

**DRAG REDUCTION OF EMULSIFIED ACID
SYSTEM IN PIPES**

BY

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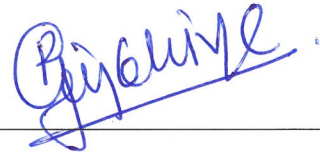


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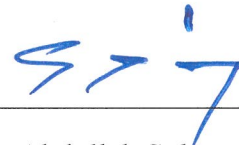
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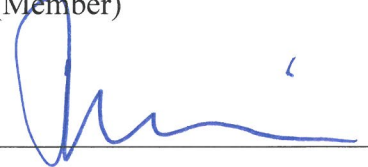
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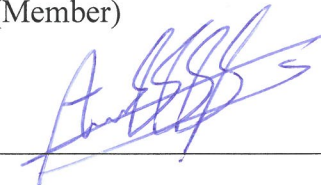
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DEDICATION

This Dissertation is dedicated to

MY BELOVED MOTHER AND FATHER,
MY WIFE, MY DAUGHTER (NOOR), MY SONS (ABDULRAHMAN AND
MOHAMMED), MY BROTHERS & SISTERS,
ALL MY FAMILY, AND FRIENDS

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LIST OF ABBREVIATIONS

EAS	:	Emulsified acid system
CNDs	:	Carbon nanodots
NM	:	Nanomaterial
OC	:	Organoclay
HCl	:	Hydrochloric acid
HF	:	Hydrofluoric acid
DRA	:	Drag-reducing agent
DR%	:	Drag reduction percentage
W/O	:	Water-in-oil emulsion
O/W	:	Oil-in-water emulsion
W/O/W	:	Water-in-oil-in-water emulsion
O/W/O	:	Oil-in-water-in-oil emulsion
IFT	:	Interfacial tension
DI	:	De-ionized
XRD	:	X-ray diffraction
XRF	:	X-ray fluorescence
PSD	:	Particle size distribution
SEM	:	Scanning electron microscopy
PV	:	Pore volume
PVBT	:	Pore volume to breakthrough
BHT	:	Bottom hole temperature
SMD	:	Sauter mean diameter
VMD	:	Volume mean diameter
S_v	:	Volume-specific surface
S_m	:	Mass-specific surface
ppm	:	Part per million

RPM	:	Revolution per minute
bpm	:	Barrel per minute
cc/min	:	Cubic centimeter per minute
μm	:	Micrometer
nm	:	nanometer
EOR	:	Enhanced oil recovery
DRP's	:	Drag-reducing polymers
HMW	:	High molecular weight
PEO	:	Polyethylene oxide
D	:	Pipe diameter.
ID	:	Inner diameter
OD	:	Outer diameter
Re	:	Reynolds number (dimensionless number)
PAM	:	Polyacrylamide
ppm	:	Part per million
PIB	:	Polyisobutylene
CTAC	:	Cetyltrimethylammonium chloride
NaSal	:	Sodium salicylate
TVP	:	Thermoviscosifying polymer
HPAM	:	Hydrolyzed polyacrylamide
Pwithout DRP	:	Pressure drop in the absence of DRP
Pwith DRP	:	Pressure drop in the presence of DRP
IOIP	:	Initial oil in place
CI	:	Corrosion inhibitor
VFD	:	Variable frequency drive

ABSTRACT

Full Name : [Ala Shafeq Abdullah AL-Dogail]
Thesis Title : [Drag Reduction of Emulsified Acid System in Pipes]
Major Field : [Petroleum Engineering]
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In the petroleum industry, well stimulation is required to enhance the productivity of oil and gas wells. Well stimulation can be done by one of two different methods, matrix acidizing, and hydraulic fracturing. The matrix acidizing process is widely used in the oil and gas industry to prolong the life of oil and gas wells and enhance production rates by removing the scales and creating channels or wormholes in the rock. The acidizing process entails the injection of acid into the wellbore to mitigate formation damage. However, conventional acidizing fluids, that are used to stimulate the carbonate reservoirs, have some limitations including high acid strength and quick reaction with scale and fines nearby to the wellbore. In addition, at elevated temperatures, they are more likely to cause corrosion in the tubing, casing, and downhole equipment. Emulsified acid systems (EAS) have been developed to overcome the conventional acid system's limitations. EAS provides reduced or retarded reaction rates of acid due to the oil's external phase, and this helps for deeper and narrower wormholes into the formation. Nevertheless, there are several drawbacks to using emulsified acids, such as low stability at high temperatures, high viscosity that restricts the pumping rate due to frictional losses, the potential for formation damage, and the difficulty of achieving homogeneous field-scale mixing. The commonly used EAS prevents injection or pumping at flow rates above 20 bpm and limits the penetration depth in the matrix or fractured systems.

Historically there is no simple solution to this problem, emulsified acid treatment designs only aim at placing the acid as fast, and deep as the friction allows it. Therefore, having lower friction characteristics would allow for higher pumping rates. The EAS is intended to be thermally stable and robust in terms of field mixing procedures. So, the objective of this study is to implement an engineered retarded acid system with low viscosity by developing effective emulsified HCl acid blends that can be delivered in the field without incurring high frictional losses, which limit their applicability.

Two different techniques were utilized to achieve the objective of this study. The first one is by adding nanomaterials (NM), which are carbon nanodots (CNDs) to the commercial formulation of EAS. The second method is to develop a new Pickering EAS utilizing organoclay (OC) as an emulsifier.

The results showed that adding CNDs to the commercial EAS formulation reduces the viscosity as well as drag in pipes without affecting the conductivity and thermal stability. So the CNDs works as viscosity reducers and drag-reducing agents (DRAs) for the EAS. Results also showed that Pickering EAS has lower drag compared to the normal EAS (with surfactant as emulsifier) even after adding the CNDs as DRA for the normal EAS.

ملخص الرسالة

الاسم الكامل: علاء شفيق عبدالله الدقيل

عنوان الرسالة: تقليل السحب لنظام الحمض المستحلب في الأنابيب

التخصص: هندسة بترول

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في صناعة النفط يتم تحفيز الآبار لتحسين وتعزيز إنتاجية آبار النفط والغاز. تتم عملية تحفيز الآبار بإحدى طريقتين مختلفتين وهما عن طريق تحميض الطبقة أو عن طريق التكسير الهيدروليكي. تستخدم عملية تحميض الطبقة على نطاق واسع في صناعة النفط والغاز لإطالة عمر آبار النفط والغاز وتعزيز معدلات الإنتاج عن طريق إزالة الرواسب وإنشاء قنوات أو ثقب دودية في الصخور. تستلزم عملية التحميض حقن الحمض في حفرة البئر للتخفيف من أضرار الطبقة. ومع ذلك فإن سوائل التحميض التقليدية، التي تستخدم لتحفيز خزانات الكربونات، لها بعض القيود بما في ذلك قوة الحمض العالية والتفاعل السريع مع الرواسب والشوائب دقيقة الحجم والقريبة من حفرة البئر. بالإضافة إلى ذلك، من المرجح أن هذه السوائل تسبب تآكلاً في الأنابيب والغلاف ومعدات قاع البئر عند درجات الحرارة المرتفعة. للتغلب على القيود للأحماض التقليدية، تم تطوير أنظمة الأحماض المستحلبة (EAS). حيث يوفر نظام الحمض المستحلب (EAS) معدلات تفاعل منخفضة أو متأخرة للحمض بسبب الطور الخارجي للزيت، وهذا يساعد على تكوين ثقب دودية أعمق وأضيق في الطبقة. ومع ذلك، لا تزال هناك بعض العيوب لإستخدام أنظمة الأحماض المستحلبة، مثل انخفاض الاستقرار عند درجات المرتفعة، وكذلك للزوجة العالية التي تقيد معدل الضخ بسبب الاحتكاك، واحتمال تضرر الطبقة، وصعوبة تحقيق خلط متجانس على الحقل. تمنع أنظمة الأحماض المستحلبة (EAS) شائعة الاستخدام الحقن أو الضخ بمعدلات تدفق أعلى من 20 برميل في الدقيقة وتحد من عمق الأختراق في الطبقة أو الأنظمة المكسورة. تاريخياً، لا يوجد حل بسيط لهذه المشكلة، حيث تتم المعالجة فقط بتصميم الحمض المستحلب ووضعها بالسرعة والعمق الذي يسمح به الاحتكاك. ولذلك، فإن تقليل الاحتكاك أو السحب لأنظمة الأحماض المستحلبة من شأنه أن يسمح بمعدلات ضخ أعلى. يهدف نظام الحمض المستحلب (EAS) إلى أن يكون مستقراً حرارياً وقوياً من حيث إجراءات الخطأ الحقلية. لذا فإن الهدف من هذه الدراسة هو تطوير نظام حمض مستحلب ميثبط هندسياً ذو لزوجة منخفضة من خلال تطوير خلطات حمض الهيدروليك المستحلب الفعالة التي يمكن تسليمها في الحقل دون تكبد خسائر احتكاك عالية تقيد تطبيقها. تم استخدام تقنيتين مختلفتين لتحقيق الهدف من هذه الدراسة. التقنية الأولى عن طريق إضافة المواد النانوية دقيقة الحجم (NM)، وهي عبارة عن نقاط نانوية كربونية دقيقة الحجم (CNDs) إلى الصيغة التجارية من نظام الحمض المستحلب (EAS). أما التقنية الثانية هي عن طريق تطوير نظام حلب مستحلب جديد (Pickering EAS) باستخدام الطين العضوي (OC) كمستحلب. أظهرت النتائج أن إضافة النقاط النانوكربونية (CNDs) إلى تركيبة نظام الحمض المستحلب (EAS) التجارية يقلل من اللزوجة وكذلك السحب في الأنابيب دون التأثير على خواص التوصيلية والثبات الحراري. ولذلك تعمل النقاط النانوكربونية (CNDs) كمخفضات لزوجة وكذلك كعوامل تقليل السحب (DRAS) لنظام الحمض المستحلب (EAS). كما أظهرت النتائج أيضاً أن (Pickering EAS) لديه سحب أقل مقارنة ب نظام الحمض المستحلب العادي (مع الفاعل السطحي كمستحلب) حتى بعد إضافة النقاط النانوكربونية كعوامل تقليل السحب لنظام الحمض المستحلب العادي (EAS).

CHAPTER 1

INTRODUCTION

Well stimulation is defined as the treatment that is used to restore or improve the productivity of oil and gas wells after formation damage caused by drilling, workover, and completion operations, where removal of the damage leads to an increase the permeability. Well stimulation can be performed by two main techniques: matrix acidizing and hydraulic fracturing. The matrix acidizing technique is carried out with a pressure lower than the fracture pressure of the reservoir, while in the case of hydraulic fracturing, the process is conducted at a pressure higher than the formation pressure. Acid systems are commonly used in the petroleum industry to stimulate carbonate reservoirs by removing the formation damage and increasing the productivity of oil and gas wells. However, managing the conventional delivery of acid deep into the reservoir while maintaining a minimum rock face dissolution is one of the critical problems in carbonate acidizing treatments. Additionally, conventional acidizing fluids are limited to some constraints such as high acid strength and rapid reaction with scale and fines near the wellbore area. Furthermore, at high temperatures, they tend to corrode tubing, casing, and downhole equipment. The EAS has become widely used in the oil and gas industry to overcome the flaws of conventional acid systems. EAS is usually formed with acid and diesel, and the diesel acts as a diffusion barrier between the acid and the rock (Fatah and Nasr-El-Din, 2010, 2008). The EAS is a water-in-oil (W/O) emulsion, in which the acid phase is encapsulated by the

diesel phase using an emulsifier (Kasza et al., 2006; Nasr-El-Din et al., 2008; Sidaoui and Sultan, 2016). The EAS thermal stability is affected by acid and emulsifier concentrations, acid and oil phase types, additives, and methods of preparation (Pandya et al., 2012; Pandya and Wadekar, 2013; Sabhapondit et al., 2012; Sidaoui et al., 2017; Wadekar and Pandya, 2014). The EAS has been considered a non-Newtonian shear-thinning fluid as the apparent viscosity is sensitive to shear changes. So the power-law model can be used to represent the EAS, where the viscosity decreases with an increase in the shear rate (Lynn and Nasr-El-Din, 2001; Nasr-El-Din et al., 2000). Many researchers conducted several studies to investigate using the EAS to stimulate the carbonate reservoirs (Al-Mutairi et al., 2008; Buijse and Van Domelen, 2000; Crowe et al., 1990; Navarrete et al., 2000, 1999; Nierode and Kruk, 1973; Siddiqui et al., 2006; K. C. Taylor et al., 2006). However, the EAS is still limited by other constraints such as low stability at high temperatures, high viscosity that restricts the pumping rate due to frictional losses, the potential for formation damage, and the difficulty of achieving homogeneous field-scale mixing. In addition, the currently used emulsified acid fluid systems hinder injection or pumping at high rates and limit the placement (depth of penetration) in the matrix or fractured system. Historically, there is no simple solution to this problem; emulsified acid treatment design only aims at placing the acid as fast, and deep as the friction allows. Therefore, having lower friction characteristics would enable higher pumping rates. The EAS has to be design with a primary focus on achieving thermal stability and robustness concerning the field mixing process.

This study aims to implement an engineered retarded, low-viscosity acid system by formulating highly efficient emulsified HCl acid blends that can be field-delivered without experiencing excessive frictional losses, which limits their applicability.

To achieve the goals of this study, two distinct methodologies were employed. Firstly, nanomaterials (NM), specifically carbon nanodots (CNDs), were utilized as viscosity-reducers and drag-reducing agents (DRAs) by incorporating them into the commercial formulation of EAS (normal EAS, which was developed by using surfactant as emulsifier). The second method involved developing a new Pickering EAS utilizing organoclay (OC) as an emulsifier. OC is defined as an organic phyllosilicate (disilicate) derived from naturally occurring clay mineral.. OC serves as both an emulsifier for preparing Pickering emulsion and a drag-reducing agent (DRA). In addition, OC offers advantages such as low cost, availability, high surface area, and environmental friendliness. This study investigates various types of OC as an emulsifier to develop a Pickering emulsified HCl system for carbonate reservoir stimulation.

1.1 Emulsions

An emulsion consists of two immiscible liquids, with one of the liquids dispersed (internal phase) into another (external phase) through the use of an emulsifier (Adewunmi et al., 2022; Israelachvili, 1994). Emulsions can be classified based on their droplet size into macroemulsions, wherein their size ranges from 0.1 to 5 μm , nanoemulsions, wherein the size ranges from 20 to 100 nm, and micellar emulsions or microemulsions, wherein the size ranges from 5 to 50 nm (Drioli, E., & Giorno, 2016). Also, emulsions can be classified based on the shape of the droplet size to monodisperse systems, which have uniform droplet size, and polydisperse emulsions, which have a wide statistical variation of droplet size (Mollet and Grubenmann, 2008; Piacentini, 2020). Another classification of emulsions is presented by (Raya et al., 2020), wherein emulsions are classified into tight emulsions,

which have very small and densely packed dispersed droplets, and loose emulsions, which have large droplets. Emulsions can be classified into four types water-in-oil (W/O), oil-in-water (O/W), water-in-oil-in-water (W/O/W), and oil-in-water-in-oil (O/W/O). However, the W/O emulsion is the most common one in the petroleum industry. Emerging emulsion processing methods such as microfluidic emulsification can be used to control and manipulate the number, and size distribution of internal droplets in multiple emulsions (Pal, 2011). According to (Tadros, 2013), macroemulsions are thermodynamically unstable and they tend to coalesce due to decreased interfacial energy, and this instability becomes more evident over time, while microemulsions are thermodynamically stable.

A Pickering emulsion is characterized as an emulsion controlled and stabilized by solid particles like silica and clay. These particles adsorb at the interface between the two phases. Extensive utility of the Pickering emulsions in the petroleum industry due to their improved thermal stability. The wettability of solid particles, at the interface between the oil and water phases, is used to determine whether the emulsion is W/O or O/W. In the case of Pickering emulsion, the liquid phase with a lower wettability tendency for solid particles assumes the role of the dispersed phase, while the liquid phase that exhibits superior wetting properties becomes the continuous phase. Pickering emulsions are renowned for their biocompatibility and environmentally friendly attributes, and they exhibit remarkable resistance to coalescence (Tang et al., 2018). Furthermore, the ionic strength significantly affects the stability of Pickering emulsions.

1.2 Drag-reducing agents (DRAs)

One of the major challenges of the flow of petroleum production systems is the drag or frictional loss, which significantly impacts flow capacity and pumping rates. The high-pressure drop during flowing conditions requires higher energy which means high cost, and thus reducing this drag leads to a reduction in the cost and saves the energy. Drag reduction is essential to increase the flow capacity and pumping rates, and drag-reducing agents (DRAs) are usually added to the fluids to reduce the drag. Drag-reducing agents (DRAs) are substances incorporated into fluids to minimize drag along the pipe wall. DRAs can be categorized into four main groups: polymers, solid particle suspensions, biological additives, and surfactants. The agents are made of polymers with high molecular weight or micellar systems, where polymers help to reduce turbulence in the pipelines which leads to a reduction of the drag in pipes, and this helps in pumping the fluid at lower pressures which leads to energy savings. DRAs are commonly used in the petroleum industry. The DRAs improve the flow capacity and help in reducing the power consumption of pumps. This feature of a DRA is vital for increasing the pump capacity and piping capacity by maintaining constant pressure drop without any changes in the pipeline conditions. The application of DRAs in the transportation of crude oil received great attention, and several studies have been conducted (Burger et al., 1982; Motier et al., 1996; Zakin et al., 1998).

The recent development of unconventional hydrocarbon exploitation has expanded the application of DRAs. Hydraulic fracturing has become an integral part of unconventional hydrocarbon production, requiring the pumping of water at a high injection rate and pressure. To achieve this high injection rate, DRAs are introduced into the water used for

hydraulic fracturing. In addition to their use in oil transportation and water injection, DRAs are gaining traction in other areas such as enhanced oil recovery (EOR) and stimulation treatments.

The co-existence of oil and water in the reservoir leads to the formation of emulsion in the petroleum production system. Emulsions, by nature, have higher viscosity compared to the individual oil and water phases. The transportation of emulsion with minimum energy consumption necessitates the use of DRAs. Conversely, certain applications, like the use of emulsified systems in EOR or stimulation, highlight another key application of DRAs in the petroleum industry.

In summary, DRAs exhibit wide applicability in different areas of the petroleum industry. Each petroleum application requires specific characteristics of the DRA. The selection, formulation, and features of DRAs are dictated by the application's requirements. For water injection and fracturing, it is necessary for DRAs to be soluble in water. Conversely, for the transportation of crude oil, DRAs need to be soluble in the oleic phase. Other applications, such as emulsion for stimulation, may require DRAs to be water-soluble or oil-soluble based on the external (continuous) phase of the emulsion. OC can be utilized as DRA for emulsion (Al-yaari et al., 2014). In this study, Carbon nanodots (CNDs) will be utilized as DRA for EAS, and OC, which can work as an emulsifier and DRA, will be utilized as an emulsifier to prepare Pickering EAS. The work of this study will be presented with details in the following chapters:

Chapter 2- A Review of Drag-Reducing Agents (DRAs) in Petroleum Industry: This paper was published in Arabian Journal for Science and Engineering.

Chapter 3- Novel Environmentally Friendly Nanomaterials for Drag Reduction of Emulsified Acid System (EAS): This paper was published in ACS Omega Journal.

Chapter 4- Development of Emulsified Acid System (EAS) Using Organoclays (OC): Rheology and Implication to the Acidizing: This paper was published in Geoenergy Science and Engineering Journal.

Chapter 5- Pickering Emulsified Acid Systems (PEAS): A Promising Approach for Reduced Drag in Matrix Acidizing: This paper was submitted to the Geoenergy Science and Engineering Journal.

CHAPTER 2

A REVIEW OF DRAG-REDUCING AGENTS (DRAS) IN PETROLEUM INDUSTRY

This paper was published in Arabian Journal for Science and Engineering:

AL-Dogail, A., Gajbhiye, R., & Patil, S. (2023). A Review of Drag-Reducing Agents (DRAs) in Petroleum Industry. *Arabian Journal for Science and Engineering*, 48(7), 8287-8305.

2.1 Abstract

Increasing the flow capacity and pumping rates is challenging in petroleum production systems due to drag or frictional losses. Drag-reducing agents (DRAs) are usually added to the fluid to reduce the drag and improve the flowing capacity or pumping rates of the fluid required for achieving the targeted flow rate or enhancing transportation efficiency. The wide variation in the oilfield systems demands distinguishing features of DRA to meet the specific requirements of the DRA relevant to the oilfield applications. The selection of DRA suitable for the oilfield systems influences the type and formulation of DRA. Oil and gas transportation in the pipeline requires oil-soluble DRA; on the other hand, injection of water requires water-soluble DRA. The requirement of an oilfield system dictates the basic characteristics of the DRA, such as polymer DRA, which can be used for the transportation of oil and gas; however, the surfactant is preferable for other systems such as drilling and fracturing applications. Also, the recent development in nanotechnology has opened a

pathway for the development of DRA for wide application in oilfield systems. This study presents a review of the published work on DRA applications in the petroleum industry. The methodology and research approaches of drag reduction relevant to oilfield systems are described and analyzed. The experimental work and case studies are also discussed while identifying the research gaps and the recommendations for research approaches and potential areas that need further investigation are highlighted in this study.

2.2 Introduction

In the petroleum industry, economic aspects are very important and usually are considered to achieve the required objective with low cost and energy. One of the major challenges of the flow of petroleum production systems is the drag or frictional loss which affects flow capacity and pumping rates. The high-pressure drop during flowing conditions requires higher energy which means high cost, and thus reducing this drag leads to minimizing the cost and energy. Drag reduction is required to increase the flow capacity and pumping rate, and drag-reducing agents (DRAs) are usually added to the fluids to reduce the drag. DRAs are defined as additives that are added to the fluids to reduce the drag on the pipe wall. DRAs can be divided into four main groups which are polymers, solid particle suspensions, biological additives, and surfactants. The agents are made of polymers with high molecular weight or micellar systems, where polymers help to decrease turbulence in the pipelines which leads to reducing the drag, and this helps in pumping the fluid at lower pressures which saves the cost and energy.

DRAs are commonly used in many oilfield applications. The oil and gas industry is one of the largest consumers of DRAs. The DRAs are introduced in different fluid systems such

as water, crude oil, refinery products, heavy oil, multiphase liquid, and chemicals as well as in drilling and fracturing fluids. The DRAs improve the flow capacity and help in reducing the power consumption of pumps. This feature of a DRA is vital for increasing the pump capacity and piping capacity by maintaining constant pressure drop without any changes in pipeline conditions.

The application of DRAs in the transportation of crude oil received great attention, and many studies were published in the literature (Burger et al., 1982; Motier et al., 1996; Zakin et al., 1998). Realizing the potential of the DRA has widened its application in other fields such as medical, chemical, refinery, and slurry transportation, as well as in the petroleum industry. Although transportation of the crude oil is an integral part of the petroleum industry, the drag-reducing agents find a place for usage in other areas of the petroleum industry.

The DRAs are also utilized for drag reduction in water injection wells. It plays a very important role in water injection when the maximum allowable operating pressure is a limiting parameter; moreover, it helps when pressure expected at the outlet of the injection well is vital for repressurizing the reservoir. DRAs (friction reducers) are one of the essential components of the drilling fluid system. The drag reduction induced by DRA makes it possible to inject the drilling fluid at the high injection rate required for efficient hole cleaning with limited pump capacity. It also helps in maintaining the pumping equipment and flowlines associated with it. The DRAs are also introduced in the fluids used for the enhanced oil recovery methods; it improves the injectivity of fluid in the formation considering the pressure constraints from the surface facilities.

In addition, the DRAs are used in the multiphase flow which is very common in the petroleum industry. The recent development of unconventional hydrocarbon exploitation brought the additional application of the DRA. Hydraulic fracturing became an integral part of unconventional hydrocarbon production. It is essential to pump the water at a high injection rate and pressure for hydraulic fracturing. To achieve a high injection rate, DRAs are introduced into the water used for hydraulic fracturing. In addition to the use of the DRA in oil transportation and water injection, the emulsion is attracting the use of the DRA in other areas such as EOR and stimulation treatments. The co-existence of oil and water in the reservoir leads to the formation of emulsion in the petroleum production system. The emulsion by nature has high viscosity compared to the individual oil and water phase. The transportation of emulsion with minimum energy leads to the usage of drag-reducing agents. In contrast, some applications such as the use of the emulsified system in enhanced oil recovery or stimulation bring forward another key application of DRA in the petroleum industry.

It can be summarized that the DRA has wide applicability in the different areas of the petroleum industry. Each petroleum application requires specific characteristics of the DRA. The selection, formulation, and features of DRA are governed by the application, and DRA is required to be developed meeting the criteria of its application for water injection and fracturing it is necessary to have DRA be soluble in water, while for the transportation of crude oil it requires to be soluble in the oleic phase. On the other hand, other applications such as emulsion for stimulation may need the DRA to be oil or water-soluble based on the external phase of the emulsion. Among the review studies on drag reduction and DRA published in the literature include a review of studies on drag reduction

with DRA by (Manfield et al., 1999), drag reduction with polymers in gas-liquid/liquid-liquid flows in pipes (Al-Sarkhi, 2010), and non-additive drag reduction by (Abdulbari et al., 2014). Earlier work on heat transfer and the role of DRA in heat transfer is well documented by (Hartnett, J. P., & Kwack, 1986; Kostic, 1994). A review of heat transfer techniques presented by (Dewan et al., 2004; Wang et al., 2011), skin friction drag reduction within the turbulent boundary layer by (Ghanadi et al., 2012), drag reduction by riblets and micro-textures in the turbulent boundary layers by (Saravi, S. S., & Cheng, 2013; West et al., 2018), and turbulent near-wall layers (Ricco et al., 2021). It should be noted that these studies address the drag reduction relevant to the aerodynamic systems.

In addition, the review of DRA such as polymer and surfactant is presented by (Abdulbari et al., 2014; Abubakar et al., 2014a; Asidin et al., 2019; Benzi, 2010; Gu et al., 2020; Perlin et al., 2016; Tiong, A. N. T., Kumar, P., & Saptoro, 2015; Xi, 2019). The applications, mechanisms, and prediction of drag reduction in flow are presented by (Al-Yaari et al., 2012; Brostow, 2008; Nesyn et al., 2018; Soares, 2020). Apart from the drag reduction in the straight pipeline or DRA type, there are reviews of the studies on the geometry of the pipe especially (Fsadni et al., 2016) followed by (Ayegba et al., 2021). A study by (Jubran et al., 2005) reviewed the research on drag reduction in single and multiphase flows in pipes. A summary of the review articles on drag reduction and DRA is shown in Table 1. It appears that there are several studies reviewing the various aspects of drag reduction and DRA application available in the literature. The list of studies addressing the use of DRA in hydraulic fracturing and drilling industry is shown in Tables 2 and 3, respectively. It appears that review studies are inadequate on drag reduction and DRA usage addressing the various applications of the petroleum industry. It perpetuates the need to review the

studies of DRA applicable to the petroleum industry. The objective of this paper is to review the studies on DRA relevant to the petroleum field applications and address the further development and possible research areas of DRA. In addition, this study also provides a detailed analysis of the experiments performed to evaluate the application of DRA and understand the mechanism of DRA. Finally, research gaps are identified and recommendations for further studies on the DRA are presented.

Table 1 List of DRA/drag reduction review papers

Reference	Paper title
(Jubran et al., 2005)	Drag-reducing agents in multiphase flow pipelines: Recent trends and future needs
(Al-Sarkhi, 2010)	Drag reduction with polymers in gas-liquid/liquid-liquid flows in pipes: A literature review
(Wang et al., 2011)	Review on drag reduction and its heat transfer by additives
(Abdulbari et al., 2013)	Going against the flow—A review of non-additive means of drag reduction
(Abdulbari et al., 2014)	Bio-polymers for improving liquid flow in pipelines—A review and future work opportunities
(Abubakar et al., 2014b)	Roles of drag-reducing polymers in single-and multi-phase flows
(Ivchenko et al., 2016)	Polyolefin drag-reducing agents (Review)
(S. Q. Liu et al., 2017; Z. Y. Liu et al., 2017)	Review of mechanical degradation and de-aggregation of drag-reducing polymers in turbulent flows
(Yunqing et al., 2017)	Analysis of drag reduction methods and mechanisms of turbulent
(Han and Choi, 2017)	Role of bio-based polymers on improving turbulent flow characteristics: Materials and application
(Han et al., 2017)	Applications of water-soluble polymers in turbulent drag reduction

(Nesyn et al., 2018)	Drag reduction in transportation of hydrocarbon liquids: From fundamentals to engineering applications
(Asidin et al., 2019)	Review of the applications and developments of drag-reducing polymer in turbulent pipe flow
(Ibrahim et al., 2019)	An overview of the most effective DRAs in crude oil pipelines
(Yang et al., 2019)	Review of friction reducers used in slickwater fracturing fluids for shale gas reservoirs
(Guo et al., 2019)	Advances in the application of biomimetic surface engineering in the oil and gas industry
(Gu et al., 2020)	Research progress on the collaborative drag reduction effect of polymers and surfactants
(Soares, 2020)	Review of mechanical degradation and de-aggregation of drag-reducing polymers in turbulent flows
(Yu et al., 2020)	Bio-inspired drag reduction: From natural organisms to artificial functional
(Souas et al., 2021)	A review on the rheology of heavy crude oil for pipeline transportation
(Ayegba et al., 2021)	Drag reduction by additives in curved pipes for single-phase liquid and two-phase flows: A review
(Utomo et al., 2021)	Drag reduction using additives in smooth circular pipes based on an experimental approach

Table 2 Application DRA/drag reduction in hydraulic fracturing

Reference	Remark
(Holtsclaw and Funkhouser, 2010)	A cross-link synthetic-polymer system for high-temperature hydraulic-fracturing applications
(Fichter et al., 2010; Ibrahim et al., 2018, 2016; Luca Gandossi, 2013; Van Domelen et al., 2017)	Use of slickwater in hydraulic fracturing to improve permeability and increase oil recovery

(Laurain, 2014)	Drag-reducing agents (DRAs) or drag-reducing polymers (DRPs) are extensively used to enhance the performance of hydraulic fracturing fluids by reducing the pressure drop
(Al-Muntasheri, 2014)	A critical review of hydraulic fracturing fluids over the last decade
(Le Brun et al., 2016)	Investigated the use of DRA for increasing injection rates. Investigated the effect of three DRA types of poly (acrylamide-co- NaAMPS) and pure PHPAAM. The drag reduction and shear stability of improved acrylamide copolymers enhanced hydraulic fracturing
(Motiee et al., 2016)	High-concentration polyacrylamide-based friction reducer used as a direct substitute for guar-based borate cross-linked fluid in fracturing operations
(Sanders et al., 2016)	Dry polyacrylamide friction reducer
(S. Q. Liu et al., 2017; Z. Y. Liu et al., 2017)	Studied the effect of the microstructure of DRA on slickwater fracturing fluid. The results explained that the viscoelasticity of slickwater is governed by the drag reducer microstructure and the viscoelasticity of the drag reducer plays an important role in the drag reduction performance
(Van Domelen et al., 2017)	Applications of viscosity-building friction reducers as fracturing fluids
(Ibrahim et al., 2018)	Developed a non-damaging FR that replaced the linear gel with an enhanced proppant-carrying capacity and reduced the potential for formation damage. The efficiency of the developed FR was compared with two conventional FRs, a salt-tolerant polymer, and a guar-based polymer
(Zhang et al., 2019)	Proposed a new type of polymer (MAS-1), which was prepared by copolymerizing acrylamide (AM), acrylic acid (AA), and 4-isopropenyl carbamoyl-benzene sulfonic acid (AMBS). The results showed that the drag reduction rate of MAS-1 was always higher than KYPAM-6A and HPAM with a shear rate ranging from 1000 1/s to 7000 1/s, which led to a reduction of the pump pressure and improved the performance of fracking
(Zhang et al., 2019)	Multifunctional viscous drag reducer optimization for unconventional hydrocarbon reservoir. The proposed a less-damaging friction reducer (FR). The molecular dynamic simulation was used to investigate the effect of encountered salts during fracturing treatment on polyacrylamide-based FRs (PAM and HPAM), also conducted some field cases, and the results showed that the proposed less-damaging FR had less formation damage compared to conventional FRs, also the proposed FR had a negligible reaction with selected salts
(An et al., 2020)	Studied the impact of slickwater fracturing fluid on the frictional properties of shale reservoir rocks with different

	carbonate contents recovered from the Longmaxi Formation in the Sichuan Basin of China. Two samples of produced water, DI water, and acidic slickwater were used to probe the chemical effects of fracturing fluids. The findings showed that the frictional properties of shale gouges were affected by slickwater, and the acidic slickwater dissolved carbonates from shale gouges
(Zhang et al., 2021)	Investigated the effect of multifunctional viscous drag reducer parameters. The four additives were the conventional polyacrylamide friction reducer EM30S, bioglue, thickener CH-1, and high-viscosity friction reducer HVFR-1. The results showed that the high-viscosity slickwater system composed of CND + HVFR-1 was more suitable for hydraulic fracturing of tight oil and gas reservoirs, and it achieved a friction reduction rate of more than 60% for unconventional oil and gas

Table 3 Application DRA/drag reduction in drilling

Reference	Remark
(Newman et al., 2007)	Investigated friction reduction for microhole CT drilling. The data indicated that as long as the axial force on the CT was less than the helical buckling load, axial vibration of the CT was effective at mitigating friction
(Zhang et al., 2012)	Presented effective lubricant which is soluble in brines and acts to reduce metal-to-metal friction. Also presented is a drag reducer that effectively reduces the hydraulic friction of completion fluids including both low and high-density applications for both monovalent and divalent brines
(Sönmez et al., 2013)	Performance analysis of drilling fluid lubricants as friction reducers in the wellbore was carried out. The effect of lubricants on mud properties (rheology, calcium, salt, pH, and mud density) was examined. None of the lubricants have significant problems
(Jahns, 2014)	Investigated the use of nanoparticles in drilling fluids, especially WBM, for reducing the generated mechanical friction between the drill string and casing. The alumina particles have a limited friction reduction, in consequence of an increasing friction factor with increasing particle concentration in the fluid
(S. Q. Liu et al., 2017; Z. Y. Liu et al., 2017)	Examined the potential improvement of the lubricating properties of drilling fluid by adding graphene and graphene oxide (GO). Results indicated that the lubricating properties of drilling fluid significantly improved by adding an appropriate amount of GO materials, while, on the other hand, the addition

	of graphene had a limited effect on the lubricating properties of drilling fluid
(Yan et al., 2018)	Experimental investigation of drilling fluids on friction coefficient of brittle gas shale at in situ temperatures. Results show that the friction coefficient decreases, induced by infiltration of drilling fluids filtrate, and the friction coefficient is more sensitive to oil-based drilling fluid filtrate than water-based. As a result of rock, strength decreasing after immersion into drilling fluids filtrate, asperities on fracture surfaces were prone to shear failure in the process of frictional sliding, and their failure products migrated with the fracture surface movement
(Adesina et al., 2018)	The experimental work was carried out on a pre-conditioned base fluid (ethylene glycol and ethanol) with silicon-oxide powder as a nanofluid to investigate the nanofluid effect on lubricity enhancement in the oil-based mud. The lubricity reduction effect observed in pre-conditioned oil-based mud can be said to be a result of the combined effect of both the nanoparticles and the based fluid
(Rafati et al., 2018)	A critical review of the application of nanoparticles in drilling fluids is presented. Wellbore stability and friction coefficient can be changed favorably using nanoparticles
(Alwasitti et al., 2019)	The enhancement of the lubrication behavior of a KCl polymer mud is fundamentally examined by adding different amounts of xanthan gum nanoparticles (XC polymer nanoparticles (NPs)), barite NPs, and lignite NPs. The coefficient of friction reduction percentage is increased with increasing nanomaterial weight, and the maximum value of the coefficient of friction reduction (more than 60%) is attained by adding 4 gm XC polymer NPs

2.3 Development of drag-reducing agents (DRAs)

The use of DRA was initiated with the sole purpose of transporting the fluids most efficiently. The transportation of fluids through the pipeline was the most common way adopted by many industries such as agriculture, chemical, flood water disposal, sewage, firefighting, mineral and mining, and aviation industries. The initial effort was made on the drag reduction to reduce the friction pressure losses due to turbulent flow (Brautlecht and Sethi, 1933; Brecht, 1935; Forrest, F., & Grierson, 1931). It involves the use of polymer

surfactant agents, bio-biopolymers, and fibers mixed to help achieve a reduction in turbulence and thus achieve the reduction in friction drop. It was followed by the research work (Tomas, 1948) developing a polymer for drag reduction in the Newtonian flow. After the use of the DRA in the Newtonian fluid, it was tested for the non-Newtonian flow. It was started by the use of sodium carboxymethyl cellulose as a bio-polymer as DRA. Further investigation on the use of surfactants and polymers as drag-reducing agents was carried out as they behave as a viscoelastic fluid (Metzner and Park, 1964; M. D. Warholic et al., 1999; M. D. Warholic et al., 1999). The reduction in turbulence is influenced by the ratio of viscous to elastic forces due to the surfactant-polymer substances. It was followed by further development of the DRAs introduced (Utomo et al., 2021) in Table 4. However, the most important sector for the DRA application appears to be the oil and gas industry. The oil and gas industry has one of the largest networks of the pipeline which is used for the transportation of single and multiphase fluids varying in physical and chemical properties as well as dimension and geometry of the pipeline. The sole purpose of the initial research on drag reduction was to reduce the power consumption or the energy loss for the transportation of crude oil through the pipeline. The trans-Alaska pipeline is one of the most phenomenal examples of the use of DRA for the drag reduction of crude oil transportation. A high molecular weight polymer with a low concentration of 1 ppm was applied downstream of the pumping section. The application of DRA was successful and promised to increase the throughput by up to 30% (Burger et al., 1982). Further application of polymer DRA in the transportation of crude oil was successful in a crude oil pipeline in Mumbai (offshore)-India, Iran-Turkey, Australia, and in the North Sea offshore pipeline. One of the challenges of the DRA application is to design a polymer suitable for the

intended hydrocarbon system (Motier et al., 1996; Nijs, 1995; Wang et al., 2011). Fluid transportation through the pipeline is an integral part of the petroleum industry, starting from the drilling to the delivery of the petroleum product to the consumer is carried out through the pipeline. The fluid from the reservoir is transported from the wellbore to the surface, the surface to the facility, and the facility to the refineries requires a pipeline. It is not only required during production but also for the injection of the fluid in the reservoir for various operations such as drilling, cementing, stimulation, fracturing, waterflooding, enhanced oil recovery, and other operations. Undoubtedly, different systems are associated with different geometries such as vertical tubing for drilling and production, and horizontal and inclined pipes with different geometries and dimensions for the transportation of fluid from the wellbore to the facility and refineries. In the plants, the fluid has to be transported through different configurations such as bends, elbows, variable cross sections, and more recently through the coil tubing units (Burger et al., 1982; Dever et al., 1962; Ercan and Ozbayoglu, 2009; Fink, 2020; Huang and Crews, 2007; Lindsay et al., 2011; Ousterhout, R. S., & Hall, 1961).

Table 4 Different review papers covering drag-reducing additives (Utomo et al., 2021)

Reference	Additive drag reduction techniques
(Lumley, 1969)	Polymer and solvent additions
(Patterson, 1969)	Polymer solutions, soap solutions, solid particle suspensions
(Hoyt, 1972)	Straight pipeline
(Virk, 1975)	Polymer additive, rotating disk, straight pipeline, flat plate
(White, A.; Hemmings, 1976)	Polymer additions, straight pipeline
(Shenoy, 1984)	Polymer additions, straight pipeline

(Berman, 1978)	Polymer additives, solid suspension solutions, biological
(Hoyt, 1986)	Additives, surfactant solutions, micellar system, polymeric system
(Zakin et al., 1998)	Anionic soap solution, nonionic solutions, zwitterionic surfactant solution, cationic surfactant solution, straight pipeline
(Nadolink and Haigh, 1995)	Bibliography of polymer additions, pipes/tubes, ducts, channels, flat plates, asymmetrical, axisymmetric bodies
(Manfield et al., 1999)	Surfactant additions, straight pipeline
(Graham, 2004)	Dilute polymer solutions, FENE spring model, spatial discretization
(White and Mungal, 2008)	Polymer solutions, straight pipeline, channels
(Al-Sarkhi, 2012)	Polymer injection, straight pipeline
(Wang et al., 2011)	Fiber suspensions, polymer solutions, surfactant solutions, straight pipeline
(Abdulbari et al., 2014)	Bio-polymer solutions, polymer injection
(Nesyn et al., 2018)	Polymer injection, rotating disk, slurry polymerization, surfactant solutions
(Xi, 2019)	FENE-P, Oldroyd-B, Giesekus models, polymer solutions Polymer solutions
(Soares, 2020)	Polymer solutions
(Ayegba et al., 2021)	Polymer solutions, curved pipes, coiled pipes, ionic surfactants, nonionic surfactants

2.4 Application of DRA in crude oil transportation

Although the DRA can be used in different systems, the most relevant application is the transportation of hydrocarbons through the pipeline. The hydrocarbon transportation in the pipeline can take place in the form of single-phase oil, single-phase gas, or multiphase in

which oil and gas mixture flows through the pipeline. Also, water production is associated with hydrocarbon production generating a multiphase mixture of oil and water or a three-phase mixture of oil, water, and gas. Also, waterflooding became a common practice of secondary recovery technique which requires a pipeline for injection of water from the facility to the well. In addition to the water sometimes surfactants, polymers, or chemicals are added to achieve the specific physical and chemical composition of water. All these applications involve the transportation of oil, water, and gas in the form of either single-phase or multiphase flow through the pipeline. These applications make it imperative to identify and investigate the application of DRA in single and multiphase flow. Historically, the main purpose of using the DRA is to reduce the drag in crude oil transportation. Several studies were carried out to investigate the different DRAs that can be used for drag reduction in crude oil transportation. These DRA's are categorized as 1) polymeric, 2) fibers, and 3) surfactants. One of the important criteria for the selection of DRA is its compatibility with crude oil. A comparison of the DRA is shown in Table 5 (Naffa'a, 2019). A study by (Den Toonder et al., 1997) reviewed the studies on DRA and the factors affecting them (Naffa'a, 2019). After identifying the different DRAs for crude oil transportation, the research focus was on improving the applicability of DRA in crude oil transportation. It mainly focused on the degradation of the DRA, as well as the effect of heat and thermal degradation of the DRA. Also, some studies have focused on the understanding of the mechanism of DRA and modeling for the prediction of drag reduction in the pipelines. Several experiments were performed to optimize the DRA concentration for obtaining the desired drag reduction without affecting the operating conditions.

Table 5 DRA comparison (Naffa'a, 2019)

DRA Type	Pros (+)	Cons (-)
Polymeric	Non-toxic and biodegradable (depending on its solubility) Quickbiodegradability for natural-based polymers Low concentration makes a significant difference	Degrades over time Loses effect in some cases (passing a pump or sharp bend due to shearing) High in cost Might be difficult to maintain (must be agitated/stored in a specific temperate) for some types Susceptible to shear degradation
Fibers	Less expensive than surfactants	N/A
Surfactants	For the fluid velocities higher than the critical shear stress (the shear rate at which surfactant micelles disappear) drag reduction is less affected compared to the polymer system When shear stress in the flow decreases to a certain level it regains the drag-reducing capability by restructuring to its original rod-like microstructures	Less drag-reducing capabilities

2.5 Application of DRAs in single/multiphase flow

In the petroleum industry, the multiphase flow of oil and water or oil–water–gas is a common occurrence in pipelines. It is mainly happening on the upstream side of the facility in which water, oil, and gas produced from the reservoir are transported to the production facility for phase separation and treatments. The fluid flows from the bottom of the wellbore to the wellhead and then the wellhead to the surface facility through the flowline has generally contains a mixture of oil, water, and gas. It is very important to design and

operate the pipeline and pumps to meet the production rates and the wellhead and facility constraints. It is also extremely important to operate wells and production facilities by maintaining the pressure drop and minimizing the issues related to flow assurance.

To address the applicability of DRA's for multiphase flow, it is necessary to identify, evaluate, and optimize the DRA in multiphase flow. (Al-Sarkhi and Hanratty, 2001a) experimentally investigated the effect of drag-reducing polymer (DRP) on flow regimes and drag reduction of oil–water flow system in a horizontal pipe. Another study by Al-Sarkhi and Hanratty (Al-Sarkhi and Hanratty, 2001b) investigated the effect of pipe diameter on drag reduction performance in annular as–liquid flow. A copolymer of polyacrylamide and sodium acrylate was used with annular air–water flow in 9.53 cm and 2.54 cm inner diameter (ID) pipes. The findings showed that the reduction of interfacial waves, which induce drop formation and assist the liquid spread around the pipe and annulus, was attributed to the drag reduction. The results also showed when all the liquid was flowing at the bottom of the pipe in a stratified pattern with a relatively smooth interface, the maximum reduction of drag was achieved. A drag reduction of up to 63% was observed in the small pipe while only a 48% drag reduction was noted in the larger pipe. A comprehensive review of the drag reduction in multiphase gas–liquid and liquid–liquid phases has been presented (Al-Sarkhi, 2010).

(Al-Yaari et al., 2009) conducted an experimental investigation of the effect of polymer concentration, polymer molecular weight, and salinity of water on drag reduction for oil–water systems flowing through 2.54 cm horizontal pipes. Their findings showed that drag reduction performance significantly affects flow patterns and drag reduction. In this study, a drag reduction of up to 65% was achieved by adding only a small amount of DRP (10-

15 ppm). Later, the effect of pipe diameter on the DRP performance for oil–water flow in horizontal pipes was investigated by (Al-Wahaibi et al., 2013). In their study, two pipe diameters (2.54 and 1.9 cm) were used to evaluate the effect of pipe diameter on drag reduction. The findings showed that by adding only 10 ppm of DRP, drag reduction increased by 60% and 45% for the pipe diameters of 2.54 cm and 1.9 cm, respectively.

(Singh et al., 2011) presented an experimental study to investigate the drag reduction by different water-soluble polymer solutions in a gravity-driven flow, where the liquid drained from a large cylindrical tank through exit pipes that had diameters of 0.289 cm and 0.4 cm. The polymers used in this study were polyacrylamide and polythene oxide. The experiments were conducted using these polymer solutions for both laminar and turbulent flow regimes through the exit pipe. The results showed that the optimum polyacrylamide concentration for optimal drag reduction was 10 ppm for laminar flow and 5 ppm for turbulent flow, while polythene oxide's optimum concentration was 20 ppm for laminar flow and 40 ppm for turbulent flow. It was also observed that the type of polymer and the type of flow in the exit pipe had an impact on the optimum concentration. The findings also showed that when the flow in the exit pipe was laminar, polyethylene oxide was a better DRA, and polyacrylamide was a better DRA when the flow in the exit pipe was turbulent.

The effect of DRP on flow patterns and drag reduction for oil–water flow in a horizontal pipe was experimentally tested by (Yusuf et al., 2012). An anionic copolymer of high molecular weight (HMW) of NaAMPS/acrylamide (ratio of 40: 60 wt. percent) was used as a DRP in an acrylic pipe of 2.54 cm inside diameter for oil–water flow. The findings indicated that the injected polymer had a significant effect on the flow patterns and their

boundary transitions. With increasing polymer concentration, drag reduction increased and reached the limit at 10 ppm concentration; also, drag reduction increased with an increase in water superficial velocity, while drag reduction decreased with an increase in oil superficial velocity.

(Abdulbari and Nour, 2012) presented an experimental study using the grafted natural polymer as a DRA. The grafted natural polymer was able to enhance the flow in pipelines containing aqueous or hydrocarbon liquids in a turbulent flow. They used Okra (*Abelmoschus esculentus*) mucilage as a DRA in water and gas–oil systems. The drag reduction experiments were performed in a closed flow loop circulation system, which is composed of two pipes with an inner diameter (ID) of 1.27 and 3.81 cm, 4 testing sections of each pipe (50 to 200 cm), tank, pump, and pressure transmitters. The main drag reduction parameters investigated in this study were Reynolds number (Re), additive concentration, and the transported media type (water, gas-oil). The findings showed that adding the grafted natural polymer had a high ability to reduce drag with a maximum drag reduction percentage (DR%) of 60%. Besides, the results showed that increasing the additive quantity increases the drag reduction, and the DR% increased with an increase in Re by using the water-soluble additive while it was decreased by an increase in Re using the oil-soluble additive. The DR% was higher in the pipe of ID 3.81 cm than in ID of 1.27 cm, and the grafted and natural mucilage showed high resistance to shear forces when circulated continuously for 200 s in the closed-loop system.

(Abubakar et al., 2014a) experimentally studied the effects of polymer properties such as molecular weight (MW), charge density, and chemical structure on the drag-reduction in single-phase water flow through a horizontal pipe. They used a 3.06 cm horizontal pipe

diameter with master solutions (1000 ppm) of ten higher molecular weight polymers. The polymers were injected with different flow rates to investigate the effect of polymer concentrations in the range of 2–40 ppm. They concluded that increasing polymer concentration up to 10 ppm increased the drag reduction and above this concentration, it reached a peak value. Also, with increasing molecular weight, the drag reduction at the maximum value increased, and the maximum drag reduction was not influenced by the increase of polymer charge density up to 13%. In other words, drag reduction is dependent on the ability of the polymer to shape and/or its flexibility to form intermolecular connections, which can be enhanced by increasing molecular weight, decreasing charge density, and making smaller side groups in the backbone of the main polymer.

A study conducted by (Al-Sarkhi, 2013) explored the effects of DRPs on stratified and slug flow regimes of a two-phase air–water system flowing in a 2.54-cm-diameter horizontal pipe. They concluded that the reduction of frictional pressure drops by adding DRP was limited to certain operational conditions of stratified flow regime, similarly, adding DRP reduced the slug frequency only at high gas and liquid superficial velocities. Also, they found adding DRP increased the liquid holdup of the two-phase system compared to air–water flow without DRP, this increase in liquid holdup was due to the decreasing of the interfacial friction of the two-phase flow after adding the DRP.

Also, (Abubakar et al., 2014b) presented a comprehensive review discussing the roles of DRP in single- and multiphase flows. They stated that most of the studies have been done on single-phase flow. Some studies investigated drag reduction in gas–liquid flow, and recently, some studies focused on using polymers in liquid–liquid flow.

(Khadom and Abdul-Hadi, 2014) conducted a study to investigate the effect of using polyacrylamide (PAM) as a DRP on Iraqi crude oil flow in pipelines. The parameters explored in this study are the concentration of additive, pipe diameter, the flow rate of the solution, and the presence of radius elbows on the percentage of drag reduction. The maximum reduction of drag was 40.64%, which was achieved at 50 ppm of PAM polymer flowing through a straight pipe diameter of 5.08 cm. To minimize the number of variables, the dimensional analysis was utilized for grouping significant quantities into dimensionless groups. The findings showed a reasonable agreement between the drag reduction observed and the estimated drag reduction with a high correlation coefficient. The findings showed that the PAM polymer was a good and effective drag-reducing agent with Kirkuk oil. The percentage of drag reduction or increased flow increased with increasing solution velocity. Also, the drag reduction percent increased with increasing additive concentration, and the additive had no impact on the physical properties of the crude oil.

(Mucharam et al., 2017) conducted an experimental study to optimize fluid flow in a pipeline and select a drag reducer during oil transportation to increase pipe flow performance. The results of this study showed that increasing DRA concentration led to increasing drag reduction. High molecular weight sulfonate polyacrylamides were used to investigate the drag reduction for oil-water flow in a 3.06 cm horizontal pipe (Eshrati et al., 2015). The investigation was conducted for tap water and oil, where the oil properties were 0.886 gm/cm³ density and 18.6 cP viscosity at 30 °C. The results revealed that the drag reduction was minimal when the polymer concentration was more than 20 ppm. Also, they concluded that oil fraction had an inversely proportional relation to the drag reduction when oil was used as the continuous phase while increasing the mixture velocity led to an

increase in the drag reduction, especially when the polymer concentration is greater than 10 ppm and the mixture velocity is greater than 1 m/s.

