl EAS viscosity (cP) vs shear rate (1/s) at 65 °C.

and the ability to modify the surface properties of other materials. CNDs can reduce the EAS viscosity by some mechanisms, one of which is adsorbing onto the surface of the emulsion droplets and creating a steric barrier that prevents the

droplets from coalescing. This reduces the friction between the emulsion droplets and the surrounding liquid, which leads to a decrease in viscosity. Another mechanism is the interaction of the CNDs with water molecules in the EAS that form

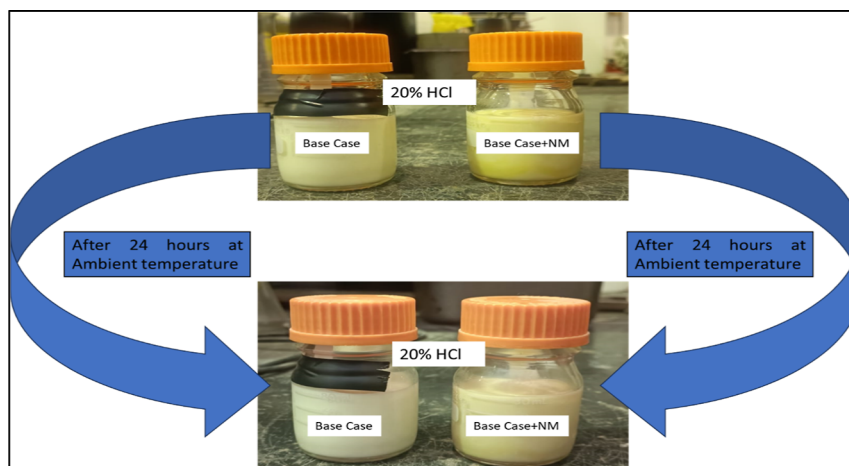


Figure 28. 20% HCl EAS stability for 24 h at 25 °C.

hydrogen bonds. This creates a network structure that traps the water molecules and reduces their mobility, which also leads to a decrease in viscosity. CNDs can also work as DRA, which means they can reduce the resistance to the flow of the EAS. This is thought to be due to the ability of the CNDs to form a boundary layer on the surface of the flow channel. This boundary layer reduces the friction between the EAs and the flow channel, which leads to a decrease in drag.

The results of this study are very promising, and further research can be done on utilizing CNDs in different petroleum industry applications. Besides, CNDs are also environmentally friendly. The findings suggest that CNDs could be used as effective viscosity reducers and DRAs for the EAS, which would lead to some benefits, such as reduced pumping costs, improved flow performance, and increased energy efficiency. More investigation is required to fully understand the mechanisms of CNDs as DRAs and viscosity reducers.

CONCLUSIONS

The following points can be concluded from this study:

- 1 The addition of the CNDs NM reduces the viscosity and drag of the EAS.
- 2 The magnitude of drag reduction is significant at the higher range of flow rates or shear rates. It is better for field operation as higher flow rates are preferable to save pumping time and cost.
- 3 The CNDs NM are compatible with the additives associated with EASs. It does not alter chemistry or other properties except for a reduction in the viscosity and drag of the EAS, which is beneficial for the industry.
- 4 The addition of CNd retains the conductivity and stability, as well as the shear-thinning behavior of the EAS.
- 5 An increase in temperature results in a reduction of the EAS viscosity; however, the CNds NM retain their efficacy at higher temperatures as well as at lower viscosities.
- 6 The HCl concentration has an insignificant effect on the EAS rheology. The performance of the CNds NM is not affected by the concentration of HCL. The drag reduction can be achieved at different HCL concentrations.
- 7 The flowing condition does not alter the rheology of the EAS. The addition of CNd reduces the viscosity and

drag, retaining the rheology before and after fluid flows at different temperatures and time durations.

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Author Contributions

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

Notes

The authors declare no competing financial interest.

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NOMENCLATURE

EAS, emulsified acid system; OC, organoclay; HCl, hydrochloric acid; HF, hydrofluoric acid; bpm, barrel per minute; DRA, drag-reducing agent; CND, carbon nanodots; W/O, water-in-oil emulsion; IFT, interfacial tension; DI, deionized; PV, pore volume; PVBT, pore volume to breakthrough; BHT, bottom hole temperature; ppm, part per million; rpm, revolution per minute; cm³/min, cubic centimeters per minute; NM, nanomaterial; VFD, variable-frequency drive; CI, corrosion inhibitor; EOR, enhanced oil recovery

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