(I. Alsurakji et al., 2018) presented a study by using both oil-soluble and water-soluble DRPs in multiphase flow. Effects of polar ZEAG18165 (water-soluble) and oil-soluble nonpolar polyisobutylene (PIB) were investigated as DRPs on pressure gradient and percentage drag reduction in multiphase flow. The findings showed that DRPs delayed the transition from low to high-frequency slug flow and the appearance of annular flow, DRPs reduced drag and pressure gradient for all different fluid phases used in their study.

Another study by (I. H. Alsurakji et al., 2018) experimentally explored the water-soluble DRPs performance in single and stratified wavy two-phase flow regimes in a horizontal pipe using the particle image velocimetry (PIV) technique. Water was used for single-phase flow and air–water was used for two-phase flow experiments. The PIV results were compared with the computational results obtained by FLUENT software. The results showed that with increasing DRP Concentration, drag reduction increased up to 45% in single-phase flow and up to 42% in two-phase flow. Also, they revealed the ability of DRP to change the structure of single-phase turbulent flow and increase the laminar layer near the pipe wall, in addition, the change of wavy stratified flow to smoothed stratified flow was observed.

The effect of using a small amount of DRP on single-phase water flow through 180° bends was investigated by (Ayegba et al., 2019). A partially hydrolyzed polyacrylamide polymer (HPAM) was used in this study, and the findings showed that in both straight pipes and U-bend, drag-reduction increased with increasing polymer concentration till it reached the

optimum concentration, after which any further increase in polymer concentration increased the drag. The results showed that the reduction of drag in straight pipes was higher than that in bends of equivalent length, where DR% was 65% in straight pipes, while 45% and 42% in downflow U-bend and horizontal U-bend, respectively.

(Yuan et al., 2022) presented an experimental study on cationic surfactants in the drag reduction of water injection pipelines. Their results showed that the cetyltrimethylammonium chloride (CTAC) had superior thixotropy. Also, they concluded that CTAC/NaSal (viscoelastic fluid) can be used as a drag reducer to reduce the drag in water injection pipelines, where CTAC/NaSal (sodium salicylate) solution had strong oil resistance and salt tolerance, they had good temperature resistance, that improved with increasing of concentration.

2.6 Application of DRAs in emulsification/mixed solutions

While addressing the multiphase flow through the pipe or application of DRA, it was assumed that the phases are dispersed and the emulsion-forming tendency was ignored. It leads to further areas to be explored in the evaluation of DRA in the emulsified solution. The type and selection of the DRA are governed by the characteristics of the emulsion, the nature of the oleic and aqueous phases, and the type of the emulsion. The effect of DRPs on the surfactant-stabilized emulsion flow of water–oil (W/O) was studied by (Al-Yaari et al., 2013). The effect of the use of oil-soluble polymers and water-soluble polymers as DRA for stable and unstable emulsions of water-in-oil (W/O) and oil-in-water (O/W) was investigated. The experiments of flow and pressure drop were performed in horizontal pipes with two different diameters 2.54 cm and 1.27 cm. The effects of DRP types,

concentration, and molecular weights on emulsion stability, viscosity, and pressure drop were studied. The findings revealed that with the addition of proper DRP, emulsion stability increased significantly and this impact was strengthened with the increase of the molecular size of DRP at ambient temperature. Emulsion stability and the effect of DRP on the stability of the emulsion decreased with increasing temperature. For all stable emulsions tested, injection of the DRP, which is soluble in the outer phase of the emulsion led to pressure drop reduction, and this influence increased with increasing DRP concentration. However, injection of DRP, which is soluble in the internal phase of the emulsion, resulted in less impact on drag reduction for unstable emulsion.

Surfactants and co-surfactants (nanoparticles) are commonly used in O/W emulsions to improve the recovery of heavy oil. A core flooding study conducted by (Pei et al., 2015) showed significant improvement in oil recovery over the surfactant stabilized emulsions, and the recovery reached 40% of the initial oil in place (IOIP) for the oil of 350 mPa viscosity at 50 °C. Also, adding surfactant helped in the emulsification of the heavy oil in the water phase to form an O/W emulsion, which is the displacement mechanism for enhanced recovery of oil by the nanoparticle-surfactant-stabilized emulsion.

The efficiency of using mixed polymer and surfactant solutions as a drag-reduction agent was experimentally investigated (Liu et al., 2018). Mixed cationic surfactant cetyltrimethylammonium chloride (CTAC) and nonionic molecular polymer-polyacrylamide aqueous solutions were used in their study, while sodium salicylate (NaSal) was used as the counter-ion salt. Six different formulations of mixed solution concentrations were used in their experiments with temperatures ranging from 25 °C to 50 °C, and as control couples, pure solutions of surfactant and polymer were used. The mixed

solution curves were divided into three zones of drag reduction which are the enhanced zone, the stable zone, and the destroyed zone. By providing a wider range of Reynolds numbers, the mixed solution system improved the drag reduction efficiency. The findings showed that the mixed solution and pure solution curves varied at low temperatures, whereas all the mixed solution curves were identical to the pure CTAC solution at high temperatures, and the low polymer concentration solution curves almost coincided with pure CTAC solution, while the high polymer concentration solution curves were slightly higher than the pure solutions. The results also showed that the temperature had more impact than concentrations while increasing the temperature to change the structures of the solution was more effective than increasing the structure quantity.

(Sokhal et al., 2019) used gum arabic and guar gum to form W/O emulsion and investigated their stability, and their effect on drag reduction. They concluded that guar gum was more stable than gum Arabic even with less concentration. The optimum concentration at which the maximum drag reduction can be obtained was selected. The maximum drag reduction was 65.9% with a guar gum solution, while only 43.26% was the maximum drag reduction with the gum Arabic solution. The reason behind the better effectiveness of guar gum than gum Arabic could be due to its polymer chain's high stability under turbulent conditions. In addition, guar gum molecules are more rigid than gum arabic.

(Atiqullah et al., 2019) experimentally explored using ultrahigh molecular weight (UHMW) drag-reducing polymers. In particular, they investigated how to enhance DRP catalyst activity and experimentally studied the novel concept underlying the current catalyst system, which involved precatalyst–cocatalyst molecular separation and cocatalyst monophenyl amine association-dissociation phenomena. The results showed that the

developed product, which is easily soluble, tripled the transportation rate for the selected grade of refinery product, which saved around 50% of pumping energy at ppm level DRA concentration.

(Chen et al., 2020) used polyether-based thermoviscosifying polymer (TVP) to improve drag reduction in slickwater hydrofracking. For similar molecular weight, a comparison between TVP and currently used HPAM was performed based on rheological properties and drag reduction. The results revealed that at low concentrations, TVP solutions showed thermos-thickening ability better than HPAM. Also, TVP is much better in reducing the drag with DR% equal to 73.45% compared with 64.29% of HPAM. Besides, at high temperatures, TVP showed a better DR% with 79.77% compared with 70.18% for HPAM.

2.7 Application of nano clay as DRAs in emulsion

Organoclay (nanoclay) is defined as an organically modified phyllosilicate (disilicate). Organoclay (OC) is derived from a clay mineral that occurs naturally. The separation of the layers due to the exchange of ions and the alteration of the chemical character of the surface of the clay allows what is known as nanocomposite to be obtained by in situ polymerization or mixing with certain polymers. Nowadays, OC polymers have widely been used as emulsifiers due to some of the advantages they offer, such as their low cost, availability, high surface area, and being environmentally friendly.

(Al-yaari et al., 2014) presented a study using OC as a DRA of surfactant-stabilized water-in-oil (W/O) emulsions. In their study, they used two different water fractions, 0.7 (concentrated) and 0.3 (diluted), two different diameters of horizontal pipes with (ID) 2.54 cm and 1.27 cm. The findings indicated that adding OC led to a significant reduction in the

viscosity of the emulsion. In the case of concentrated W/O emulsions, a 25% reduction was observed in the pressure drop of emulsion in both horizontal sections when OC was added, while no pressure drop reduction was observed in the laminar flow region for diluted W/O emulsion with 0.3 water fraction.

The effect of Cloisite 20A nano clay particles on the efficiency and stability of W/O emulsions at various temperatures ranging from 25 °C to 45 °C was experimentally investigated by (Khalid et al., 2020). The findings showed that compared to the dispersion without nano clay, the presence of Cloisite 20A stabilized the W/O emulsions, as well as nano clay concentration, affecting the emulsion viscosity depending mainly on the fractions of the water volume. The emulsion viscosity was reduced effectively by a small amount of nano clay, while higher nano clay concentrations contributed to an increase in emulsion viscosity. They concluded that the influence of fluid temperature on the reduction of pressure drops was greater than the effect of nano clay concentration.

2.8 Application of friction reducers in fracturing applications

The recent development of unconventional hydrocarbon resources suggests that it will be the main source of energy in the future. The fracturing process is essential to exploit and sustain production from unconventional resources. As hydraulic fracturing involves the injection of water at high rates, it requires reducing frictional pressure drop to lower the pumping cost as well as performing the fracturing job at given pumping capabilities. Also, it is necessary to have a high viscosity of the fracturing fluid to transport proppant to the fractures. The high viscosity leads to an increase in friction pressure drop and necessitates to use of a friction-reducing agent for efficient fracturing operation. Typical polymeric

DRA's are not suitable due to degradation when exposed to typical conditions of fracturing such as flow rates, pH, and temperature. Also, the breaking of these polymers will reduce the viscosity and will deposit in the subsurface requiring cleaning treatment.

A study by (Kim et al., 2011) investigated the effect of pH in the presence of surfactant on the polymeric DRA. The high efficiency of the DRA is observed at a higher value of pH (pH=11) compared to the low pH environment (pH=4 and 7). The surfactant/solvent system is sensitive to the pH environment. The presence of ionic charges on the surfactant molecule is affected by the pH. Similarly, the biopolymers extracted from the bacteria are very sensitive to the pH environment. The pH of the system will affect the performance of the DRA and should be considered for the selection of the DRA. The incorrect selection of pH may result in an undesired chemical reaction and may not get the desired performance of the DRA; however, few studies were conducted on addressing the pH effect on drag reduction or DRA performance. In addition, the pH significantly alters the performance of nano clay. The presence of surface charge on clay surfaces can significantly alter the performance due to the pH. In drilling, bentonite clays are commonly used as a viscosifier. The bentonite clays can give high viscosity in a high pH environment. Hence, careful selection of the clay type and pH is necessary for its application. Nevertheless, there are many types of clays available; each one has its characteristics governing its application. It opens another area for the development of the DRA for fracturing applications. The nano clay can be a suitable DRA for the fracturing application. The thermal stability, compatibility with water, and economics are advantageous for the use of nano clay as a DRA in fracturing operations.

2.9 Mechanism of DRAs in drag reduction

The mechanism of the DRA in reducing the drag is still not clearly understood. Earlier studies stated that reduction in the turbulence due to the addition of the DRA is responsible for the drag reduction. The turbulence in the pipe is considered the cause of higher friction with the pipe, and hence, reducing the interaction between the pipe and fluid is assumed to be the main mechanism of the drag reduction with DRA. However, a simple experimental facility with pressure drop measurement as a function of velocity and pressure drop may not reveal the mechanism of the DRA. These experiments can be utilized for the selection and optimization of the DRA. Most of the studies have employed this approach for evaluating the performance of DRA. The performance of the DRP is estimated using the drag reduction percentage (DR%) which can be calculated by the following equation:

$$\text{DR}\% = \frac{\Delta P_{\text{without DRP}} - \Delta P_{\text{with DRP}}}{\Delta P_{\text{without DRP}}} \times 100 \quad (1)$$

One of the mechanisms responsible for the DRA is proposed by (Lumley, 1969). According to Lumley, the drag reduction due to the addition of the polymer is caused by the elongation of the polymer molecules which increases the thickness of the viscous sublayer, while (Joseph et al., 1986) and (De Gennes, 1986) stated that drag reduction is caused by the elastic behavior of the polymer.

Further development of the modeling on drag reduction was based on the formulating correlation for the friction factor. In this approach, other variables such as pipe roughness as well as the concentration of the DRA were introduced; however, the mechanism of drag

reduction remains unaddressed. Also, the effect of pipe geometry, curvature, bend, and inclination are not addressed as far as drag reduction is concerned.

2.10 Applications of DRAs in oilfield systems

DRAs are usually added to the oilfield systems to improve the transport of oil and gas through pipelines by increasing the pumping rates and flow capacity of pipelines. Several experimental and numerical studies were conducted to investigate the reduction of drag by adding DRAs. (Tomas, 1948) was the pioneer in using polymers for drag-reduction purposes. The polymers that can reduce drag are called drag-reducing polymers (DRPs). Since then, several studies of using DRA or DRP have been conducted to understand the mechanism of DRPs to reduce the drag, and to investigate and propose commercial and new chemicals for the most efficient use (Otten and Fayed, 1976; Sylvester and Brill, 1976; Thwaites et al., 1976), Warholic et al. (M. D. Warholic et al., 1999; Michael D. Warholic et al., 1999).

One of the most successful applications of DRP was conducted in the trans-Alaska pipeline system by adding 10 ppm of oil-soluble polymers, which greatly improved the pipeline flow rates (Burger et al., 1982). Polyethylene oxide (PEO) was used as DRP in multiphase flow by (Oliver, D. R., & Young Hoon, 1968). (Greskovich and Shrier, 1971) used a DRP with a slug air–water flow system and found a 40% drag reduction when DRP was added. Another study for slug flow was conducted by (Rosehart et al., 1972), and the results showed higher drag reduction compared with single-phase flow, On the contrary, lower drag reduction was presented by (Saether et al., 1989). Significant drag reduction in a flowing fluid was observed when only a small amount of HMW polymers were added

(Yusuf et al., 2012). Later studies discovered that OC could be used as a drag-reducing agent to reduce the pressure drop of emulsion flow in pipes, where adding OC to emulsion leads to a reduction in the viscosity and thus reduction of friction factor (Al-yaari et al., 2014). It seems OC is working effectively as a DRA with low cost compared with other DRAs.

A summary of using DRAs in different applications of the petroleum industry is shown in Table 6, while an example of a drag reduction system is shown in Figures. 1 and 2. Figure 1 shows the drag reduction flow loop system, available at the Research Institute at King Fahd University of Petroleum and Minerals, while Figure. 2 shows a schematic of the flow loop (Khalid et al., 2020). This flow loop consists of two barrels (200 L for each barrel) with a pump for each barrel, a DRP tank with an additive injection reciprocating pump, and two flowmeters connected to the two streamlines. The length of the stainless pipes is 5 m, divided into horizontal and vertical sections, with an outer diameter of 1.27 cm (0.5 inches), and an inner diameter, of 1.016 cm (0.4 inches). Two pressure transducers to measure the pressure difference are located on the horizontal section, one differential pressure transducer measures across 1 m length, and another transducer measures along 1.5 m, to detect the small pressure difference. The horizontal section contains an acrylic section at the end of the pipe to visualize the flow behavior.

Table 6 The summary of DRA in petroleum applications

Authors year	Investigation	DRAs/DRPs	Remarks
(Singh et al., 2011)	DR in gravity-driven flow	Different water-soluble polymer Polyacrylamide and polyethylene oxide	Polyacrylamide's optimum concentration for optimal DR was 10 ppm for laminar flow and 5 ppm for turbulent flow

			Polythene oxide's optimum concentration was 20 ppm for laminar flow and 40 ppm for turbulent flow The type of polymer and type of flow in the exit pipe had an impact on the optimum concentration When the flow in the exit pipe was laminar, polyethylene oxide was a better DRA and polyacrylamide was a better DRA when the flow in the exit pipe was turbulent
(Yusuf et al., 2012)	Effect of DRP on flow patterns and DR of oil-water flow in a horizontal pipe	An anionic copolymer of HMW with 40 wt. %: 60 wt.%NaAMPS/acrylamide was used as DRP	The injected polymer had a significant effect on flow patterns and their boundary transitions With increasing polymer concentration, DR increased and reached the limit at 10 ppm concentration DR increased with increasing water superficial velocity, while DR decreased with increasing oil superficial velocity
(Abdulbari and Nour, 2012)	DR	Grafted natural polymer Okra (Abelmoschus esculentus) mucilage as a DRA in water and gas-oil systems	Adding the grafted natural polymer had a high ability to reduce drag with a maximum DR% of 60% Increasing the additive quantity increases the DR and DR% increases with increasing Re by using the water-soluble additive DR was decreased by increasing Re by using the oil-soluble additive The DR% was higher in the pipe of ID 3.81 cm than the ID of 1.27 cm, and the grafted and natural mucilage showed high

			resistance to shear forces when circulated continuously for 200 s in the closed-loop system
(Al-Yaari et al., 2013)	Effect of DRPs on surfactant stabilized emulsion flow of W/O Effect of Oil soluble and water-soluble polymers as DRA for W/O and O/W emulsions	N/A	With the addition of proper DRP, emulsion stability increased, and this impact was strengthened with the increase of molecular DRP at ambient temperature Emulsion stability and the effect of DRP on the stability of the emulsion decreased with increasing temperature Injection of the DRP, which is soluble in the outer phase of the emulsion led to pressure drop reduction, and this influence increased with increasing DRP concentration
(Abubakar et al., 2014a)	Effects of polymer properties on drag reduction in single-phase water flow through a horizontal pipe	Polymers	DR depends on the ability of the polymer to shape and/or its flexibility to form intermolecular connections, which can be enhanced by increasing molecular weight, decreasing charge density, and making smaller side groups in the backbone of the main polymer
(Abubakar et al., 2014b)	Comprehensive review study to discuss the roles of DRPs in single- and multiphase flows	N/A	Most of the studies that have been done are for single-phase flow and some of the studies conducted for gas-liquid flow, recently there have been some studies focused on using polymers in liquid-liquid flow
(Khadom and Abdul-Hadi, 2014)	Effect of using polyacrylamide (PAM) as DRP on Iraqi	PAM	A reasonable agreement between the DR observed and the estimated DR with

	crude oil flow in pipelines The parameters explored are the concentration of additive, pipe diameter, the flow rate of the solution, the presence of radius elbows		a high coefficient of correlation PAM polymer was a good and effective DRA with Kirkuk oil DR% or flow increased with increasing solution velocity DR% increased with increasing additive concentration, and the additive had no impact on the physical properties of the crude oil
(I. Alsurakji et al., 2018)	Using oil-soluble and water-soluble (DRPs) in multiphase flow	Effects of polar ZEAG18165 (water-soluble) and oil-soluble Nonpolar polyisobutylene (PIB) was investigated as (DRP)	DRPs have delayed the transition from low to high-frequency slug flow and the appearance of annular flow, besides DRPs reduced drag and pressure gradient for all different flow phases used in their study
(Liu et al., 2018)	The efficiency of using mixed polymer and surfactant solutions as DRAs	Polymer and surfactant solutions	The mixed solution and pure solution curves varied at low temperatures, whereas all the mixed solution curves were identical to the pure CTAC solution at high temperatures and the low polymer concentration solution curves almost coincided with pure CTAC solution and the high polymer concentration solution curves were slightly higher than the pure solutions The temperature had more impact than concentration, where increasing the temperature to change the structures of the solution was more effective than increasing structure quantity

(Ayegba et al., 2019)	Effect of using a small amount of (DRP) on single-phase water flow through 180° bends	Partially hydrolyzed polyacrylamide polymer	In both straight pipes and U-bend, DR increased with increasing polymer concentration till it reached the optimum concentration, after which any further increase in polymer concentration increased the drag The DR in straight pipes was higher than that in bends of equivalent length, where DR% was 65% in straight pipes, while 45% and 42% in downflow U bend and horizontal U-bend, respectively
(Chen et al., 2020)	Improving the DR in slickwater hydrofracking	Polyether-based thermoviscosifying polymer (TVP)	At low concentrations, TVP solutions showed thermos-thickening ability better than HPAM TVP is much better in reducing the drag with DR% equal to 73.45% compared with 64.29% of HPAM. Besides, at high temperatures, TVP showed a better DR% with 79.77% compared with 70.18% for HPAM



Figure 1 A 3D image of the drag duction flow loop system (Khalid et al., 2020)

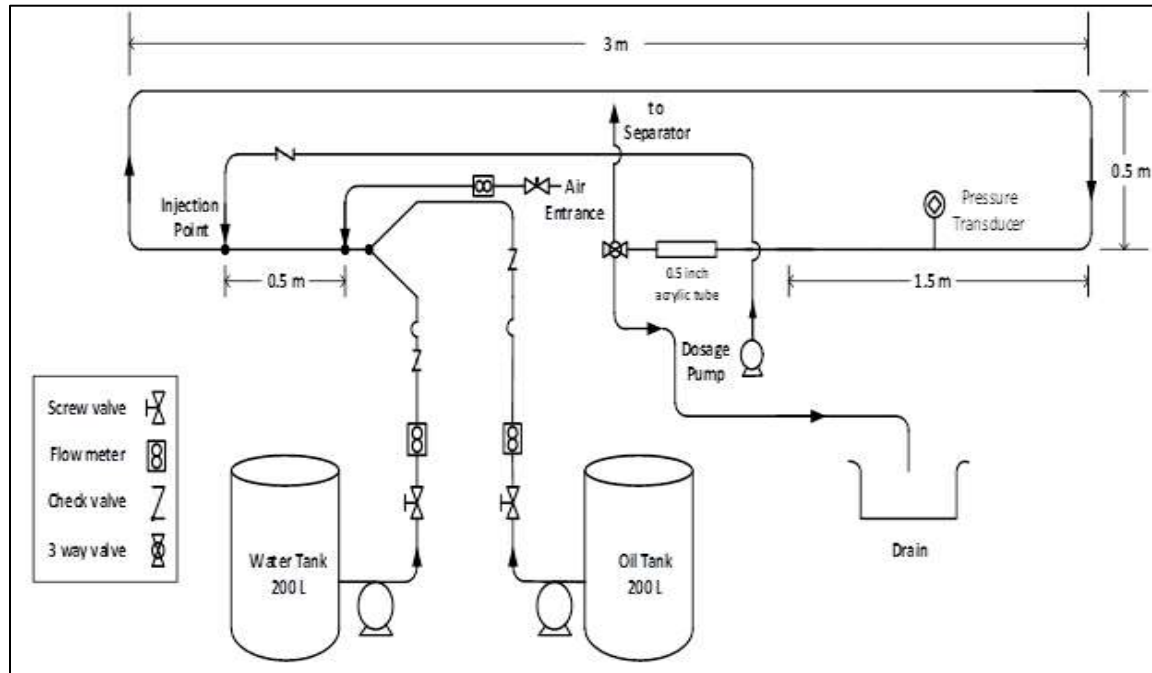


Figure 2 Schematic of the drag reduction flow loop system (Khalid et al., 2020)

2.11 Case studies

DRA found application in different industries such as agriculture, chemical, flood water disposal, sewage, firefighting, mineral and mining, and aviation industries. It has been successfully applied in many fields and shows promising results. In lieu of the scope of the study, three cases of the petroleum industry's DRA application for oil transportation and water injection are illustrated.

2.11.1 Kaji-Semoga Sumatera, Indonesia

The Kaji-Semoga (KS) field is located in the southern part of Sumatera, Indonesia. In the initial reservoir, the estimation speculated that pick production of the field would reach 40,000 BOPD. An 8" 148 km (92 miles) pipeline was built to handle the production of the KS field. However, with the further development of the field, peak production was forecasted to be around 68 MBOD. To accommodate the additional production with the already set-up pipeline DRA was applied. A field trial was conducted with the application of DRA. The field trial turned out to be successful by increasing the flow capacity by 32.15% with the introduction of 24.5 ppm DRA (Prasetyo, 2003). The success of the field trial with drag reducer injection operating costs around US\$ 0.50/barrel increments the KS field production; 63 MBOD was delivered to the existing pipeline. The DRA application increased throughput up to 90% from the baseline capacity of the KS field. It allowed a net share increment of about \$22 million to a production terminal EXSPAN Nusantara and the government of Indonesia to have a net share increment of about \$126 within 1.5 years.

2.11.2 Ukpokiti Field, Niger Delta

Joseph and Ajioka, 2010, presented a case study of using DRA to improve water injectivity in the Ukpokiti field in the Niger Delta. 40,000 barrels of water per day (BWPD) is the expected amount to be injected into the Ukpokiti field, however, only 30,000 BWPD was the amount that could be injected. They used the Conoco drag reducer (CDR) as DRA, and the field results showed that the optimum injection increase of 13% was obtained when 20 ppm of CDR was injected. Also, the test had no harmful impact on the environment.

2.11.3 Mumbai offshore field

Tiwari et al., 2016 presented a case study of the DRA application in the pipeline handling high water cut fluid from a mature field in the Mumbai offshore region. In mature oil fields, usually water cuts increase with time, and an economically appropriate technique is needed to control the water cut. DRA was utilized to address the problem of high frictional pressure drops in pipelines. A field trial was performed for 4 days with an initial DRA injection dosage of 200 ppm. Incremental production of 250 barrels of oil per day (~8–10% of oil production from satellite) was obtained for a DRA concentration of 100 ppm.

2.12 Research gap and future research directions

The high frictional pressure losses associated with the turbulent flow are minimized by the addition of DRA (Brautlecht and Sethi, 1933; Brecht, 1935; Forrest, F., & Grierson, 1931). The preliminary concept of drag reduction assumes that the polymeric DRA induces the laminar sublayer in the turbulent flow and is responsible for the drag reduction. It was suggested that drag reduction occurs through the interaction between elastic macromolecules and macrostructures in turbulent flow (Al-Sarkhi, 2010; Kim, O. K., &

Choi, 1996). It was further supported by the velocity profile, alterations in boundary-layer momentum transfer, and viscous sublayer phenomena (De Gennes, 1986; Joseph et al., 1986; Lumley, 1969). In addition, the correlation for the friction factor was formulated to simulate the drag reduction effect. However, the precise mechanism of drag reduction remains unaddressed. Also, the effect of pipe geometry, curvature, bend, and inclination are not addressed as far as drag reduction is concerned. The drag reduction phenomenon at the molecular level is also unknown. These gaps are required to be addressed by combining the knowledge of fluid mechanics, thermodynamics, and chemistry to improve the understanding of the drag reduction and function of a DRA. Advanced experimental methods such as particle velocimetry, laser Doppler, velocity profiling, microscopic studies, and numerical simulation insights into the structure and interaction should be adopted to understand the drag reduction mechanism (Ayegba et al., 2021; Edomwonyi-Otu et al., 2021; Jubran et al., 2005; Wang et al., 2011).

Realizing the potential of polymers as DRA many studies were conducted, a review of polymeric DRA is presented by (Utomo et al., 2021). In addition, the surfactant or the combination of surfactant and polymer was evaluated for drag reduction (Ayegba et al., 2021; Broniarz-Press et al., 2007; Hoyt, 1986; Zakin et al., 1998). There is a long list of polymers and surfactant solutions that can act as a DRA. Introducing the parameters such as polymer concentration, and surfactant concentration along with the surfactant-polymer types will make numerous DRA's to evaluate the efficacy of the drag reduction (Tiong et al. 2015). Hence, it is necessary to study the characteristics at the molecular level and the functional groups distinguishing them. It will help in identifying the concentration of

polymer/surfactant or synthesizing it with the functional group and capabilities (Gu et al., 2020).

The application of DRA in the petroleum industry requires a different approach. One of the main features required by DRA is capability with the harsh environment such as flow rates, temperature, salinity, and constituents of hydrocarbon. Many times, the polymers tend to degrade with a high shear rate or temperature on the other hand surfactants are not compatible with high temperature, salinity, or hydrocarbon compounds (Abubakar et al., 2014b; I. Alsurakji et al., 2018; I. H. Alsurakji et al., 2018; Ayegba et al., 2019). It requires identifying DRA suitable for the petroleum application. The limitation imposed by the harsh conditions can be overcome by new DRAs such as nanoclay which are more resilient to harsh conditions (Al-yaari et al., 2014). The DRA should be tested at the representative condition of application and should be evaluated considering multiphase, emulsion, pH, wetting degree of fluid on the tubular, pipe geometry, flow patterns, representative fluid properties, and water cut. For application purposes, correlation models for pipe diameter scale-up will be required. These applications require advanced equipment such as spectroscopy, high-performance liquid chromatography (HPLC), X-ray diffraction (XRD), X-ray fluorescence (XRF) as well as flow loops for evaluating the performance of DRA under harsh conditions.

2.13 Concluding remarks

The review of the research conducted on the DRA suggests that DRAs have a wide range of applications in the oil and gas industry. The complex nature and distinguished requirements necessitate an independent approach for the further development of DRAs.

The chemical nature of DRA and its conditions are vital for the development of DRA for oilfield systems. There are numerous studies reported on drag reduction that are available in the literature that do not apply to oil and gas operations; thus, there is a need to analyze and discuss these further to identify the future research direction. The following are the research gaps identified based on the review reported in this study.

1. The application of the DRA in the transportation of crude oil has driven the research in drag reduction in crude oil pipelines. Many studies evaluating the effect of different DRA in evaluating its performance and optimization are presented in the literature. however, the mechanism of the drag reduction with DRA is not revealed.
2. The geometry of the pipe is very important for petroleum applications such as drill pipe, annulus, and coiled tubing which have not been adequately addressed concerning its relevance to drag reduction. Also, the flow direction and flowthrough bends, curves, and elbows certainly require further research.
3. The pipe friction factor is very important in the petroleum production system as it changes with time. The effect of pipe condition on the drag reduction application needs further investigation. The effect of pipe conditions for the drag reduction application needs further investigation.
4. The multiphase flow in the pipes is common in the petroleum industry and requires to be addressed in perspective of the different drag-reducing agent and their effect on the flow regime, phase separation, and fluid properties.

5. In line with the single-phase flow, the effect of pipe inclination and flow direction requires to be investigated for the multi-phase flow with the inclusion of a drag-reducing agent.

6. The fracturing fluid requires a different approach for drag reduction. The effect of temperature, salinity as well and degradation of DRA on the drag-reduction performance needs to be evaluated.

7. Emulsion is desirable in some applications such as EOR or stimulation and undesirable while it is transported through the pipeline. However, in both scenarios, it is advantageous to reduce the drag for the emulsion system. Identifying the right type of DRA is very challenging due to the complex nature of emulsions, and the compatibility of the DRA.

8. Nanoparticles appear to be a promising material for drag reduction. There are several types of non-materials available; however, the application of these materials as DRAs demands considerable research work. The following are the recommendations for bridging the research gaps on DRA and drag reduction applications in the petroleum industry.

1. The mechanism of drag reduction is not fully understood. It requires combining the knowledge of fluid mechanics, thermodynamics, and chemistry to improve the understanding of the drag reduction and function of a DRA.

2. Advanced experimental methods and instruments such as particle velocimetry, laser Doppler, and velocity profiling will strengthen the research on understanding drag reduction further.

3. The flow direction and flow through bends, curves, and elbows certainly require further research.
4. The effects of pipe inclination and flow direction require to be investigated for the multiphase flow with the inclusion of a drag-reducing agent.
5. The emerging DRA such as nanomaterials needs to be studied with advanced methods such as spectroscopy, and high-performance liquid chromatography (HPLC) to identify the function groups, surface chemistry for identification of materials, and possible usage of these materials as a DRA.
6. The microscopic view may give insights into the structure and interaction required to be studied for the DRA. It can provide new approaches for the development of DRA.
7. Experimental techniques as well as the experimental setup to study DRA behavior under flow conditions are required to be developed.
8. The numerical approach for simulation in capturing the mechanism can be explored for further understanding and validating the function of DRA.
9. The wide range of applicability of the DRA in the petroleum industry can have a significant impact on pumping costs, improved efficiency, and operational safety. The DRAs need to be developed as per the nature and requirements of the oilfield system. There is not a unique DRA suitable for all conditions. The market is available for the DRA, and research will continue to grow in this area.

CHAPTER 3

NOVEL ENVIRONMENTALLY FRIENDLY

NANOMATERIALS FOR DRAG REDUCTION OF

EMULSIFIED ACID SYSTEM (EAS)

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3.1 Abstract

Matrix acidizing is a technique that is widely used in the petroleum industry to remove the scales and create channels in the rock. Removal of scales and creating channels (Wormhole) enhances productivity. Conventional acidizing fluids such as hydrochloric acid (HCl) for carbonate and a mixture of hydrofluoric acid (HF) + 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 reaction with scale and particles. Emulsified acid systems (EAS) are used to address these drawbacks. EAS can create deeper and narrower wormholes by reducing the reaction rate of the acid due to the external oil phase. However, EAS has a much higher viscosity compared to conventional acidizing

fluids. The high viscosity of EAS leads to high drag that restricts pumping rates and consumes energy.

This study aims to utilize environmentally friendly and widely available nanomaterials as drag-reducing agents (DRA) of 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 usually smaller than 10 nanometers. CNDs are characterized by biocompatibility and chemical stability. This study investigates the use of CNDs as DRA For EAS. Several experiments have been conducted to investigate the CNDs as 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 thermal stability for the range of temperatures and rheological properties of the EAS were evaluated to meet the criteria of field operation. Then flow experiment of EAS was conducted before and after adding the CNDs to investigate its efficacy in drag reduction of EAS.

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 of EAS showing its compatibility with the field formulation. The drag reduction was observed at the range temperatures investigated in the study. The conductivity, stability, and rheology experiments for the sample taken after the flow experiment are consistent ensuring CNDs are worked as DRA. The developed EAS with CNDs is robust in terms of field mixing procedures and thermally stable. The CNDs can be used as DRA with EAS which will reduce drag in pipes, increasing pumping rates and saving energy.

3.2 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 done 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 formation. These cracks allow oil and gas to flow more easily to 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 with scale and fines, and corrosion of the tubing, casing, and downhole equipment at high temperatures.

The EAS is one of the solutions to the limitations of conventional acid systems. 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 (Fatah and Nasr-El-Din, 2010, 2008). 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 (AL-Dogail et al., 2023b; Kasza et al., 2006; Nasr-El-Din et al., 2008; Sidaoui and Sultan, 2016). 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 (Lynn and Nasr-El-Din, 2001; Nasr-El-Din et al., 2000).

Many researchers have studied the use of EAS to stimulate carbonate reservoirs (AL-Dogail et al., 2023b; Al-Mutairi et al., 2008; Buijse, 1997; Buijse and Van Domelen, 2000; Crowe et al., 1990; Mahmoud et al., 2023; Navarrete et al., 2000; Nierode and Kruk, 1973; Siddiqui et al., 2006; K. C. Taylor et al., 2006). 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 or 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 nanometers. 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 they are likely to become increasingly important in the future.

This study aims to utilize environmentally friendly and chemically stable CNDs as DRA for EAS. More specifically, this study investigates CNDs as viscosity reducers and DRA 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 EAS before and after adding the CNDs.

Acidizing is a technique required in the oil and gas industry to stimulate the wells and enhance the productivity of oil and gas wells. Conventional acidizing fluids that are used in the petroleum industry for well-stimulations of carbonate reservoirs are hydrochloric acid (HCl) or a combination of hydrofluoric (HF) and hydrochloric (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 (Huang et al., 2013).

As a solution to these issues, alternative acid systems have been developed to operate at high temperatures without causing damage to downhole equipment. Examples of such acid systems include a mixture of tricarboxylic acids, amino carboxylic acids, and dicarboxylic acids (Huang et al., 2013). By utilizing these innovative acid systems the oil and gas industry can overcome some limitations of the conventional acidizing fluids. However, these alternative acids are still limited to specific carbonate reservoir conditions, also these acids have complex formulations, compatibility issues, as well as corrosion problems still being less corrosive compared to the conventional acidizing fluids. So that a need for

another acidizing liquid is required to overcome these limitations. 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 EAS, 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 15-28 %) is commonly used (Adewunmi et al., 2022; Al-Mutairi, S. H., Hill, A. D., 2008; Sayed and Nasr-El-Din, 2011). 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 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 (Huang et al., 2013). 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 one thousand 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 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 well stimulation and overall reservoir performance. The preparation

methods of emulsified acids significantly impact 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 (Al-Mutairi, S. H., Hill, A. D., 2008). 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 7 summarizes the studies of developments on the EAS.

Table 7 Summary of the development of EAS

Authors	Findings
(De, 1933)	Pioneering researchers first utilized acid-in-oil emulsion in well-stimulation
(Al-Anazi et al., 1998)	Field application of emulsified acid in carbonate reservoir
(Hoefner et al., 1987)	Role of acid diffusion in matrix acidizing
(Mohamed et al., 1999)	Acid stimulation of water injectors and saltwater disposal wells in carbonate reservoir
(Nasr-El-Din et al., 2000)	Stimulation of water-disposal wells using Acid-in-Diesel emulsions
(Sayed and Nasr-El-Din, 2011)	Effect of emulsifier concentration and acid volume fraction on the elastic properties of emulsified acids
(Pandya et al., 2012)	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)	Optimization of a 26% HCl-based EAS was performed for stimulating high-temperature carbonate reservoirs Effects of two different corrosion inhibitors at various temperatures and time durations

(Madyanova et al., 2012)	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)	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 threefold increase in core permeability improvement compared to conventional acid systems
(Sidaoui and Sultan, 2016)	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 EAS. The small droplet size of the emulsion contributed to its higher viscosity
(Sidaoui et al., 2017, 2016)	Utilization of waste oil as the external phase of a 70:30 acid/oil ratio with 15 % HCl in an EAS Developed HCl-waste oil EAS demonstrated shear-thinning behavior, exhibiting favorable rheological properties
(Sidaoui et al., 2018)	Investigate adding iron control and chelating agents to EAS stability and its reaction with dolomite Stable EAS was achieved without iron control, and with the inclusion of less concentration of the chelating agents
(Sayed et al., 2018)	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-inch core sample pumping
(Aldakkan et al., 2018)	A proposed acid system with a combination of a potent acid with a highly soluble organic compound Achieved a remarkable four-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)	Replace surfactants with specific nanoparticles Developed EAS with waste oil showed superior 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)	Developed Jatropha oil-based EAS, which exhibited superior thermal stability, a more environmental alternative for acidizing
(Sokhanvarian et al., 2019)	Formulated a stable EAS for HPHT 149 C (300 F) with non-aromatic nonionic surfactant. Non-ionic surfactants provide stable EAS and exhibit superior performance with low acid pore volume breakthrough (PVBt) at 149 C (300 F)

(Jafarpour et al., 2019)	Designed a novel multi-batched acid system designed for heterogeneous carbonate reservoirs. The developed EAS is effective in stimulating complex carbonate reservoirs
(Sayed et al., 2021)	A low-viscosity single-phase acid system acid fracturing. The system consists of a pre-engineered blend of an alkyl sulfonic acid and strong mineral acid. Exhibited comparable performance to 15 wt% HCl-EAS in terms of diffusion and reduced drag
(Al-Sabea et al., 2022)	Developed low-viscosity, polymer-free acid retarded system and successful case study in the west Kuwait field. The acid system consists of robust mineral acid HCl, with a non-damaging retarding agent. Exhibited great promise compared to the EAS
(Zakaria et al., 2022)	Developed 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., 2023b)	Investigated different types of organoclays (OC) as emulsifiers to develop Pickering EAS. Selected types of OCs can be used as emulsifiers to develop Pickering EAS with good thermal stability and low viscosity at high shear rates

These studies represent only a portion of the ongoing research aimed at improving acid stimulation techniques for enhanced efficiency and environmental considerations in the oil and gas industry. They demonstrate 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 EAS to overcome the limitation of conventional acid fluid for stimulation. EAS involves acids dispersed in an external oil phase, offering benefits like reduced corrosion and controlled reaction rates. The EAS formulations required for well stimulation are required to be stable at 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 formulations include macro and microemulsions, low-viscosity systems, and formulations with alternative components like nanoparticles or waste oil. Factors influencing EAS stability and performance include emulsifier concentration, acid-to-oil ratio, and temperature. Researchers have proposed diverse solutions to optimize 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 emulsion but not the emulsified acid system. It should be noted that the achieving drag reduction of the emulsion cannot be translated to the drag reduction of the EAS. The nature of EAS needs to be considered while addressing the drag reduction of EAS. It includes compatibility of the material with acid and ensuring the formation of an emulsion that is thermally stable and possesses characteristics of an emulsion that is ready to use considering operating and field conditions. This requires rigorous experiments and laboratory set-up 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 EAS, temperature, flow rates, and the acidic nature of the fluid. The results are encouraging as it reduces the drag of EAS meeting field preparation and operation requirements. The indigenous material is compatible with the acid system and ready to be tested in the field.

3.3 Methodology

To achieve the objectives of this study, the EAS was prepared using a commercial formula and this is considered as the base case, and then the necessary tests were conducted. The acid phase-to-diesel phase ratio for all prepared EAS was 70:30. The prepared base case EAS was investigated by different tests, and these tests include conductivity, pH test, drop-test, rheology, and thermal stability. 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, firstly the base case EAS was prepared in large amounts (30-40 liters), 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, and again the flow rates were recorded against the pressure drop readings. Samples of the EAS base case and 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 have been presented in this section in detail.

3.3.1 Materials and equipment

Materials utilized in this study include lab-grade hydrochloric acid (HCl) with 37 wt.% concentration, industrial-grade hydrochloric acid (HCl) with 26 wt.% concentration, deionized (DI) water, commercial diesel from a gas station, EAS formula including one corrosion inhibitor, one inhibitor intensifier, two iron controls, and one emulsifier (surfactant). Equipment required to perform this study includes high shear mixer/homogenizer (IKA T 25 digital ULTRA-TURRAX homogenizer with titanium acid-resistant shaft and speed range of 3000-25000 RPM), magnetic stirrer, rheometer (Anton-Paar MCR-702 Rheometer), See-through Oven, test tubes, conductivity and pH meter (Thermo Scientific-Orion StarA215 pH/Conductivity Benchtop Multiparameter Meter), high-speed mixer/homogenizer (TAISITESMART JRJ-300SH-220V high-speed homogenizer lab disperser emulsifier capacity 40L 200-11000 r/min 510W digital display blender), drag reduction unit (flow loop).

3.3.2 Emulsified acid system (EAS) preparation

EAS was prepared based on the commercial formula with the ratio of 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 acid in the EAS were 15 and 20 %. Firstly, the emulsifier (surfactant) was added with a specific concentration according to the formula to the diesel, and they mixed using the homogenizer at 6000 RPM for 2-3 minutes, while the 37 % lab-grade HCl acid was titrated with DI water in a separate beaker to the required concentration 15, 20 %

using a magnetic stirrer for 1-2 minutes. Then, the corrosion inhibitor 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 with 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 mixing at 6000 RPM.

3.3.3 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 O/W emulsion if the dispersion takes place in a beaker containing water, while the emulsion is W/O emulsion if it takes place in a beaker containing diesel. To confirm the acidity of the prepared EAS, the pH was measured.

3.3.4 Thermal stability

Thermal stability is essential to guarantee that the prepared EAS reaches the formation in its original form. The thermal stability was explored at three different temperatures (25, 80, and 120 250 °C) using high-temperature graduated glass tubes and a see-through oven. By visually observing the EAS separation every 10 minutes for the first 30 minutes, then every hour after the first 30 minutes for the next 2-3 hours, and finally after 24 hours, thermal stability was carried out simply and easily. The EAS separation volume was plotted

against the time, and the photographs of the graduated glass tubes were taken before and after heating in the oven.

3.3.5 Rheology

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

3.3.6 Flow experiment

The EAS was prepared based on the commercial formula as the base case with large amounts (30-40 Liter) 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 variable frequency drive (VFD), tank, pressure transducer, and 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 variable frequency drive and the reading of pressure drop against flow rates is recorded. This procedure is followed covering the range 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 EAS (15 and 20 %) before and after adding CNDs.

3.4 Results and discussion

3.4.1 Emulsified acid system (EAS) preparation

The EAS was prepared with the ratio of 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 minutes, while the 37 % lab-grade HCl acid was titrated with DI water in a separate beaker to the required concentration of 15 % using a magnetic stirrer for 1-2 minutes. Then, the corrosion inhibitor 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 mixing 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 EAS with 20 % HCl acid concentration.

3.4.2 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, the drop-test was carried out to ensure that the EAS is a W/O emulsion. The electrical conductivity results show values close to zero, and that means the external phase is diesel and the prepared EAS is a W/O emulsion. According to pH measurements, the EAS is an extremely acidic solution. The drop-test results show that the EAS is a W/O emulsion since it is dispersed in diesel, not in the water.

3.4.3 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 3 shows the separation volume as a function of time for the EAS at the three different temperatures (25, 80, and 120 °C), while Figure 4 shows photographs of the EAS in the test tubes before and after being taken from the oven after 24 hours.

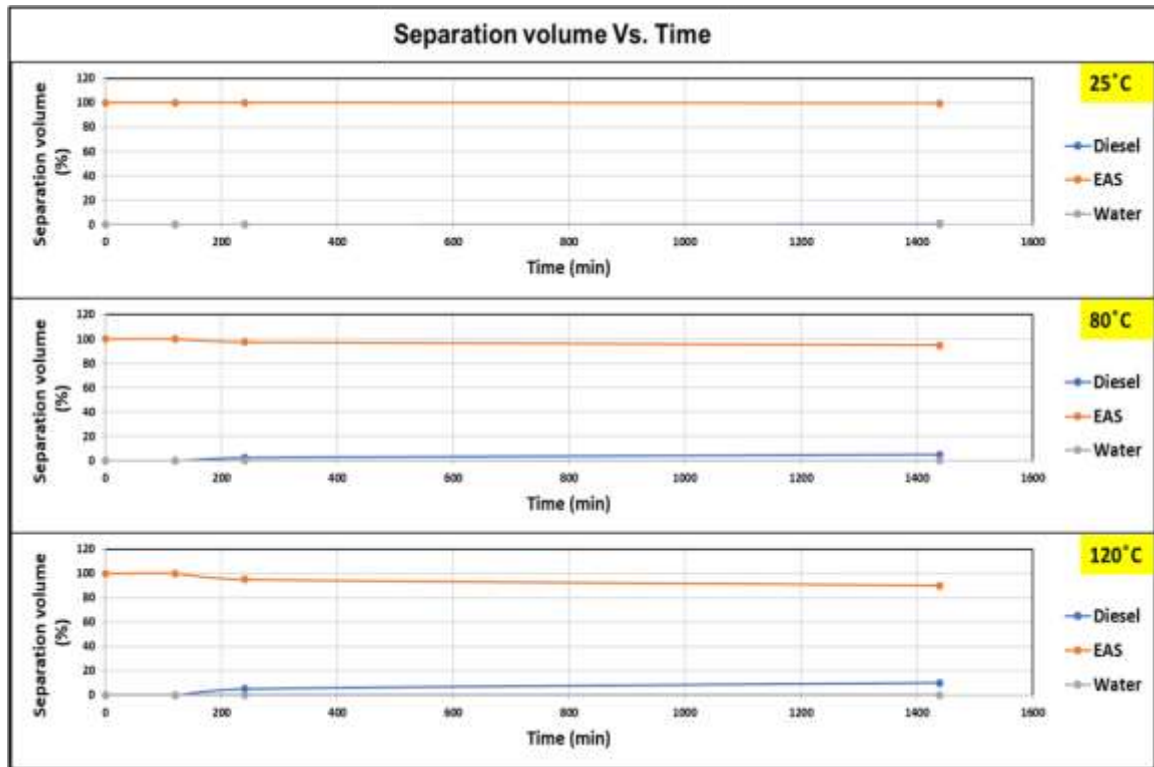


Figure 3 Separation volume of the EAS at three different temperatures (EAS+0.4% NM as an example)

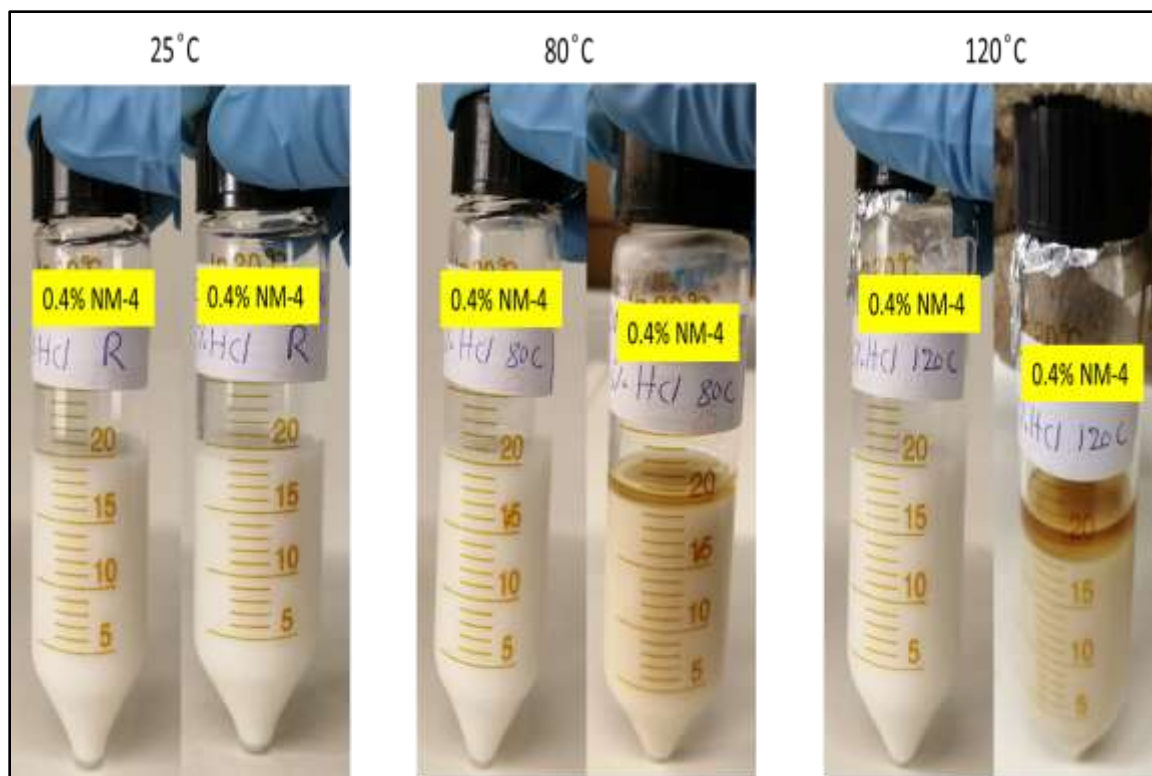


Figure 4 Photo of the EAS at three different temperatures before and after oven (EAS+0.4% NM as an example)

3.4.4 Rheology

Rheological properties were explored for the prepared EAS. Firstly, the viscosity was measured at different shear rates which ranged from 0.1 to 10001/sec at 65 °C for all prepared EAS with and without nanomaterials (CNDs) at 15 % HCl acid concentrations as shown in Figure 5. Adding CNDs to the EAS reduces the viscosity as shown in Figure 5 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 6 shows the shear stress as a function of the shear rate for the prepared EAS with CNDs.

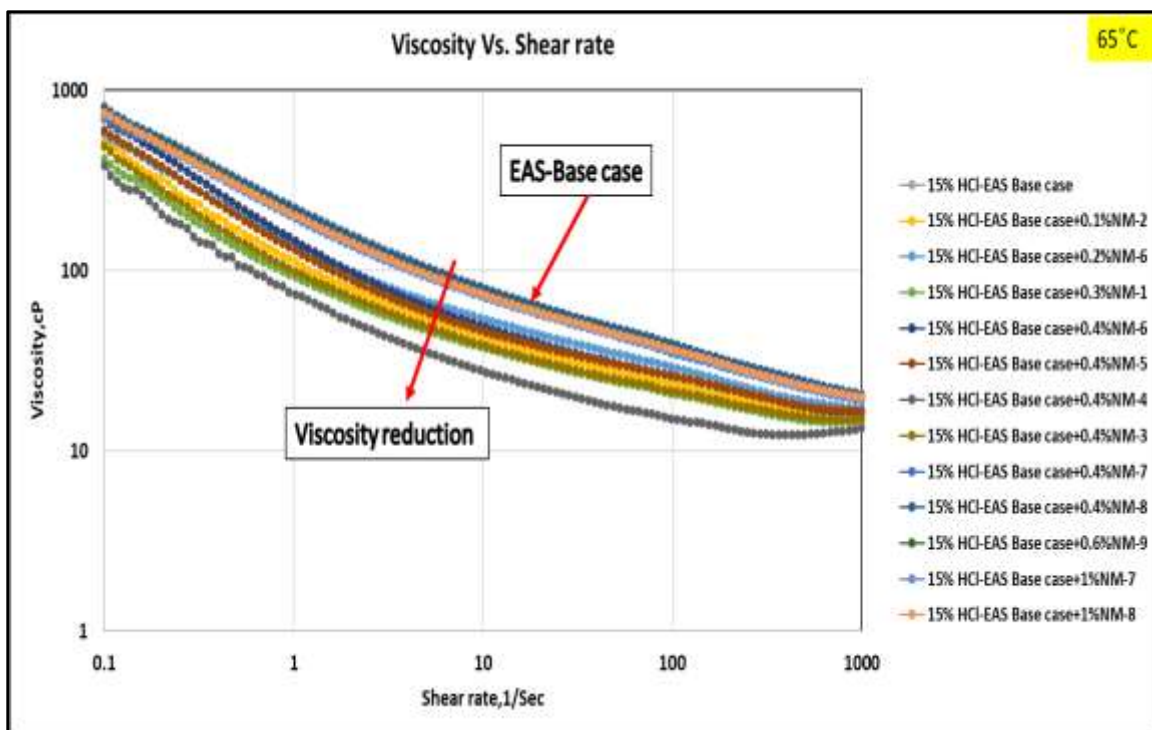


Figure 5 15% HCl EAS viscosity (cP) vs. shear rate (1/sec) at 65 °C

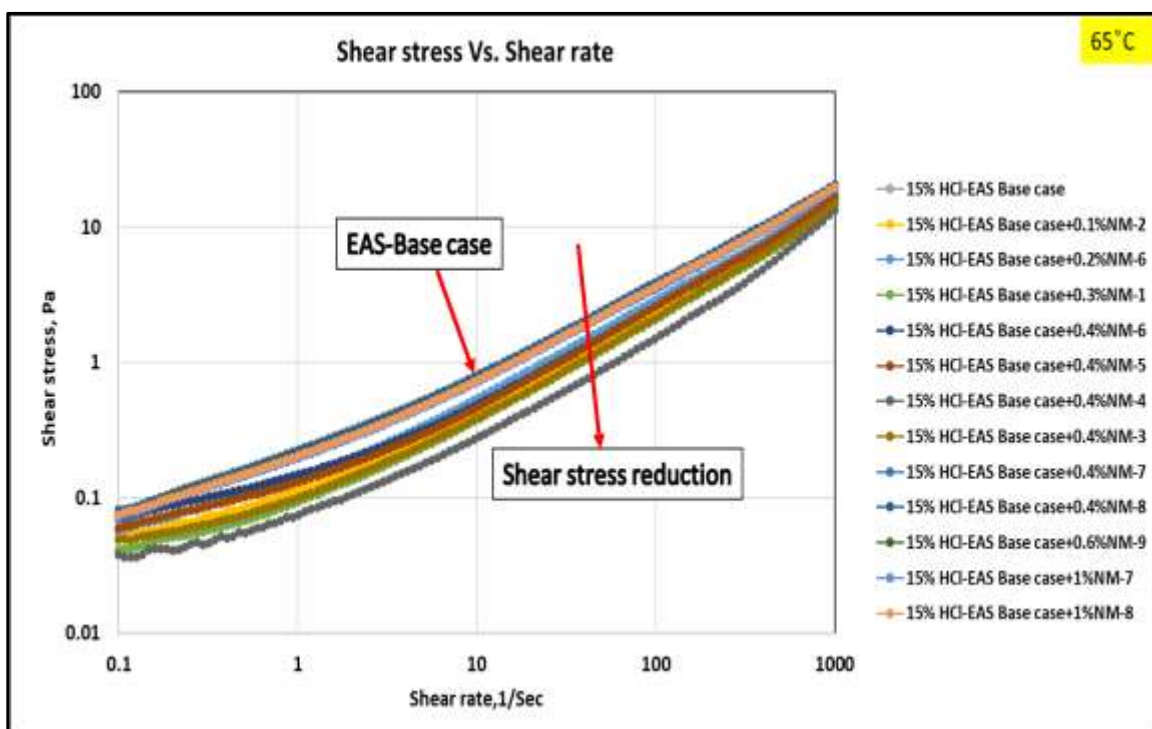


Figure 6 15% HCl EAS shear stress (Pa) vs. shear rate (1/sec) at 65 °C

Firstly, all experiments (preparation, conductivity, drop-test, thermal stability, and rheology) were repeated three times (at 15% HCl) to ensure the repetition. Figures 7 and 8 show the viscosity and shear stress as a function of shear rate, respectively for these prepared EAS. 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 shown in Figures 9 and 10. After that, the same nanomaterial (NM-4) was tested with another corrosion inhibitor, and the viscosity and shear stress as a function of the shear rate are shown in Figures 11 and 12. Also, a sample was taken from the flow loop after the flow experiment of EAS with the same nanomaterial (NM-4), and the viscosity was compared with the base case as shown in Figure 13. Figure 14 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 5, 7, 9, 11, and 13 adding nanomaterials (CNDs) reduces the viscosity of the EAS at different conditions, including different HCl acid concentrations, different corrosion inhibitors, and the sample of EAS after the flow experiment. Furthermore, all experiments (preparation, conductivity, drop-test, thermal stability, and rheology) were repeated (at 15% HCl) with another batch of the same nanomaterial (NM-4) at the same concentration (0.4%). Figures 15 and 16 show the rheology results of the new batch of NM-4, which again shows adding NMs reduces the viscosity of the EAS.

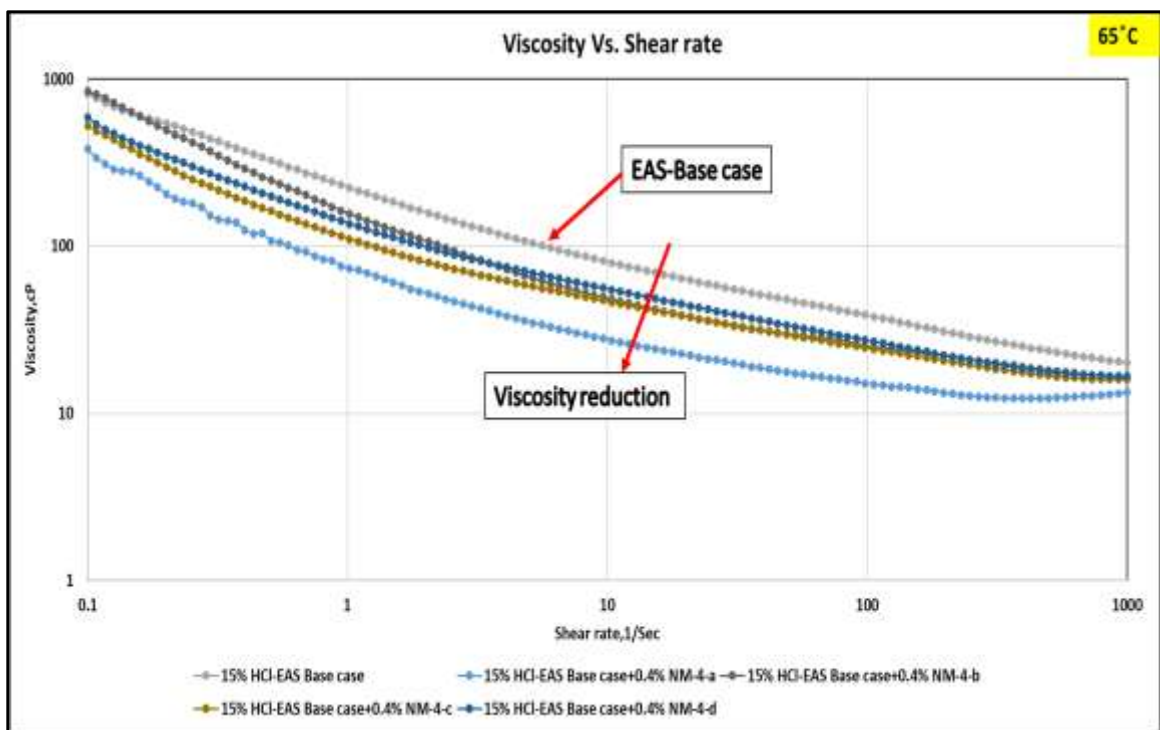


Figure 7 15% HCl EAS viscosity (cP) vs. shear rate (1/sec) at 65 °C (repeated 3 times)

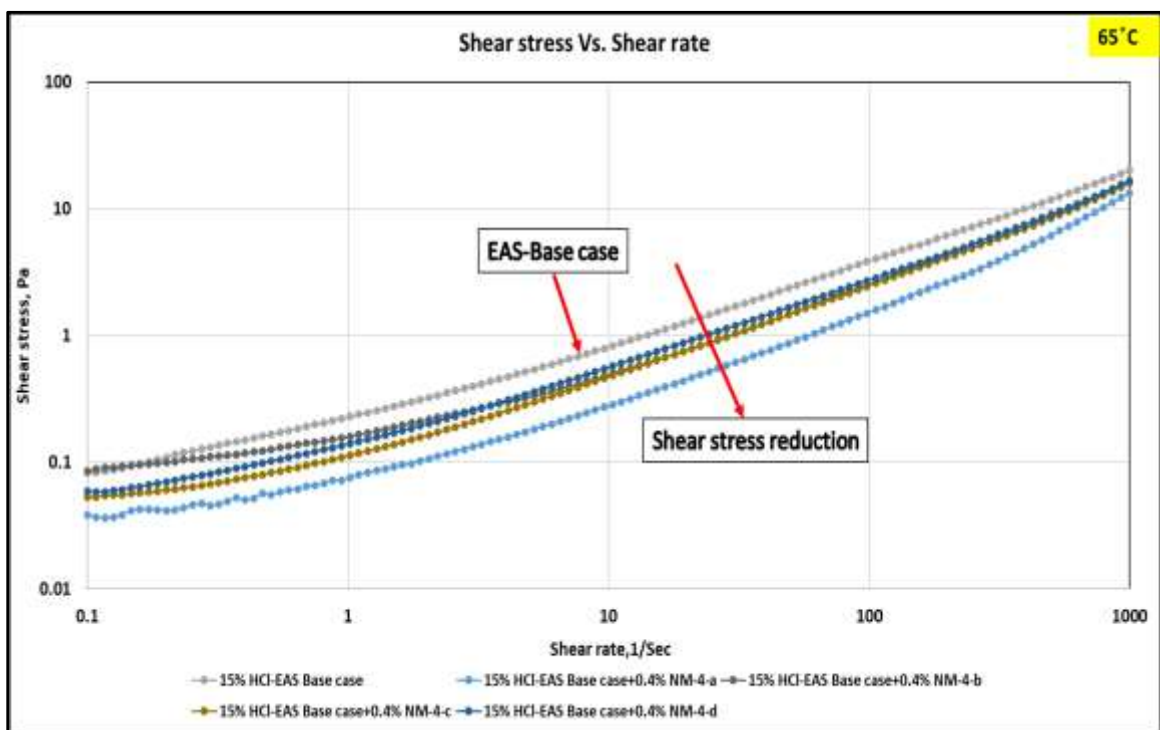


Figure 8 15% HCl EAS shear stress (Pa) vs. shear rate (1/sec) at 65 °C (repeated 3 times)

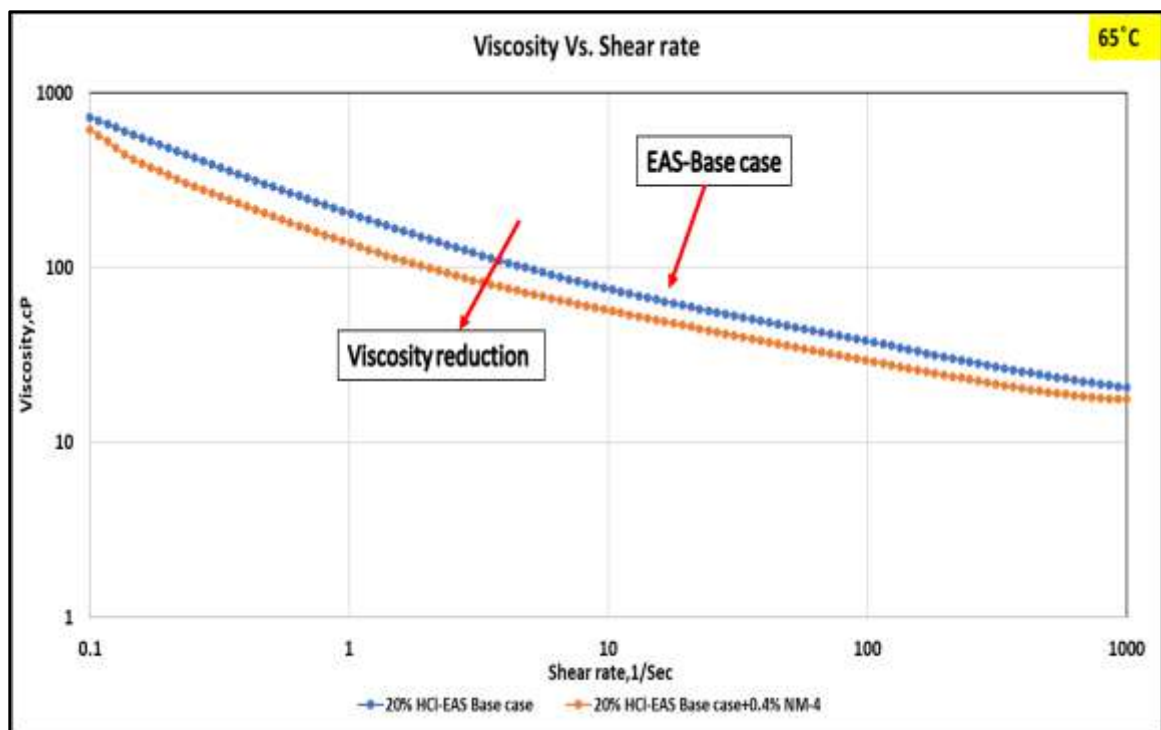


Figure 9 20% HCl EAS viscosity (cP) vs. shear rate (1/sec) at 65 °C

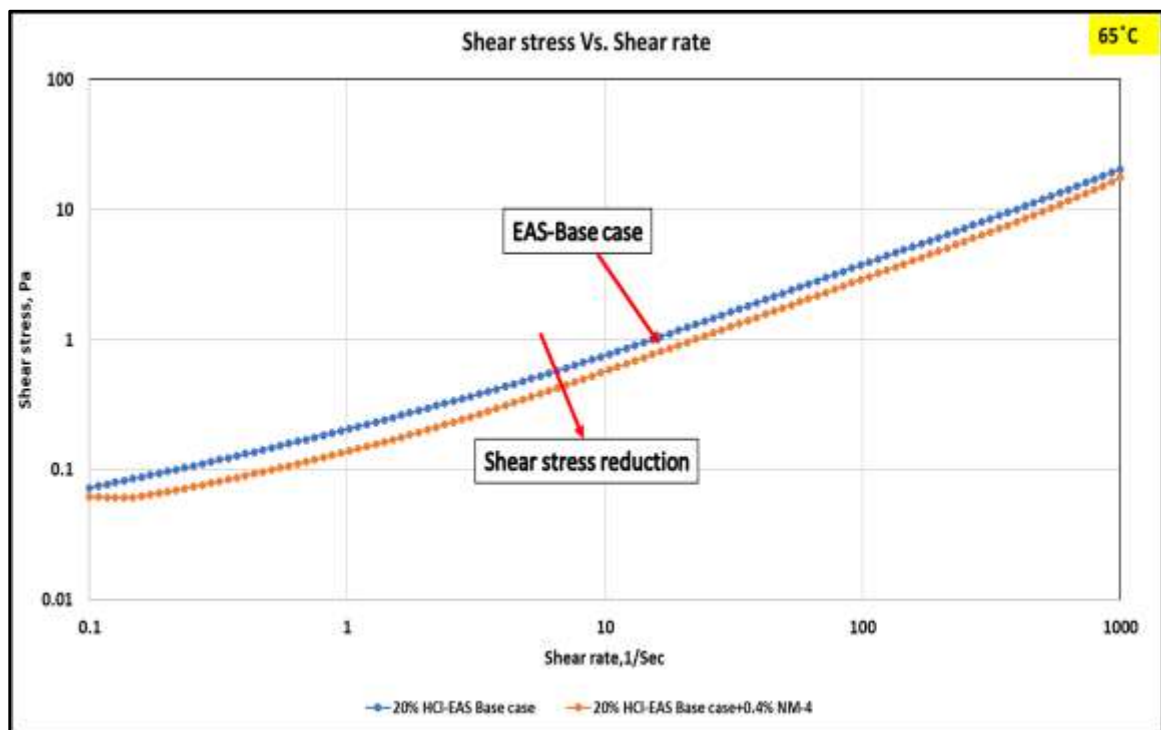


Figure 10 20% HCl EAS shear stress (Pa) vs. shear rate (1/sec) at 65 °C

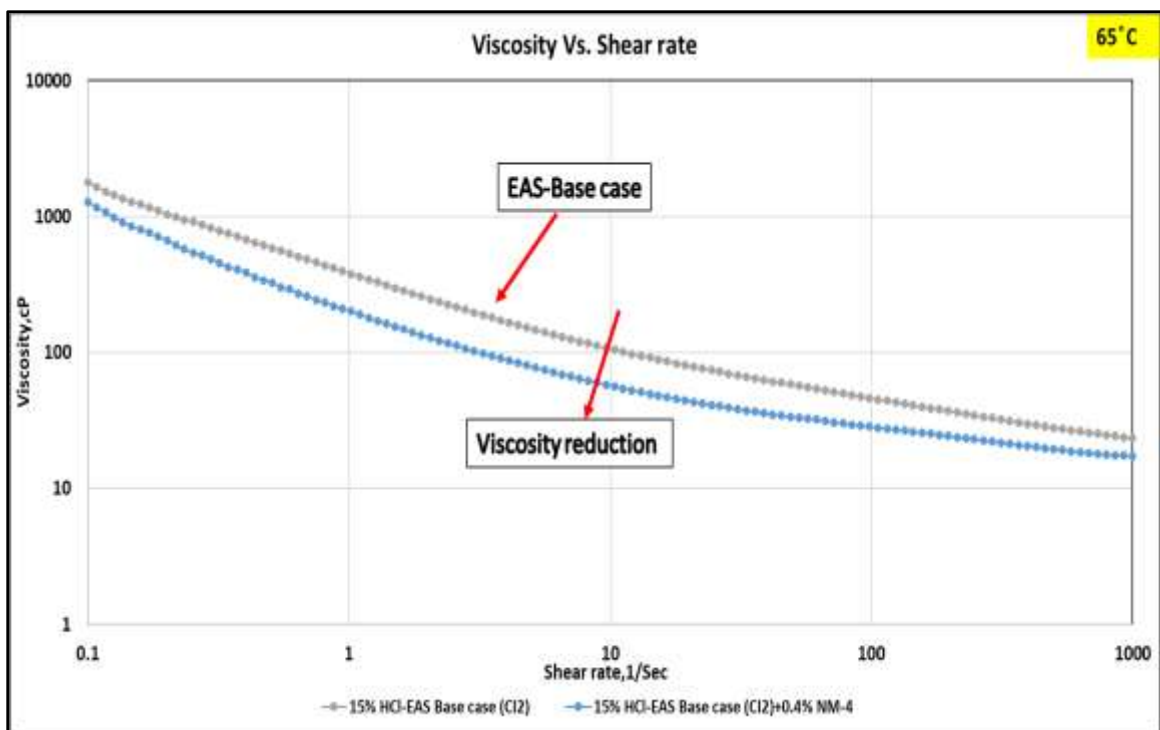


Figure 11 15% HCl EAS viscosity (cP) vs. shear rate (1/sec) at 65 °C (Tested with another corrosion inhibitor)

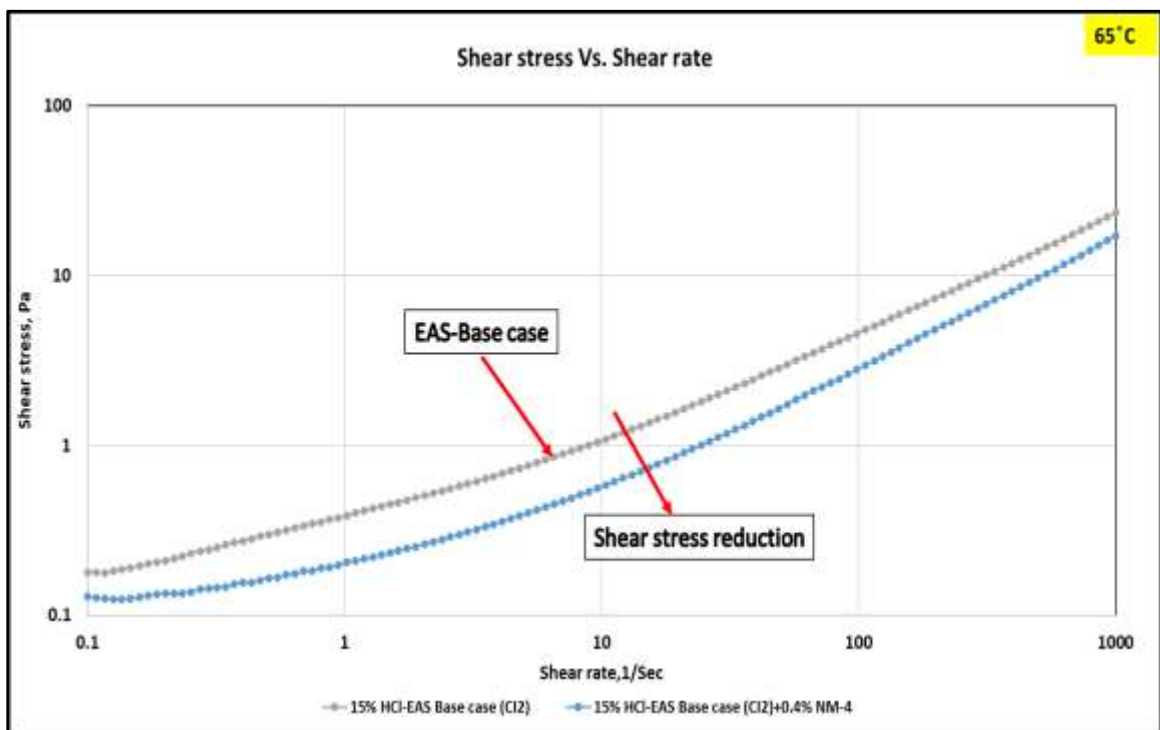


Figure 12 15% HCl EAS shear stress (Pa) vs. shear rate (1/sec) at 65 °C (Tested with another corrosion inhibitor)

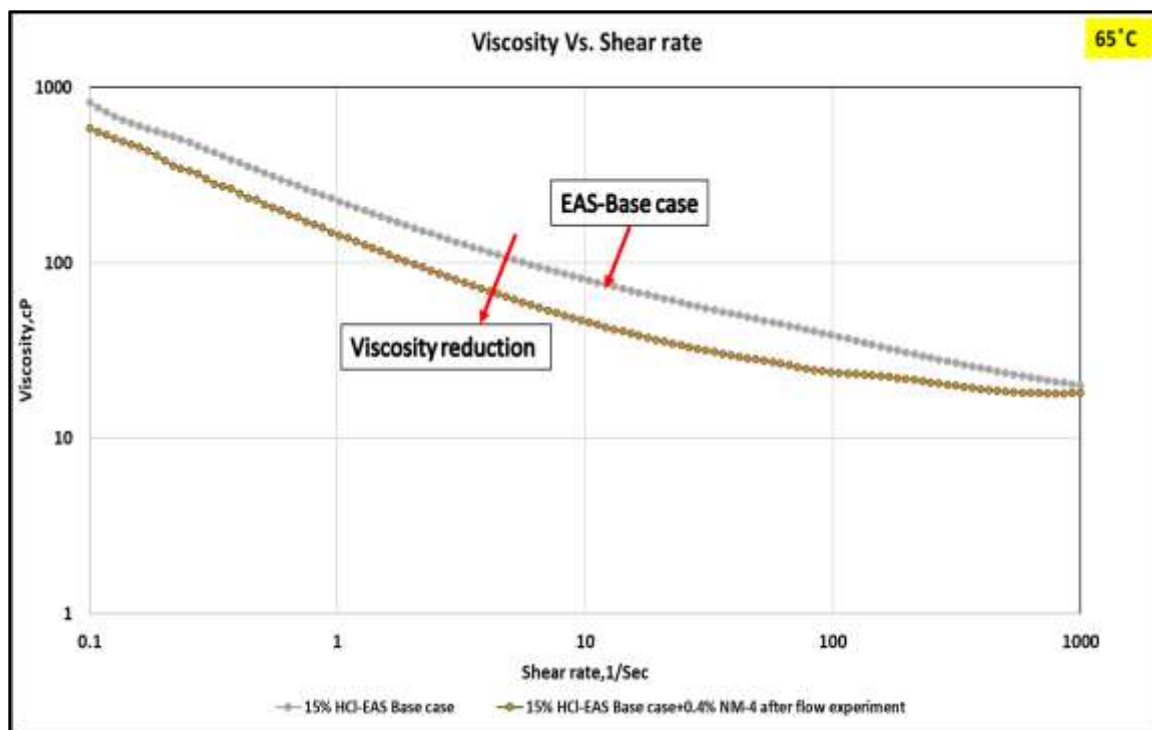


Figure 13 15% HCl EAS viscosity (cP) vs. shear rate (1/sec) at 65 °C (Sample after flow experiment)

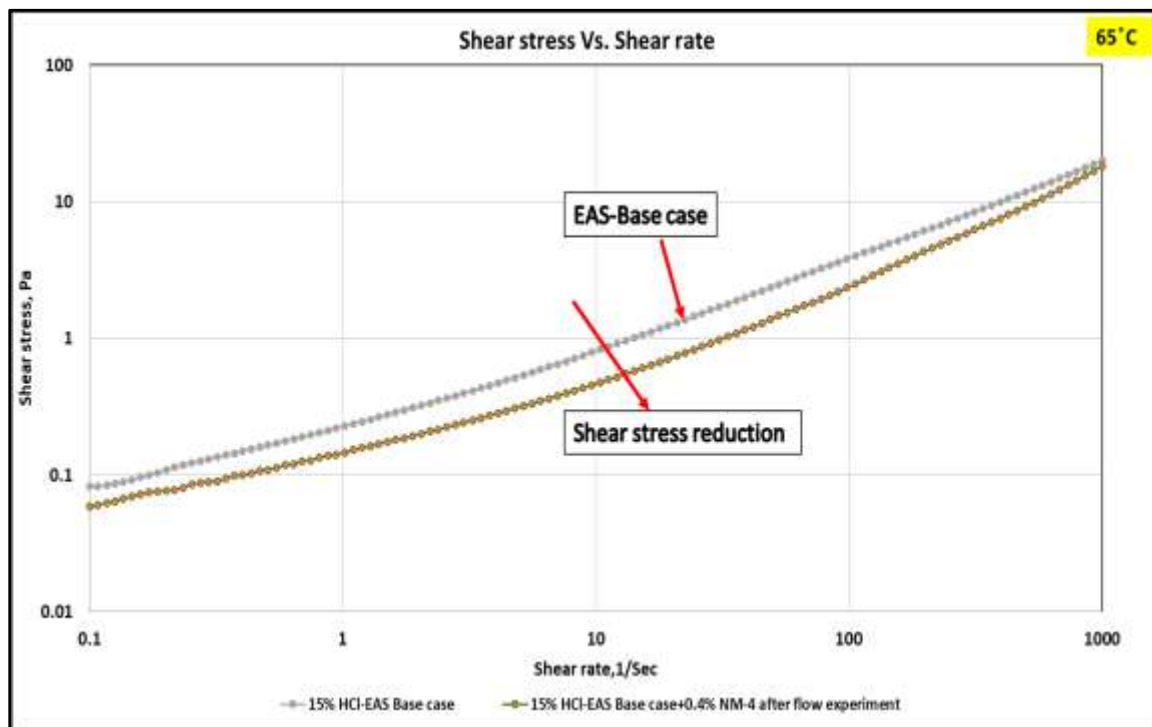


Figure 14 15% HCl EAS shear stress (Pa) vs. shear rate (1/sec) at 65 °C (Sample after flow experiment)

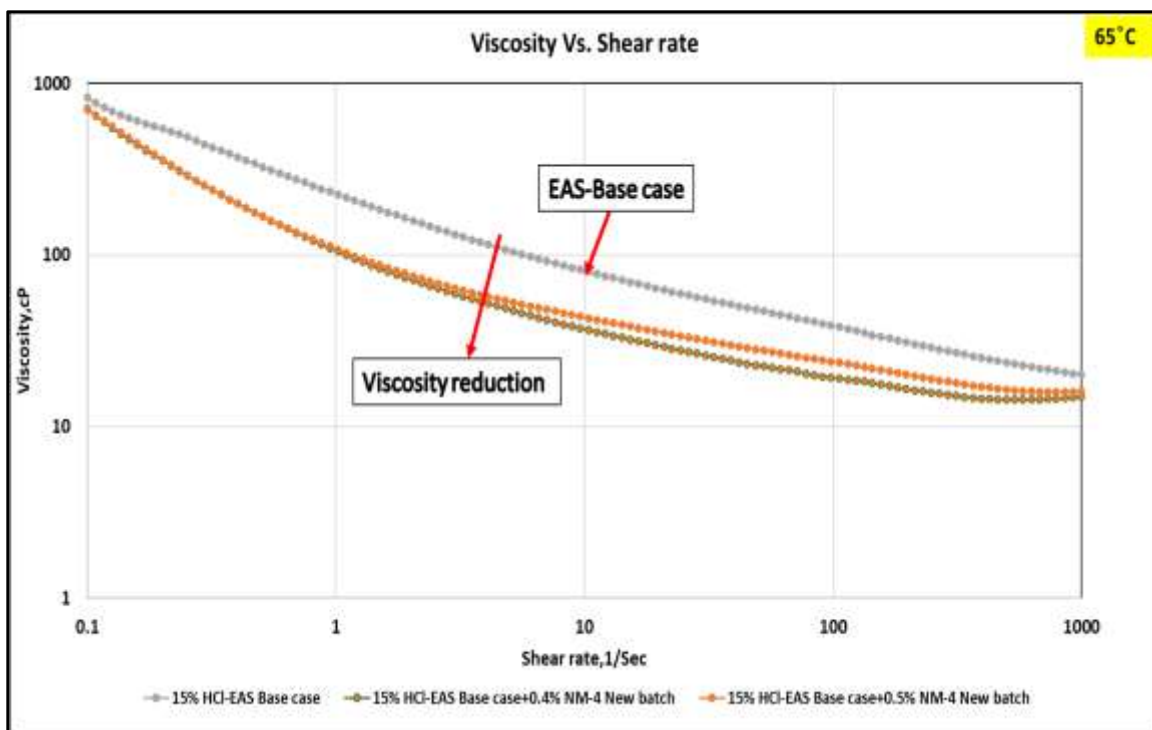


Figure 15 15% HCl EAS viscosity (cP) vs. shear rate (1/sec) at 65 °C (New batch)

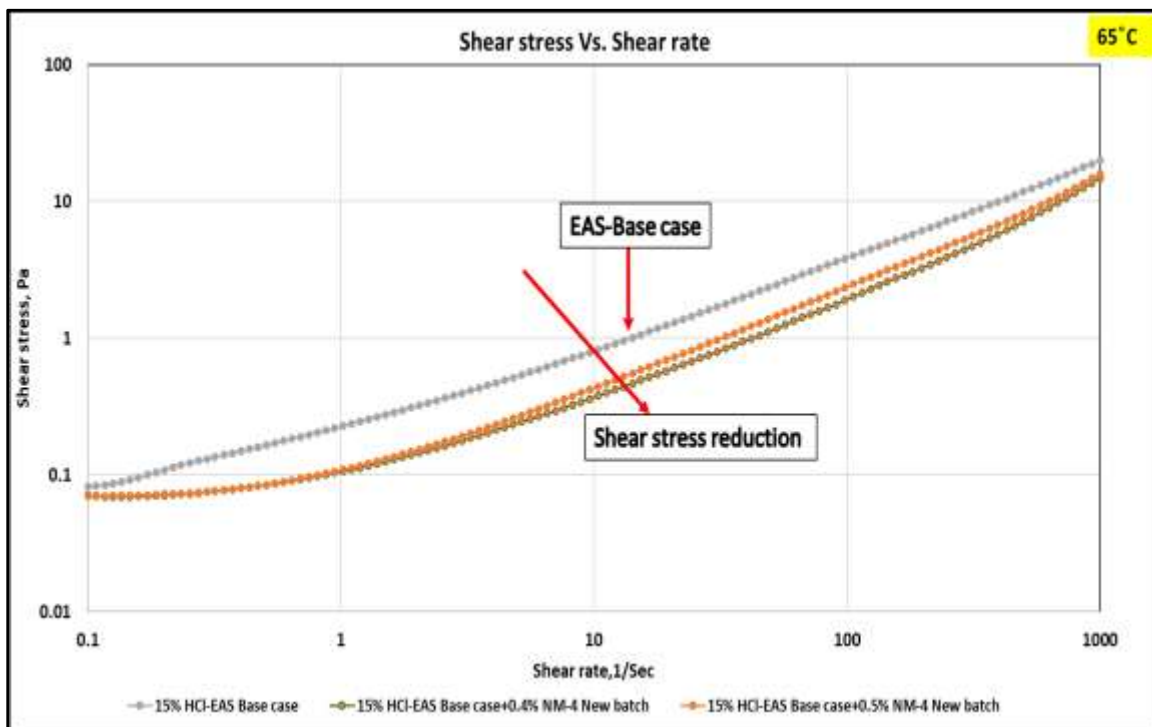


Figure 16 15% HCl EAS shear stress (Pa) vs. shear rate (1/sec) at 65 °C (New batch)

3.4.5 Drag reduction

The Drag reduction unit (flow loop) was utilized to conduct the drag reduction experiments. Firstly the drag reduction unit was calibrated with diesel as shown in Figure 17, then the EAS was prepared in large quantities (30-40 Liter) as shown in Figure 18. 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.

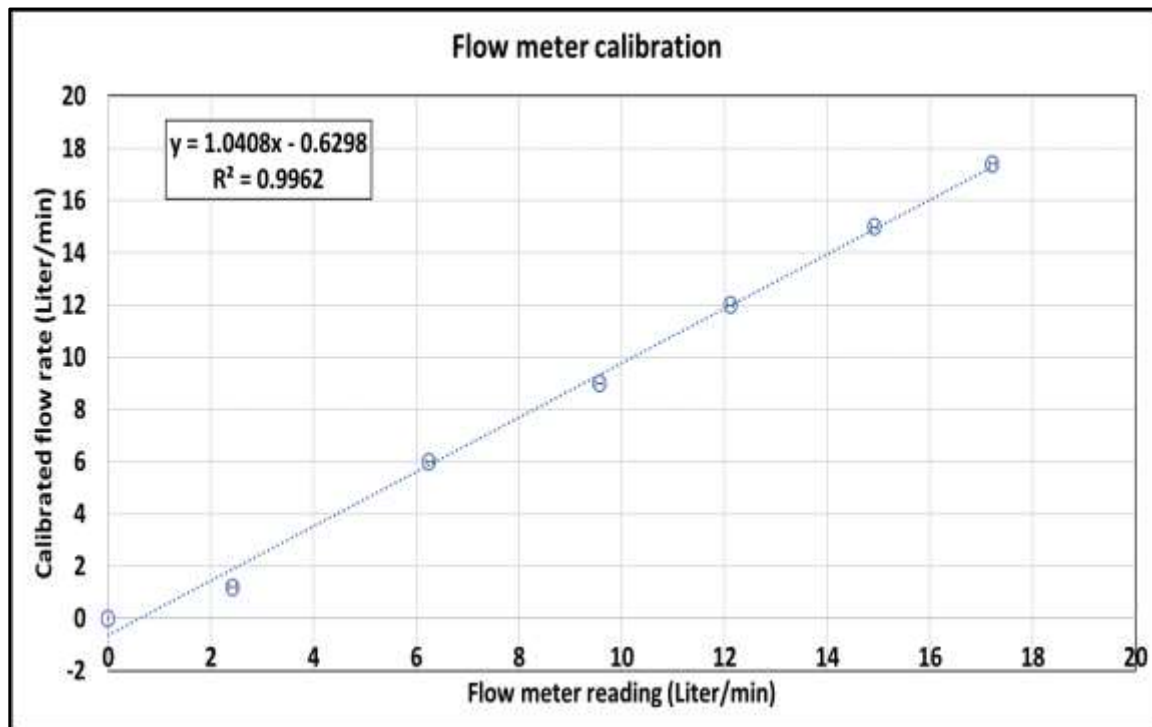


Figure 17 The drag reduction flow loop calibration with diesel

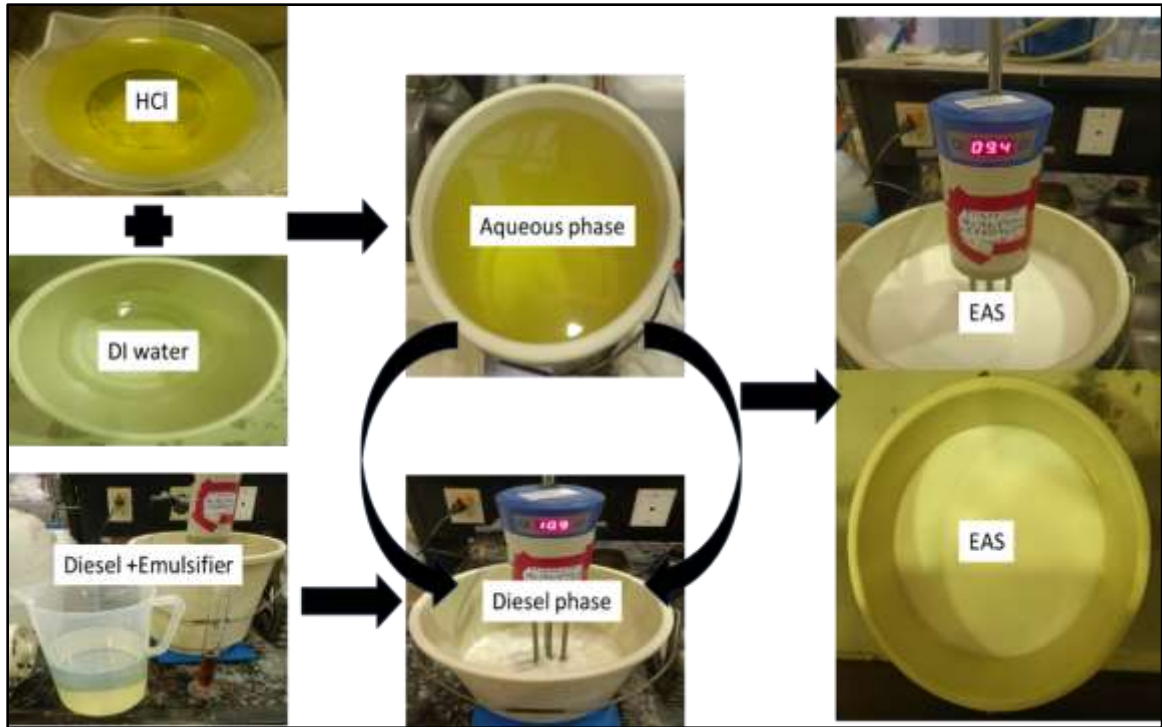


Figure 18 EAS preparation for flow experiment

Two different HCl concentrations of EAS were investigated in the flow experiments (15 and 20 %). The pressure drop of the base case of 15% HCl-EAS was plotted against the flow rates at ambient temperature (25 C) as shown in Figure 19. Figure 19 shows that pressure drop increases with an increase in the flow rate. However, the increase in pressure drop with flow rate is non-linear hence 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 EAS. The shear stress decreases with an increase in shear rate attributing to the shear thinning behavior.

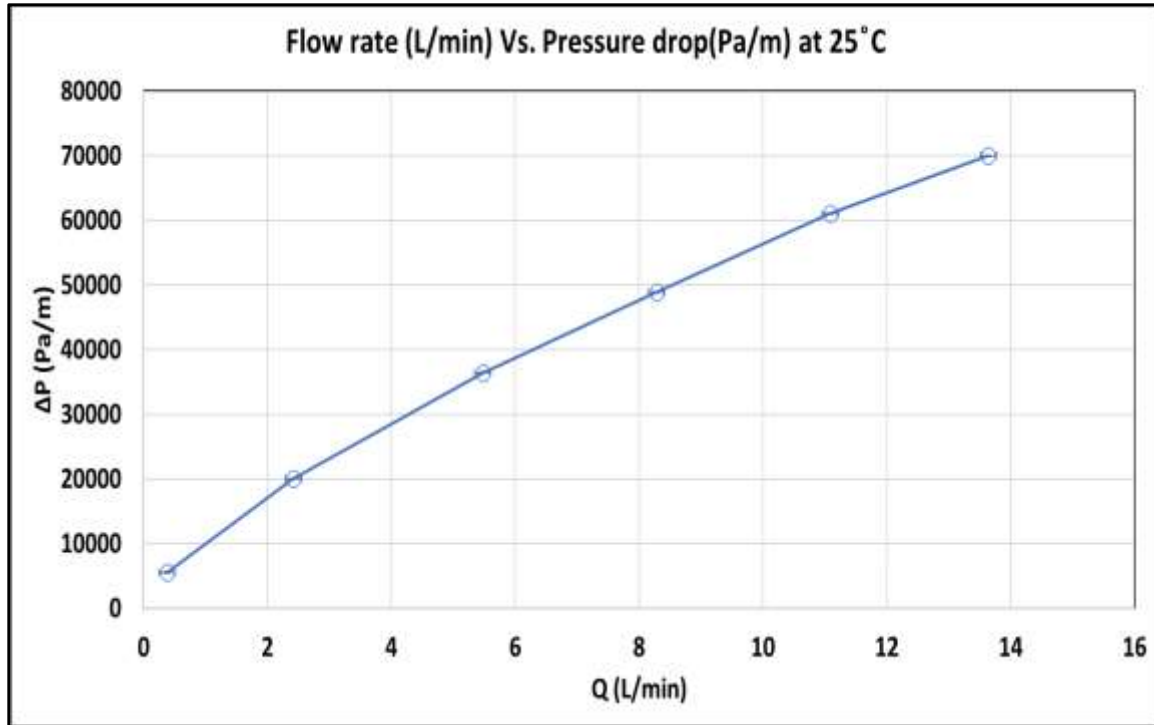


Figure 19 Flow experiment of 15% HCl-EAS (Base case) at 25 °C

The effect of temperatures on the flow behavior of the EAS is shown in Figure 20 (15% HCl-EASn(base case)). Figure 20 shows that the increase in temperature causes a reduction in the 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 psi/ft (1 psi~6895 Pa) at 40 C, and 7.5 psi/ft (1 psi~6895 Pa) at 50 C. It indicates that the changes in the viscosity of EAS are insignificant at high temperatures. These results are consistent with the results from rheology experiments, where a reduction in the viscosity of EAS was observed with an increase in temperature.

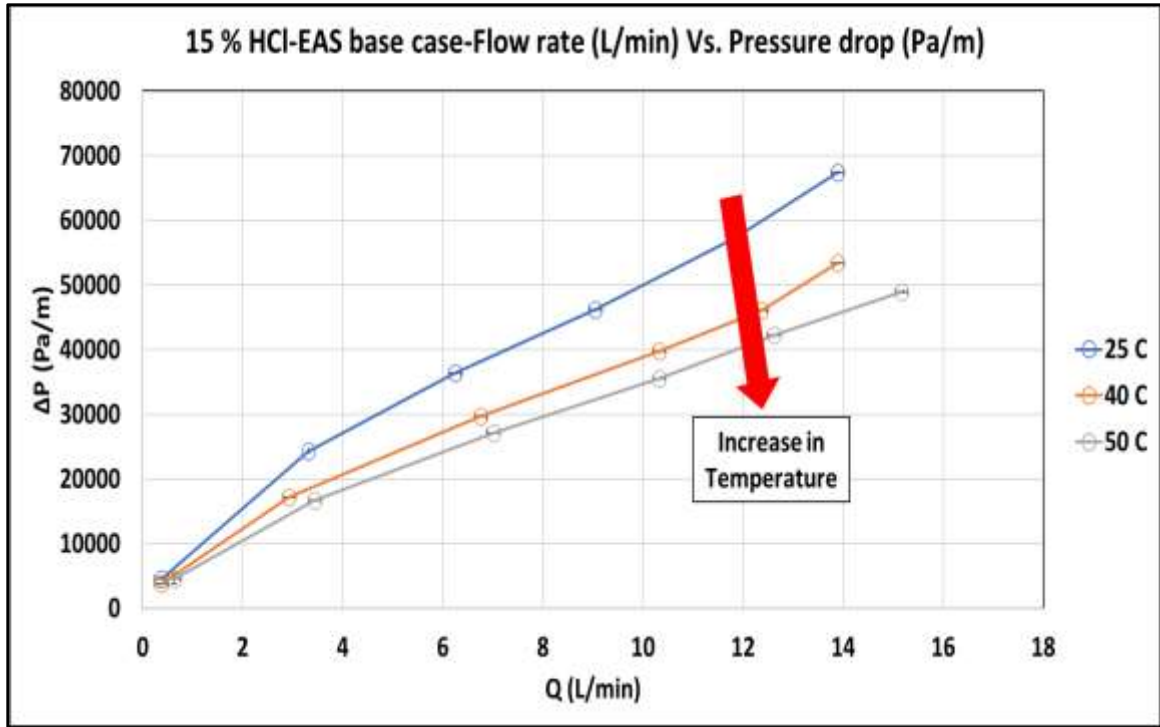


Figure 20 Effect of temperatures on the 15% HCl-EAS (Base case) flow experiment

Figure 21 shows the drag reduction of the EAS with the aid of NM (CND). Figure 21 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 21 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 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 the range of flow rates and temperatures.

It is evident from Figure 21 that the drag reduction can be achieved by the addition of NM (CND) to the EAS. The magnitude of drag reduction appears to be significant at higher

flow rates compared to the 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) observed. The reduction in the drag due to the addition of the NM can be ascribed to hydrodynamic stabilization, turbulence suppression, and steric stabilization (Esfandiari et al., 2020; Luo et al., 2021; Shaw, 2020). CNDs can form a layer on the surface of the fluid, which reduces the friction between the fluid molecules, and as a result reduction in the viscosity of the fluid occurs and the fluid can flow more easily (Sworna et al., 2023). This study does not reveal the exact mechanism of the drag reduction. The main complexities associated with the CND are its chemical nature and the interaction of the CND at the molecular level. Another challenge is the interaction of CND with additives used for the preparation of the EAS.

Figure 22 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 21, the only difference is the pressure drop and flow 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 Figures 23 and 24, respectively. It can be observed that the addition of NM even at the high temperature helps in drag reduction. The magnitude of the drag reduction was decreased with an increase in temperature. Adding NM to the 15% HCl-EAS reduces the drag at 40 C, while the drag reduction was small at 50 C. It should be noted that at higher temperatures the pressure drop /viscosity values of EAS acid are lower compared to the base case, however, the trends show higher drag reduction with an increase in flow rates which is generally practiced in the field operation.

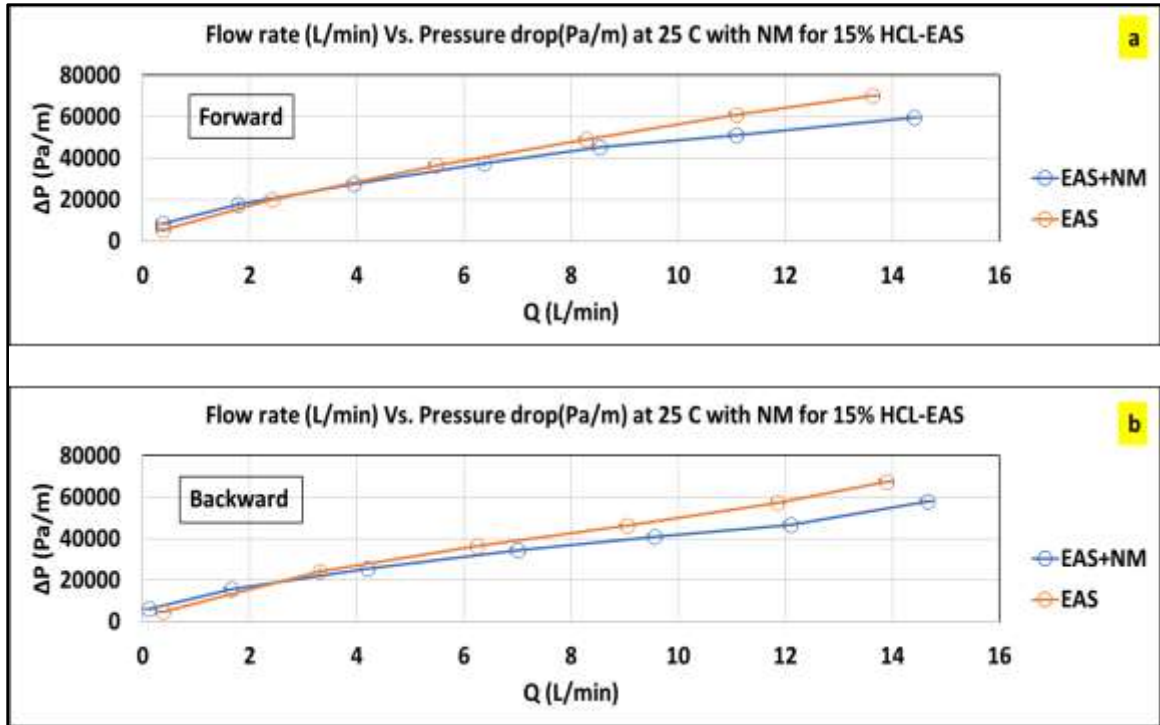


Figure 21 Effect of adding NM to the 15% HCL-EAS (Base case) pressure drop at 25 C

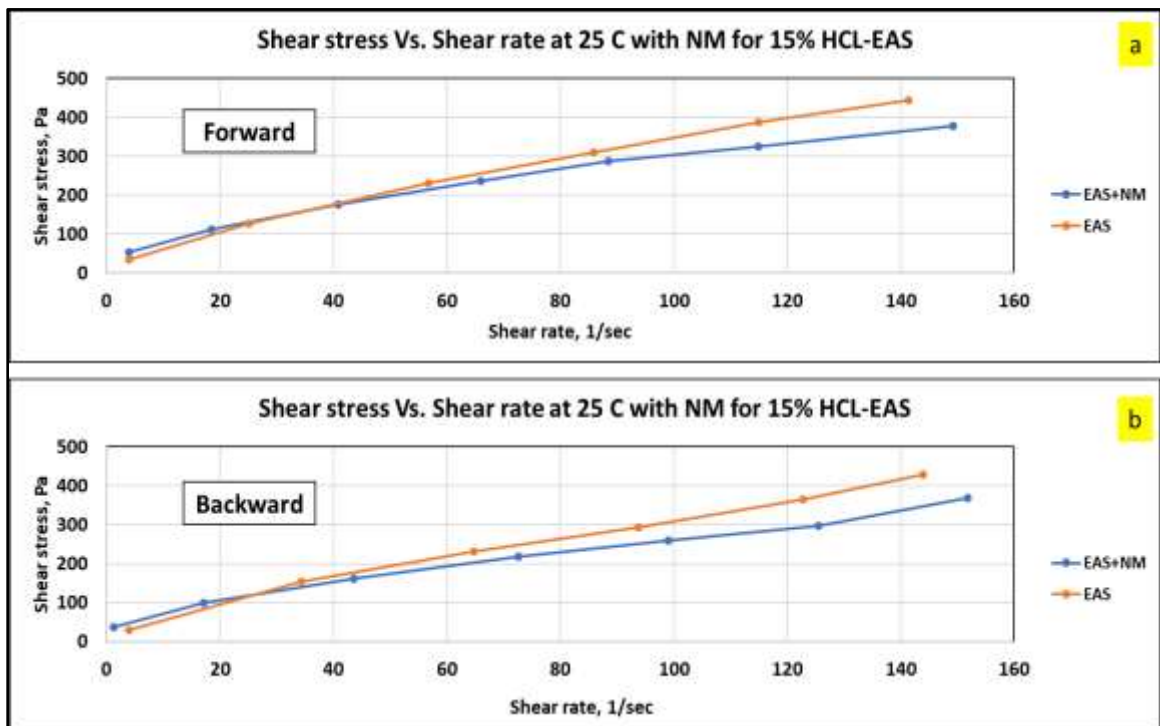


Figure 22 Effect of adding NM to the 15% HCL-EAS (Base case) shear stress at 25 C

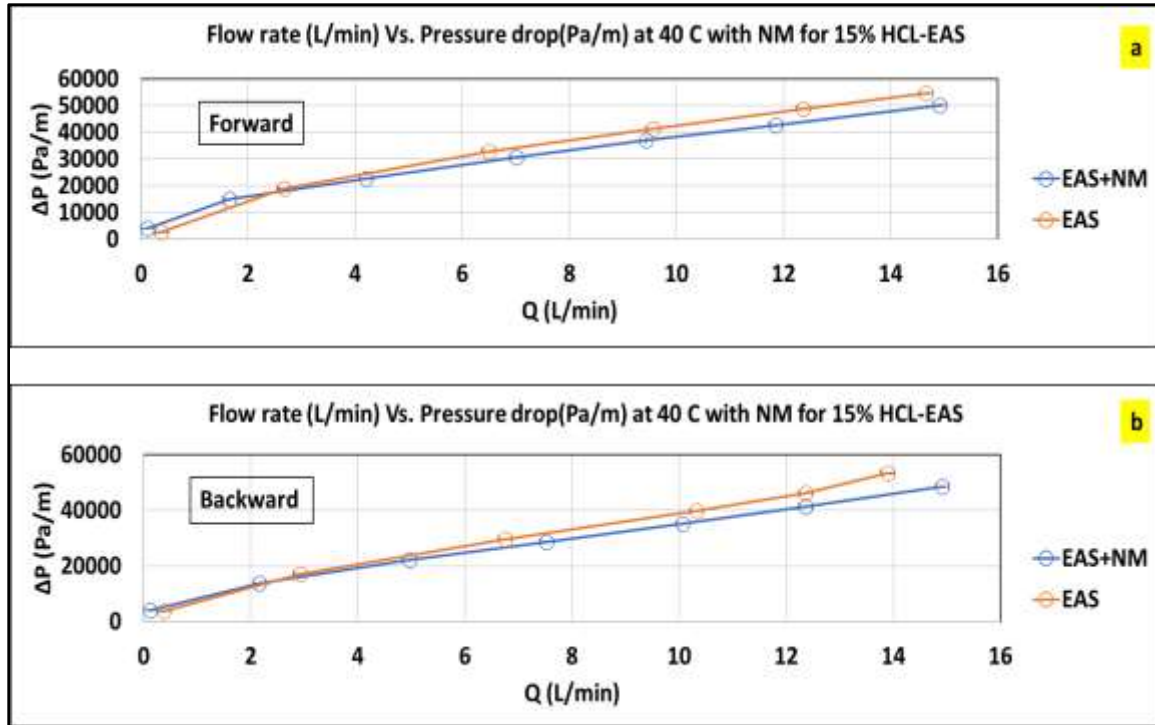


Figure 23 Effect of adding NM to the 15% HCL-EAS (Base case) at 40 °C

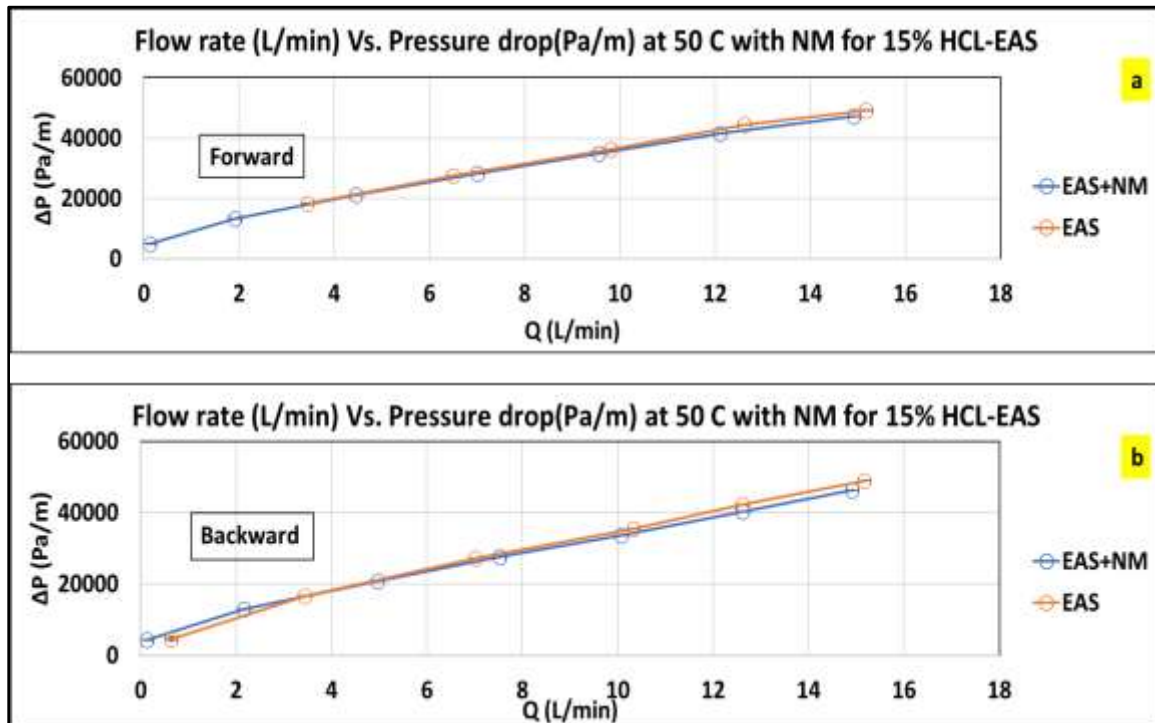


Figure 24 Effect of adding NM to the 15% HCL-EAS (Base case) at 50 °C

In addition, the flow experiment for the 20% HCl-EAS before and after adding NM was conducted using the drag reduction flow loop covering the range of flow rates and temperature comparable with 15% HCl-EAS. The effect of increasing the temperatures on the flow experiment of 20% HCl-EAS (base case) is shown in Figure 25. 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 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.

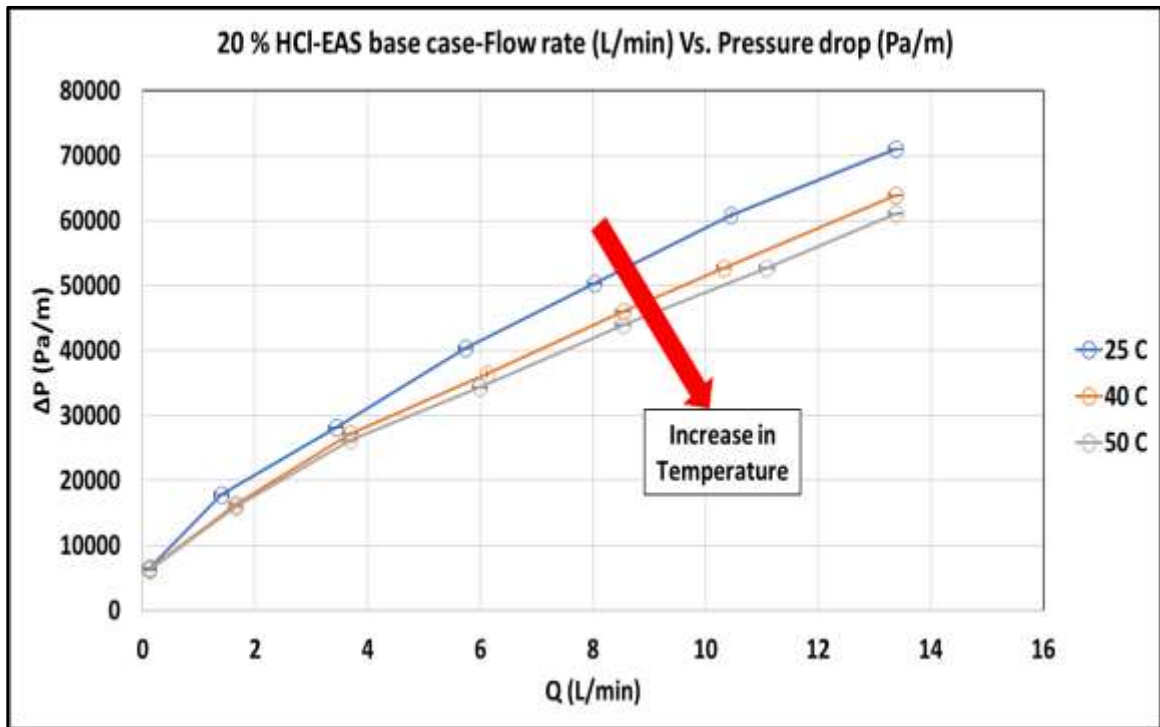


Figure 25 Effect of temperatures on the 20 % HCl-EAS flow experiment

Figure 26 shows the comparison between the pressure drop of 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.

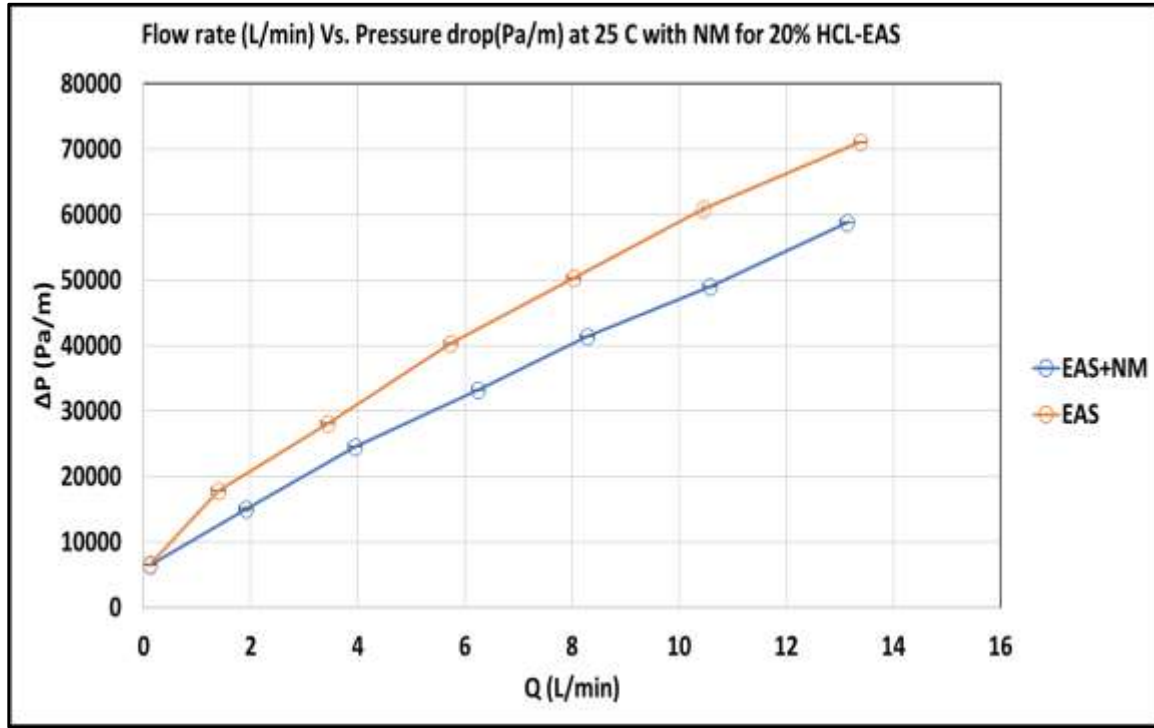


Figure 26 Effect of adding NM to the 20% HCl-EAS pressure drop at 25 °C

After that, the flow experiment of the 20 % HCl-EAS+NM was done at higher temperatures (40 and 50 C) as shown in Figures 27 and 28, 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 15% HCl emulsion i.e. 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 CNDs NM for achieving the drag reduction of EAS irrespective of viscosity and temperature.

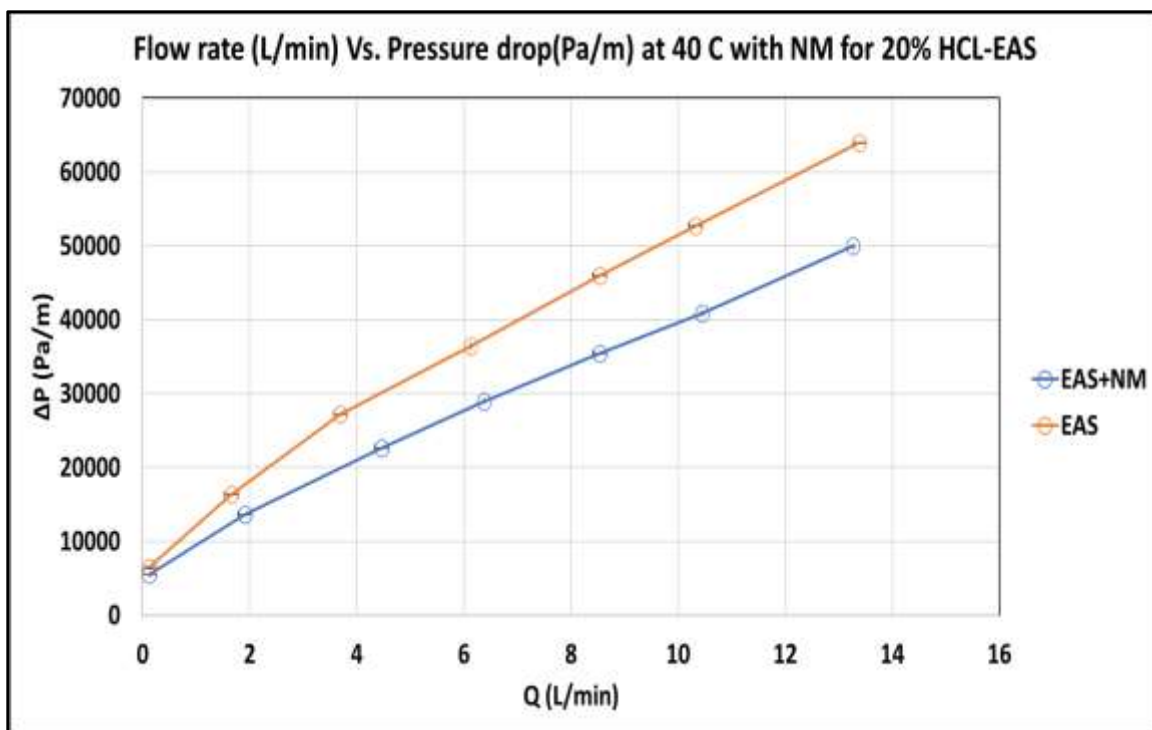


Figure 27 Effect of adding NM to the 20 % HCL-EAS at 40 °C

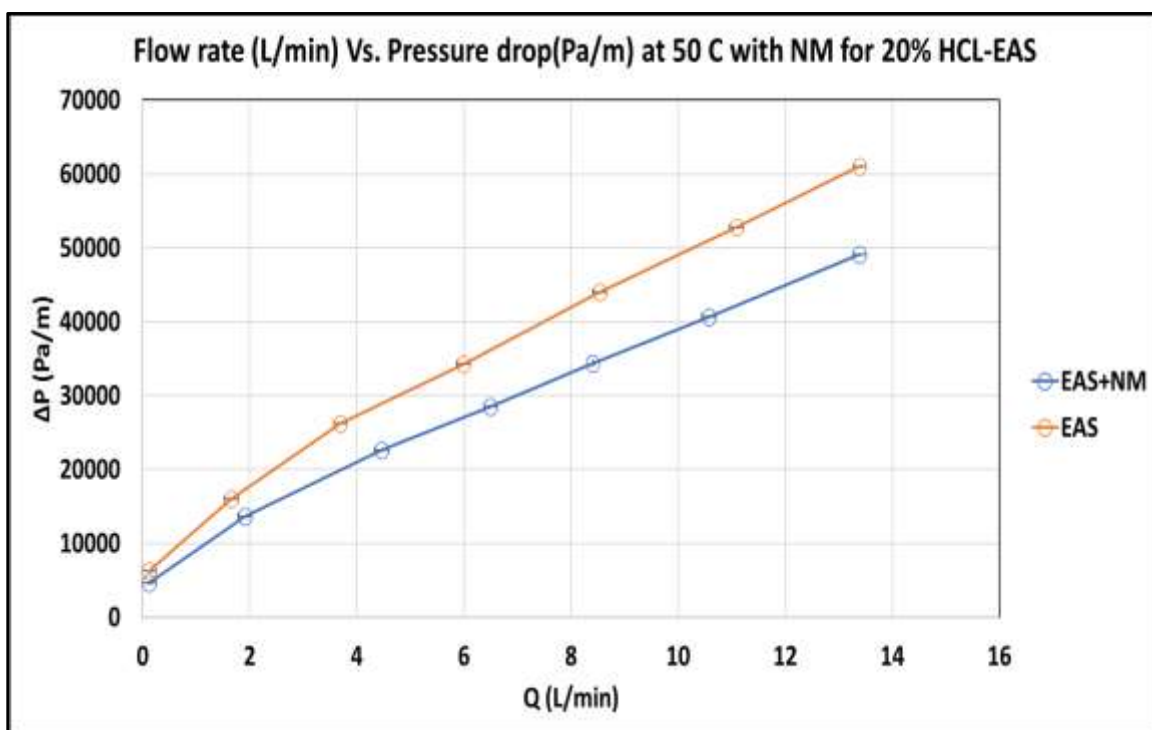


Figure 28 Effect of adding NM to the 20 % HCL-EAS at 50 °C

Further, a sample of the 20% HCl-EAS (base case), as well as for the 20% HCL at 40 and 50 C was collected for analysis to ensure it retains the rheological behavior after the flow experiment. The samples were analyzed for rheology using a rheometer. Figure 29 shows the viscosity as a function of share rates for the 20 % HCl-EAS samples that were taken from the flow loop before and after adding NM. It is evident from Figure 29 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 hours as shown in Figure 30.

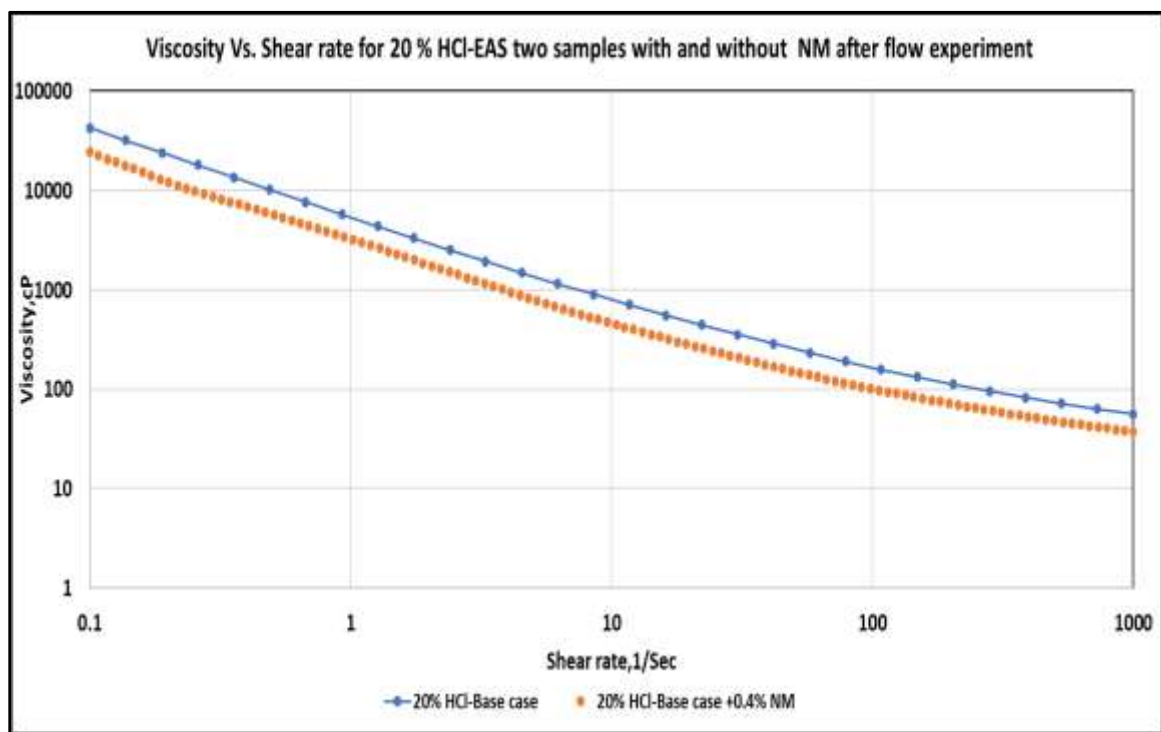


Figure 29 20 % HCl EAS viscosity (cP) vs. shear rate (1/sec) at 65 °C

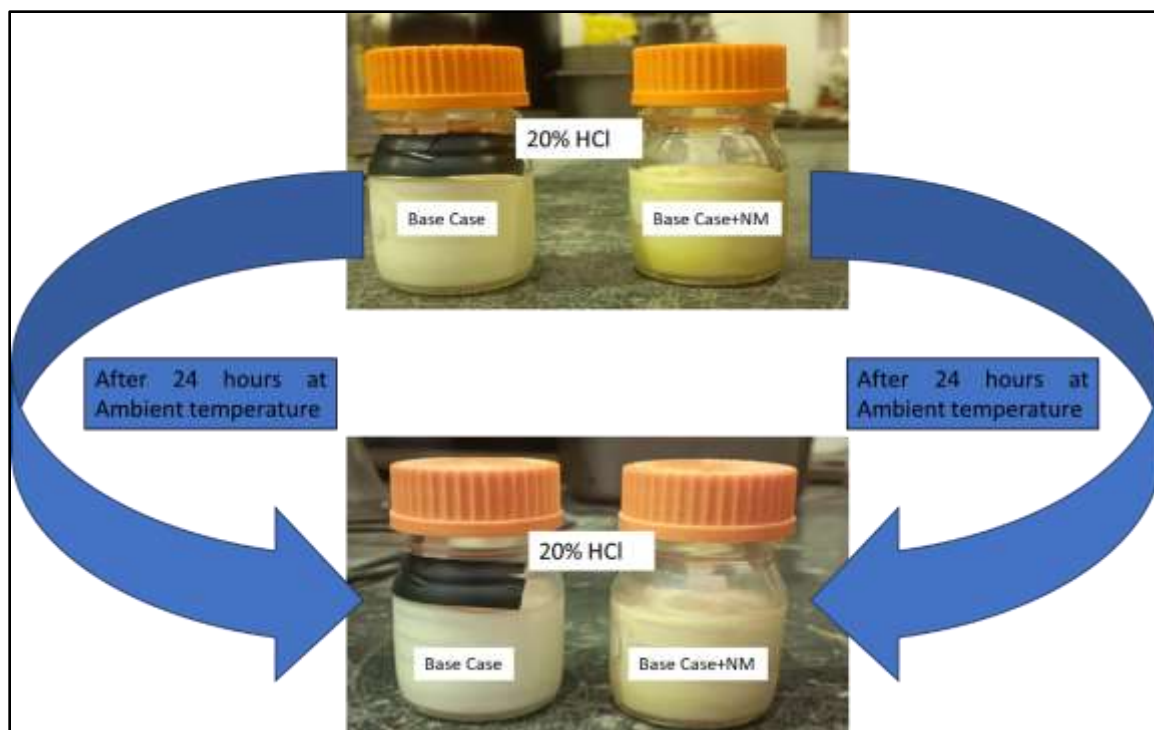


Figure 30 20 % HCl EAS stability for 24 hours at 25 °C

3.4.6 Discussion

Carbon nanodots (CNDs) show potential to be used in the petroleum industry because they are showing promising results in different applications in the oil and gas industry (Alsaba et al., 2020; Hajiabadi et al., 2020; Lu et al., 2007; Mady and Kelland, 2020; Negin et al., 2016; Yang et al., 2015). 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 high surface area and tunable surface chemistry, so they can be utilized as catalysts for many processes such as hydrocracking and reforming, which improve the refining operations efficiency. CNDs are promising surface-active agents for altering the wettability from strongly oil-wet to water-wet in the carbonate reservoirs (Sakthivel et al., 2024). CND can be used as nanofluids for heat transfer as well as it can be used as a corrosion inhibitor (CI), where CNDs 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 (Sadeghalvaad et al., 2023), 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 (Negin et al., 2016), where CNDs can alter the interfacial tension (IFT), wettability, and viscosity and as a result, enhance the oil displacement and increase the oil recovery (Kanj et al., 2020; Okunade et al., 2021; Sakthivel et al., 2024, 2021, 2019; Yekeen et al., 2020). 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 the wellbore stability (Shaw, 2020). This paper explored the utilization of CNDs as viscosity reducers for EAS, as well as DRA for the EAS.

CNDs can work as viscosity reducers and DRA for fluids, and there are different mechanisms for CNDs to work as DRA and viscosity reducers, these mechanisms include hydrodynamic stabilization, turbulence suppression, and steric stabilization (Chauhan, D. S., Quraishi, M. A., & Verma, 2022). CNDs can form a layer on the surface of the fluid, which reduces the friction between the fluid molecules, and as a result reduction in the viscosity of the fluid occurs and the fluid can flow more easily (Sworna et al., 2023). A similar mechanism was given for the nano-material for drag reduction in hydraulic fracturing fluid, horizontal pipe as well and multiphase flow (Esfandiari et al., 2020; Luo et al., 2021; Pouranfard et al., 2015; Sun et al., 2016).

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 and this helps in reducing the fluid viscosity and improving the flow (Nyholm and Espallargas, 2023; Sakthivel et al., 2019). 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 (Kanj et al., 2020; Sakthivel et al., 2024). 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, so interfering with their formation can reduce the drag.

In general, the mechanism by which CNDs work as viscosity reducers and DRA depends on different factors, including the type of CNDs, CNDs' concentration, the fluid they are added, and the conditions under which they are used. Utilizing the CNDs as viscosity reducers or DRA has some advantages, including 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 DRA is still in the early stages of development, but it offers many advantages that help reduce 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 nanometers. CNDs are characterized by some unique properties, including a high surface area, good dispersibility in water and other liquids, and the ability to modify the surface properties of other materials. CNDs can reduce the EAS viscosity through various mechanisms, one of which involves 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, leading to a decrease in viscosity. Another mechanism involves the interaction of the CNDs with water molecules in the EAS, forming hydrogen bonds. This creates a network structure that traps water molecules and reduces their mobility, also leading to a decrease in viscosity. CNDs can also function as DRAs, reducing the resistance to the flow of the EAS. This is thought to be due to the ability of CNDs to form a boundary layer on the surface of the flow channel, reducing the friction between the EAS and the flow channel and resulting in decreased 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 environmentally friendly. The findings suggest that CNDs could be used as effective viscosity reducers and DRA for the EAS, leading to 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 DRA and viscosity reducers.

3.5 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 EAS. It does not alter chemistry as well as other properties except for the 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 the reduction of the EAS viscosity, however, the CNDs NM retain its efficacy at higher temperatures as well at lower values of 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 the flowing of the fluid at different temperatures and time durations.

CHAPTER 4

DEVELOPMENT OF EMULSIFIED ACID

SYSTEM (EAS) USING ORGANOCCLAYS (OC):

RHEOLOGY AND IMPLICATION TO THE

ACIDIZING

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Ala, A. D., Gajbhiye, R., Sultan, A., Solling, T., Patil, S., & Alsarkhi, A. (2023). Development of emulsified acid system (EAS) using organoclays (OC): Rheology and implication to the acidizing. *Geoenergy Science and Engineering*, 212022.

4.1 Abstract

Matrix acidizing is a well-stimulation technique extensively used in the petroleum industry to increase well productivity by removing scales and creating channels in the rocks. However, conventional acidizing fluids used in this process have some limitations including rapid reactions with scale and fines, high acid strength, and corrosion of equipment at high temperatures. To address these issues, an emulsified acid system (EAS) is used in fracturing and acidizing operations for carbonate reservoirs to improve well

productivity by removing formation damage. EAS can help to improve well productivity by creating deeper and narrower wormholes through reduced reaction rates of acid due to the external oil phase. However, EAS has limitations such as low stability at high temperatures, high viscosity that restricts pumping rates, potential formation damage, and difficulty in achieving homogenous mixing. Pickering emulsions, which use solid microparticles as a stabilizer instead of surfactants, show promise in overcoming these challenges due to their easy preparation, good thermal stability, and low viscosity at high shear rates.

This study investigates the use of various types of organoclays (OC) for developing emulsified HCl acid systems for carbonate reservoirs. Several experiments were conducted to demonstrate and evaluate the use of OC for EAS and to improve field operations. To advance the development of EAS, a meticulous process was undertaken to select and optimize OCs as the key component. This process included mineral characterization by XRD and XRF techniques, optimization of OC concentration (250–1000 ppm), and mixing speed (4000–8000 RPM). The thermal stability of the EAS was evaluated for a temperature range of 25–160 °C and a comprehensive analysis of EAS rheology ($0.1\text{--}1000\text{ sec}^{-1}$) was performed. Conductivity, drop-test analysis, as well as micrographic analysis, were carried out to ensure the formation of an inverted emulsion. It was found that the required mixing speed was 6000 RPM and the optimum OC concentration was 500 ppm for developing a stable invert emulsion.

The viscosity of the EAS shows increasing trends with an increase in temperature at the low shear rates (below 10 sec^{-1}); however, at high shear rates (higher than 10 sec^{-1}), the EAS viscosity decreases with temperature. The study concludes that OCs are promising

emulsifiers for creating EAS with good thermal stability and low viscosity at high shear rates. The EAS formulated using OC proved to be robust and thermally stable, making them suitable for field mixing procedures. Additionally, the OCs used in the study are cost-effective, readily available, environmentally friendly, and have a high surface area, making them advantageous as an emulsifier.

4.2 Introduction

Well stimulation is defined as the treatment that is used to restore or improve the productivity of oil and gas wells. Well stimulation can be performed by two main techniques, matrix acidizing, and hydraulic fracturing. The matrix acidizing technique is carried out with a pressure lower than the fracture pressure of the reservoir, while in the case of hydraulic fracturing, the process is conducted at a pressure higher than the formation pressure.

Acid systems are commonly used in the petroleum industry to stimulate the carbonate reservoirs by removing the formation damage and increasing the productivity of oil and gas wells. However, managing the convective delivery of acid deep into the reservoir while maintaining a minimum rock face dissolution is one of the critical problems in carbonate acidizing treatments. Besides, conventional acidizing fluids are limited to some constraints such as high acid strength and rapid reaction with scale and fines near the wellbore area, also at high temperatures, they tend to corrode tubing, casing, and downhole equipment.

The EAS has become widely used in the oil and gas industry to overcome conventional acid systems' flaws. EAS is usually formed with acid and diesel, and the diesel acts as a diffusion barrier between the acid and the rock (Fatah and Nasr-El-Din, 2010, 2008). The

EAS is a water-in-oil (W/O) emulsion, in which the acid phase is encapsulated by the diesel phase using an emulsifier (Kasza et al., 2006; Nasr-El-Din et al., 2008; Sidaoui and Sultan, 2016). The EAS has been considered a non-Newtonian shear-thinning fluid as the apparent viscosity is sensitive to shear changes. So the power-law model can be used to represent the EAS, where the viscosity decreases with an increase in the shear rate (Lynn and Nasr-El-Din, 2001; Nasr-El-Din et al., 2000).

Many researchers conducted several studies to investigate using the EAS to stimulate the carbonate reservoirs (Al-Mutairi, S. H., Hill, A. D., 2008; Buijse and Van Domelen, 2000; Crowe et al., 1990; Navarrete et al., 2000; Nierode and Kruk, 1973; Siddiqui et al., 2006; K C Taylor et al., 2006). However, the EAS is still limited by other constraints such as low stability at elevated temperatures, high viscosity that restricts the pumping rate due to frictional losses, the potential for formation damage, and the difficulty of achieving homogeneous field-scale mixing.

In addition, the currently used emulsified acid fluid systems prevent injection or pumping at low flow rates and limit the placement (depth of penetration) in the matrix or fractured system. Historically, there is no simple solution to this problem, emulsified acid treatment design only aims at placing the acid as fast, and deep as the friction allows it. Therefore, having lower friction characteristics would allow for higher pumping rates.

Organoclay (OC) is defined as an organic phyllosilicate (disilicate), and it is derived from a clay mineral that occurs naturally. OC can be used as an emulsifier to prepare Pickering emulsion meanwhile it can be used as a drag-reducing agent (DRA). In addition, OC has some advantages such as its low cost, availability, high surface area, and being

environmentally friendly. The EAS is intended to be robust in terms of field mixing procedures and thermal stability with time.

The objective of this study is to implement an engineered retarded acid system with low viscosity by developing effective emulsified HCl acid blends that can be delivered in the field without incurring high frictional losses which limit their applicability. In particular, this study aims to investigate using different types of OC as an emulsifier to develop a Pickering emulsified HCl system for carbonate reservoir stimulation. The procedures of Pickering EAS preparation, thermal stability, and rheological properties have been presented in detail.

4.3 Literature review

The emulsion is defined as the colloidal dispersion of one liquid which is called the disperse phase (internal phase) and in another liquid is called the continuous phase (external phase). The two phases are immiscible liquids (Adewunmi et al., 2022; Israelachvili, 1994). Emulsions can be classified into four different types water-in-oil (W/O), oil-in-water (O/W), water-in-oil-in-water (W/O/W), and oil-in-water-in-oil (O/W/O). However, the widest form of emulsion in the oil and gas industry is W/O emulsion. To control and manipulate the number, size, and size distribution of internal droplets in multiple emulsions, emerging emulsion processing methods such as microfluidic emulsification could be used (Pal, 2011).

Generally, emulsions are unstable and they can be categorized based on their kinetic stability into three types, loose emulsions which are those emulsions stable for only a few minutes, the emulsions that are stable for tens of minutes are called medium emulsions,

while those emulsions that are stable for hours/days are named as tight emulsions. The stability is affected by many factors such as heavy polar materials, small solids, including organic (asphaltenes, waxes) and inorganic (clays, scales, products of corrosion), temperature, distribution of droplet size, brine pH, and brine composition (Kokal, 2008). A pH influences the emulsion stability and severe emulsion upsets always occur due to solid precipitation, mainly asphaltenes, after acid stimulation, and as a result, a tight and very stable emulsion will be formed which may kill the well. So an appropriate acid treatment design is imperative to prevent emulsion upsets.

Pickering emulsion is defined as the emulsion that is controlled and stabilized by solid particles such as silica and clay, these particles adsorb onto the interface between the two phases. Pickering emulsions can be widely used in the petroleum industry due to their improved thermal stability. In general, the wettability of solid particles, at the interface between oil and water phases, is used to determine the Pickering emulsion W/O or O/W. In the case of Pickering emulsion, the dispersed liquid phase is the one that wets solid particles lower than the second liquid phase has better wetting capacity, and becomes the continuous phase and the other becomes the dispersed phase. Pickering emulsion is considered a biologically compatible and eco-friendly emulsion; besides that, it is more stable against coalescence (Tang et al., 2018). Furthermore, the strength of ions plays an important role in the stability of Pickering emulsion. (Xie et al., 2018) explored the effects of some parameters on Pickering emulsion, these parameters included particle concentration, pH, homogenization speed, type of oil, and particle size distribution, and they concluded that emulsion stability increased with increasing particle concentration, and

homogenization speed, whereas pH and oil type, had a negligible effect on the emulsion stability.

4.3.1 Emulsified acid system (EAS)

Conventional acidizing liquids, such as hydrochloric acid (HCl) are widely used to stimulate the carbonate reservoirs. It has a high acid strength and a rapid reaction with scales and fines closest to the wellbore. Also, at high temperatures, they cause problems for tubing, casing, gravel pack screen, and downhole pumps. In addition, above 93 °C, HCl is not recommended in some cases due to its damaging impact on the formation (Huang et al., 2013). Some acid systems can be used without damaging the downhole equipment at high temperatures, such as mixtures of tricarboxylic acids, amino carboxylic acids, and dicarboxylic acids (Huang et al., 2013).

A combination of two immiscible fluids is defined as an emulsion, wherein one fluid is called the internal phase or dispersed phase, while the other fluid is named the external phase or continuous phase. For an EAS, the diesel is a continuous or external phase surrounding the HCl droplets that form an emulsion of acid-in-diesel. A concentrated (15–28 percent) HCl acid is usually used in the oil and gas industry (Adewunmi et al., 2022; Al-Mutairi, S. H., Hill, A. D., 2008). The EAS is widely used for fracturing and acidizing operations in carbonate reservoirs to improve the formation permeability and increase oil and gas production., The EAS causes reducing or retarding rates because of the oil's external (outer) phase and as a result, deeper and narrower wormholes can be formed.

An emulsifier is used to emulsify the aqueous acid with oil and to increase the EAS's stability with temperature. Sometimes very small particles are used such as colloidal clay

particles and/or nanoparticles for the formation of emulsion. The stabilized emulsified acid system consists of at least one oil, a solution of aqueous acid containing at least one acid, at least one emulsifier, and acid-insoluble nanoparticles, having an average particle size of one thousand nanometers or less (Huang et al., 2013). The acids emulsified with oil, typically diesel, can minimize corrosion of pumping and downhole equipment, and reduce the rates of reaction with carbonate formation at elevated temperatures, providing deep penetration of active acid into the formation. The physical properties of the emulsified acids are highly influenced by the preparation methods, so the analysis of emulsified acids by their droplet size distribution integrates its chemical composition and gives the emulsified acid a specific description and thus reproducible properties (Al-Mutairi, S. H., Hill, A. D., 2008).

De, 1933 was a pioneer in using acid-in-oil emulsion. The EAS is either a macro or microemulsion (Al-Anazi et al., 1998; Hoefner et al., 1987), however, the macro emulsions are the most widely used in the field due to their larger droplet size and they require less emulsifier (Al-Anazi et al., 1998; Kasza et al., 2006; Mohamed et al., 1999; Nasr-El-Din, H. A. et al., 2000; Sayed and Nasr-El-Din, 2011). (Pandya et al., 2012) developed a unique EAS with a combination of three intensifiers for the stimulation of very high-temperature carbonate reservoirs. The proposed EAS can be used for the stimulation of carbonate reservoirs with bottom-hole temperatures (BHT) up to 163 °C°. In addition, they presented a better understanding of the effect of the intensifiers in the EAS.

Sabhapondit et al., 2012 experimentally optimized the 26% HCl-EAS blend for the stimulation of high-temperature carbonate reservoirs. Two different corrosion inhibitors were explored at different temperatures and durations, the results showed that optimizing

the balanced concentration of inhibitor and emulsifier was crucial for designing a good EAS blend.

Madyanova et al., 2012 presented a case study of a matrix stimulation for high-temperature carbonate formation of the Sungai Kenawang (SKN) onshore gas-condensate field, located at the southwest part of the Jambi Merang block in the South Sumatra province of Indonesia. The process was performed through a combination of emulsified and viscoelastic self-diverting acids. They concluded that using highly retarded high-temperature EAS and high-temperature viscoelastic surfactant significantly stimulated the entire interval with a higher productivity index.

Cairns et al., 2016 experimentally investigated an improved EAS in a systematic approach for deeper well stimulation. The investigated parameters include pore pressure, flow rate, acid-rock contact time, and fluid treatment composition. The results showed that the developed stabilized system was three times better than the conventional acid system in terms of core permeability improvement.

Umar et al., 2016 studied the effect of water content, shear rate, shear stress, and temperatures on 30 days aged W/O emulsion, where the consequence of different water cuts and the presence of emulsifier on W/O emulsion were investigated. Also, the W/O emulsions' rheological properties were investigated with different water cuts at two different temperatures (25 and 60 °C). The findings indicated that emulsifier, water content, shear rate, and temperature highly impacted the rheology and stability of W/O emulsions.

Sidaoui and Sultan, 2016 presented an experimental study of the EAS to investigate the factors affecting the HCl emulsified stability based on thermal stability and rheology. The

findings indicated no significant change in the emulsified acid stability when the concentration of the emulsifier changed from 0.5 to 1.5 vol %. Also, the small droplet size of the emulsion means it is more viscous. Besides, the apparent viscosity decreased with increasing temperature.

Further, Sidaoui et al., 2017, 2016 extended the work by using waste oil as the external phase of a 70:30 acid to oil with 15% HCl- EAS. The results revealed the potential of using waste oil as an external phase to prepare the EAS for high-temperature carbonate reservoirs. In addition, the developed HCl-waste oil EAS was a shear-thinning fluid. Another study by Sidaoui et al., 2018 investigated the effect of iron control and chelating agents on the EAS stability and reaction with dolomite. The results showed that the most stable EAS was achieved with no iron control and with little concentration of the chelating agent.

Sayed et al., 2018 presented a low-viscosity retarded acid system for the stimulation of high-temperature carbonate reservoirs. The proposed acid system reduced the free water in the system and consequently prevented a full dissociation of the acid. The results showed that the proposed acid system required only 0.28 pore volume (PV) to achieve a breakthrough in a core sample of 12 inches, which is low PV compared to some EAS, also the fluid viscosity was much less compared with EAS which will help to reduce the drag and increase the pumping rate.

Aldakkan et al., 2018 developed an engineering low-viscosity retarded acid system. The acid system was proposed by combining the use of a strong acid with an organic compound that is highly soluble in the acid. The results showed that the reduction in the core weight

loss to dissolution using the developed acid system was four times compared to the normal 15-wt percent HCl. Besides, their developed acid system showed negligible corrosion and delayed acid reaction with calcite.

Ahmed et al., 2018 proposed a highly stable and cheap EAS to stimulate deep wells in carbonate reservoirs. They used specific nanoparticles as an alternative to surfactants. Core flooding experiments were conducted to investigate the effectiveness of the developed EAS in stimulating deep limestone reservoirs and the results were compared with the conventional EAS that was formed using diesel. The results showed that the diesel EAS was better at low injection rates, while the developed EAS with waste oil was better at high injection rates. They concluded that diesel EAS was superior in the stimulation process. Furthermore, they concluded that the stability of EAS was impacted by some factors such as emulsifier concentration, acid-to-oil ratio, acid and oil types, chemical additives, and preparation methods.

Yousufi et al., 2019 replaced diesel with an environmentally friendly oil to prepare the EAS for matrix acidizing of carbonate rocks. The oil was synthesized from *Jatropha curcas* oil, and the results showed that *Jatropha* oil-based EAS can be used and replace the diesel in preparation for the EAS for matrix acidizing. In addition, the results showed better thermal stability compared to diesel-based EAS. Furthermore, the *Jatropha* oil-based EAS has low toxicity with high fatty acid content.

Sokhanvarian et al., 2019 developed a stable EAS at 149 °C, using a non-aromatic non-ionic surfactant for HPHT wells. The results showed that a non-ionic surfactant can be used

to prepare a stable EAS and a superior stimulation with low acid PVBT at 149 °C with the developed EAS.

Jafarpour et al., 2019 developed a multi-batched acid system to increase the stimulation efficiency of heterogeneous carbonate reservoirs. The results showed that the developed multi-batch acid stimulation system was efficient in the stimulation of heterogeneous carbonate reservoirs. Sayed et al., 2021 proposed a low-viscosity single-phase acid system for acid fracturing in deep carbonate reservoirs at high temperatures. The developed acid system was comprised of a pre-engineered blend of an alkyl sulfonic acid and a strong mineral acid. The results were similar to 15 wt% HCl EAS in terms of diffusion coefficient. In addition, the low viscosity led to a reduction in drag and as a result high pumping rates through the tubular.

Al-Sabea et al., 2022 developed a low-viscosity polymer-free acid retarded system, and they presented a successful case study performed in the west Kuwait field. Their proposed acid system combines the use of a strong mineral acid (e.g. HCl) with a non-damaging retarding agent that allows deeper penetration of the HCl acid into the formation. The results showed that the proposed acid system was promising compared to the EAS which pumped in a nearby well. In addition, the developed acid system reduced environmental concerns, as well as costs.

Zakaria et al., 2022 developed a novel low-viscosity, single-phase, polymer-free delayed HCl acid system for stimulation of high-temperature carbonate reservoirs. Their results showed that the developed delayed HCl acid system required less acid pore volume to breakthrough (PVBT) compared to HCl acid at all injection rates. In addition, using a low

viscosity delayed HCl acid improved the acid penetration to access deeper reservoir area, which helped to reach a successful acid stimulation process.

4.3.2 Organoclay (OC)

Organoclay (OC) is defined as an organically modified phyllosilicate (disilicate). Organoclay is derived from a clay mineral that occurs naturally. The separation of the layers due to the exchanges of ions and the alteration of the chemical character of the surface of the clay allows what is known as nanocomposite to be obtained by in situ polymerization or mixing with certain polymers. Recently, OC polymers have become widely used as emulsifiers, as well as DRA due to some advantages of physical properties such as high surface area, reduced drag, and higher thermal stability (Ray and Bousmina, 2005), they are low cost, available, and environmentally friendly.

Mohamed et al., 2018 conducted a study to explore the use of OC as a stabilizer in high temperature and high salinity conditions for W/O emulsions. The findings of their study showed that with increasing concentration of the proposed OC, the stability of the emulsion was improved, where the total separate volume decreased by a factor of 4.8 when the OC (Colisite 15 A) concentration increased from 600 to 1000 ppm due to reduction in interfacial tension (IFT). Increasing the concentration of OC (Cloisite 15 A) from 300 to 1000 ppm led to an improvement by a factor of 2 in the stability of an emulsion prepared using 6% polyethylene glycol-2 ether (PEG-2E). They concluded that at high temperatures (more than 100 °C) and high salinity (more than 200, 000 ppm), OC materials can be used as emulsifiers.

The effect of Cloisite 20 A Nano-Clay particles on the efficiency and stability of W/O emulsions at various temperatures ranging from 25 to 45 °C was experimentally investigated by (Khalid et al., 2020). The findings showed that compared to the dispersion without Nano-Clay, the presence of Cloisite 20 A stabilized the W/O emulsions, as well as Nano-Clay concentration, affecting the emulsion viscosity depending mainly on the fractions of the water volume. The emulsion viscosity was reduced effectively by a small amount of Nano-Clay, while higher Nano-Clay concentrations contributed to an increase in emulsion viscosity. They concluded that the influence of fluid temperature on the reduction of pressure drops was greater than the effect of Nano-Clay concentration. The effect of OC has been studied on the electrical properties of a polyethylene blend by (Shaw et al., 2019). Changes in electrical properties were observed with the inclusion of organoclay, which helps to boost the transport of charges under direct current (DC) fields. Al-yaari et al., 2014 presented a study using OC as a DRA of surfactant-stabilized water-in-oil (W/O) emulsions. In their study, they used two different water fractions, 0.7 (concentrated) and 0.3 (diluted), two different diameters of horizontal pipes with (ID) 2.54 cm and 1.27 cm. The findings indicated that adding OC led to a significant reduction in the viscosity of the emulsion. In the case of concentrated W/O emulsions, a 25% reduction was observed in the pressure drop of emulsion in both horizontal sections when OC was added, while no pressure drop reduction was observed in the laminar flow region for diluted W/O emulsion with 0.3 water fraction.

The existing literature suggests that there is a continued demand for the development of an EAS that exhibits robustness during field mixing procedures and maintains thermal stability over time. Additionally, there is a need for such EAS to possess low viscosity,

utilizing readily accessible, cost-effective, and environmentally friendly materials. The motivation of this research is to overcome the limitations of the current EAS in terms of thermal stability and rheology, and evaluation of using different types of OCs to develop an EAS.

4.4 Methodology

To achieve the objectives of this study, the Pickering EAS was prepared, and the necessary tests were performed. First, all OC types that are used in this study were characterized using different analytical techniques. Then, these OC types were screened to select the types that can be used as an emulsifier and form Pickering EAS. After that, the Pickering EAS was prepared at a 70:30 acid-to-diesel ratio using the selected OC. After, the prepared EAS was evaluated by performing different tests, including conductivity, pH test, drop-test, rheology, and thermal stability. Several acid emulsions were prepared, where diesel was mixed with the emulsifiers (OC), and the aqueous phase. After mixing the OC with diesel, acid was added progressively while mixing. The methodology and procedures used for the preparation and evaluation of the EAS have been presented in detail in the following section.

4.4.1 Materials and equipment

Materials used in this study include lab-grade hydrochloric acid (HCl) at 37 wt% concentration, de-ionized (DI) water, commercial diesel from a gas station, and OC provided by BYK company.

Equipment required to experiment includes high shear mixer/homogenizer (IKA T 25 digital ULTRA-TURRAX® homogenizer with titanium acid-resistant shaft and speed

range of 3000–25000 RPM), magnetic stirrer, rheometer (Anton-Paar MCR-702 Rheometer), See-through Oven, test tubes, conductivity and pH meter (Thermo Scientific™-Orion StarTMA215 pH/Conductivity Benchtop Multiparameter Meter).

4.4.2 Material characterization

X-ray diffraction (XRD) was performed to determine the crystalline constitution of different types of OC to evaluate the mineral composition and determine the quantitative mineralogy of OC. Also, X-ray fluorescence (XRF) was performed on different OC samples to measure the elemental composition of OC and the chemical characteristics of OC in the development of EAS. Zeta potential was measured for all types of OC using an Anton-Paar Particle size analyzer: Litesizer 500. pH and conductivity were measured using conductivity and pH meter (Thermo Scientific™-Orion StarTMA215 pH/Conductivity Benchtop Multiparameter Meter).

4.4.3 Emulsified acid system (EAS) preparation

Several EAS were prepared at a ratio of 70:30 acid-to-diesel ratio, where diesel represents the continuous or external phase. The concentration of HCl acid in the EAS was 15%; however, the effect of HCl concentration was investigated at 20 and 25%. To achieve the homogenization of the EAS, first, the emulsifier (OC) was added with a specific concentration in ppm to the diesel, and they mixed using the homogenizer at 6000 RPM for 5–7 min. The 37% lab-grade HCl acid was mixed with DI water for the required HCl acid concentration of 15, 20, or 25% using a magnetic stirrer for 2–3 min. Then the aqueous phase (acid phase) was added to the oil phase (diesel phase) by a syringe-drop-wise with an addition rate of 3 cc/min while mixing at 6000 RPM. Emulsifier (OC) concentration was investigated for different OC types.

4.4.4 Conductivity/ pH, and drop-test

After the preparation of the Pickering EAS, the electrical conductivity was measured to ensure that the prepared EAS is a W/O emulsion (the external phase is diesel), if the electrical conductivity reading is near zero, indicating 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. If the dispersion occurs in the beaker containing water the emulsion is O/W emulsion, while if the dispersion occurs in the beaker containing diesel the emulsion is W/O emulsion. The pH was measured to ensure the acidity of the prepared EAS.

4.4.5 Thermal stability

To ensure that the prepared EAS retains the formation in its original form, thermal stability is imperative. Thermal stability was studied at four different temperatures (25, 65, 90, and 120 °C) using Pyrex graduated glass tubes and a see-through oven. Thermal stability was performed simply and quickly using visual observation by monitoring the EAS separation every 10 min for the first 30 min, and then after 1 hr. after the first 30 min for 2–3 hrs. and after 24 hrs. Photographs of the graduated glass tubes were taken at different times, and the breaking of EAS in the aqueous and oleic phases was plotted versus time.

4.4.6 Rheology

An acid-resistant bob/cup setup of the Anton Paar rheometer MCR- 702 was used to measure the rheological properties. The setup requires a 15.9 ml volume of the prepared EAS. The temperature was set at 65 °C. The shear rate ranges from 0.1 to 1000 sec^{-1} , and every test required a time of 2 hours. In addition, the temperature was investigated by

utilizing the rheometer at two other temperatures (25 and 45 °C) besides 65 °C for one type of the prepared Pickering EAS.

4.5 Results and discussion

4.5.1 Material characterization

Twelve different OC types were characterized using different analytical techniques including XRD, XRF, zeta potential, pH, and conductivity. The XRD and XRF results for all twelve OC types are shown in Tables 8 and 9, respectively.

The results of XRD and XRF provide insight into the role of mineral structure and chemistry in the formation of emulsion and its stability. Among the clays investigated in this study, only four clays (Claytone-SF, Claytone-IMG-400, Claytone-ER, and Cloisite 20 A) were able to form stable emulsions. The results of XRD show that four out of the five OCs that formed Pickering EAS contain Montmorillonite with different percentages. Only one (Claytone-3) of the five OCs does not contain Montmorillonite, however, Claytone-3 is alone among the 12 OCs investigated in this study that contains Halite (7.8%), Clintonite-1M (33.1%), Oligoclase (7.9%). Also, it can be seen from the XRD table (Table 1) that the quartz is found only in three OCs (Claytone-SF, Claytone-3, and Claytone-IMG-400) out of the 12 and all these three OCs formed Pickering EAS. In addition, Illite is only found in two OCs (Claytone-ER, and Claytone-3) and both of them formed Pickering EAS. Also, Clinocllore is only found in Claytone-IMG-400 and this OC can form Pickering EAS. The other clays (Laponite EP and Laponite-RDS) were not able to form EAS. The XRF results show Laponite EP and Laponite-RDS high quantities of Na and Mg. The Montmorillonite clay has the advantage of forming the stable emulsion

however it is not always guaranteed that having Aluminium and Silica will form the stable emulsion. The absence of Aluminium and Silica in Laponite EP and Laponite-RDS indicated by XRF can be considered as one of the reasons for its inability to develop stable EAS. The ability of certain organoclays to form Pickering emulsified acid systems while others can not is likely related to their structural and compositional characteristics.

Zeta potential was measured for all twelve OC samples using the Anton-Paar-Particle size analyzer: Litesizer 500. The 500 ppm of each OC was added and mixed with DI water using a magnetic stirrer at 1500 RPM for a 1-hour duration. In addition, pH, and conductivity were measured for these samples (DI water + 500 ppm OC). The results of the zeta potential for 500 ppm of OC in DI water measured at 25 °C are shown in Table 10, while Figure 31 shows the zeta potential distribution function. The zeta potential test is used to measure particle charge in liquid, and it varies between -100 mV and +100 mV. Figure 31 shows the zeta potential as a function of relative frequency. It should be noted that the range of zeta potential -600 mV to +600 mV is for the zero frequency. The values of OC zeta potential are shown in Table 10.

The results show that zeta potential values vary between (-55 to +45 mV) for all OC samples. The values of zeta potential other than (-30 to +30 mV) represent a stable and highly dispersed particle (Duffy et al., 2012). The results show some OC has zeta potential values in the range of (-30 to +30 mV), and this may be due to OC being considered oil-soluble, and only partially water-soluble. This is due to the modification of the surface charge of the clay to make it preferentially soluble in the oleic phase and not in the aqueous phase. However, the test was performed for OC with DI water due to the limitation of the cell of the device. The pH and conductivity values are also shown in Table 10.

Table 8 XRD analysis for 12 organoclay types

OC Type/Contents	Claytone-AF	Claytone-SF	Claytone-EM	Claytone-ER	Claytone-HT	Claytone-40	Claytone-3	Claytone-APA	Claytone-IMG-400	Cloisite 20A	Laponite-EP	Laponite-RDS
Montmorillonite [%]	91.7	83.4	-	32.1	-	99.7	-	35.6	71.1	99.5	-	-
Cristobalite [%]	0.4	-	-	-	-	0.3	-	21.4	-	0.5	-	-
Orientite [%]	8	13.5	-	-	-	-	-	43.1	-	-	-	-
Quartz [%]	-	3.1	-	-	-	-	5.5	-	0.2	-	-	-
Vermiculite [%]	-	-	1	-	-	-	-	-	-	-	100	-
Illite-1M (NR) [%]	-	-	99	-	99.5	-	-	-	-	-	-	-
Anorthite, Na-bearing, syn [%]	-	-	-	-	0.5	-	-	-	-	-	-	-
Clinochlore [%]	-	-	-	-	-	-	-	-	28.7	-	-	-
Illite [%]	-	-	-	67.9	-	-	45.6	-	-	-	-	-
Denningite [%]	-	-	-	-	-	-	-	-	-	-	-	52.9
Valentinite, syn [%]	-	-	-	-	-	-	-	-	-	-	-	47.1
Halite [%]	-	-	-	-	-	-	7.8	-	-	-	-	-
Clintonite-1M [%]	-	-	-	-	-	-	33.1	-	-	-	-	-
Oligoclase [%]	-	-	-	-	-	-	7.9	-	-	-	-	-

Table 9 XRF analysis for 12 organoclay types

OC type/Minerals	Na	Mg	Al	Si	P	S	Cl	K	Ca	V	Mn	Fe	Zn	Sr	Rh
Claytone-3	26.22	12.78	26.46	32.17	0	0.32	1.28	0.08	0.27	0	0	0.41	0	0	0
Claytone-40	0	10.96	33.45	53.4	0.01	0.01	0.5	0.13	0.19	0.01	0	1.33	0	0.01	0
Claytone-IMG-400	6.12	10.41	34.65	47.12	0	0.03	0.37	0.02	0.14	0	0	1.11	0	0	0
Claytone-AF	0	11.07	32.73	53.15	0.01	0.01	1.39	0.13	0.16	0.01	0	1.32	0	0	0
Claytone-APA	0	10.03	34.89	52.72	0.01	0.14	0.99	0.01	0.1	0	0	1.11	0	0	0
Claytone-EM	0	9.8	35.74	52.48	0.01	0.05	0.59	0.02	0.1	0	0	1.22	0	0	0
Claytone-ER	0	9.93	35.92	52.01	0.01	0.03	0.52	0.03	0.11	0	0	1.44	0	0	0
Claytone-HT	0	9.8	35.33	52.96	0.01	0.03	0.44	0.02	0.16	0	0	1.25	0	0	0
Claytone-SF	0	11.5	34.16	52.09	0.01	0.03	0.88	0.03	0.08	0	0	1.23	0	0	0
Cloisite 20A	0	11.35	33.43	53.25	0.01	0	0.52	0.11	0.17	0.01	0	1.15	0	0	0
Laponite-EP	50.06	43.39	0.01	6.2	0.01	0.01	0.15	0	0.17	0	0	0	0	0	0
Laponite-RDS	57	38.11	0.04	4.58	0.24	0.02	0	0	0	0	0	0	0	0	0

Table 10 Zeta potential, pH, and Conductivity analysis for 12 organoclay types

OC/ Zeta potential	Zeta Potential	Standard deviation	Electrophoretic mobility	Conductivity	Distribution peak	pH	Conductivity
	(mV)	(mV)	$\mu\text{m}^2\text{cm/Vs}$	mS/cm	(mV)	pH	$\mu\text{S/cm}$
Claytone 3	29.71	0.64	2.19	0.09	32.53	7.37	52.58
Claytone 40	-16.94	1.13	-1.25	0.04	-16.19	7.13	7.71
Claytone APA	40.80	1.51	3.01	0.04	37.20	7.15	17.81
Claytone AF	-10.26	2.95	-0.76	0.12	-14.27	7.39	11.83
Claytone EM	44.88	1.16	3.31	0.02	46.16	6.85	7.099

Claytone ER	-6.30	0.71	-0.46	0.06	-5.01	6.62	6.915
Claytone HT	11.97	4.23	0.88	0.03	15.30	7.16	8.10
Claytone IMG 400	-4.87	0.71	-0.36	0.04	-3.62	6.77	16.14
Claytone SF	10.21	2.36	0.75	0.03	2.91	6.31	13.88
Cloisite 20A	30.59	0.57	2.25	0.03	32.90	7.66	11.13
Laponite RDS	-1.68	4.13	-0.12	0.21	2.82	9.71	117.6
Laponite EP	-54.13	0.97	-3.99	0.08	-51.72	8.72	40.63

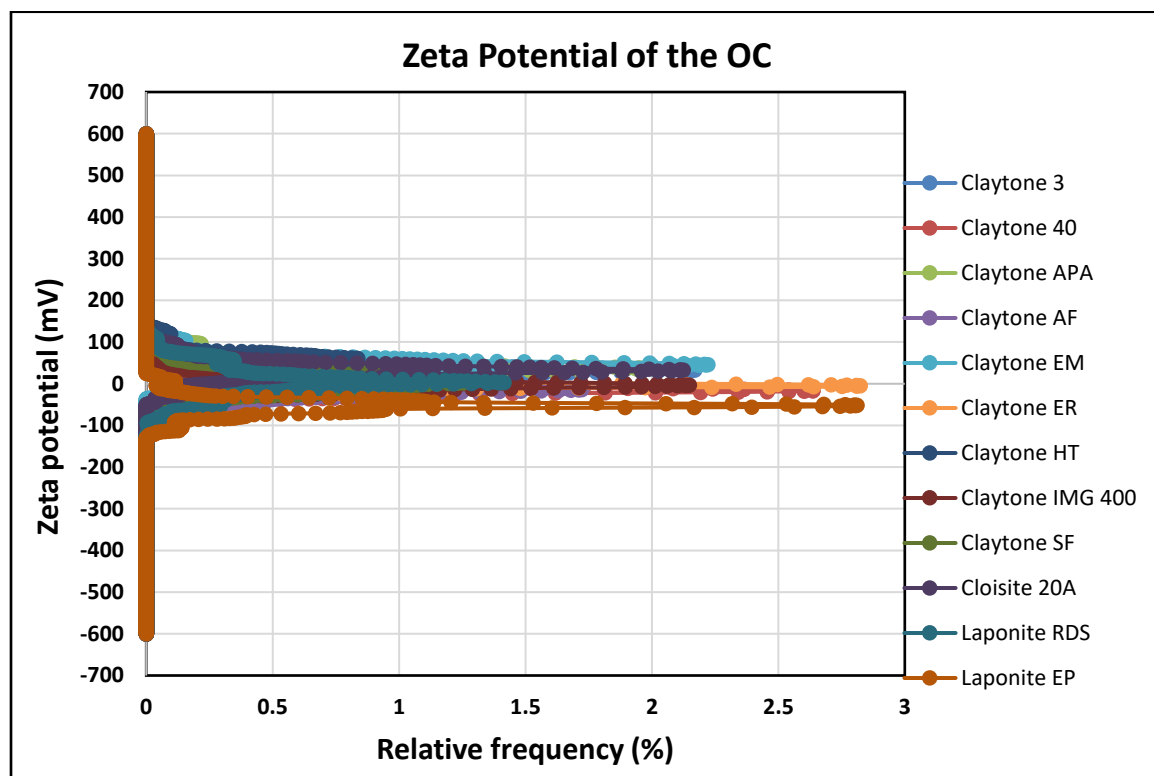


Figure 31 Zeta potential distribution function

4.5.2 Emulsified acid system (EAS) preparation

Twelve organoclays are screened to check the possibility of using them as an emulsifier for Pickering EAS. All the OC was tested at a concentration of 1000 ppm, some of them formed EAS, while others did not form the EAS. The EAS was prepared by following the procedure explained in the methodology section to achieve the homogenization of the EAS,

Figure 32 shows the steps of preparation of the EAS. The letters (a, b,c, and d) in Figure 32 represent the following steps:

- a. Adding the emulsifier (OC) with a specific concentration in ppm to the diesel (30% of the total volume).
- b. Mixing the OC with diesel using the homogenizer at 6000 RPM for 5–7 min, then the aqueous phase (acid phase) (70% of the total volume) was added to the oil phase (diesel phase) by a syringe drop-wise at a rate of 3 cc/min while mixing at 6000 RPM. The aqueous phase was prepared using 37% lab-grade HCl acid diluted with DI water for the required HCl acid concentration using a magnetic stirrer for 2–3 min.
- c. The photo shows the mixing process during the preparation of the EAS.
- d. The photo shows the EAS (after preparation).

A photograph of EAS was taken after preparation. Also, the conductivity of the prepared EAS and drop-test analysis was performed to ensure that the EAS is an inverted emulsion (W/O emulsion). Figure 33 shows an example of the prepared Pickering EAS using Claytone-ER, conductivity measurement, and drop-test in water and diesel. Also, a micrograph was taken using (BX51 Petrographic Microscope) with 500 μm resolution directly after preparation. Figures 34 and 35 show the micrographs of the Pickering EAS prepared by Claytone-SF, and Claytone-ER, respectively. After that, the prepared EAS was tested for thermal stability at different temperatures (25, 65, 90, and 120 $^{\circ}\text{C}$). Table 11 shows the results of screening all OC types. It was found that among the twelve OCs investigated in the study, only five OCs (Claytone SF, Claytone 3, Claytone ER, Claytone IMG 400, and Cloisite 20 A) were able to form Pickering EAS when they were used as an

emulsifier at a concentration of 1000 ppm. These five OCs were investigated for the concentration of 500 ppm, and the results showed that there was no significant change in the thermal stability for 500 ppm concentrations compared with EAS prepared with 1000 ppm concentration. However, little reduction in viscosity was observed when the concentration of OC was reduced to 500 ppm.



Figure 32 EAS preparation steps

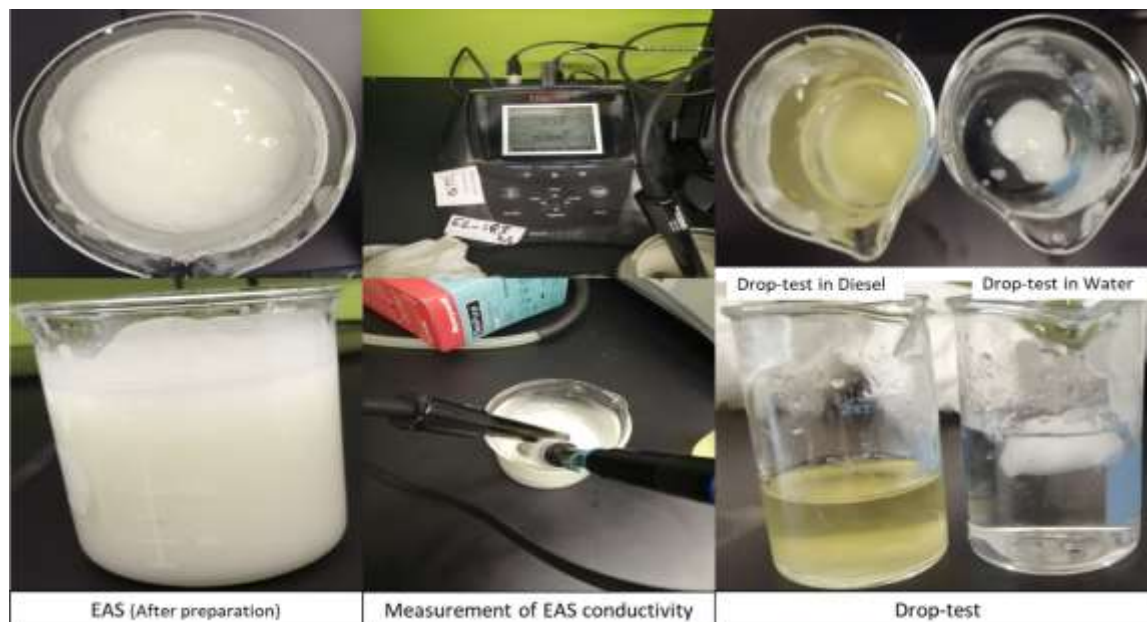


Figure 33 Example of the Pickering EAS prepared using Claytone-ER, Conductivity measurement, and drop-test

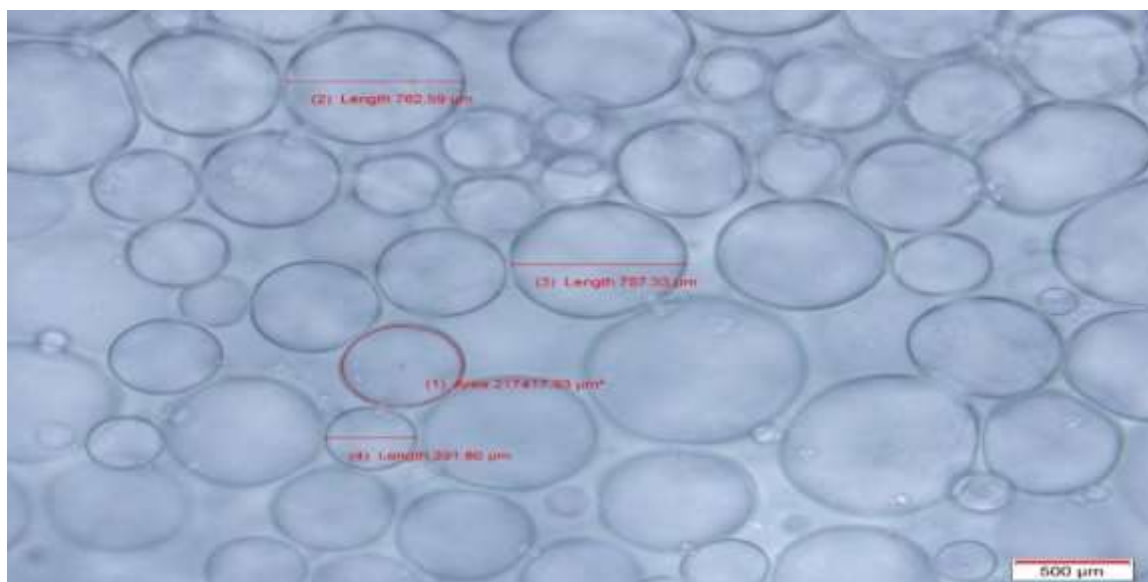


Figure 34 Micrograph of the Pickering EAS prepared by Claytone-SF

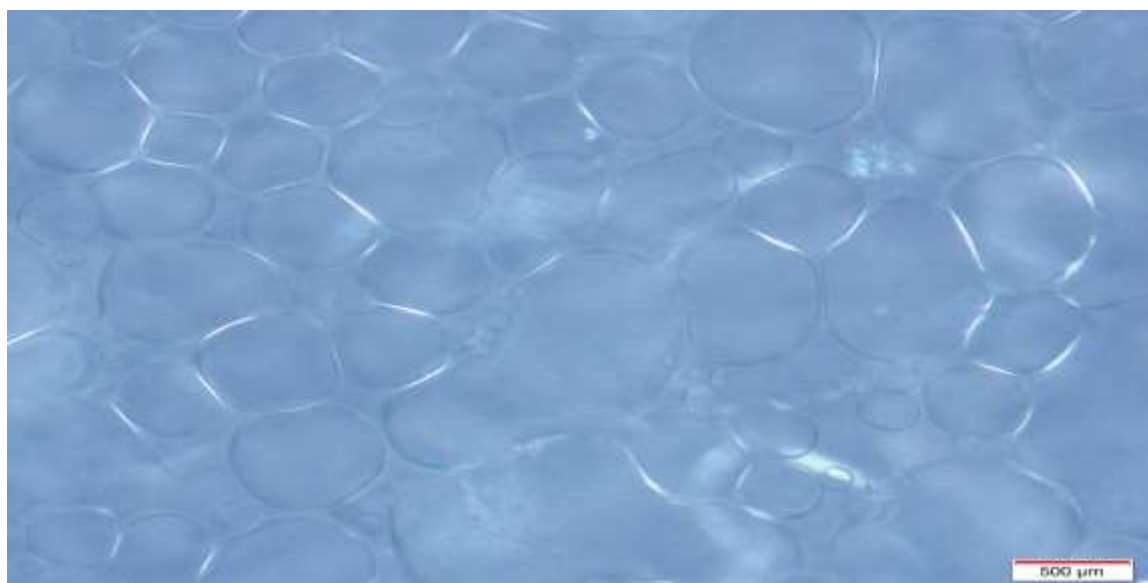


Figure 35 Micrograph of the Pickering EAS prepared by Claytone-ER

The best four organoclays as emulsifiers to form EAS were Claytone-SF, Claytone-3, Claytone-IMG 400, and Claytone-ER, which are all organoclays that have been modified with quaternary ammonium salts. The quaternary ammonium salts used to modify the clay allow it to become highly compatible with organic solvents, oils, and other hydrophobic substances.

Table 11 Screening OC to prepare EAS

Emulsifier	Concentration	Mixing Speed	Acid addition Rate	EAS	Thermal Stability			
					25 °C (Room)	65 °C	90 °C	120 °C
	ppm	RPM	CC/min					
Claytone-SF	1000	6000	3	Yes	Stable	Stable	Stable	Stable
Claytone-IMG-400	1000	6000	3	Yes	Stable	Stable	Stable	Stable
Claytone-ER	1000	6000	3	Yes	Stable	Stable	Stable	Stable
Claytone-3	1000	6000	3	Yes	Stable	Stable	Stable	Stable
Cloisite 20A	1000	6000	3	Yes	Stable	Stable	Stable	Stable
Claytone-EM	1000	6000	3	Yes	Stable	Not Stable	Not Stable	Not Stable
Claytone-AF	1000	6000	3	Yes	Stable	Not Stable	Not Stable	Not Stable
Claytone-40	1000	6000	3	No	Not Stable	-	-	-
Claytone-APA	1000	6000	3	No	Not Stable	-	-	-
Claytone-HT	1000	6000	3	No	Not Stable	-	-	-
Laponite-EP	1000	6000	3	No	Not Stable	-	-	-
Laponite-RDS	1000	6000	3	No	Not Stable	-	-	-

Cloisite 20 A has excellent properties such as a high aspect ratio, good thermal stability, and good dispersion properties. These organoclays can dissolve in oil or diesel, which allows the development of stable emulsions. The modification of the clay mineral structure with quaternary ammonium salts changes the clay's surface properties, making it hydrophobic and able to interact with the oil or diesel phase. The selection of the appropriate quaternary ammonium salt for organoclay modification depends on the specific

application and the properties required of the EAS, such as stability, viscosity, and thermal stability.

It should be noted that the OC concentration plays a critical role in the formation of stable emulsions. The release of the acid from the EAS can be controlled by fine-tuning the OC concentration. The release profile of acid from Pickering EAS depends on several parameters, including the concentration and type of acid used, the type and concentration of nanoparticles used, the temperature and pressure of the reservoir, and the pore size distribution of the formation. It will also ensure the encapsulation of the acid in the diesel phase while pumping through the tubular at a high shear rate and prevent corrosion due to acid. Therefore, it is essential to carefully optimize the Pickering EAS formulation to ensure a desirable release profile that maximizes the acid's effectiveness and minimizes the potential for formation damage.

4.5.3 Conductivity/ pH, and drop-test

The electrical conductivity and acidity of the prepared Pickering EAS were measured using a conductivity and pH meter. Also, a drop-test analysis was performed to confirm that the Pickering EAS is a W/O emulsion. The results of electrical conductivity show values near zero, ensuring the external phase is diesel and the prepared Pickering EAS is a W/O emulsion. pH values show that the Pickering EAS is highly acidic, the pH values range between 0 and 1. The drop-test confirmed that the Pickering EAS is a W/O emulsion since it is dispersed in diesel, not in the water as shown in Figure 36.

In addition, a micrograph after the preparation of the emulsion was taken to confirm the formation of an emulsion. Figure 34 shows a micrograph of EAS developed using Claytone

SF at 25 °C temperature, which confirms the formation of a stable emulsion immediately after the preparation of the emulsion. The results of the conductivity test, drop-test analysis, and micrograph ensure the formation of a stable inverted emulsion.

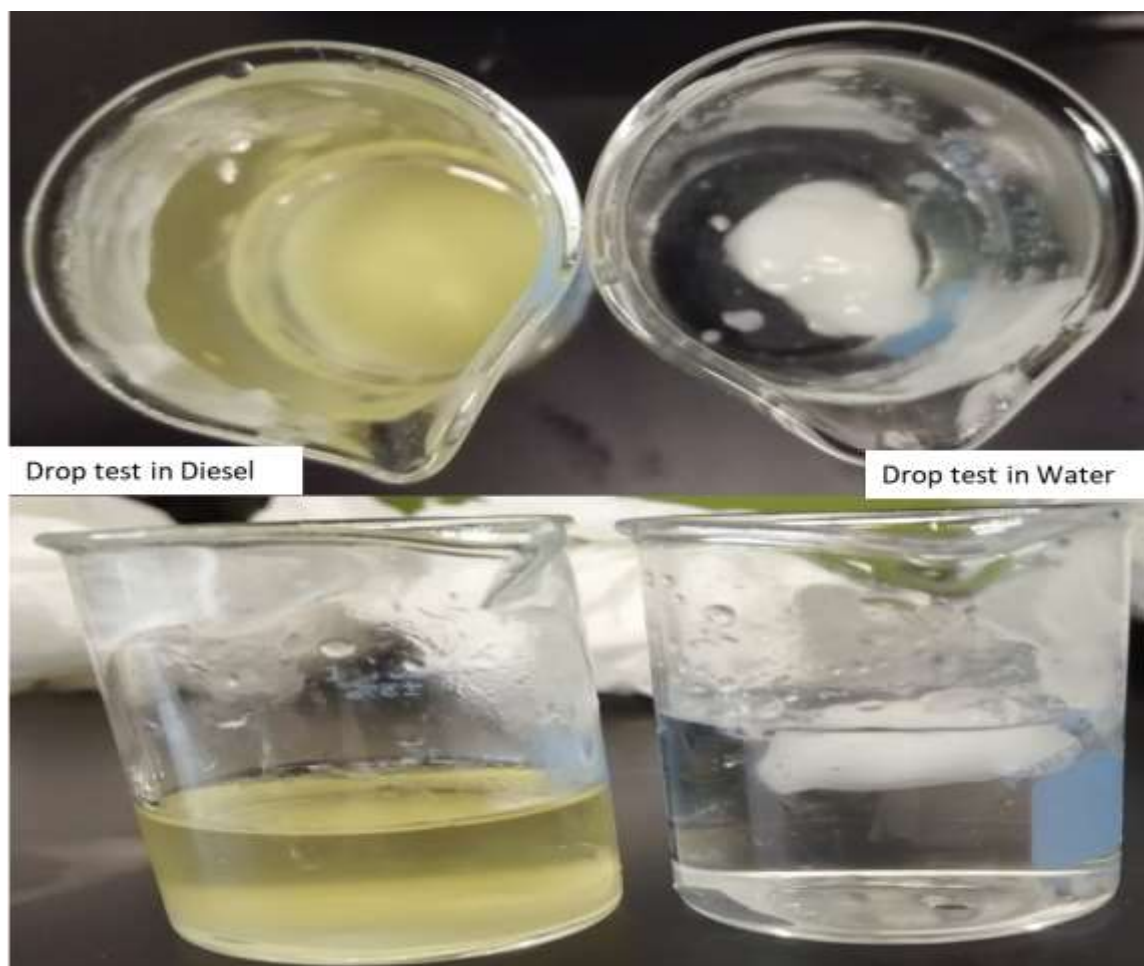


Figure 36 Drop-test of Pickering EAS using Claytone –SF in diesel (Left), in water (right)

4.5.4 Thermal stability

Thermal stability of emulsion refers to the time for which emulsion can stay in stable emulsion form. The emulsified acids are considered to be stable if it does not experience a complete phase separation between the oil phase and the aqueous phase. The EAS should be thermally stable for the operation time of the stimulation job. It will ensure that acid is

encapsulated in the diesel phase before it is placed into the targeted area for stimulation treatment. Once it has been placed in the targeted area the breaking of the EAS will initiate an acid-rock reaction. It also ensures that acid is not in contact with the tubular as well as surface and subsurface equipment. A typical range of thermal stability of 8–10 h is considered in this work, although, it varies based on the volume of the acid to be injected, targeted formation depth, injection rate as well as well configuration.

Thermal stability was studied at four different temperatures (25, 65, 90, and 120 °C) using Pyrex graduated glass tubes and a see-through oven. The results showed that the prepared Pickering EAS is thermally stable even at high temperatures. Figures 37–41 show the separation volume with time for the Pickering EAS prepared with the Claytone SF as an example at the four different temperatures. Figure 37 shows thermal stability at 25 °C temperature for EAS prepared with Claytone SF. The EAS at 25 °C temperature was stable for 24 h. Similarly, the EAS is stable for 24 h at 65 °C as shown in Figure 38.

For the higher temperature of 90 °C, a slight volume of the diesel appears after 1 h; however, this volume remains constant for 24 h Suggesting the EAS system is thermally stable as shown in Figure 39. Similarly, the EAS was stable for 24 h after a slight amount of diesel at the initial stage which is shown in Figure 40 at a temperature of 120 °C. It should be noted that the appearance of a slight quantity of diesel does not mean the EAS is unstable. This volume remains constant for the period for which the stability of the EAS is targeted. The separation of the aqueous phase (acid) from the EAS is considered an indication of unstable EAS. The conductivity test and drop test were conducted at the end of the time to ensure the aqueous phase remained encapsulated in the diesel phase.

Furthermore, the thermal stability of the developed Pickering EAS was tested at a very high temperature of 160 °C and 300 psi using an aging cell and the results show the prepared Pickering EAS is thermally stable at high temperatures. The Pickering EAS conductivity was measured after 24 h when the sample was taken from the oven and it shows a very small value of 0.263 $\mu\text{S}/\text{cm}$ which means it is a W/O emulsion and that is confirmed by conducting the drop-test in water and diesel. The pH value was also measured after 24 h when the sample was taken from the oven and it was 0.37 which means the prepared EAS is still strongly acidic. Figure 41 shows a photograph of the Pickering EAS prepared by ClaytoneSF with its drop-test after 24 h when taken from the oven at 160 °C. Figure 42 shows the thermal stability of the Pickering EAS prepared using Claytone IMG 400 at 90 and 120 °C, while Figure 43 shows the thermal stability of the same Pickering EAS at 160 °C. The results show that the EAS prepared with Claytone IMG 400 is stable at 160 °C.

It can be inferred from the results that the Pickering EAS formulated using OCs is thermally stable up to the temperature of 160 °C tested in this study. It should be noted that the separation of EAS in the oil phase should not be referred to as unstable EAS, the acid remains encapsulated as there is no change in the aqueous phase. In the field operation, the injection period for the acid system is in the range of 8–10 h which is much less than the 24 h tested in this work. The higher range (more than 160 °C) of the temperature was not tested in this study due to the limitation of the glassware sustaining the higher temperature. It should be noted that the stability of the emulsion can be adjusted by fine-tuning the clay concentration as per the field operation requirement. The fine-tuning of the OC concentration is further explored in the discussion section.

Photographs were taken before and after the oven. Figure 44 is an example of the prepared EAS with Claytone-ER, before and after oven at 120° C for the 15% HCl prepared Pickering EAS.

Another thermal stability example of the prepared EAS with Claytone-SF, before and after oven at 120°C for the 20 and 25% HCl prepared Pickering EAS is shown in Figure 45.

Also, A micrograph was taken using (BX51 Petrographic Microscope) with 500 μm after 24 h in the oven at different temperatures. Figure 46 shows the micrographs of the Pickering EAS prepared by Claytone-SF.

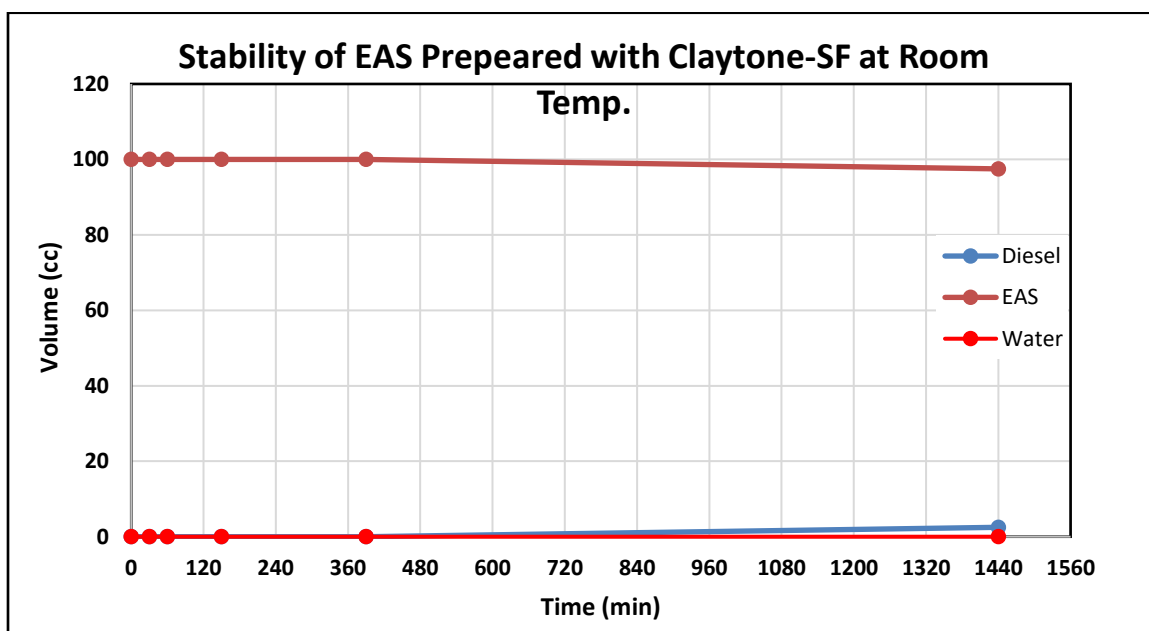


Figure 37 Separation volume of Pickering EAS prepared with 500 ppm of Claytone-SF at room temperature

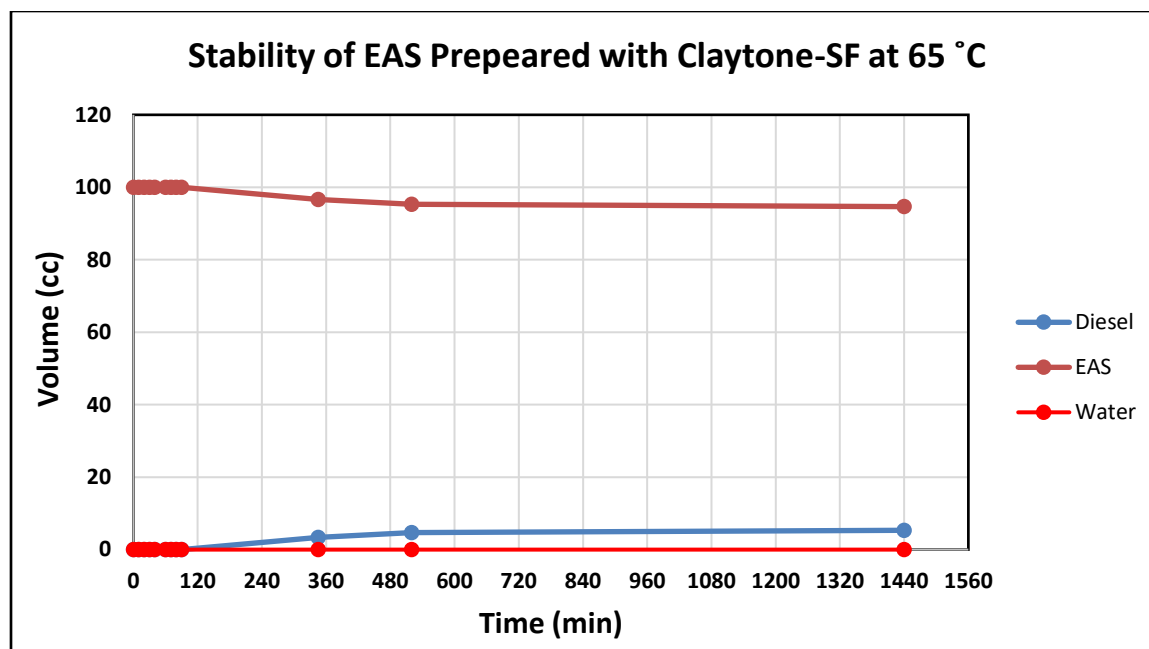


Figure 38 Separation volume of Pickering EAS prepared with 500 ppm of Claytone-SF at 65 °C

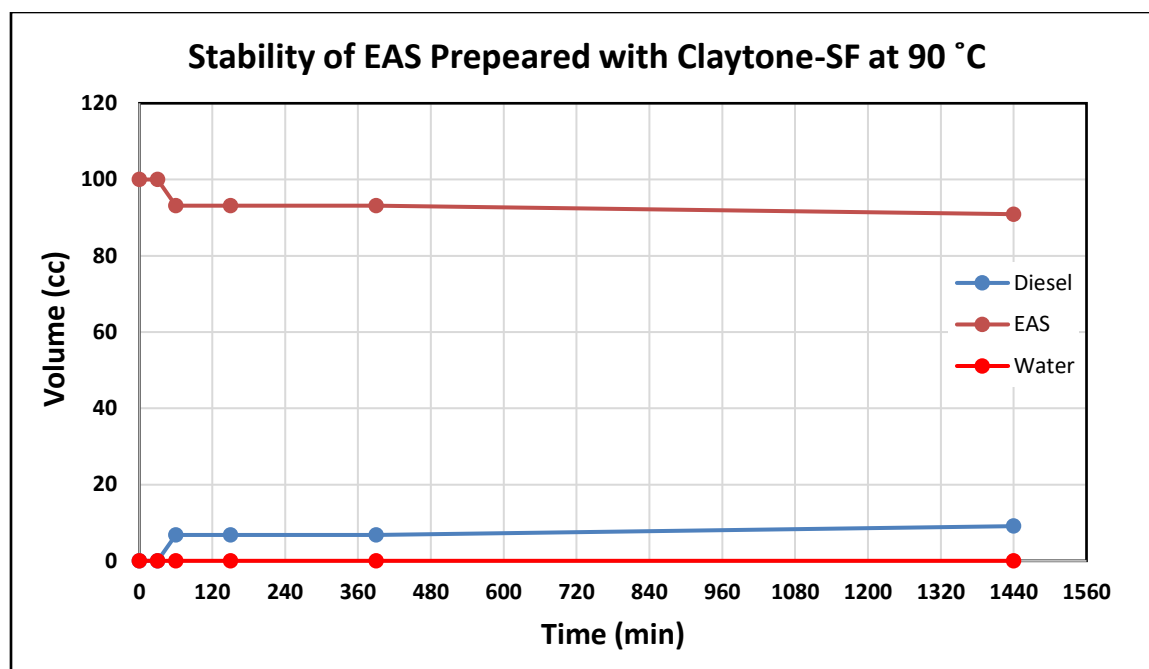


Figure 39 Separation volume of Pickering EAS prepared with 500 ppm of Claytone-SF at 90 °C

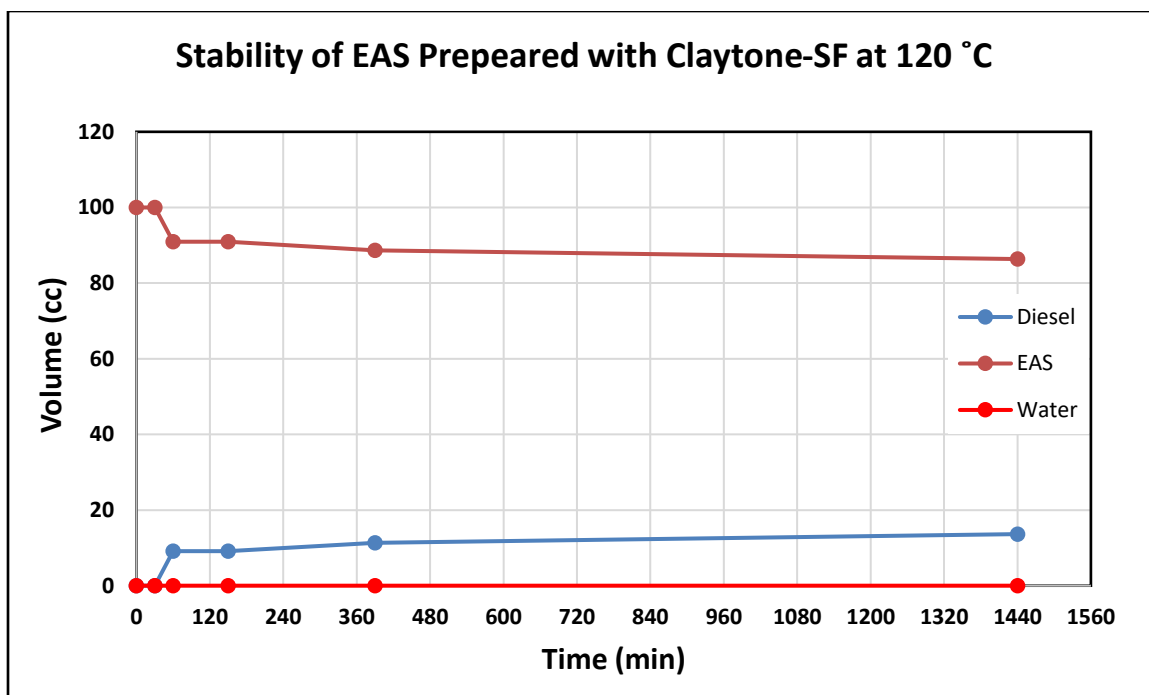


Figure 40 Separation volume of Pickering EAS prepared with 500 ppm of Claytone-SF at 120 °C

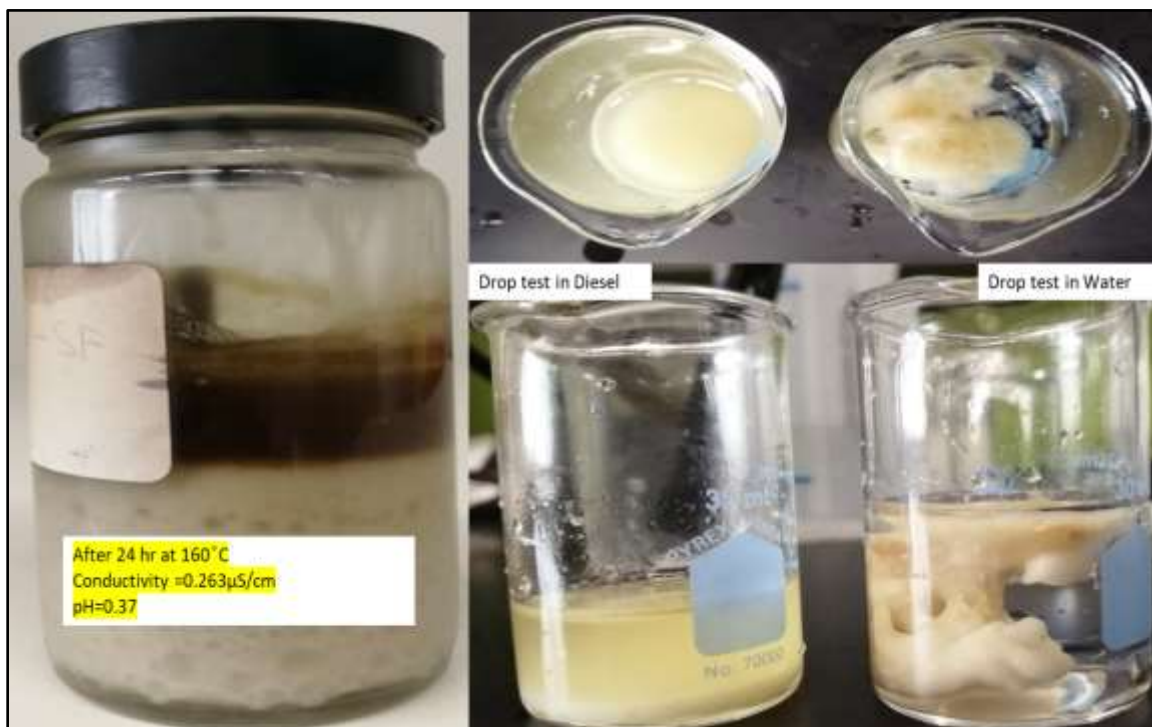


Figure 41 Stability of Pickering EAS prepared with 500 ppm of Claytone-SF after 24 hr at 160 °C and its drop-test

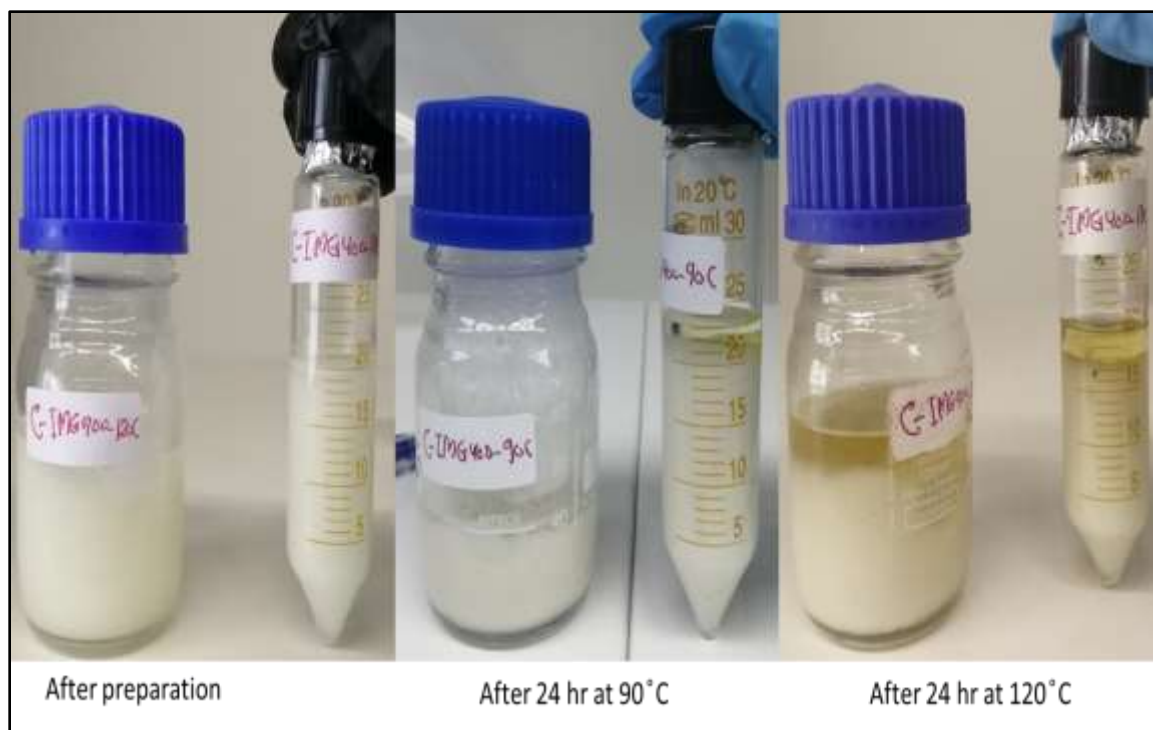


Figure 42 Stability of Pickering EAS prepared with 500 ppm of Claytone-IMG 400 after 24 hr at 90 and 120 °C



Figure 43 Stability of Pickering EAS prepared with 500 ppm of Claytone-IMG 400 after 24 hr at 160 °C

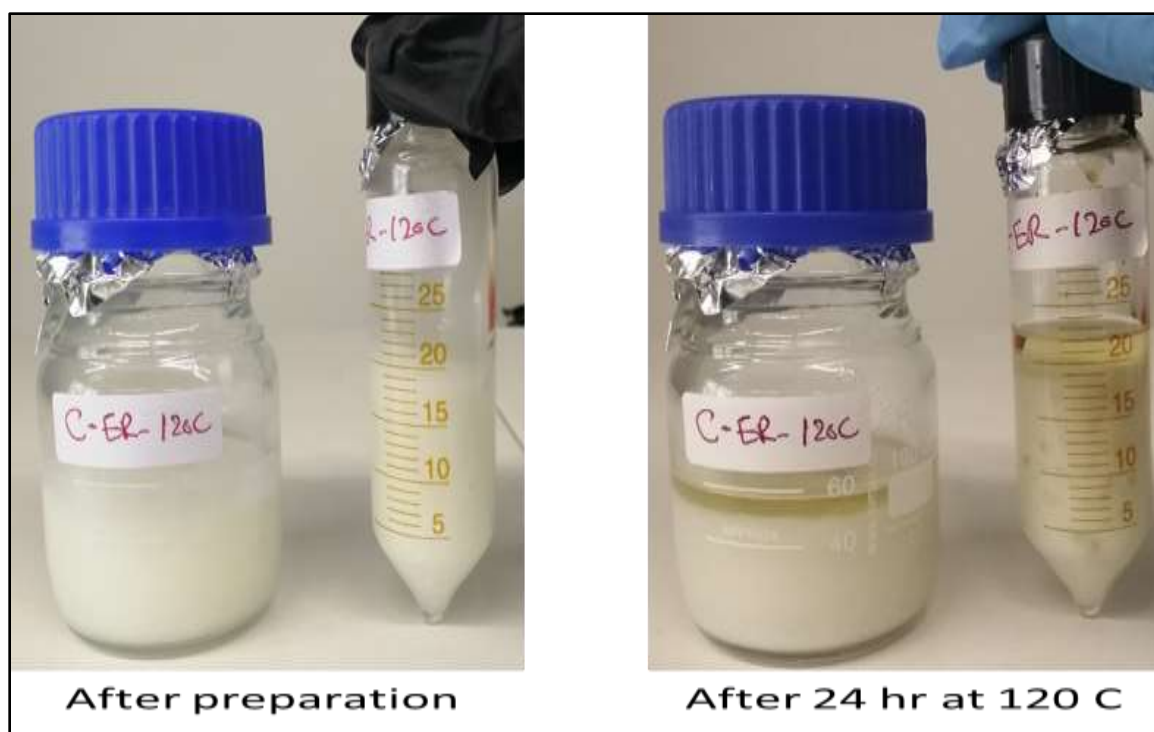


Figure 44 Thermal stability of the prepared EAS with Claytone-ER with 15% HCl at 120 °C

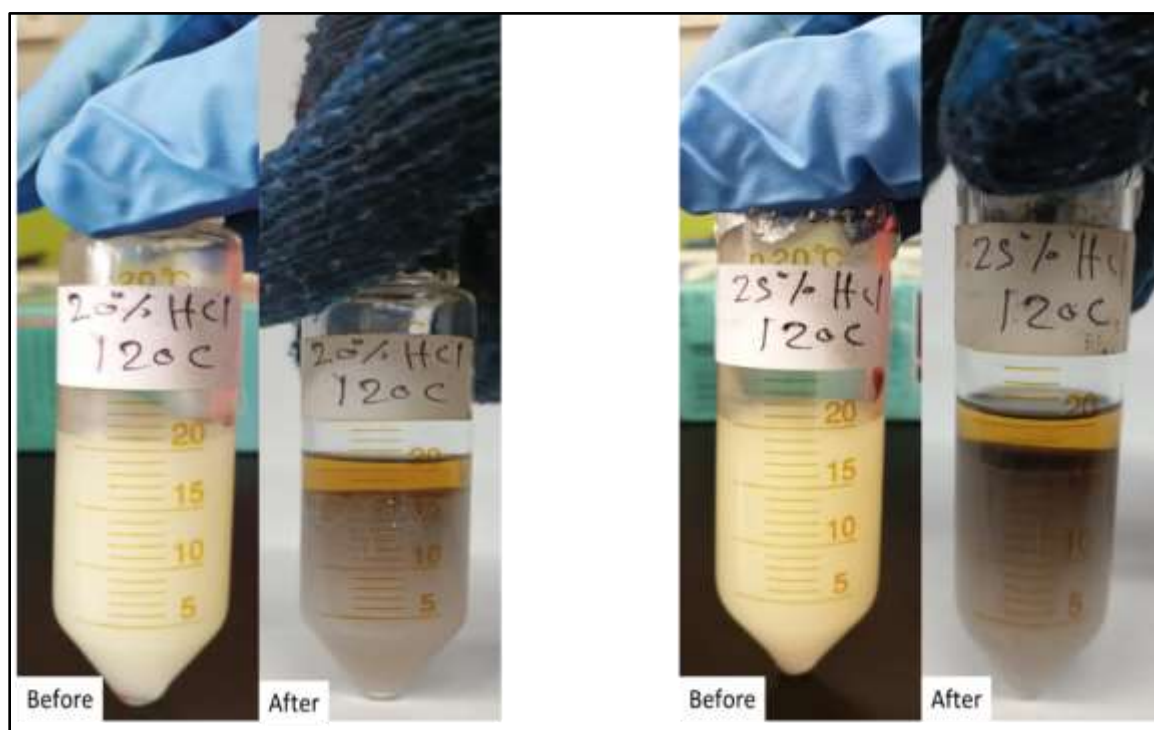


Figure 45 Thermal stability of the prepared EAS with Claytone-SF with 20, and 25 HCl% at 120 °C

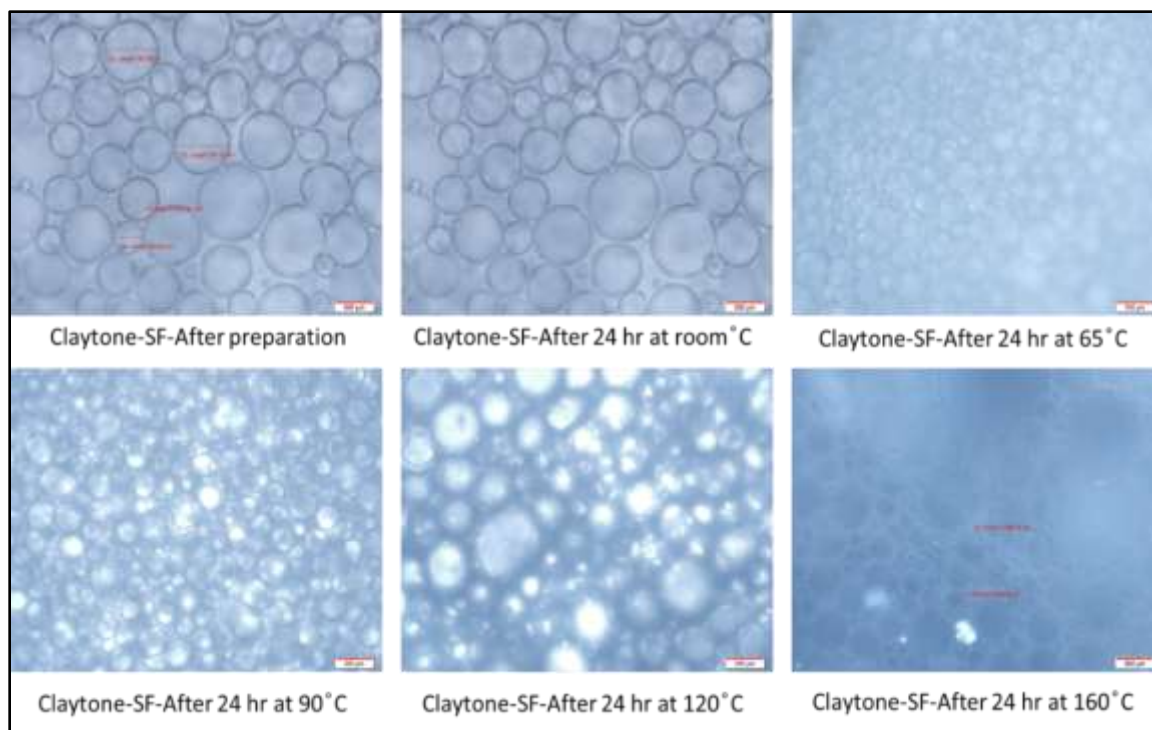


Figure 46 Micrographs of the Pickering EAS prepared by Claytone-SF 500 ppm with 15% HCl

4.5.5 Rheology

Rheological properties were studied for the prepared Pickering EAS. Firstly, the viscosity was measured at different shear rates from 0.1 to 1000 sec^{-1} at 65 °C for all prepared Pickering EAS at 1000 ppm emulsifier (OC) concentrations. The results of rheology in the form of viscosity as a function of the shear rate are shown in Figure 47. Figure 47 shows the trends of the viscosity as a function of the shear rate. It can be inferred that the EAS prepared using the OCs shows shear thinning behavior as the viscosity decreases with the shear rate. Also, the trends are consistent for all the EAS prepared using OC.

However, it should be noted that the range of the viscosity varies based on the type of OC. At low shear rates (0-10 sec^{-1}) the range of viscosity can be categorized into three regions i. e low-viscosity (100–1000 cP), medium-viscosity (1000–10,000 cP), and high-viscosity (10,000–100,000 cP). The EAS prepared using OCs (Claytone ER, Claytone 3, and

Claytone IMG 400) were given high viscosities. While the other categories of OCs (Claytone EM and Cloisite 20 A) have a low magnitude of viscosity. It is also important to note that this magnitude is 100 times less than the OCs with high viscosity. On the other hand, OC ClaytoneEM gives the average magnitude of viscosity for the EAS with different clays considered in this study.

Claytone-SF, Claytone-ER, and Claytone-3 are water-washed hectorite clay modified with quaternary ammonium salts that provide thermal stability and excellent suspension properties. The rheology of the EAS developed using these clays shows shear thinning behavior. Cloisite 20 A and Claytone-IMG 400 are organophilic clays that enable them to be thermally stable and have excellent properties such as a high aspect ratio, good thermal stability, and good dispersion properties. The EAS developed using these clays also shows shear thinning behavior. The clay mineral and the associated group of the salt group are the main rationales for the variation in the magnitude of viscosity. The particle size distribution did not have significant differences for the clays used in this study.

At a medium shear rate ($10\text{--}100\text{ sec}^{-1}$), the viscosity for EAS with OC follows similar trends to the high shear rate region except for the EAS with ClaytoneEM which shows constant viscosity up to a shear rate of 200 sec^{-1} . For high shear rates ($500\text{--}1000\text{ sec}^{-1}$) the trends are similar to the low shear rate region and EAS shows shear thinning behavior. The viscosity of EAS varies with the type of OC clay used for the EAS system indicating that each of the OC has a different effect on the viscosity of EAS although all of them can form the EAS by replacing the emulsifier. It hints at further investigation to check the effect of the concentration of the OCs used for EAS.

To evaluate the effect of OC concentration on the rheology of EAS, another set of the EAS was formulated using OCs with a concentration of 500 ppm instead of 1000 ppm following the same procedure explained earlier. After preparing the EAS, it was tested for conductivity, drop-test, and thermal stability. The EAS prepared with an OC concentration of 500 ppm passed the conductivity and drop-test. Also, reducing the (OC) concentration from 1000 ppm to 500 ppm does not affect the thermal stability of the EAS.

Further, the EAS prepared at 500 ppm concentration was tested for the rheology performance. Figure 48 shows viscosity as a function of the shear rate for the EAS system prepared using 500 ppm OCs. Unlike the conductivity and thermal stability test, the rheology of the EAS system appears to be affected by the concentration of clays. The reduction in the concentration of the OC for the EAS decreases the viscosity of the EAS, especially at the high shear rates. Most of the viscosities of the EAS are below 10 cP compared to the EAS for OCs with a concentration of 1000 ppm where viscosity is higher than 10 cP for some of the clay.

To examine the impact of varying concentrations on viscosity, rheology plots were plotted for Claytone-SF at different concentration levels. These plots depict the variation of viscosity with shear rates.

As shown in Figure 49, the viscosity of the EAS prepared with 500 ppm of OC is decreased as compared to the EAS prepared with 1000 ppm of OC at a high shear rate region. There is no change in the viscosity at the low shear rate region; however, the difference in the magnitude of viscosity at the high shear rate region is significant. This suggests that it is necessary to conduct all the tests when preparing the EAS with OC. Merely satisfying the

criteria of conductivity, drop-test, and thermal stability in an EAS may not be enough to determine the appropriate OC concentration. The rheological properties play a crucial role in ensuring the successful delivery of the EAS into the target formation.

To determine the required concentration of OC for the Pickering EAS, the Pickering EAS was prepared with Claytone-ER at three different concentrations (250, 500, and 1000 ppm). The prepared EAS was not thermally stable with OC of 250 ppm concentration, while it is thermally stable at 500 and 1000 ppm OC concentrations. Similar results were seen for the other clays considered in this study.

The effect of temperature on the Pickering EAS was studied at three different temperatures (25, 45, and 65 °C). Figure 50 shows the effect of temperature on the rheology of the EAS prepared with 500 ppm OC Claytone SF. As shown in Figure 50, the viscosity of the Pickering EAS increased with increasing temperature at the low shear rate (below 10 sec^{-1}); however, at a shear rate higher than 10 sec^{-1} , the EAS viscosity decreased with increasing temperature.

In the EAS, numerous factors are interconnected, highlighting the significance of evaluating the operational implications of key factors. The HCl concentration is one of the factors that control the rate of reaction in the carbonate acidizing which is the target application of EAS. The HCl concentration is varied depending on the reservoir or well under consideration, Hence, the effect of HCl concentration was also investigated for preparing the EAS with OCs. Three different concentrations of HCl (15, 20, and 25%) are investigated for the conductivity, stability, and rheology of the EAS. The effect of HCl concentration (15%–25%) does not alter the conductivity and stability of the EAS.

However, the HCl concentration has a minor effect on the rheology of the EAS. As shown in Figure 51, increasing the HCl concentration led to a very small reduction of viscosity.

The rheology of the EAS is a vital parameter when it comes to operation. It should be noted that the rheology will govern the placement of the EAS in the reservoir. It is required to place the EAS deep into the reservoir in a short time. Hence the rheology will be important for pumping the fluid from the surface to the wellbore with minimum energy and time. On the other hand, it will also signify the propagation of the EAS into the reservoir i.e. in porous media. In light of this, the EAS system's rheological properties were investigated at three different shear rates (10, 30, and 70 sec^{-1}). As shown in Figure 52, viscosity is plotted as a function of shear stress at three different shear rates. It can be seen that the trends of the viscosity at different shear rates indicate the shear thinning behavior. Furthermore, the time-dependent behavior is evaluated for the EAS system. As shown in Figure 53, the viscosity of the EAS at different shear rates indicates that the viscosity of EAS decreases with time exhibiting the thixotropic behavior. In addition to evaluating the visco-elastic behavior, the storage and loss modulus as a function of shear strain and angular frequency were investigated.

As shown in Figure 54, the storage and loss modulus were plotted with shear strain, and both moduli show a linear relationship with strain up to a value of 0.008. This suggests that within this range of shear strain, the EAS response to deformation is predominantly elastic, meaning it can recover its original shape after the applied stress is removed. Further, the storage and loss modulus are plotted as a function of angular frequency as shown in Figure 55. Figure 55 shows that there is no intersection between the storage and loss modulus for the shear strain of 0.1 and above. This implies that at higher shear strains, the material's

response becomes dominated by viscous behavior, where energy is dissipated rather than being stored elastically. In other words, the material loses its ability to recover its original shape and exhibits a more fluid-like behavior. The EAS requires to be injected at high velocity to save operation time and penetrate deeper into the formation before the EAS becomes unstable. This suggests that the specific range of interest lies within the higher shear strain, where the material behaves more like a fluid and can effectively perform its intended function. It may have an intersection below the shear strain 0.1, however, this range was not evaluated as the objective of the EAS application is to inject it at high velocity to save the operation time and deeper into the formation before the EAS becomes unstable. The comparison of the storage and loss modulus indicates the EAS is dominated by elasticity. It indicates material retains its ability to store elastic energy and can potentially recover its shape after deformation. This characteristic is desirable for the EAS application, as it suggests that the material can effectively propagate through the formation and maintain its integrity while injecting at high velocities.

The developed Pickering emulsified acid systems (EAS) using organoclays were compared with another EAS prepared by using a surfactant at the same conditions of mixing speed, HCl concentration, and temperature. In terms of thermal stability, almost all of them (Pickering EAS, and Surfactant EAS) were thermally stable. However, in terms of rheology, it was found the Pickering EAS has low viscosity compared with surfactant EAS at high shear rates as shown in Figure 56. This reduction in the viscosity of OC EAS compared with the emulsion formulated using a surfactant at a high shear rate is comparable with the finding reported by (Al-yaari et al., 2014), in which reduction in the viscosity was observed for the emulsion prepared with organoclay compared to the

emulsion formulated using a surfactant. It should be noted that the study by (Al-yaari et al., 2014), was for water-in-oil emulsion and not the EAS.

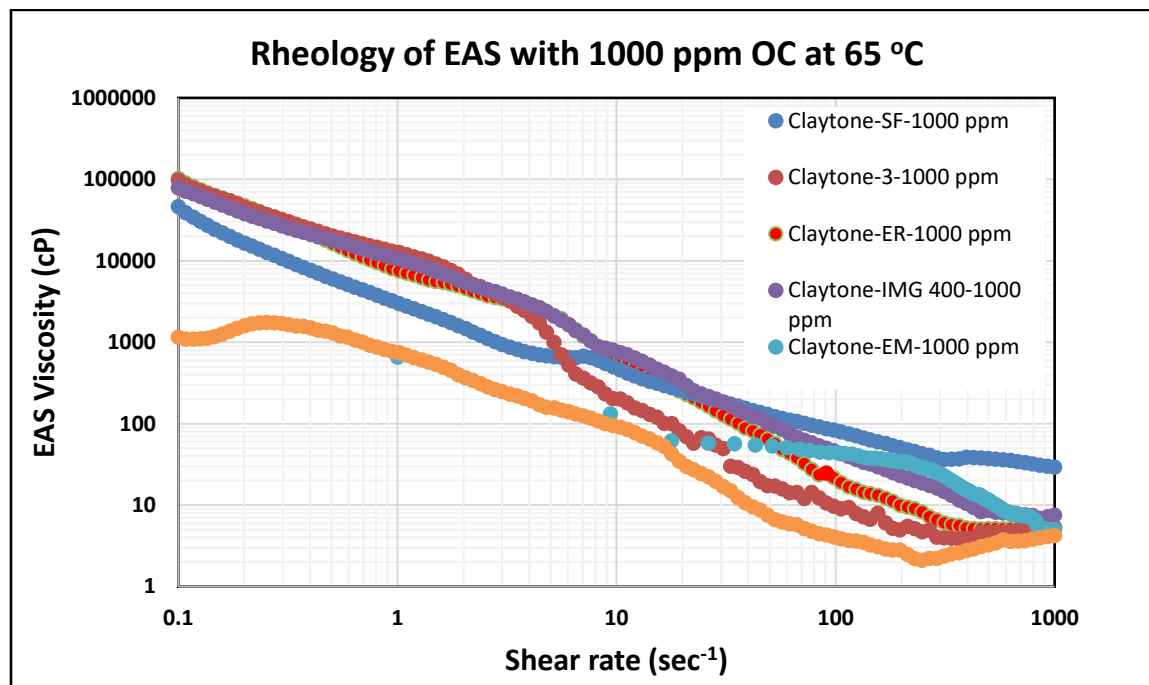


Figure 47 EAS Viscosity (cP) Vs. the shear rate at 1000 ppm OC concentration at 65 °C

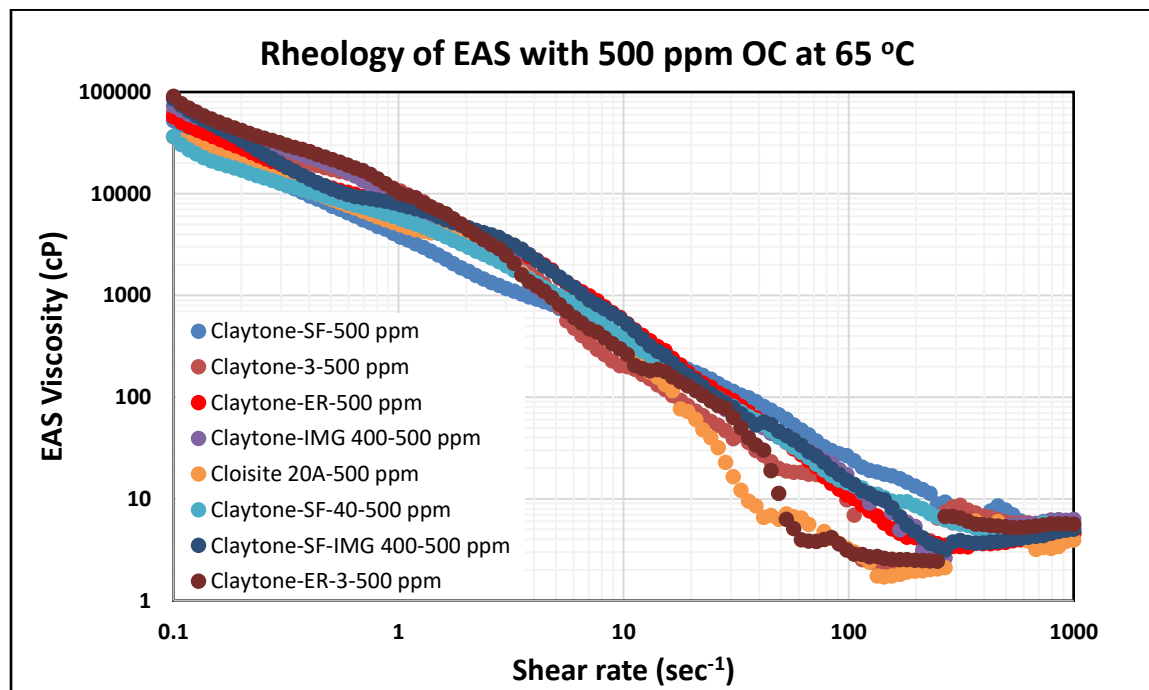


Figure 48 EAS Viscosity (cP) Vs. the shear rate at 500 ppm OC concentration at 65 °C

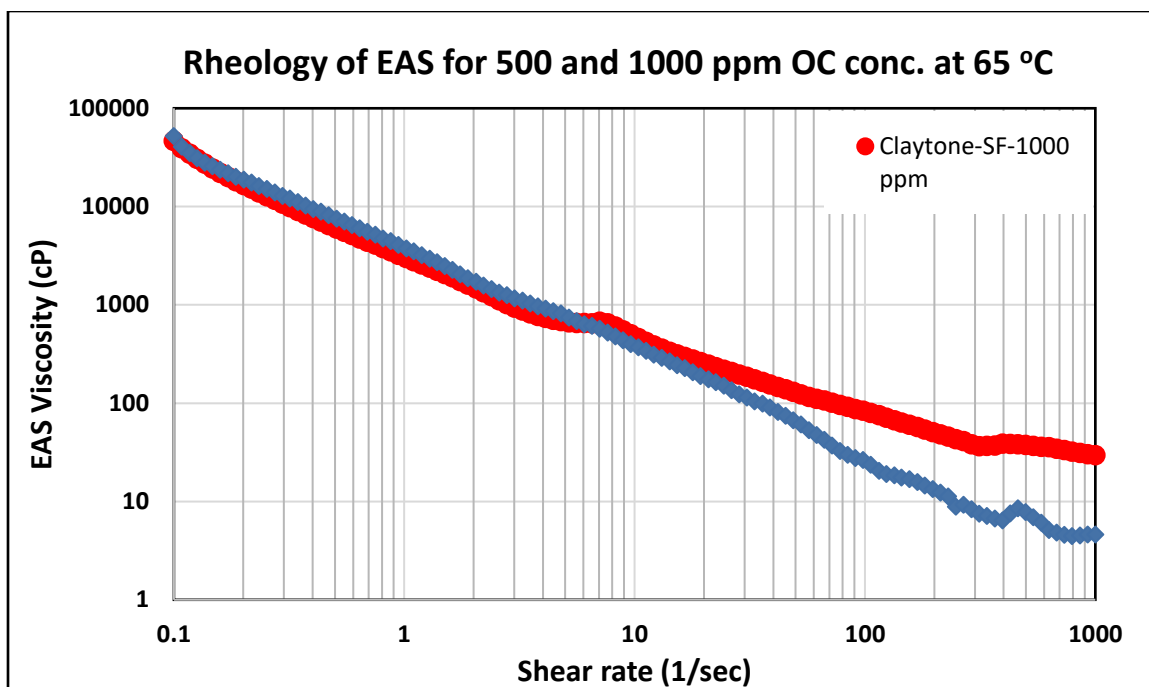


Figure 49 EAS Viscosity (cP) Vs. the shear rate at 1000, and 500 ppm Claytone SF at 65 °C

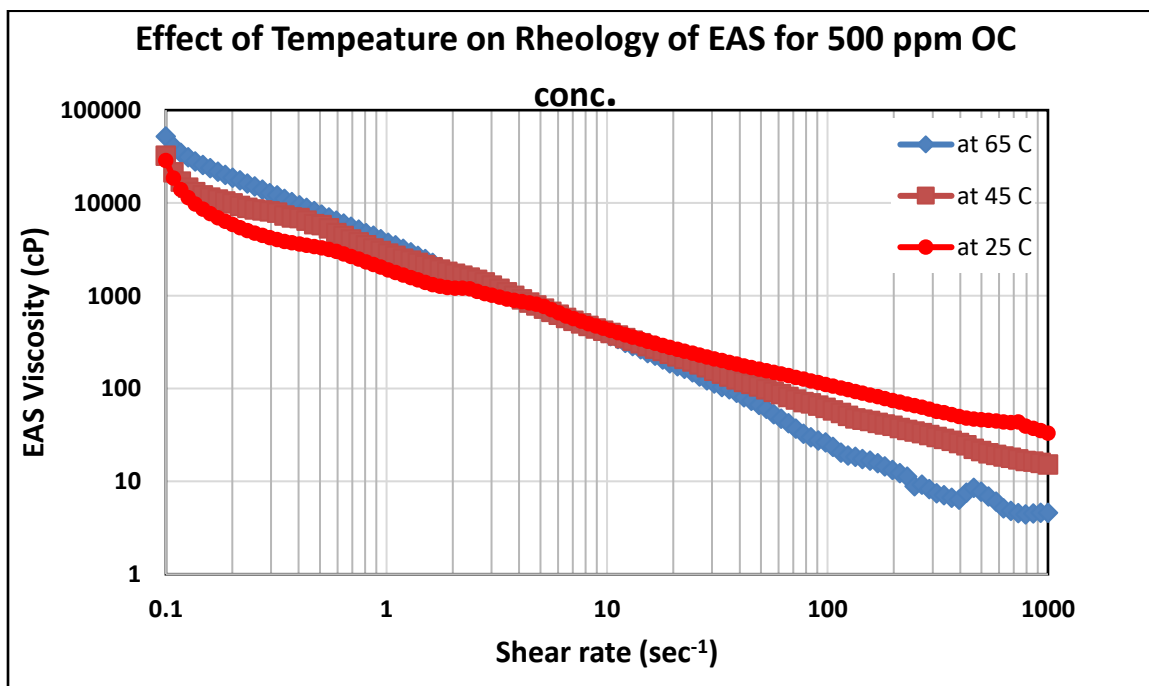


Figure 50 EAS Viscosity (cP) Vs. the shear rate with 500 ppm of Claytone SF at different temperatures

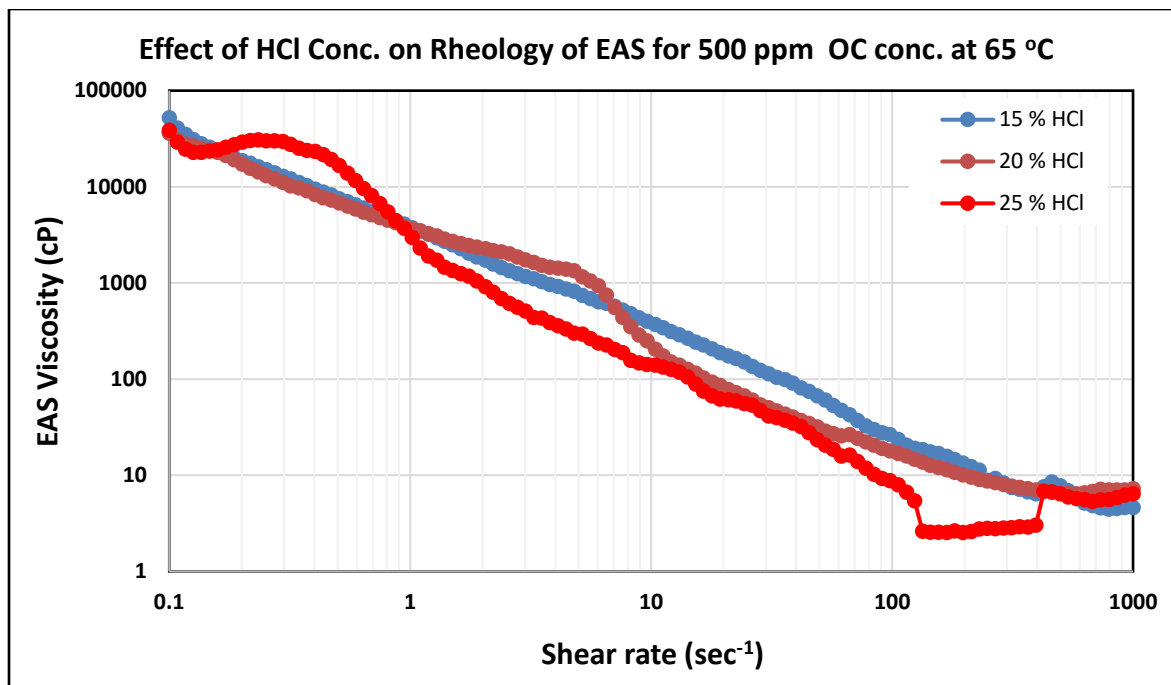


Figure 51 EAS Viscosity (cP) Vs. Shear rate for 500 ppm of Claytone SF at different HCl concentrations at 65 °C

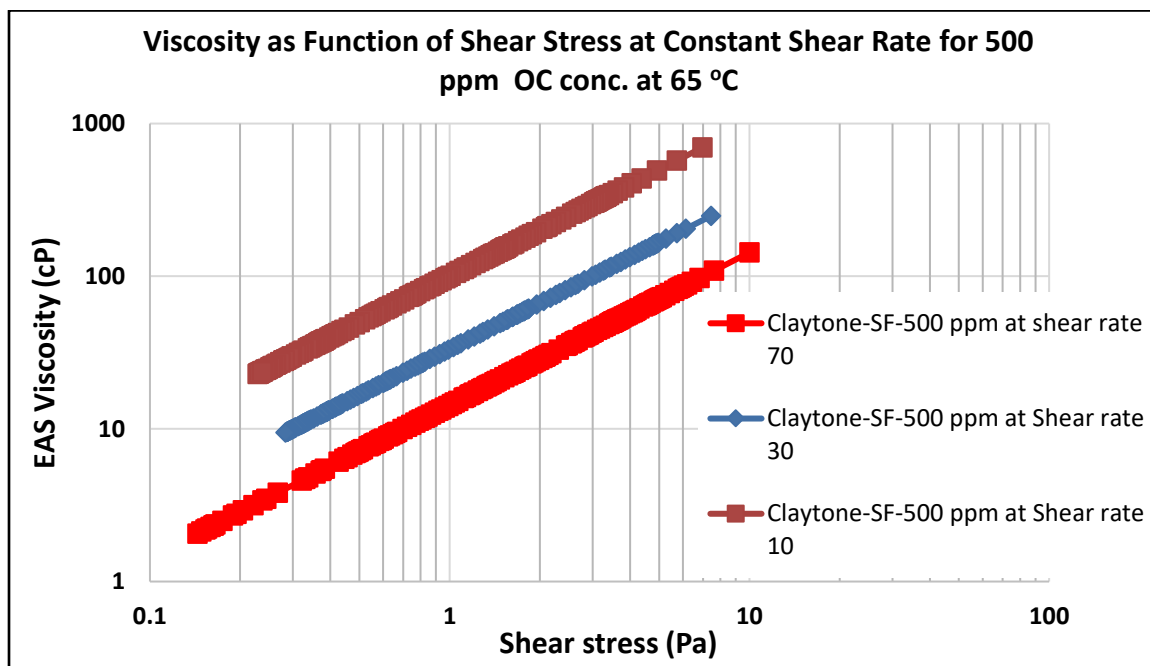


Figure 52 EAS Viscosity (cP) Vs. the shear stress with 500 ppm for Claytone SF at different shear rates at 65 °C

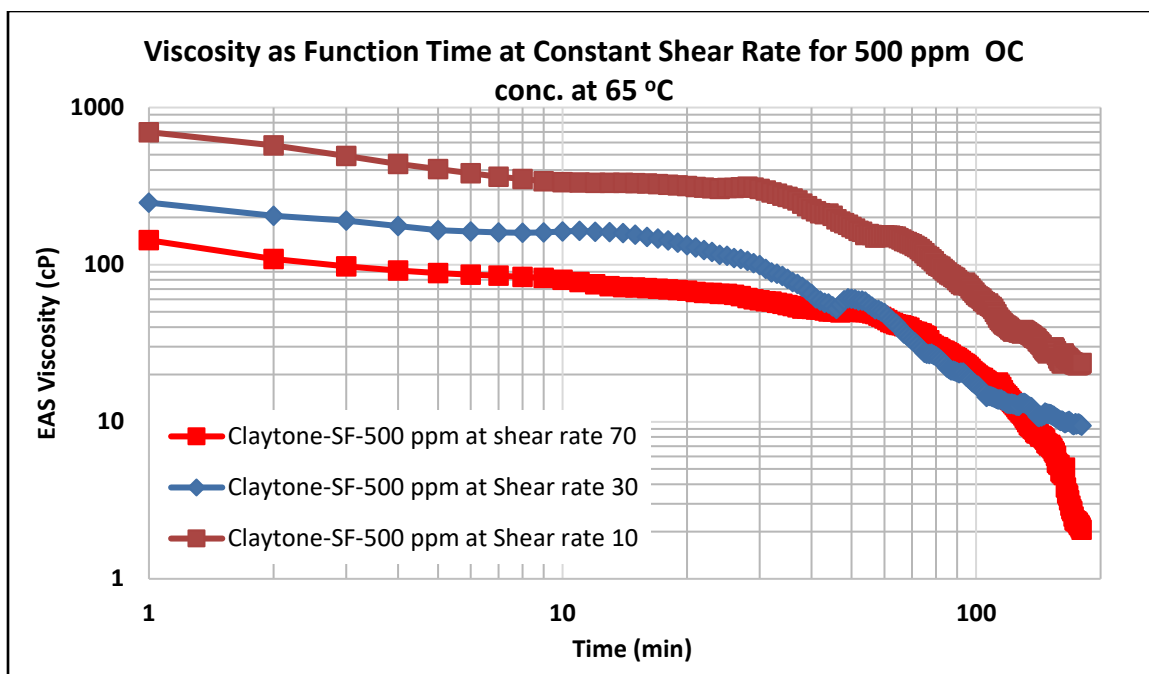


Figure 53 EAS Viscosity (cP) Vs. Time for 500 ppm Claytone SF at different shear rates at 65 °C

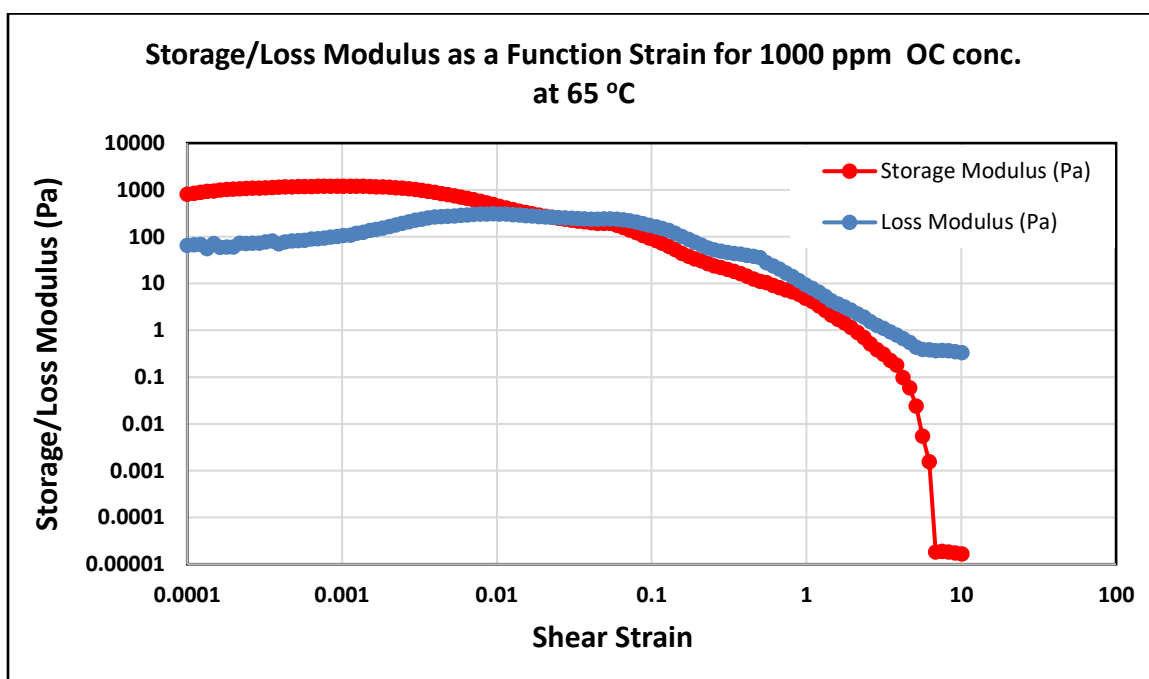


Figure 54 Storage/loss modulus (Pa) Vs. the shear strain for 1000 ppm Claytone SF at 65 °C

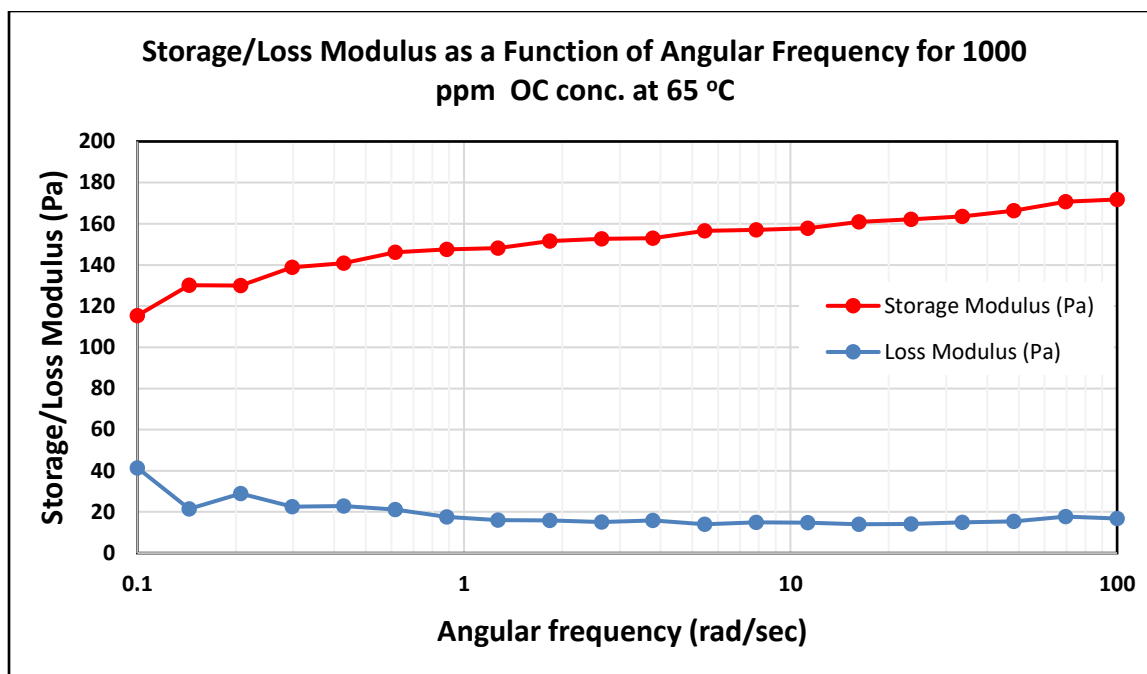


Figure 55 Storage/loss modulus (Pa) Vs. Angular Frequency for 1000 ppm Claytone SF at 65 °C

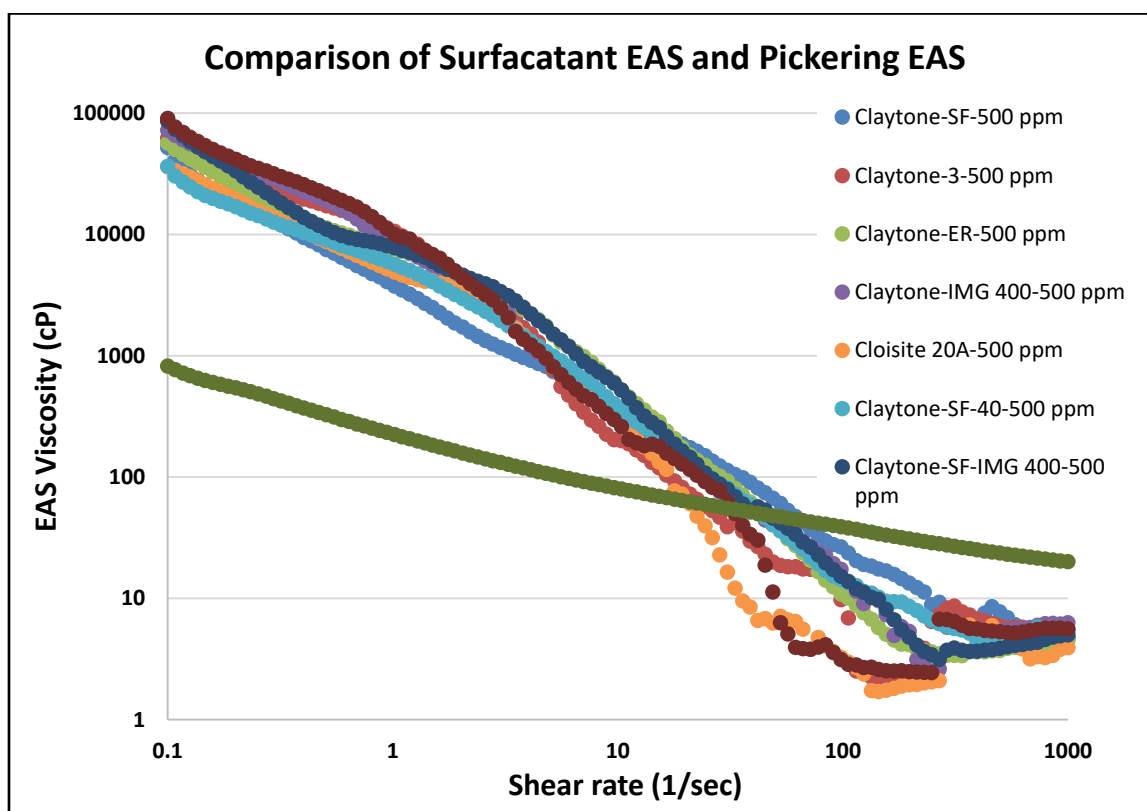


Figure 56 Comparison between Surfactant EAS and Pickering EAS at 65 °C

4.5.6 Discussion

This study details the development of an Emulsified Acid System (EAS) using Organoclays (OC). The EAS system developed using OC was tested for conductivity, drop test, and thermal stability. A comprehensive investigation of EAS rheology was conducted, as it is a critical parameter for operational effectiveness. Various types of OCs were explored for EAS formulation. However, only five OCs (Claytone-SF, Claytone-IMG-400, Claytone-ER, Claytone-3, Cloisite 20 A) can give stable EAS for all examined temperatures in this study, two OCs (Claytone-EM, Claytone-AF) provides EAS which is stable only at 25 °C temperature and rest of the OCs (Claytone-40, Claytone-APA, Claytone-HT, Laponite-EP, Laponite-RDS) were not able to formulate EAS. The clays that were not able to formulate the EAS are mainly due to the dispersible media, which is diesel in this study. The first group of clays comes from the family of organophilic phyllosilicates (Claytone-40, Claytone-APA, Claytone-HT), these clays are easily dispersible in the diesel due to the high polarity of compounds (Aromatic and Aliphatic). These clays are more suitable for a non-polarity medium. In addition, the other group of OC (Laponite-EP, Laponite-RDS) belongs to the silicates group and is not dispersible in the diesel due high polarity of compounds. As the EAS is an inverted emulsion system the clays are required to be dispersed in the diesel which is a continuous phase of EAS.

The OCs (Claytone-SF, Claytone-IMG-400, Cloisite 20 A) is a modified form of the montmorillonite i.e. alkyl quaternary ammonium bentonite. The Claytone-E and Claytone-3 show a percentage of illite. These clays are modified to disperse in organic compounds such as diesel used in this study. These clays can formulate the inverted emulsion and are

known to be used in oil-based mud as a rheology modifier. These clays also provide stability to the emulsion and are thermally stable.

Rheological variation among tested clays for EAS is influenced by parameters such as mixing speed, mixing time, acid concentration, and temperature. The five clays underwent further testing for influencing parameters. Optimizing these parameters is crucial for complementing the presented work.

The stability of EAS and release time for the acid are very important from a field operation perspective. The concentration of OC clay plays a crucial role in achieving the optimum stability and acid release time from EAS. A desirable release profile ensures that the acid penetrates deep into the formation and dissolves the mineral scale, enhancing the flow of oil and gas. However, if the acid is released too quickly or too slowly, the optimum output of the acidizing will not be achieved such as creating channels or etching the rock, reducing the effectiveness of the stimulation treatment. The release time of acid requires to be addressed by considering the factors that govern the acid release from the EAS system. They include the concentration and type of acid, the type and concentration of OC, pressure, and temperature as well as the pore size distribution of the formation. Considering the scope of the study the refinement for the desired OC concentration was carried out.

The result of the optimization of OC for controlling the release profile of acid from EAS is shown in Figs. 27–28. The Clayton SF was not able to form EAS at 200 ppm concentration. However, it can form EAS at 250 ppm, 300 ppm, and higher concentrations. Figure 57 shows the stability of EAS with 250 ppm Clayton SF for 1hr, 3 h, and 5 h and at a constant temperature of 90 °C. Similarly, Figure 58 shows the stability of EAS with 300

ppm Clayton SF at 1hr, 3 hr, and 5 hr at a constant temperature of 90 °C. It was found that a concentration of 250 ppm as well as 300 ppm was able to form the EAS. The comparison in terms of concentration indicates more stability for higher concentration or slow release of acid from EAS. Also, the comparison of the acid release as a function of time indicates that the concentration of OC can be fine-tuned for the desired requirement of stability and acid release time from the EAS. It should be noted that conducting pertinent research is imperative in the development and optimization of EAS. The release profile of acid from EAS is a crucial factor that impacts well stimulation because it determines the effectiveness of the treatment and the potential for formation damage. By carefully optimizing the EAS formulation, it is possible to achieve a desirable release profile that enhances well productivity without causing damage to the formation. In summary, several factors influence the formulation of the EAS. This work provides a guideline for the development of the EAS using OCs. It provides insight into the material characterization, mixing process, mixing speed, as well testing of the formulated EAS in terms of conductivity, thermal stability, and rheology. The rheological parameters are studied in detail considering the implication of the EAS for acidizing as it needs to be transported from the surface to the wellbore through pipes/tubing where it is subjected to high velocity and then placed into the reservoir which is porous media in the flow velocity is remarkably low, especially for the viscous medias such as EAS.

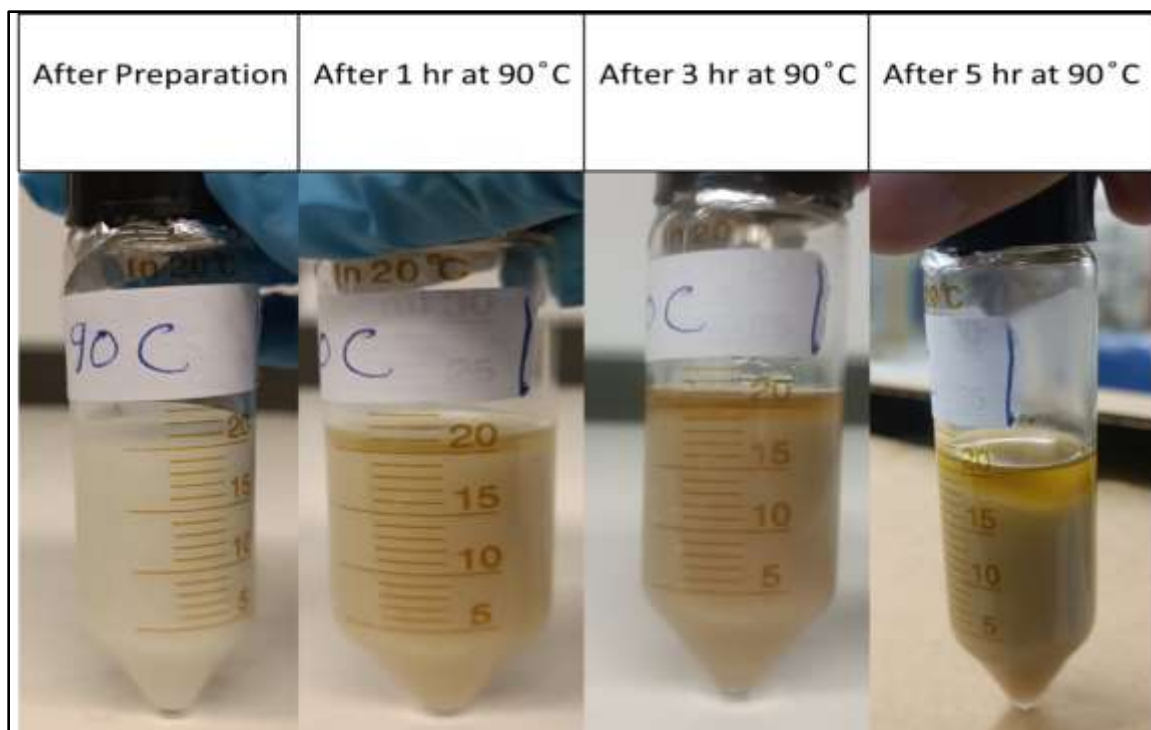


Figure 57 Stability /acid release profile of EAS at 1hr, 3hr, and 5hr for 250 ppm Claytone SF at 90 °C

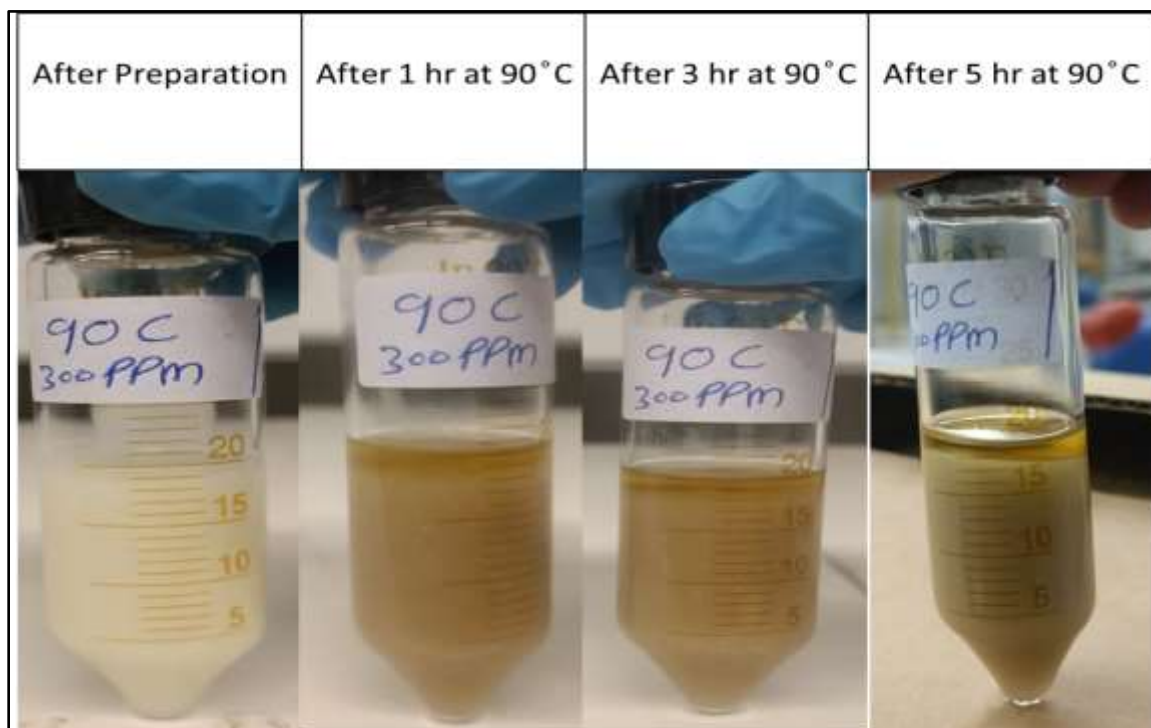


Figure 58 Stability /acid release profile of EAS at 1hr, 3hr, and 5hr for 300 ppm Claytone SF at 90 °C

4.6 Conclusions

The following points can be concluded from this study:

1. Twelve different OCs were investigated in this study for the development of the EAS. Among the tested OCs five clays (Claytone-SF, Claytone-IMG-400, Claytone-ER, Claytone-3, and Cloisite 20 A) can give stable EAS for all the temperatures tested in this study.
2. These clays (Claytone-SF, Claytone-IMG-400, Claytone-ER, Claytone-3, Cloisite 20 A) can be used as an emulsifier to prepare Pickering EAS with good thermal stability, and representative rheological characteristics.
3. Two OCs (Claytone-EM, Claytone-AF) provide EAS and were able to provide stability only at 25 °C temperature and the other five OCs (Claytone-40, Claytone-APA, Claytone-HT, Laponite-EP, Laponite- RDS) were not able to formulate EAS.
4. The insight into the performance of the OCs based on the dispersible nature of OCS in the media could be the criteria for the selection of OC for the development of EAS.
5. The reduction in the concentration of OCs from 1000 to 500 ppm has a negligible effect on the thermal stability, however, it has a significant impact on the rheological behavior of the EAS. The OC concentration of 200 ppm was not able to formulate the EAS.
6. The viscosity of the EAS shows increasing trends with increasing temperature at the low shear rate (below 10sec^{-1}) however, at a shear rate higher than 10sec^{-1} , the EAS viscosity decreases with increasing temperature. At the low shear rate, the

Pickering EAS has high viscosity compared to the conventional EAS, however at the high shear rate the Pickering EAS has low viscosity compared to the conventional EAS.

7. Increasing the HCl concentration has a very small or negligible reduction of viscosity of the Pickering EAS.
8. There are several interrelated factors (mixing speed, mixing time, acid concentration, OCs concentration, temperature) affecting the development and performance of the EAS system, and further study to evaluate the influence of these parameters.

CHAPTER 5

PICKERING EMULSIFIED ACID SYSTEM

(PEAS): A PROMISING APPROACH FOR

REDUCED DRAG IN MATRIX ACIDIZING

This paper was submitted in Geoenergy Science and Engineering :

Ala, A. D., Gajbhiye, R., Sultan, A., Solling, T., Patil, S., & Alsarkhi, A. (2023). Pickering emulsified acid systems (PEAS): A promising approach for reduced drag in matrix acidizing *Geoenergy Science and Engineering*, 212022.

5.1 Abstract

Matrix acidizing is a commonly used technique in the petroleum industry to remove scale and create pathways within rock formations, a process known as "wormholing." This method significantly enhances well productivity. Traditionally, hydrochloric acid (HCl) is used as the acidizing fluid for carbonate reservoir stimulation. However, HCl acid solutions have certain drawbacks, including high acidity, susceptibility to corrosion at elevated temperatures, and rapid reactivity with scale and particles.

To address these limitations, emulsified acid systems (EAS) are utilized. EAS can generate narrower and deeper wormholes by slowing down the acid's reaction rate through the

introduction of an external oil phase. However, EAS has a higher viscosity than standard acidizing fluids, resulting in increased resistance during pumping and higher energy consumption.

The Pickering emulsified acid system (PEAS), formulated using organoclays (OC) as an emulsifying agent, offers superior performance compared to typical EAS that employ surfactants. PEAS enhances acid penetration and interaction with reservoir rocks by leveraging the solid particles of OC, ultimately improving reservoir stimulation. PEAS is also better suited to reservoir conditions. Organoclays possess unique attributes that make them applicable across various applications in the petroleum industry, including enhanced thixotropy, compatibility, and eco-friendliness. OCs can exhibit slippery or lubricious characteristics and reduce friction due to their distinct structure and qualities.

This study investigated the drag reduction of PEAS and compared it with EAS prepared using surfactants. Several flow experiments were conducted to study the drag reduction of PEAS. The results showed that PEAS has a lower drag than EAS prepared with surfactant for two different HCl concentrations (15 and 20%). The drag reduction was observed at the range of temperatures investigated in the study. Conductivity, stability, and rheology experiments were conducted on samples taken after the flow experiments, and the results showed that PEAS is robust in terms of field mixing procedures and thermally stable. The lower drag associated with PEAS can be a promising approach for drag reduction, which can help in faster pumping rates, deeper placement of acid, and efficient wormhole formation using environmentally friendly OC.

5.2 Introduction

Well stimulation is a method for enhancing oil and gas flow from a well, and it can be done using two different methods, matrix acidizing, and hydraulic fracturing. Matrix acidizing uses acids to dissolve rock formations and create channels and wormholes for oil and gas to flow through. This is carried out at a pressure lower than the reservoir's fracture pressure. Hydraulic fracturing uses high-pressure fluids to create cracks in the rock formations. These cracks allow oil and gas to flow more easily to the wellbore. At a pressure greater than the formation pressure, hydraulic fracturing is carried out. Table 12 shows the well stimulation techniques.

Table 12 Well stimulation techniques

Method	Pressure	Description
Matrix acidizing	Lower than the formation fracture pressure	Uses acids to dissolve rock formations and create channels for oil and gas to flow through
Hydraulic fracturing	Higher than the formation fracture pressure	Uses high-pressure fluids to create cracks in the rock formation. These cracks allow oil and gas to flow more easily to the wellbore.

HCl acid systems are frequently employed in the petroleum industry to improve the well productivity of oil and gas by removing the formation damage in carbonate reservoirs. Delivering acid deep into the reservoir while limiting rock face dissolution is difficult, though. The drawbacks of conventional acidizing fluids are their extreme acidity, quick interaction with scale and particles, and corrosion of the tubing, casing, and downhole equipment at high temperatures.

One of the solutions to overcome the drawbacks of traditional acid systems is to use the EAS. EAS typically consists of acid and oil (usually diesel), where diesel functions as a diffusion barrier separating the acid within the EAS from the surrounding rock (Fatah and Nasr-El-Din, 2010, 2008). EAS belongs to the category of water-in-oil (W/O) emulsions, wherein an emulsifier is used to seal the acid phase inside the diesel phase (AL-Dogail et al., 2023b; Kasza et al., 2006; Nasr-El-Din et al., 2008; Sidaoui and Sultan, 2016). EAS is classified as a non-Newtonian shear-thinning fluid, indicating that its viscosity changes with the shear rate. The EAS rheological property can be adequately described by the power-law model, where the viscosity decreases as the shear rate increases (Lynn and Nasr-El-Din, 2001; Nasr-El-Din, H. A. et al., 2000).

Numerous investigations on the use of the EAS to stimulate carbonate reserves have been carried out by many researchers (AL-Dogail et al., 2023b; Al-Mutairi et al., 2008; Buijse, 1997; Buijse and Van Domelen, 2000; Crowe et al., 1990; Mahmoud et al., 2023; Navarrete et al., 2000; Nierode and Kruk, 1973; Siddiqui et al., 2006). Nevertheless, EAS still has some limitations such as low stability at high temperatures, high viscosity that restricts pumping rates, the potential for formation damage, and the challenge of achieving homogeneous field-scale mixing. Furthermore, the presently used EAS can not be pumped or injected at low flow rates and limits the depth of penetration in the matrix or fractured systems. Addressing this problem is still challenging, and the emulsified acid treatment design has only aimed at placing the acid as rapidly and deeply as possible. Consequently, the reduction of drag in pipes would allow for higher pumping rates, increase the flow capacity, and conserve energy (AL-Dogail et al., 2023a).

Organoclay(OC), often referred to as nano clay, represents an organically modified phyllosilicate, specifically a disilicate compound. OC is derived from clay minerals that occur naturally. The process involves the separation of clay layers through ion exchange and surface chemical modifications, enabling the creation of nanocomposites either through in situ polymerization or by blending with specific polymers. Nowadays, OC has gained widespread utility, particularly as an emulsifier due to its advantages such as low cost, availability, high surface area, and eco-friendliness. OC can be used as drag drag-reducing agent (DRA) for W/O emulsion (Al-yaari et al., 2014; Khalid et al., 2020), where OC reduces the W/O emulsion viscosity, and as a result the reduction in drag occurs.

The purpose of this study is to experimentally explore the drag reduction of PEAS. Several flow experiments have been conducted to study the drag reduction of PEAS. Detailed explanations of the PEAS preparation, thermal stability, rheological characteristics, and flow experimentation processes have been provided.

5.3 Literature review

A category of colloidal systems known as emulsions consists of two immiscible liquids in which one liquid disperses into tiny droplets within the other liquid phase (Adewunmi et al., 2022; Israelachvili, 1994). The liquid phase that forms the dispersed droplets is referred to as the internal phase, while the surrounding liquid is known as the continuous phase, often termed the external phase. Water-in-oil (W/O), oil-in-water (O/W), water-in-oil-in-water (W/O/W), and oil-in-water-in-oil (O/W/O) are the four primary forms of emulsions. In the petroleum industry, the W/O emulsion is the most typical kind. Emerging emulsion processing techniques, including microfluidic emulsification, can be used to regulate the

number, size, and size distribution of the droplets in an emulsion. Microfluidic emulsification uses tiny channels to produce emulsions with high droplet consistency. This technique has the potential to improve the performance of emulsions in a wide range of applications (Pal, 2011).

Emulsions represent inherently unstable mixtures comprising two immiscible liquids. They can be systematically classified into three distinct categories based on their temporal stability characteristics: loose emulsions, which are stable for a few minutes; medium emulsions, characterized by stability lasting approximately ten minutes; and tight emulsions, which are stable for hours or even days (Abdulredha et al., 2020; Tambe, D. E., & Sharma, 1993). Several variables can affect an emulsion's stability, including the presence of heavy polar elements, tiny solids (both organic and inorganic), temperature, the distribution of droplet sizes, and the pH and content of the brine (Kokal, 2008). Notably, the stability of the emulsion is substantially impacted by the pH of the brine. Following acid stimulation, several emulsion upsets can occur due to the precipitation of solid materials, primarily asphaltenes. This precipitation process can give rise to the formation of a tightly bonded and exceedingly stable emulsion, which can kill the well. Hence, it is essential to design an appropriate acid treatment to prevent emulsion upsets.

Acidizing is a stimulation technique used in the petroleum industry to stimulate oil and gas wells and enhance the productivity of wells. HCl and a combination of HF and HCl are the conventional acidizing fluids that are frequently employed in the petroleum industry to stimulate carbonate reservoirs. However, these fluids have some limitations such as high acid strength, leading to quick reactions with scales and fines near the wellbore. Additionally, at high temperatures, they pose challenges for tubing, casing, gravel pack

screens, and downhole pumps. In some circumstances, using HCl acid above 93°C is not recommended due to its potential to damage the formation (Huang et al., 2013). Alternative acid systems can be used as a solution to the issues of conventional acidizing fluids, and these systems include a mixture of tricarboxylic acids, amino carboxylic acids, and dicarboxylic acids (Huang et al., 2013). However, these alternative acids are still limited to specific carbonate reservoir conditions, also these acids have complex formulations, compatibility issues, as well as corrosion problems still being less corrosive compared to the conventional acidizing fluids. So that a need for another acidizing liquid is required to overcome these limitations. EAS has become widely used in the petroleum industry as a solution to the limitations of conventional acid systems.

Two immiscible fluids are combined to form an emulsion; the internal phase, also known as the dispersed phase, and the external phase, sometimes known as the continuous phase. When the continuous phase or external phase (diesel) envelops the HCl droplets, an acid-in-diesel emulsion, a type of W/O emulsion, is formed. A concentrated HCl acid (usually ranging from 15–28%) is frequently utilized in the oil and gas industry (Adewunmi et al., 2022; Al-Mutairi, S. H., Hill, A. D., 2008). To maximize oil and gas production and improve formation permeability, the EAS is frequently used in fracturing and acidizing procedures within carbonate reservoirs. The presence of 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.

To create an EAS by mixing the aqueous acid phase with the diesel phase and improving its stability at high temperatures, an emulsifier is needed. Very small particles, including

clay particles and/or nanoparticles, are included in the EAS to provide this stability (Huang et al., 2013). The stabilized EAS is made up of oil, an aqueous acid solution including one or more acids, at least one emulsifier, and acid-insoluble nanoparticles with an average particle size of 1000 nanometers or less. In oil and gas operations, emulsified acids, acids that have been mixed with oil, usually diesel, offer some benefits. They aid in reducing downhole equipment corrosion as well as the rate of carbonate reservoir reactions, especially at high temperatures. This improves well stimulation and overall reservoir performance by allowing the active acid to permeate deeply into the formation. Emulsified acids' physical characteristics are strongly influenced by how they are made (preparation method). 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 (Al-Mutairi, S. H., Hill, A. D., 2008). This method is essential for getting consistent and predictable outcomes from emulsified acid treatments, which ensures their usefulness in a variety of oilfield circumstances.

5.3.1 Emulsified acid system (EAS)

De, 1933 was a pioneering researcher who first utilized acid-in-oil emulsion in well stimulation. EAS can exist in either macro or microemulsion forms (Al-Anazi et al., 1998; Hoefner et al., 1987). However, macro emulsions, distinguished by their larger droplet size and requiring less emulsifier, are the most commonly used in the field (Al-Anazi et al., 1998; Kasza et al., 2006; Mohamed et al., 1999; Nasr-El-Din et al., 2000; Sayed and Nasr-El-Din, 2011). In a notable development, Pandya et al. (2012) introduced a novel EAS formulation for the stimulation of extremely high-temperature carbonate reservoirs, and

the developed formulation incorporates three intensifiers. This novel EAS was specifically designed for use in carbonate reservoirs with bottom-hole temperatures (BHT) of up to 163° C. Additionally, their research provided valuable insights into the impact of the intensifiers on the EAS performance, contributing to a deeper understanding of the stimulation process. The findings of Pandya et al. (2012) offer promising prospects for effectively enhancing production in challenging high-temperature carbonate reservoirs.

In a study conducted by Sabhapondit et al. (2012), the experimental optimization of a 26% HCl-based EAS was performed for stimulating high-temperature carbonate reservoirs. The researchers investigated the effects of two different corrosion inhibitors at various temperatures and time durations. The results highlighted the critical importance of finding the right balance between the inhibitor and emulsifier concentrations to design an effective and efficient EAS blend. This optimization process is essential for achieving a well-tailored EAS formulation capable of effectively stimulating high-temperature carbonate reservoirs while mitigating potential corrosion issues.

Madyanova et al. (2012) conducted a case study on matrix acidizing stimulation applied to a high-temperature carbonate reservoir, specifically the Sungai Kenawang (SKN) gas-condensate field situated in the southwestern part of the Jambi Merang block in south Sumatra province, Indonesia. This field is a high-temperature carbonate reservoir. Emulsified and viscoelastic self-diverting acids were used in conjunction with the stimulation process. The researchers observed that using highly retarded high-temperature EAS along with high-temperature viscoelastic surfactant led to significant stimulation throughout the targeted interval, resulting in a notably higher productivity index. Their

findings demonstrate the potential effectiveness of this approach in enhancing well-performance high-temperature carbonate formation.

Cairns et al. (2016) conducted a comprehensive experimental study aimed at enhancing well-stimulation through an improved EAS. Their investigation involved 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 threefold increase in core permeability improvement compared to conventional acid systems. This promising outcome highlighted the potential of the improved EAS as a valuable solution for achieving deeper and more effective well stimulation in various reservoir conditions.

Umar et al. (2016) investigated the impact of various factors on 30-day-aged W/O emulsions. The study examined the effects of various water cuts, the presence of an emulsifier, and the effects of water content, shear rate, shear stress, and temperatures on the emulsion. Additionally, the rheological properties of the W/O emulsions were analyzed at two different temperatures (25 and 60° C) with varying water cuts. The findings demonstrated that the rheology and stability of the W/O emulsions were significantly influenced by the presence of the emulsifier, water content, shear rate, and temperature. This study sheds light on the complex interplay of these factors and their impact on the behavior of W/O emulsions, providing valuable insights for applications in the oil and gas industry.

Sidaoui and Sultan (2016) experimentally investigated the factors influencing the stability of HCl-EAS. They focused on thermal stability and rheology of the EAS. The results revealed that varying the emulsifier concentration from 0.5 to 1.5 vol % did not significantly affect the stability of the emulsified acid. Additionally, the small droplet size of the emulsion contributed to its higher viscosity. Furthermore, as the temperature increased, the apparent viscosity of the EAS decreased.

Sidaoui et al. (2017, 2016) expanded their research by exploring the utilization of waste oil as the external phase of a 70:30 acid/oil ratio with 15 % HCl in an EAS. As a result of the findings, waste oil has the potential to be a useful external phase for constructing EAS intended for high-temperature carbonate reservoirs. Additionally, the created HCl-waste oil EAS displayed shear-thinning behavior and had advantageous rheological characteristics. In a separate study, Sidaoui et al. (2018) focused on the investigation of adding iron control and chelating agents to EAS stability and its reaction with dolomite. The findings indicate that the most stable EAS was obtained with an initial chelating agent concentration and without iron control.

Using a unique low-viscosity retarded acid system, Sayed et al. (2018) stimulated high-temperature carbonate reservoirs. The proposed acid system successfully decreased the amount of free water within the system, preventing the acid from completely dissociating. The findings showed that a 12-inch core sample of the suggested acid system needed an additional 0.28 pore volume (PV) to make a breakthrough. It differs from EAS in that it has a lower PV need, which has benefits for fluid viscosity. When compared to conventional EAS, the fluid viscosity of the suggested acid system was significantly lower, which reduced pumping drag and allowed for higher pumping rates.

Through the use of engineering methods, Aldakkan et al. (2018)) created a novel low-viscosity retarded acid system. Their suggested acid system combined a strong acid with an organic molecule that is very soluble in water. According to the testing findings, the proposed acid system significantly reduced core weight loss owing to dissolving by a factor of four when compared to the standard 15-weight percent HCl acid. They also found that the corrosion impacts of their unique acid system were negligible and that the acid reaction with calcite was delayed.

A highly stable and cost-effective EAS for stimulating deep wells in carbonate reservoirs was proposed by Ahmed et al. (2018). They exploited particular nanoparticles as an alternative to traditional surfactants. The effectiveness of the produced EAS in stimulating deep limestone reservoirs was assessed using core flooding experiments, and the outcomes were contrasted with those of a typical EAS formed using diesel. According to the findings, the created EAS with waste oil outperformed the diesel EAS in the stimulation process and worked better at low injection rates. The results also showed that the emulsifier concentration, acid-to-oil ratio, types of employed acids and oils, chemical additives, and the manner of preparation all had an impact on EAS stability.

By substituting ecologically friendly oil for diesel when creating an EAS for matrix acidizing of the carbonate rocks, Yousufi et al. (2019) created a green method of doing so. They created the oil from *Jatropha curcas* oil using a synthetic process, and they showed that diesel could be successfully replaced by the *Jatropha* oil-based EAS for matrix acidification. Particularly noteworthy was the fact that the *Jatropha* oil-based EAS outperformed the traditional diesel-based EAS in terms of thermal stability. The experimental findings also showed that the *Jatropha* oil-based EAS had minimal toxicity

and a high fatty acid content. This characteristic enhances its potential as a safer and more environmentally conscious alternative for acidizing operations in the oil and gas industry.

Sokhanvarian et al. (2019) successfully formulated a stable EAS suitable for high-pressure-high-temperature (HPHT) wells, operating at 149° C. They utilized a non-aromatic non-ionic surfactant to develop the EAS. The experimental findings showed that the non-ionic surfactant effectively enabled the preparation of a stable EAS, which exhibited superior performance in well stimulation with low acid pore volume breakthrough (PVBT) at 149° C.

Jafarpour et al. (2019) introduced a novel multi-batched acid system designed to enhance the stimulation efficiency of heterogeneous carbonate reservoirs. The findings demonstrated that the developed multi-batch acid stimulation technique proved highly effective in stimulating such complex carbonate reservoirs, leading to improved reservoir performance.

Sayed et al. (2021) designed a low-viscosity single-phase acid system tailored for acid fracturing in deep carbonate reservoirs operating at high temperatures. This acid system was a pre-engineered mixture of a powerful mineral acid and an alkyl sulfonic acid. According to the experimental findings, the created acid system performed similarly in terms of diffusion coefficient to 15-weight percent HCl-EAS. Furthermore, the low viscosity of the acid system minimized drag, which allowed for high pumping rates through the tubular and helped with effective well stimulation in deep carbonate reservoirs.

Al-Sabea et al. (2022) devised a novel low-viscosity, polymer-free acid retarded system and completed a case study in the west Kuwait field. A non-damaging retarding agent was

combined with a powerful mineral acid, such as HCl, in their novel acid system to enable deeper penetration of the HCl acid into the formation. Compared to the EAS injected into a neighboring well, the experimental findings demonstrated that the proposed acid system showed considerable promise. Furthermore, the developed acid system offered additional benefits by reducing environmental concerns and minimizing costs. This novel approach presents an attractive solution for effective well stimulation in the west Kuwait field, promoting greater reservoir productivity and optimizing hydrocarbon recovery. Moreover, the environmentally friendly and cost-efficient nature of the proposed acid system further strengthens its viability for application in various oil and gas operations.

Zakaria et al. (2022) introduced an innovative and polymer-free delayed HCl acid system with low viscosity, specifically designed for stimulating high-temperature carbonate reservoirs. The results showed that the developed delayed HCl acid system required a reduced acid PVBT compared to standard HCl acid at all injection rates. Moreover, the utilization of this low-viscosity delayed HCl acid system enhanced acid penetration, allowing for access to deeper reservoir areas and contributing to the success of the acid stimulation process.

AL-Dogail et al. (2023b) investigated different types of organoclays (OC) as emulsifiers to develop Pickering EAS. The results showed that some types of OCs can be used as emulsifiers to develop Pickering EAS with good thermal stability and low viscosity at high shear rates.

In summary, it can be seen that several studies have explored the formulation of EAS to overcome the limitation of conventional acid fluid for stimulation. EAS involves acids

dispersed in an external oil phase, offering benefits like reduced corrosion and controlled reaction rates. The EAS formulations required for well stimulation are required to be stable at 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 like nanoparticles or waste oil. Factors influencing EAS stability and performance include emulsifier concentration, acid-to-oil ratio, and temperature. Researchers have proposed diverse solutions to optimize 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 emulsion but not the emulsified acid system. It should be noted that the achieving drag reduction of emulsion cannot be translated to drag reduction of the EAS. The nature of EAS needs to be considered while addressing the drag reduction of EAS. It includes compatibility of the material with acid and ensuring the formation of an emulsion that is thermally stable and possess characteristics of an emulsion that is ready to use considering operating and field condition. This requires rigorous experiments and laboratory set-up for testing the EAS and its drag reduction.

This study experimentally investigates the drag reduction of PEAS. The PEAS 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 EAS, temperature, flow rates, and the acidic nature of the fluid. The results are encouraging when they are compared with surfactant EAS.

5.4 Methodology

To achieve the objectives of this study, the PEAS was prepared utilizing OC as an emulsifier. The acid phase-to-diesel phase ratio for all prepared EAS was 70:30. Several acid emulsion formulations were prepared, where diesel was mixed with the emulsifier (OC), and the aqueous phase, which includes acid that was added while the mixing process was on with a specific addition rate. In the flow experiment, firstly the 15% HCl-PEAS was prepared in large amounts (30-40 liters), and the flow rates of the PEAS flowing through the flow loop were recorded against the pressure drop readings. Then similarly, the 20% HCl-PEAS was prepared, and again the flow experiment was conducted. Optimization of OC concentrations was investigated during the flow experiment of 15 and 20 % HCl-PEAS. After that, samples of the PEAS were taken from the flow loop after flow experiments, and the conductivity, pH test, drop test, rheology, and thermal stability at ambient temperature were explored. The methodology and procedures have been presented in this section in detail.

5.4.1 Materials and equipment

Materials utilized in this study include commercial diesel from a gas station, an emulsifier (OC), de-ionized (DI) water, and industrial-grade hydrochloric acid (HCl) with a concentration of 26-weight percent. High-speed mixer/homogenizer (TAISITESMART JRJ-300SH-220V high-speed homogenizer lab disperser emulsifier capacity 40L 200-

11000 r/min 510W digital display blender), magnetic stirrer, drag reduction unit (flow loop), rheometer (Anton-Paar MCR-702 Rheometer), test bottles, conductivity and pH meter (Thermo Scientific™-Orion StarTMA215 pH/Conductivity Benchtop Multiparameter Meter), and 510W digital display blender are among the instruments needed to conduct this study.

5.4.2 Emulsified acid system (EAS) preparation

PEAS was prepared in large batches (30–40 liters) using a 70:30 acid-to-diesel ratio, where 70% refers to the aqueous phase, also known as the acid phase, which is the dispersed phase, and 30% refers to the diesel phase, which is the continuous or external phase. The PEAS has HCl acid concentrations of 15 and 20 percent. First, a predetermined amount of emulsifier (OC) was added to the diesel, and they were mixed using a homogenizer at 10,000 RPM for 7-8 minutes. At the same time, 26% industrial-grade HCl acid was titrated with DI water in a different beaker to the necessary concentration of 15, and 20% using a magnetic stirrer for 1-2 minutes. Then, the aqueous phase (acid phase) was added to the oil phase (diesel phase) progressively while mixing at 10,000 RPM with a specific addition rate of 300 cubic centimeters per minute (cc/min).

5.4.3 Flow experiment

The required amount for one flow experiment is 30-40 liters. The prepared PEAS was pumped through the flow loop (drag reduction unit), and this flow loop consisted of a gear pump with variable frequency drive (VFD), tank, pressure transducer, and 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 variable frequency drive and the reading of pressure drop against flow rates is recorded. This procedure is followed covering the range flow rates starting from low to high and then high to low to check the hysteresis. The flow experiments were done for two different HCl concentrations PEAS (15 and 20 %).

A sample of the PEAS was taken from the flow loop after finishing the flow experiment, and the following tests were conducted.

5.4.4 Conductivity/pH, and drop-test

To confirm that the PEAS sample, which was collected from the flow loop, is a W/O emulsion (the external phase being diesel), the electrical conductivity was tested. If the electrical conductivity reading is close to zero, it is likely a W/O emulsion. Moreover, to confirm that it is a W/O emulsion, a drop-test was also conducted. To conduct the drop test, 20 ml of water and 20 ml of diesel were added to two separate beakers along with 1 ml of the PEAS. If the dispersion occurs in a beaker containing water, the emulsion is an O/W emulsion, and if it occurs in a beaker containing diesel, the emulsion is a W/O emulsion. The pH was measured to confirm the PEAS's acidity.

5.4.5 PEAS stability

PEAS stability was explored at an ambient temperature for the sample taken from the flow loop using high-temperature graduated glass bottles. By visually observing the EAS separation every 10 minutes for the first 30 minutes, then every hour after the first 30 minutes for the next 2-3 hours, and finally after 24 hours, thermal stability was carried out

simply and easily. Photographs of the graduated glass bottles were taken before and after 24 hours.

5.4.6 Rheology

The rheological properties were assessed using the Annton Paar rheometer MCR-702, which has an acid-resistant bob/cup setup. A 15.9 ml volume of the PEAS is needed for the setup being used. All rheology measurements were performed at different temperatures. Every test took 30 minutes, while the shear rate ranged from 0.1 to 1000 1/sec.

5.5 Results and discussion

5.5.1 Emulsified acid system (EAS) preparation

The PEAS was prepared in large quantities (30-40 liters) with the ratio of 70:30 acid-to-diesel ratio, where the HCl acid concentration in the PEAS was 15 %. The emulsifier (OC) was added to the diesel, and they mixed using the homogenizer at 10000 RPM for 7-8 minutes, while the 26 % industrial-grade HCl acid was titrated with DI water in a separate beaker to the required concentration of 15 % using a magnetic stirrer for 1-2 minutes. Then the aqueous phase (acid phase) was added to the oil phase (diesel phase) progressively while mixing at 10000 RPM with a specific addition rate of 300 cc/min. Then, the prepared PEAS was tested for conductivity, pH, and drop test before the flow experiment. Figure 59 shows the PEAS preparation by adding the aqueous phase to the diesel phase while mixing at 10000 RPM. The same preparation procedures were followed for EAS with 20 % HCl acid concentration.



Figure 59 PEAS preparation

5.5.2 Flow experiment (drag reduction)

The Drag reduction unit (flow loop) shown in Figure 60 was utilized to conduct the drag reduction experiments. Firstly the drag reduction unit was calibrated with diesel as shown in Figure 61, then the prepared PEAS was pumped through the flow loop and the pressure drop was recorded using a pressure transducer at different flow rates. Figure 62 shows the procedures of the PEAS flow experiment through the drag reduction flow loop.

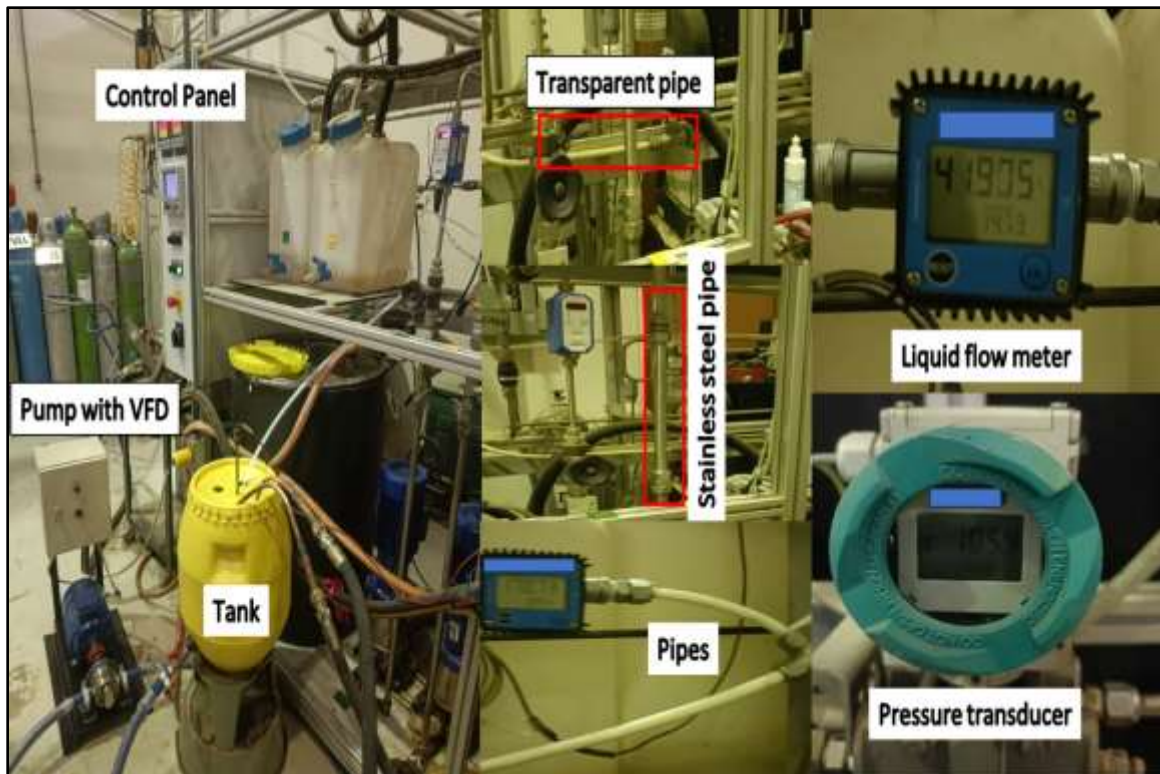


Figure 60 Drag reduction flow loop system

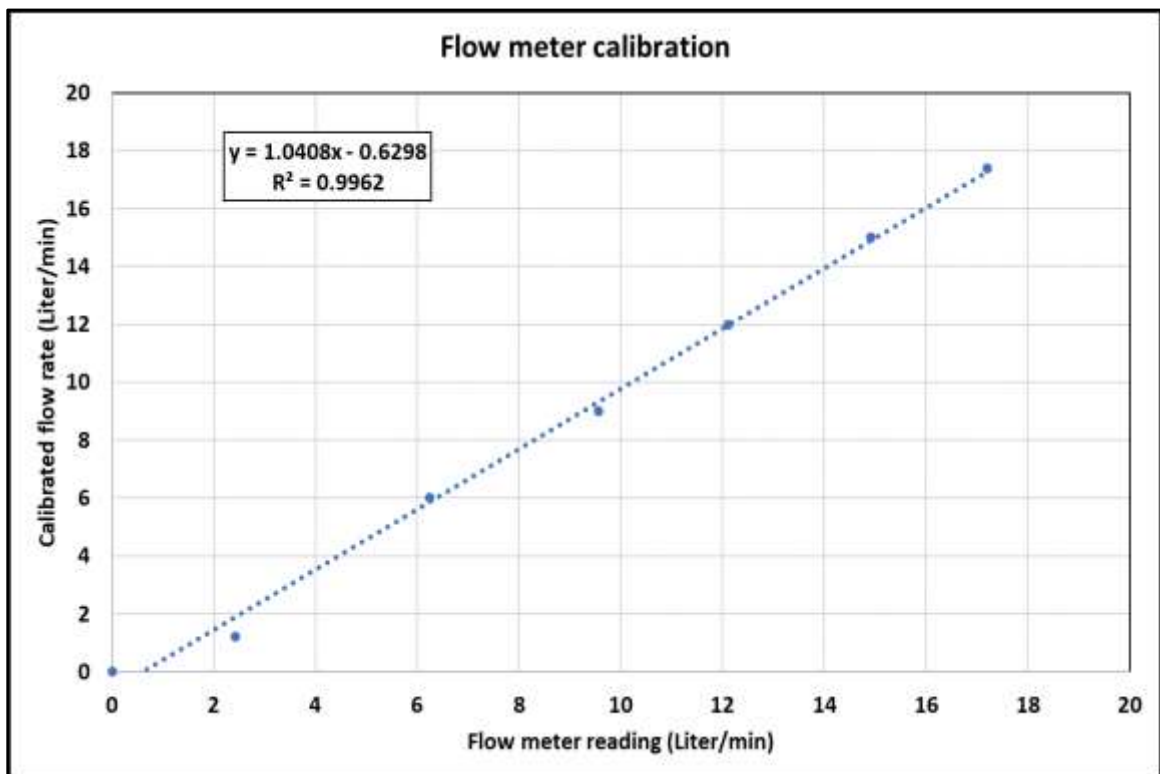


Figure 61 The drag reduction flow loop calibration with diesel



Figure 62 PEAS flow experiment

Two different HCl concentrations of PEAS were investigated in the flow experiments (15 and 20 %). The pressure drop of 15% HCl-PEAS was plotted against the flow rates at ambient temperature (25° C) as shown in Figure 63. Figure 63 shows that pressure drop increases with an increase in the flow rate. However, the increase in pressure drop with flow rate is non-linear hence PEAS can be classified as a non-Newtonian fluid. Figure 64 shows the shear stress as a function of the shear rate for the 15% HCl-PEAS at 25 °C. It is evidence that the pressure drop (shear stress) and flow rate (shear rate) show the shear thinning behavior of PEAS. The shear stress decreases with an increase in shear rate attributing to the shear thinning behavior.

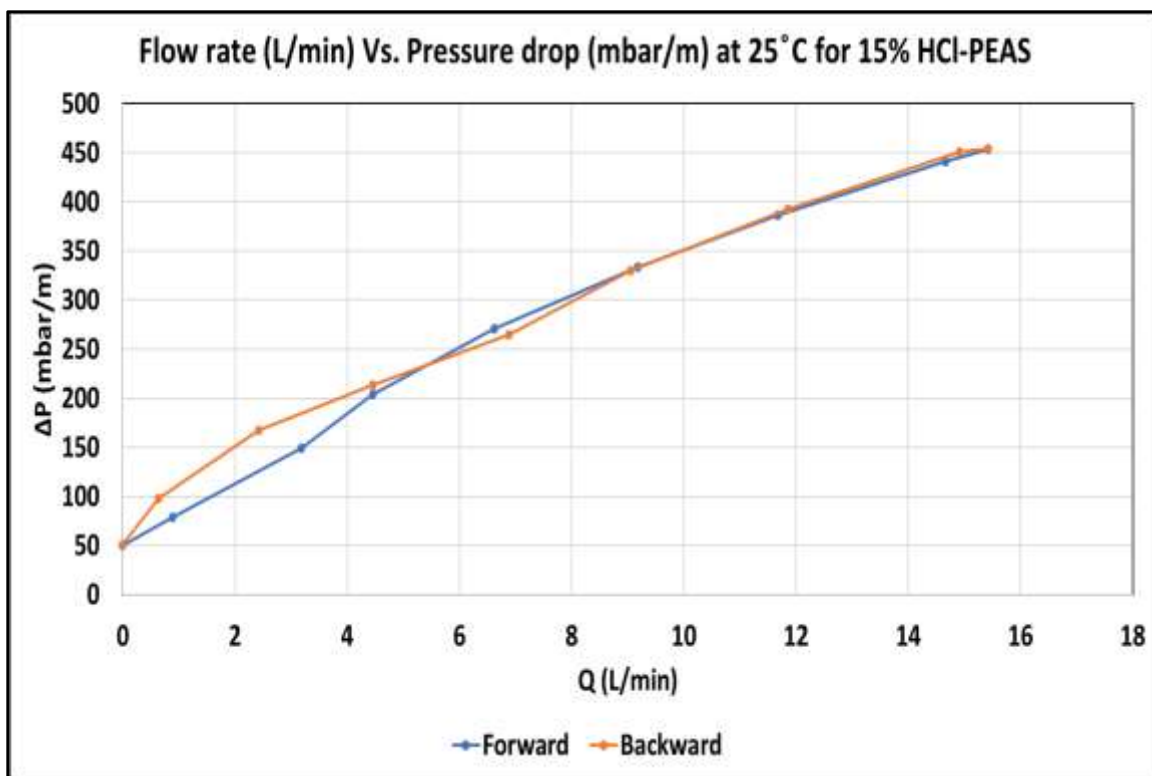


Figure 63 Flow experiment of 15 % HCl-PEAS at 25 °C

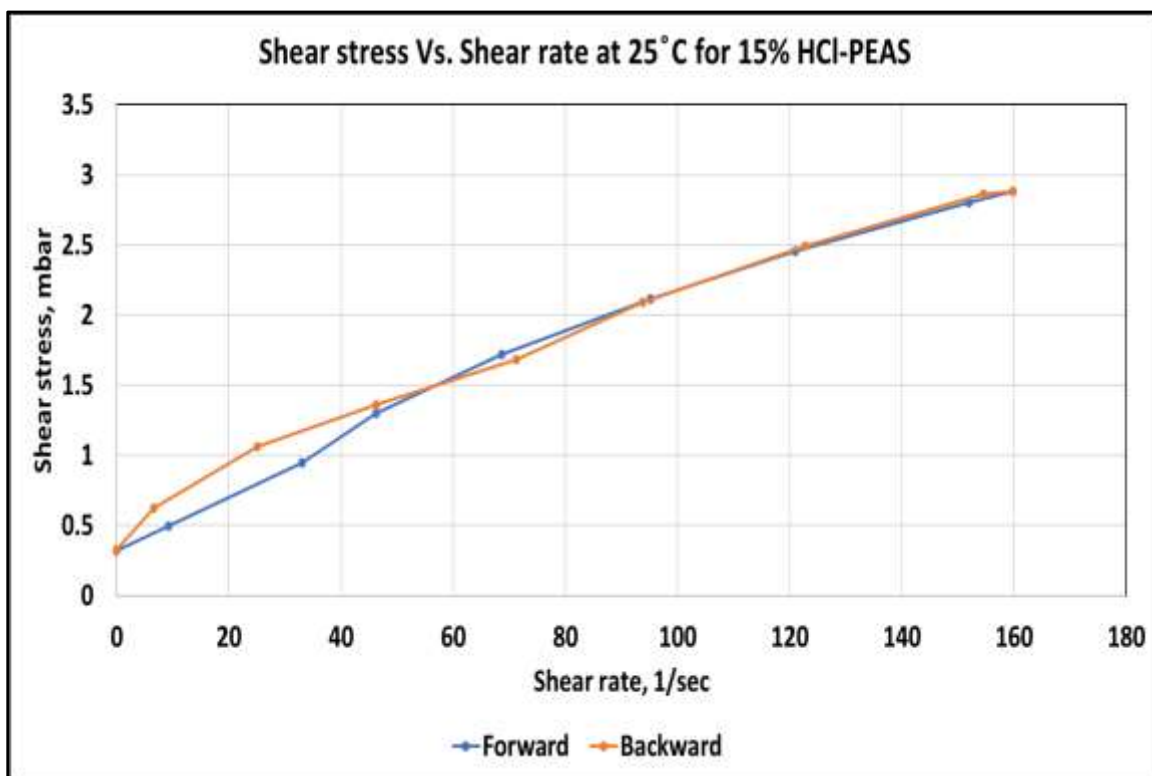


Figure 64 Shear stress vs. shear rate of 15 % HCl-PEAS at 25 °C

The effect of temperatures on the flow behavior of the PEAS is shown in Figure 65 (15% HCl-PEAS). Figure 65 shows that the increase in temperature causes a reduction in the pressure drop. The changes in the viscosity at high temperatures are minimal. For a constant rate of 10 L/min, the pressure gradient is 350 mbar/m at 25°C, 300 mbar/m at 40°C, and 295 mbar/m at 50°C. It indicates that the changes in the viscosity of PEAS are insignificant at high temperatures. These results are consistent with the results from rheology experiments, where a reduction in the viscosity of PEAS was observed with an increase in temperature. Figure 66 shows the shear stress as a function of the shear rate for the 15% HCl-PEAS at different temperatures (25, 40, and 50 °C).

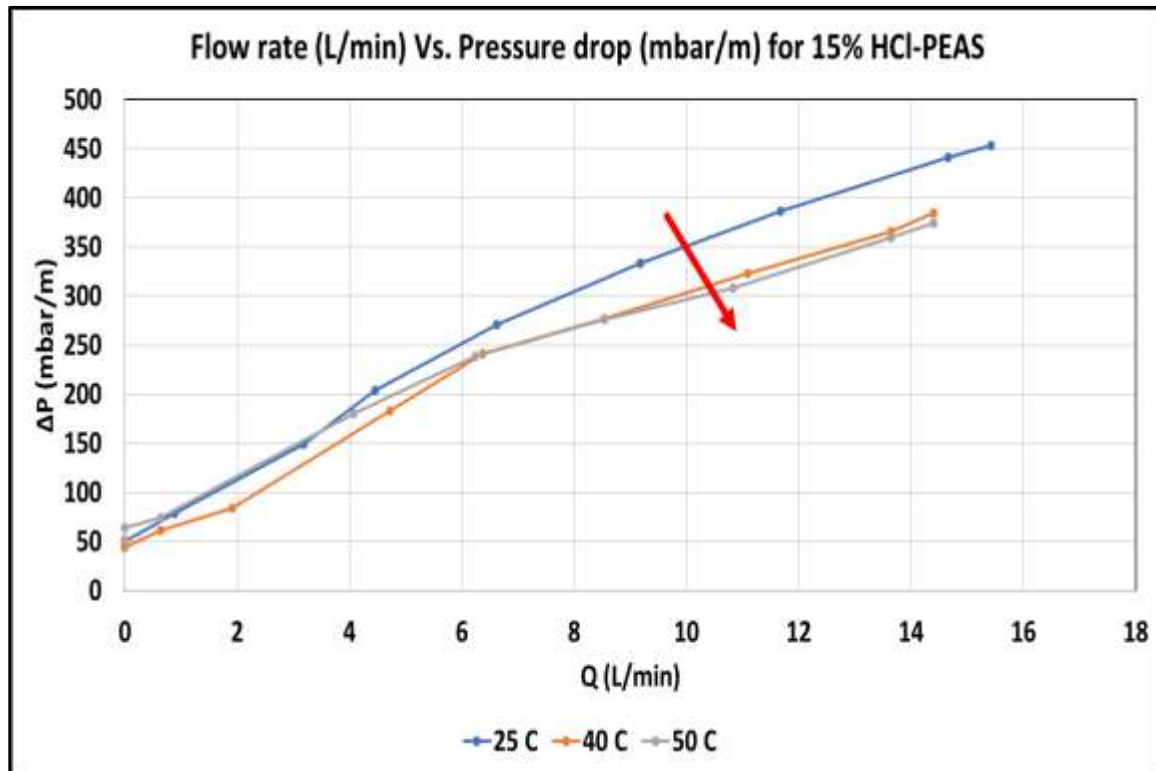


Figure 65 Effect of temperatures on the 15 % HCl-PEAS flow experiment

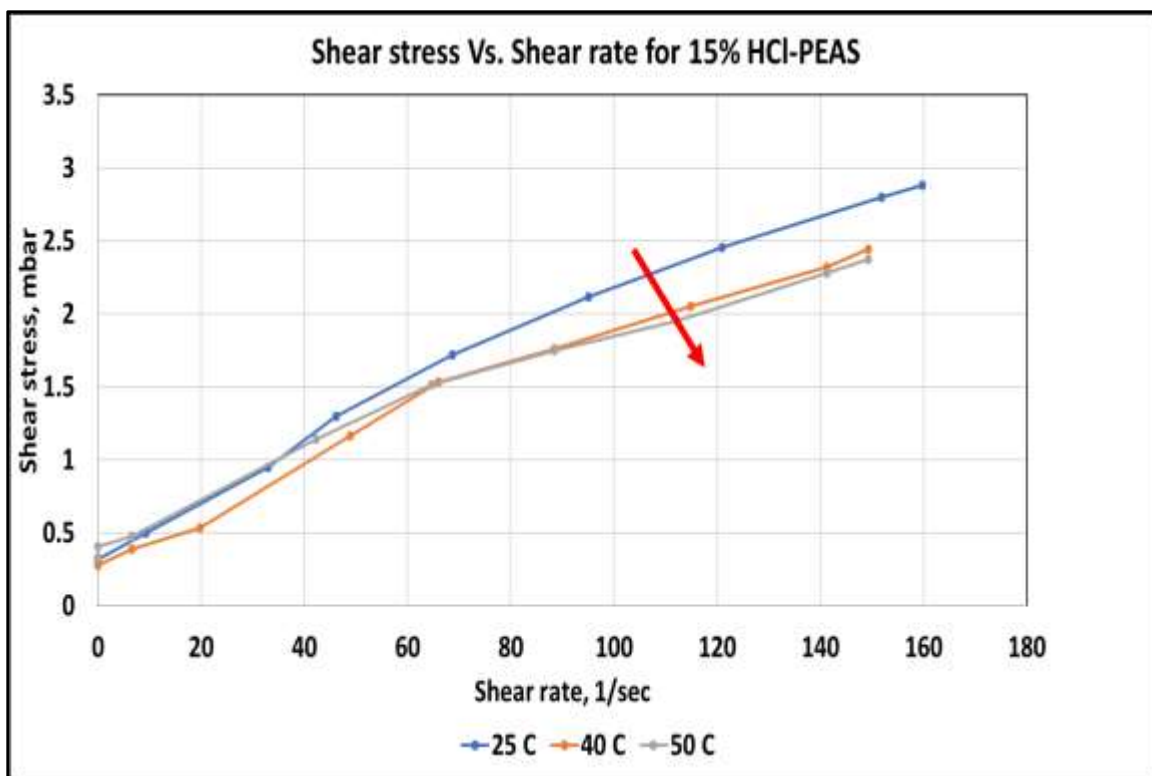


Figure 66 Shear stress vs. shear rate of 15 % HCl-PEAS at different temperatures

Similarly, Figure 67 shows the pressure drop increases with an increase in the flow rate for 15% HCl-PEAS at 50 °C, and it can be inferred from Figure 63 and Figure 67, that there is no effect of hysteresis for the flow experiment of 15% HCl-PEAS. The optimum OC concentration for 15% HCl-PEAS was 750 ppm. It should be noted that PEAS can be prepared with 500 ppm OC concentration, however it was broken during the flow experiment. The braking of the emulsion was not observed during the rheometer test as it was not subjected to dynamic flow conditions. This shows the importance of flow dynamics when the system is subjected to hydrodynamic conditions expected during the field operation. The EAS which appears to be stable during the rheology test might not work in the dynamic conditions and is required to be tested in dynamic conditions before implementing in the field operations.

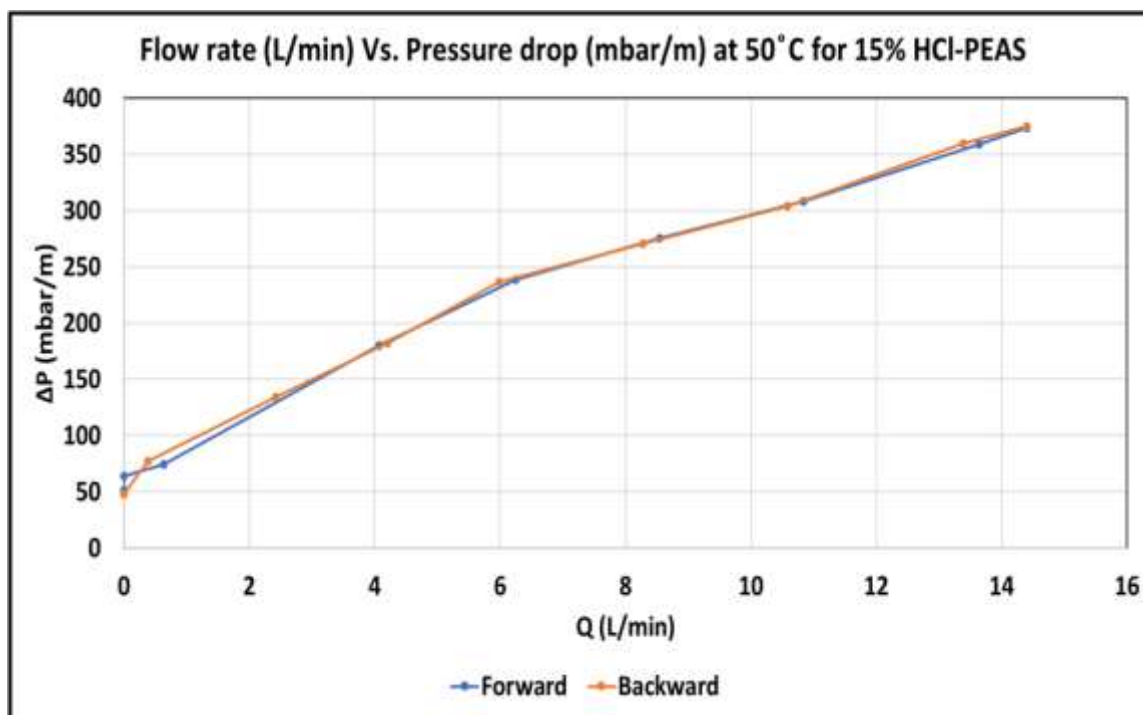


Figure 67 Flow experiment of 15 % HCl-PEAS at 50 °C

Figure 68 shows the comparison between two flow experiments of 15% HCl-PEAS prepared with two different OC concentrations (750 and 1000 ppm). The pressure drop at a high concentration of OC(1000 ppm) is higher compared to the PEAS with 750 ppm. Hence, it is important to optimize OC concentration. The lower concentration of OC (500 ppm) can give a stable emulsion when tested with a rheometer, however, the emulsion was broken when tested in the dynamic flow loop condition. On the other when the concentration of OC increased to 1000 ppm the emulsion was stable in the dynamic environment however the pressure drop was much more compared to 500 ppm OC concentration. This indicated the need to optimize the OC concentration which can retain the stable emulsion and provide low pressure drop required for faster pumping and placement of the acid deeper into the formation.

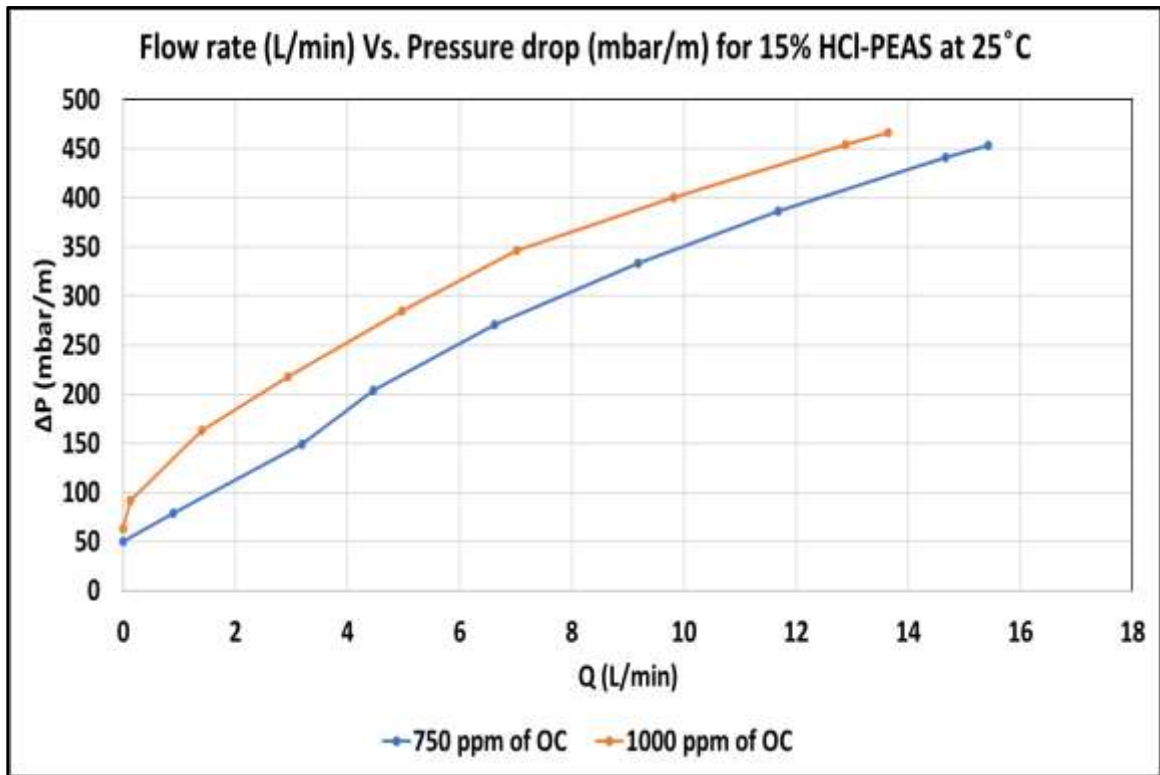


Figure 68 Flow experiment of 15 % HCl-PEAS at 25 °C for two different OC concentrations

Further to explore the effect of the HCl concentration on the drag reduction flow experiment was conducted for the 20% HCl-PEAS. The pressure drop of 20% HCl-PEAS was plotted against the flow rates at ambient temperature (25°C) as shown in Figure 69. Figure 69 shows that pressure drop increases with an increase in the flow rate. However, the increase in pressure drop with flow rate is non-linear hence PEAS 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 PEAS. The shear stress decreases with an increase in shear rate attributing to the shear thinning behavior. Figure 70 shows the shear stress as a function of the shear rate for the 20% HCl-PEAS at 25 °C. It can be inferred from Figure 69, that there is a small effect of hysteresis on the flow experiment.

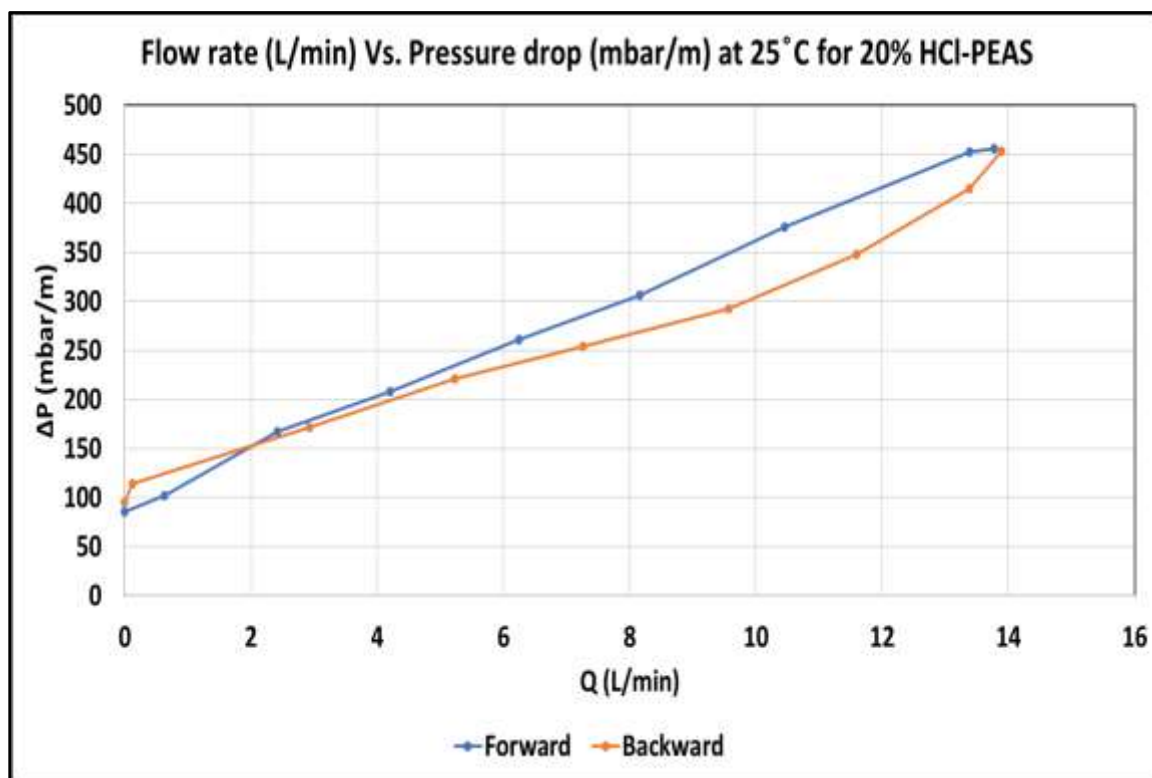


Figure 69 Flow experiment of 20 % HCl-PEAS at 25 °C

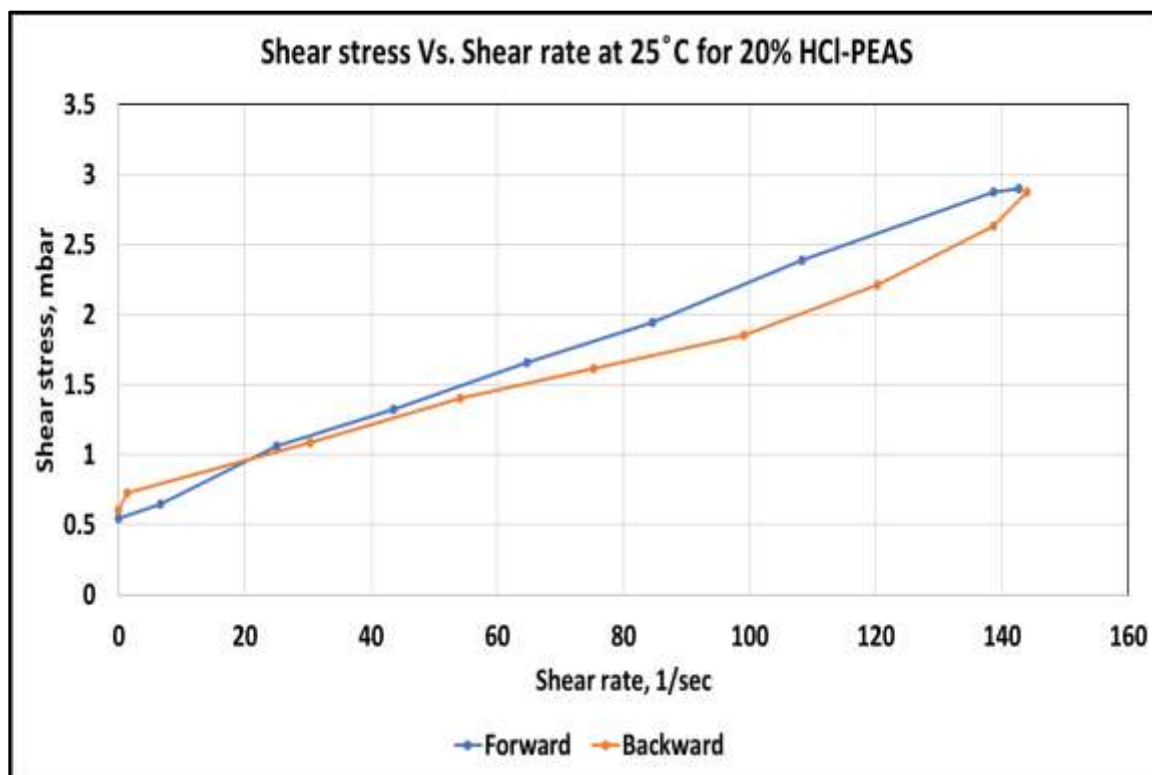


Figure 70 Shear stress vs. shear rate of 20 % HCl-PEAS at 25 °C

The effect of temperatures on the flow behavior of the PEAS (20 % HCl-PEAS) is shown in Figure 71. Figure 71 shows that the increase in temperature causes a reduction in the pressure drop. The changes in the viscosity at high temperatures are minimal. For a constant rate of 10 L/min, the pressure gradient is 370 mbar/m at 25°C, 260 mbar/m at 40°C, and 245 mbar/m at 50°C. It indicates that the changes in the viscosity of PEAS are insignificant at high temperatures. These results are consistent with the results from rheology experiments, where a reduction in the viscosity of PEAS was observed with an increase in temperature. Figure 72 shows the shear stress as a function of the shear rate for the 20 % HCl-PEAS at different temperatures (25, 40, and 50 °C).

The optimum OC concentration for 20 % HCl-PEAS was 1000 ppm. This emphasizes the importance of OC concentration which is required to be optimized based on the concentration of HCL and stability in the dynamic condition. The 750 ppm OC concentration is optimal, for the 15% HCl however, 1000 ppm of OC concentration is needed for the emulsion to be stable in dynamic conditions for 20% HCL. The PEAS formulated using 500, and 750 ppm of OC were broken during the flow experiment.

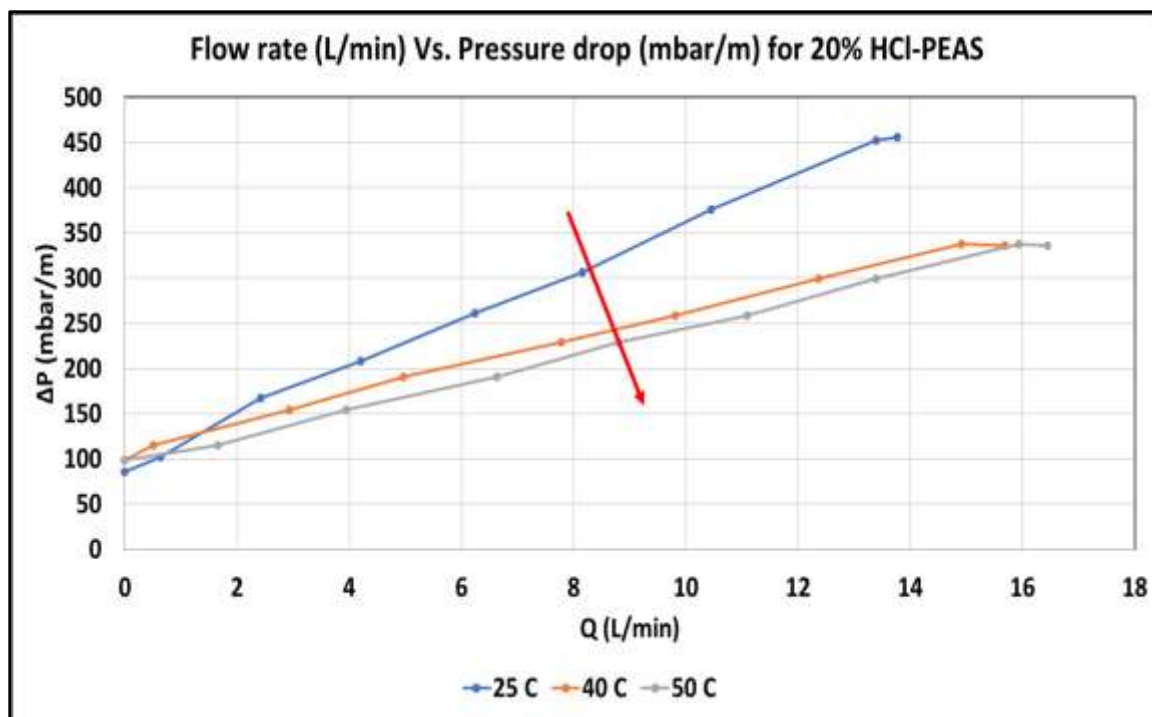


Figure 71 Effect of temperatures on the 20 % HCl-PEAS flow experiment

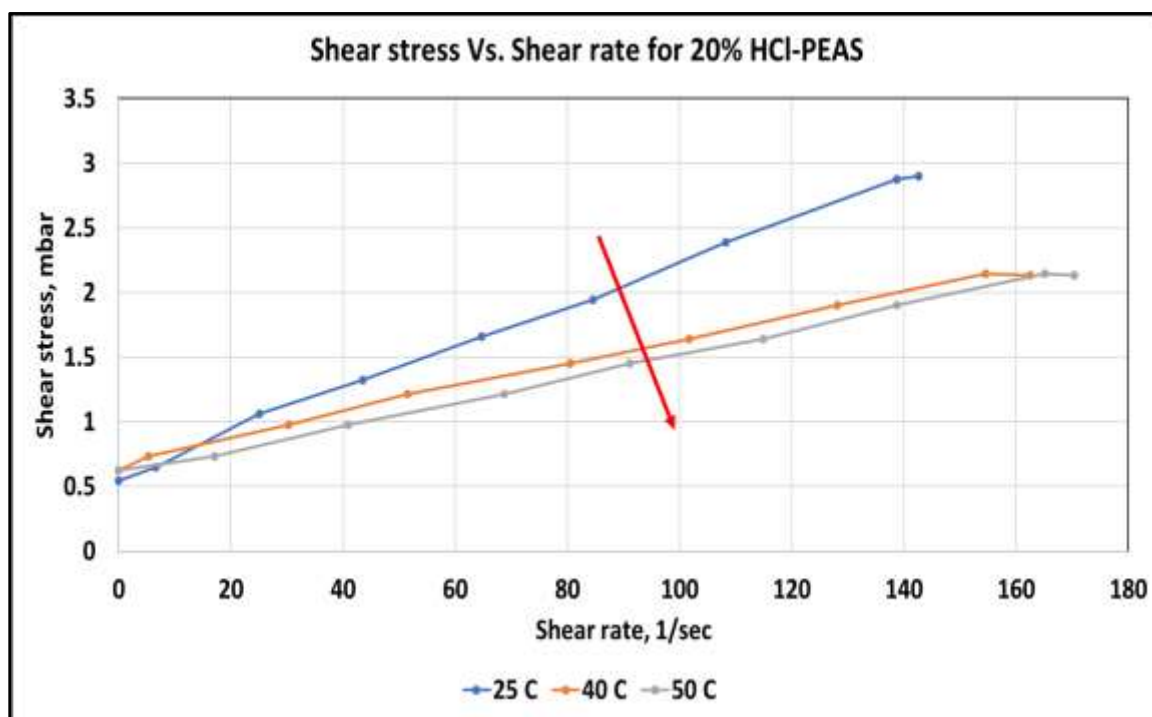


Figure 72 Shear stress vs. shear rate of 20 % HCl-PEAS at different temperatures

5.5.3 Conductivity/pH, and drop-test

To ensure retaining the properties of the PEAS after subjecting to dynamic conditions the sample of PEAS was tested before and after the flow loop experiment. The main tests conducted on the samples collected after the flow loop experiments are conductivity, pH, drop test, stability, and rheology. These tests confirm that the PEAS properties are not altered after being subjected to the hydrodynamic conditions. The conductivity/pH meter was used to measure the electrical conductivity and the acidity of the PEAS for the two samples (15 and 20 HCl%) taken from the flow loop after the flow experiments. Table 13 shows the values of the pH and electrical conductivity of the two samples, while Figure 73 shows the electrical conductivity and pH measurement using conductivity and pH meter. In addition, the drop-test was carried out to ensure that the PEAS is a W/O emulsion. The electrical conductivity results show values are zero, and that means the external phase is diesel and the PEAS samples are W/O emulsions. According to pH measurements, the PEAS is an extremely acidic solution. The drop-test results show that the PEAS samples are W/O emulsions since they are dispersed in diesel, not in the water. Figure 74 shows an example of the drop-test of PEAS in water and diesel.

Table 13 Electrical conductivity and pH of the PEAS

PEAS Sample	OC concentration	Electrical conductivity, $\mu\text{S/m}$	pH
15 % HCl-PEAS	750 ppm	0	1.64
20 % HCl-PEAS	1000 ppm	0	1.14

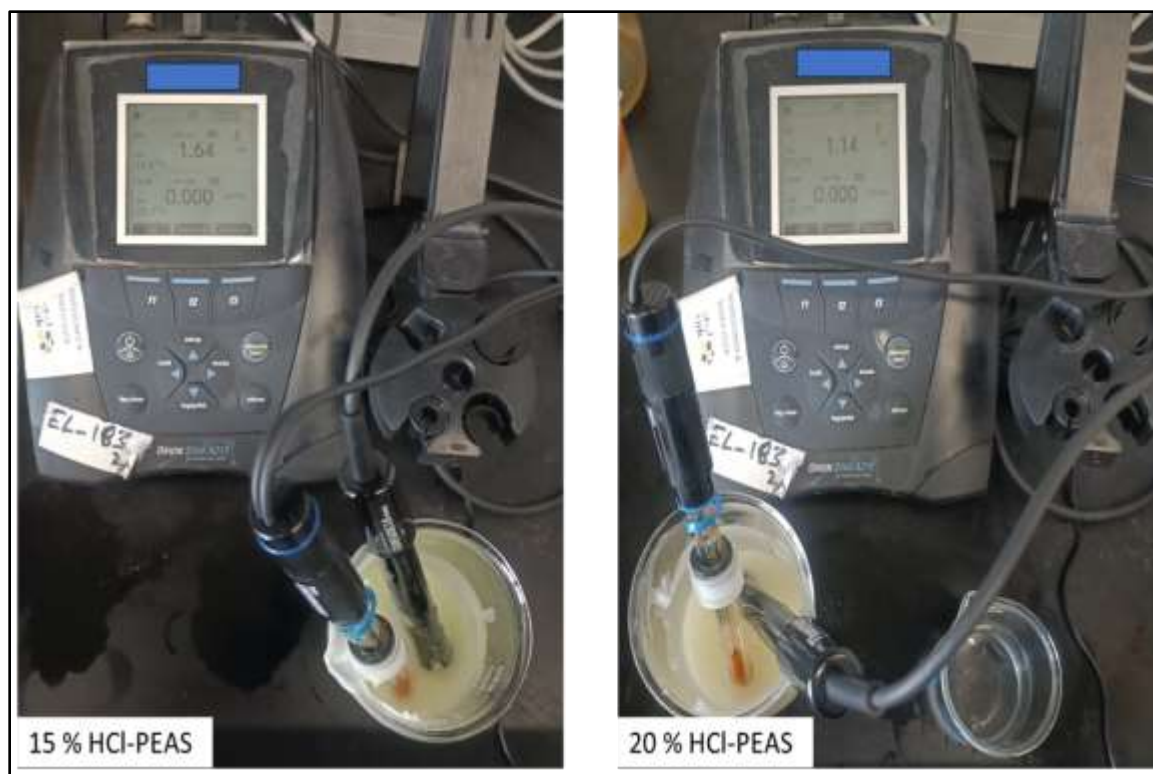


Figure 73 Electrical conductivity and pH for two PEAS samples

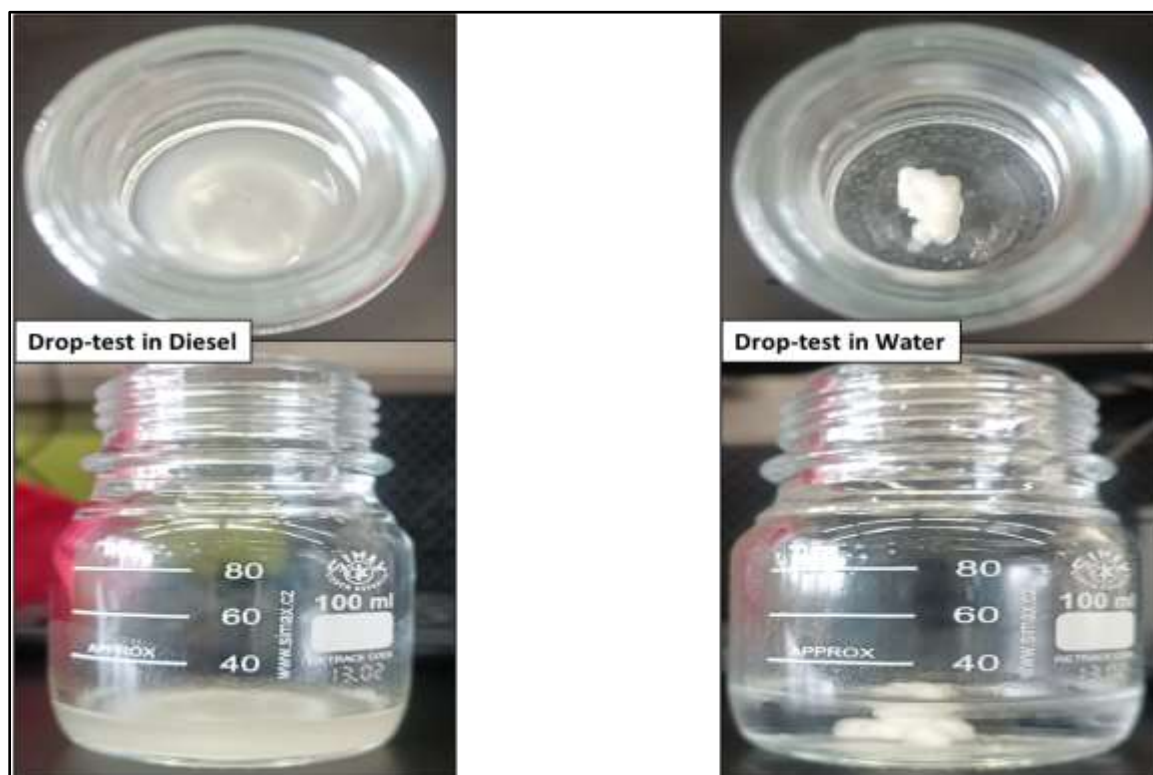


Figure 74 Drop-test of the PEAS

5.5.4 PEAS stability

PEAS stability was investigated at an ambient temperature (25 °C) for the samples taken from the flow loop after the flow experiments. By visually observing the PEAS separation every 10 minutes for the first 30 minutes, then every hour after the first 30 minutes for the next 2-3 hours, and finally after 24 hours. A photograph of the graduated glass bottle was taken before and after 24 hours as shown in Figure 75.



Figure 75 20 % HCl-PEAS stability for 24 hours at 25 °C

5.5.5 Rheology

Rheological properties were explored for the PEAS samples that were collected from the flow loop after the flow experiments. Firstly, the viscosity was measured at different shear rates which ranged from 0.1 to 10001/sec at two different temperatures (25 and 50°C) for both 15 and 20 % HCl-PEAS. Figure 76 shows the viscosity of 15 % HCl-PEAS as a

function of the shear rate for the OC concentration of 750 ppm, while Figure 77 shows the shear stress as a function of the shear rate for the same sample (15 % HCl-PEAS at 750 ppm of OC). It can be inferred from Figure 76 that increasing temperature led to a reduction of the viscosity of the 15 % HCl-PEAS. Similarly, Figure 78 shows the viscosity of 20 % HCl-PEAS as a function of the shear rate for the OC concentration of 1000 ppm, while Figure 79 shows the shear stress as a function of the shear rate for the same sample (20 % HCl-PEAS at 1000 ppm of OC). Increasing the temperature led to a reduction of the viscosity for the 20 % HCl-PEAS as shown in Figure 78. Viscosity comparison between two OC concentrations, 750 and 1000 ppm for the 15 % HCl-PEAS at 25 °C is shown in Figure 80, which shows a small difference in the viscosity plot at low shear rates (less than 10 1/sec).

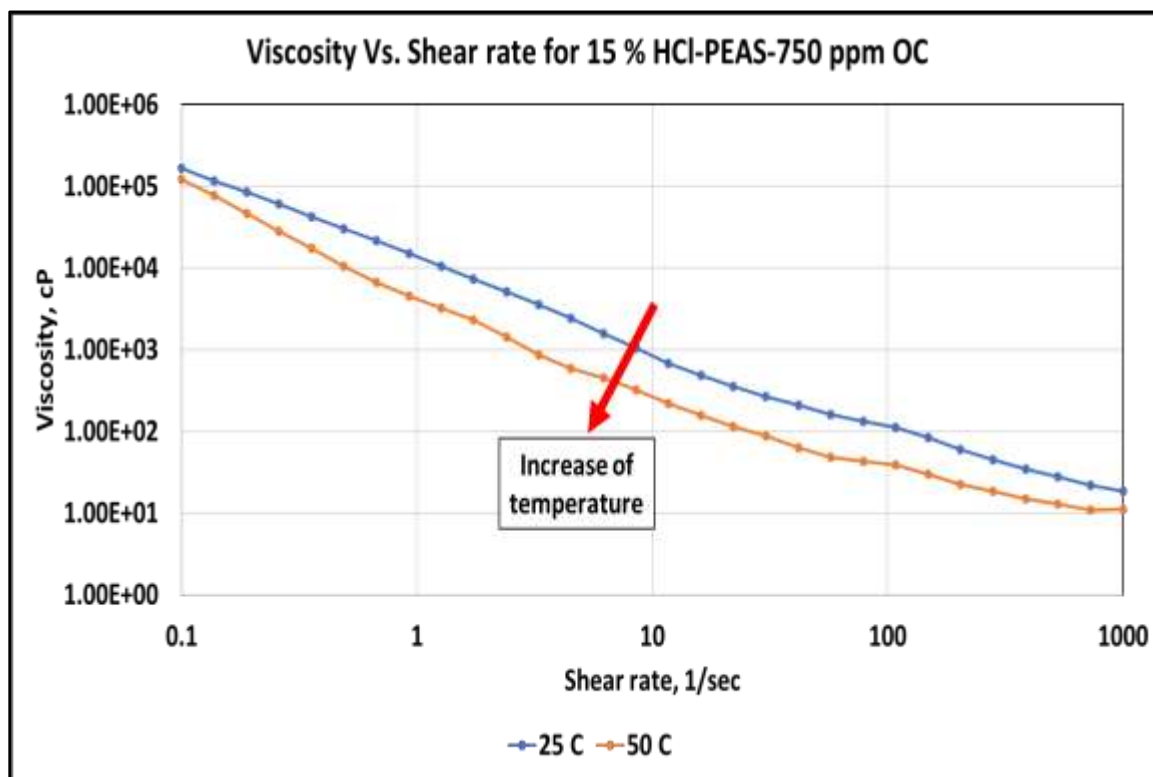


Figure 76 Viscosity vs. shear rate for 15 % HCl-PEAS-750 ppm OC

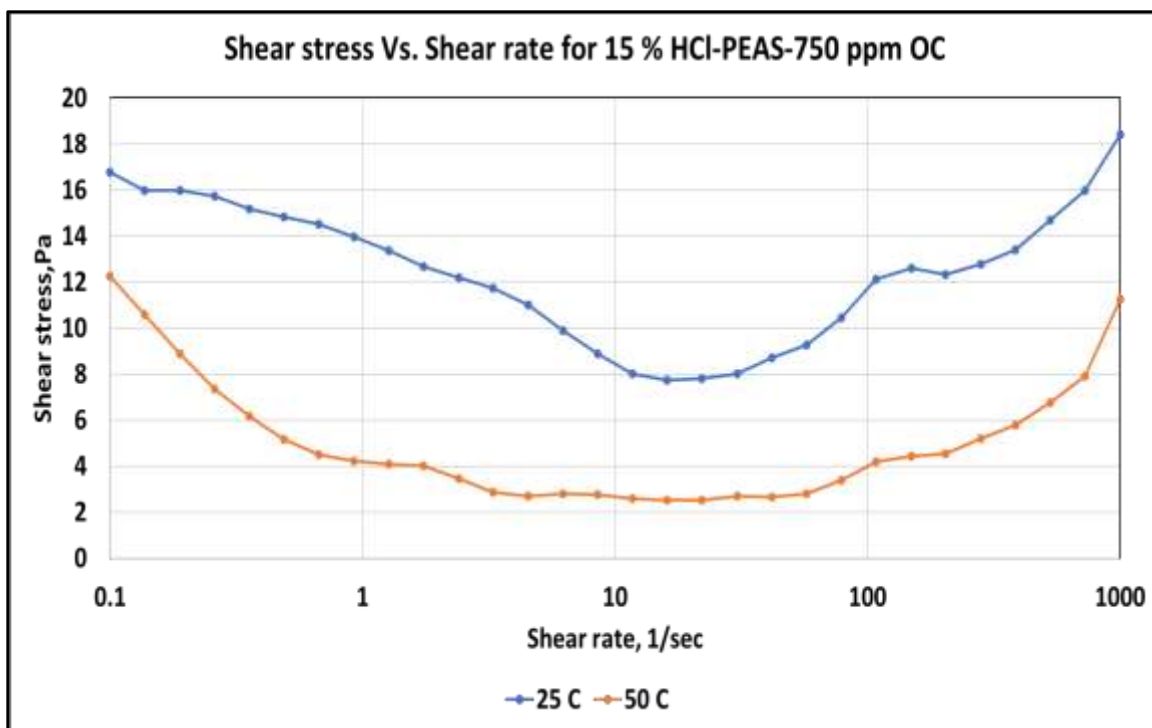


Figure 77 Shear stress vs. shear rate for 15 % HCl-PEAS-750 ppm OC

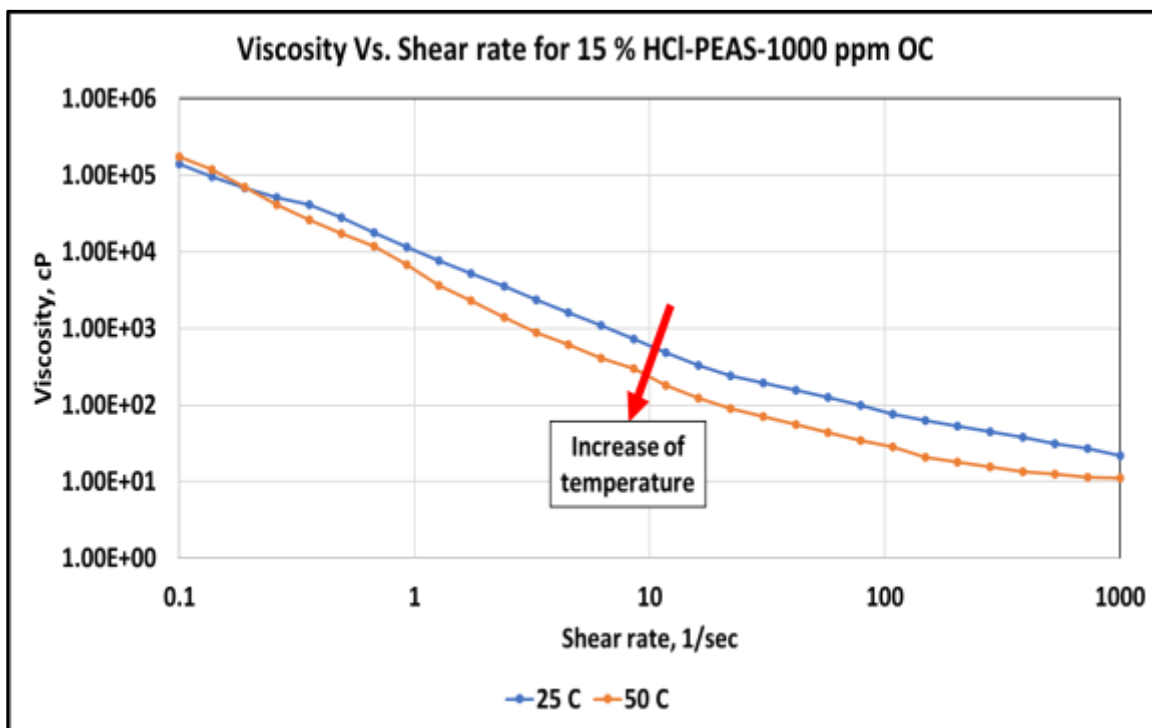


Figure 78 Viscosity vs. shear rate for 20 % HCl-PEAS-1000 ppm OC

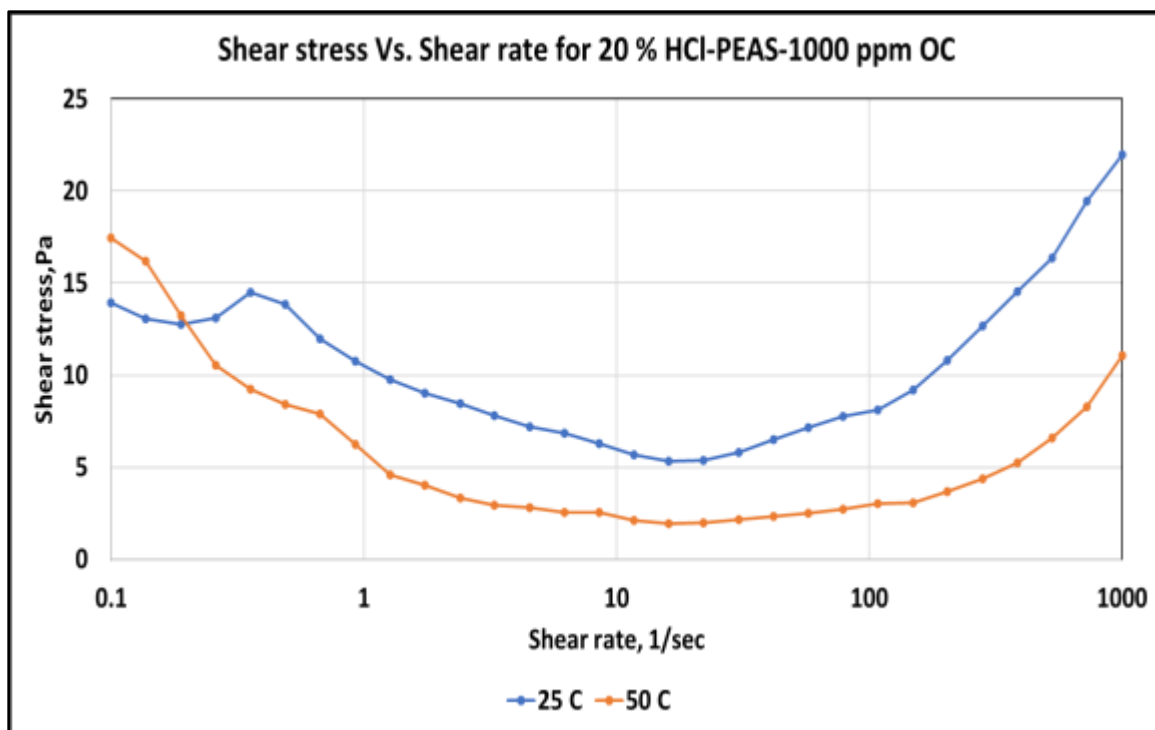


Figure 79 Shear stress vs. shear rate for 20 % HCl-PEAS-1000 ppm OC

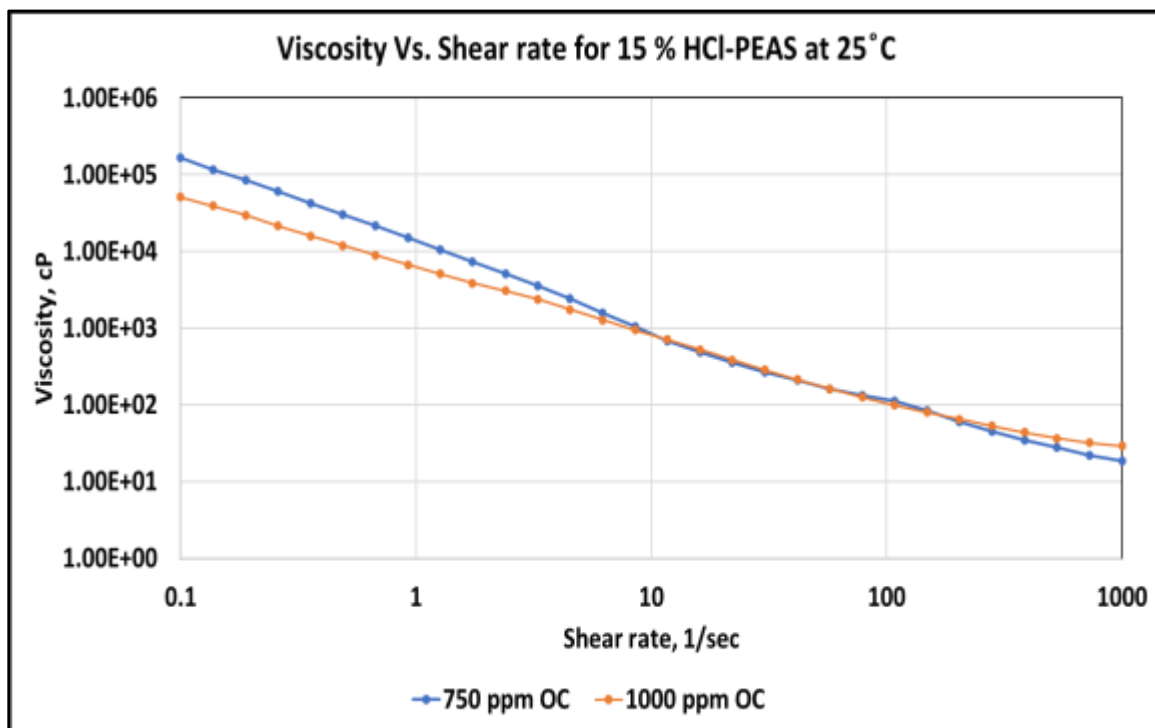


Figure 80 Viscosity vs. shear rate for 15 % HCl-PEAS at 25 °C

The rheology results for the 15 % HCl-PEAS were compared with the results of (AL-Dogail et al., 2023b) at the same temperature of 65 °C as shown in Figure 81. The only difference between the 15% HCl-PEAS samples in the Figure 81 is the OC concentrations, where the OC concentrations of (AL-Dogail et al., 2023b) are 500, and 1000 ppm, while the sample of this study is 750 ppm of OC.

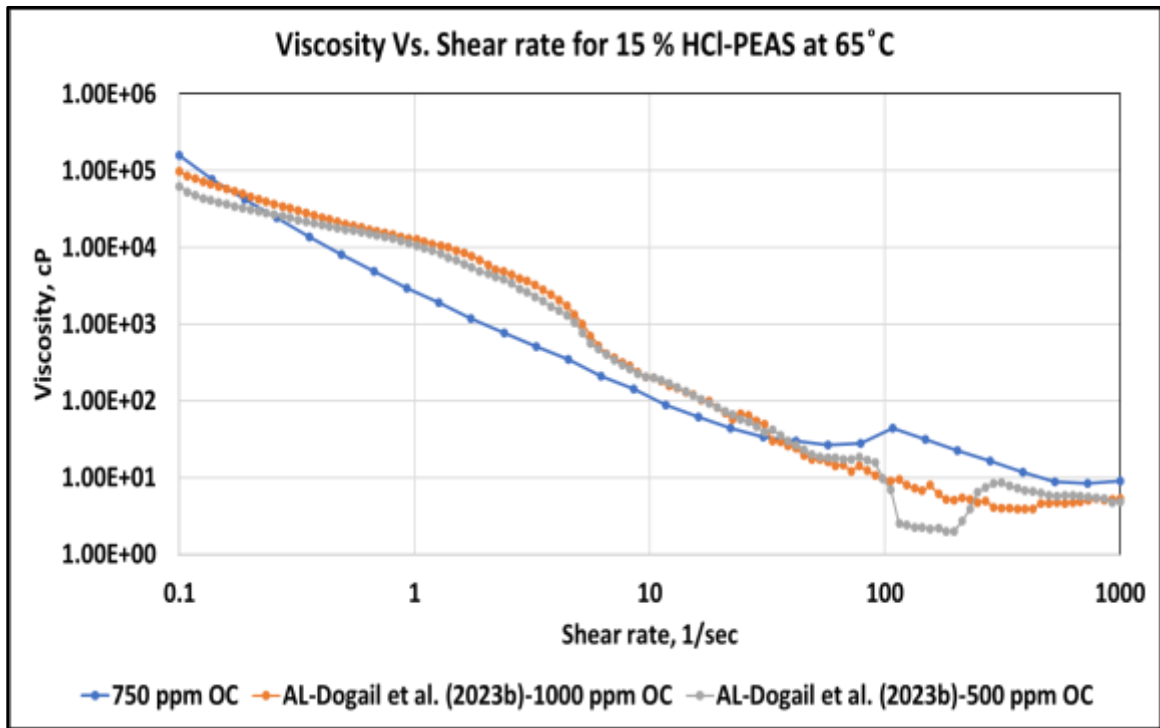


Figure 81 Viscosity comparison with (AL-Dogail et al., 2023b) at 65 °C

5.5.6 Discussion

This work explores the drag of the PEAS developed using OC. The PEAS systems developed using OC were pumped through the flow loop to investigate the drag at different conditions of flow rates, HCl concentrations, OC concentrations, and temperatures. In addition, the conductivity, pH, drop test, stability, and rheology were investigated for the samples collected from the flow loop after the flow experiments. The flow results of the PEAS are promising in terms of drag, where the results show that the PEAS have lower

drag compared to the surfactant-EAS at the temperatures investigated in this study (25-50 o C). Figure 82 and Figure 83 show the comparison between 15 % HCl-PEAS with the 15 % HCl-surfactant EAS at 25 and 50 o C, respectively. It can be inferred from Figure 82 and Figure 83 that PEAS is much better than surfactant-EAS in terms of lower drag.

Similarly, Figure 84 and Figure 85 show the comparison between 20 % HCl-PEAS with the 20 % HCl-surfactant EAS at 25 and 50 o C, respectively. It can be inferred from Figure 84 and Figure 85 that PEAS has lower drag compared to the surfactant-EAS at both investigated temperatures. The OC used in this study was able to disperse in organic compounds such as diesel used in this study. This OC can formulate the inverted emulsion and is known to be used in oil-based mud as a rheology modifier. The used OC also provides stability to the emulsion and is thermally stable. PEAS developed using OC as an emulsifier can be more compatible with reservoir conditions. OCs have unique properties making them applicable in different applications in the petroleum industry. These properties include enhanced thixotropy, compatibility, and environmental friendliness. OCs can show slippery or lubricious as well as reduced friction behavior due to their distinct structure and characteristics. OCs can significantly reduce the viscosity of fluids, and when they are incorporated into EAS, they help decrease the overall viscosity of the system. This property facilitates the pumping and injection of the EAS into the wellbores or reservoirs, making the process more efficient.

OCs can serve as Drag Reducing Agents (DRAs), minimizing frictional resistance as EAS flows through pipes. This drag reduction effect enhances the fluid's flowability, reduces energy consumption, and allows for smoother transportation of EAS within the wellbore. OCs possess emulsifying properties, enabling them to stabilize the emulsion formed when

acid combines with the external phase (typically oil) in EAS. This stable emulsion helps disperse the acid evenly, ensuring better contact with the reservoir rock and enhancing the effectiveness of acid treatments. OCs are often preferred over conventional chemical additives due to their environmentally friendly nature. They are non-toxic and biodegradable, reducing the environmental impact of acid treatments. OCs benefit from the slippage effect as they can reduce friction between particles or surfaces in a fluid. This slipperiness results from OCs' ability to create a lubricating layer between fluid components, reducing overall resistance and promoting smoother flow.

In summary, Organoclay additives (OCs) offer numerous advantages in EAS, such as viscosity reduction, drag reduction, emulsification, environmental compatibility, and a slipperiness effect. These properties make them valuable additives for enhancing the efficiency and effectiveness of acid treatments in various petroleum applications. The results of this study are very promising, and further research can be conducted to explore the utilization of OCs in different petroleum industry applications. Moreover, OCs are environmentally friendly.

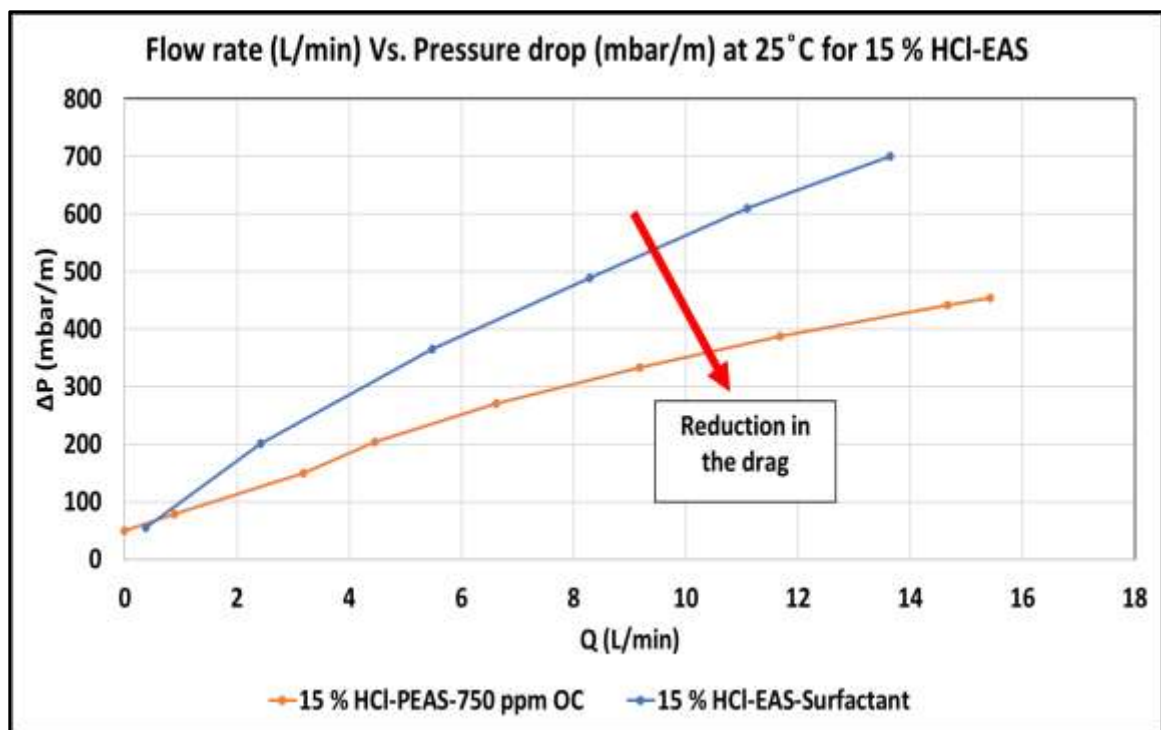


Figure 82 Comparison between 15% HCl-PEAS and 15 % HCl-surfactant EAS at 25 °C

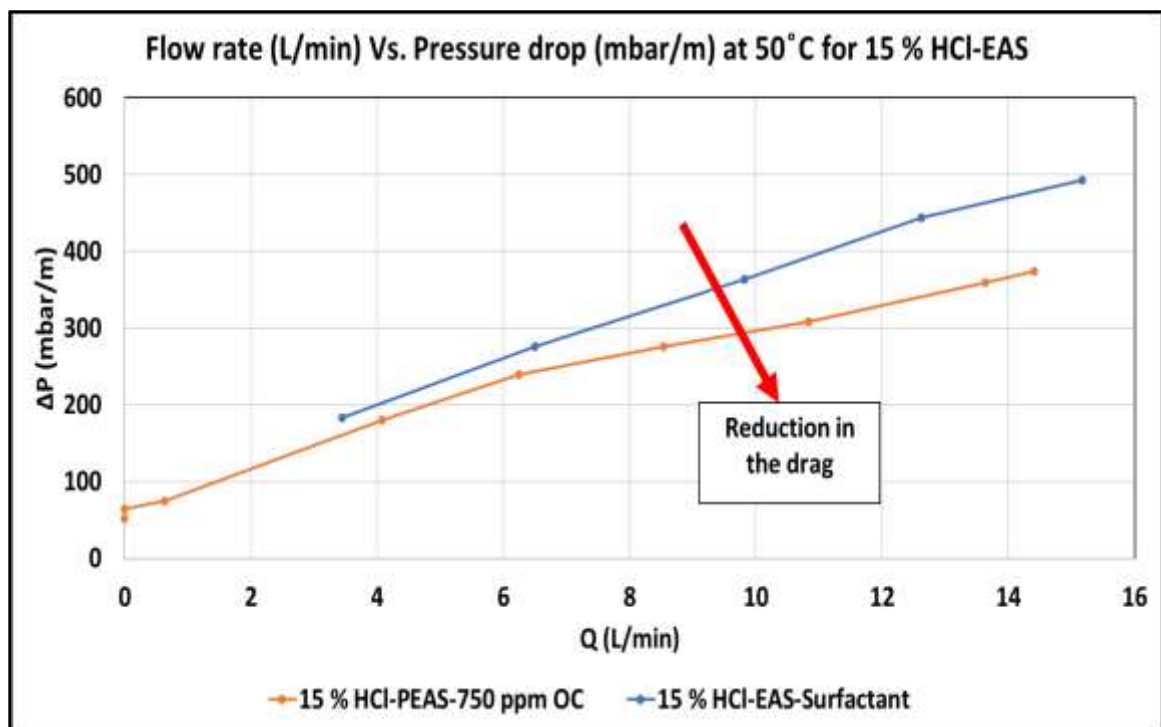


Figure 83 Comparison between 15% HCl-PEAS and 15 % HCl-surfactant EAS at 50 °C

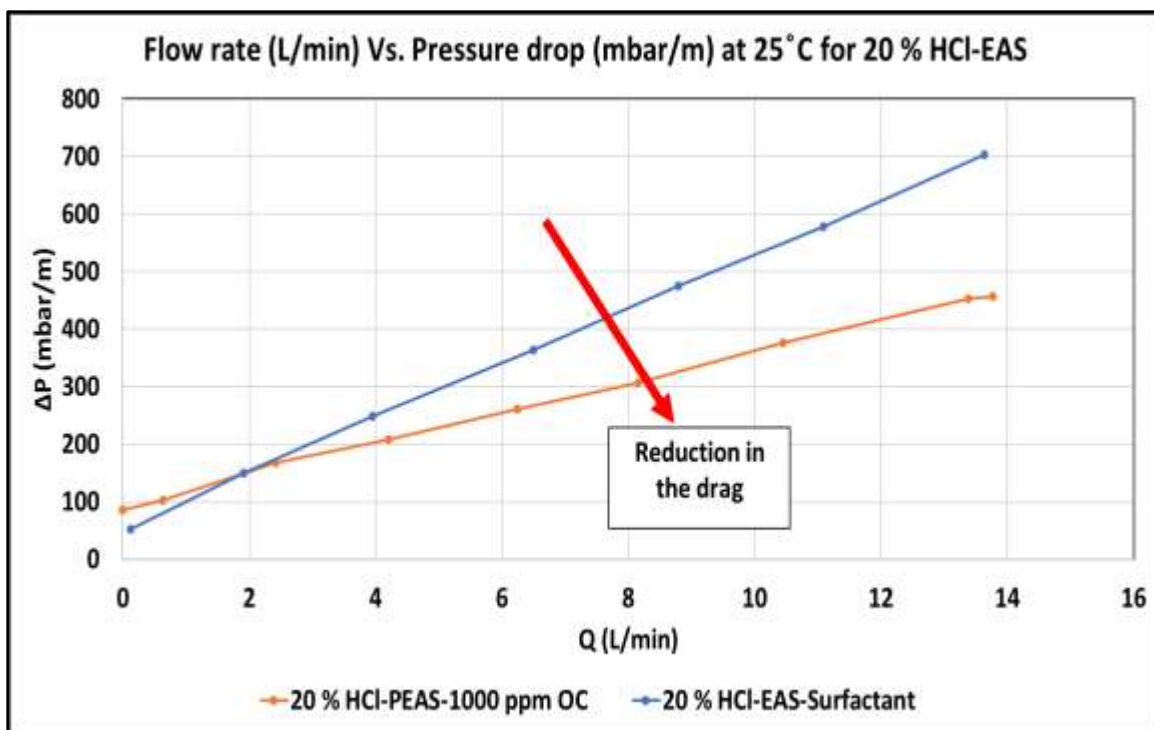


Figure 84 Comparison between 20 % HCl-PEAS and 20 % HCl-surfactant EAS at 25 °C

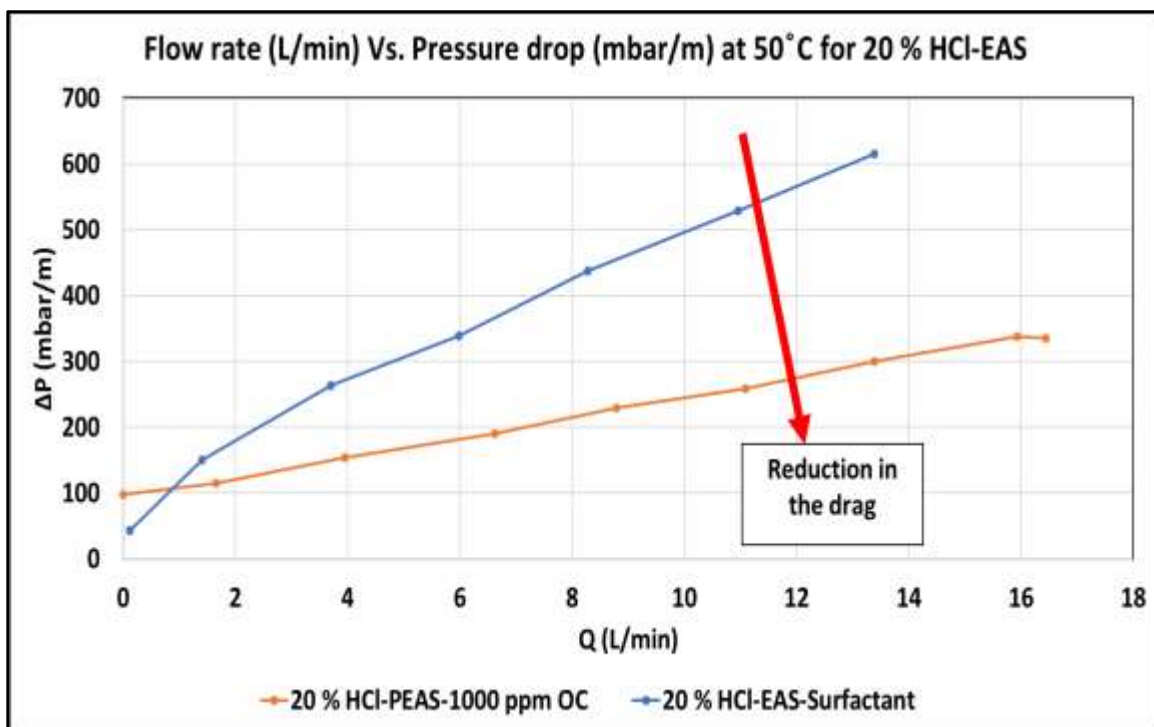


Figure 85 Comparison between 20 % HCl-PEAS and 20 % HCl-surfactant EAS at 50 °C

5.5.7 Conclusions

The following points can be concluded from this study:

1. The PEAS has lower drag compared to the surfactant-EAS at all temperatures investigated in this study (25, 40, 50 °C) for both HCl concentrations investigated in this study (15 and 20 %).
2. The drag reduction values are 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. Pressure drop reduction was observed with an increase in temperature for both 15 and 20 % HCl-PEAS.
4. The conductivity, pH stability, and rheology results for the PEAS samples taken from the flow loop after the flow experiments show its inverted emulsion (W/O) with strong acidity as well as the shear-thinning behavior. It also shows the PEAS does not alter the properties after being subjected to the dynamic flow conditions.
5. The optimization of OC concentration is important to ensure the PEAS is stable at hydrodynamic conditions.
6. A lower concentration of OC may provide a stable system tested with a rheometer however it may not be stable when subjected to the dynamic conditions experienced during field operation.
7. The high OC concentration can provide stable PEAS however the associated drag will be much higher compared to the optimized OC concentration.
8. Also, the concentration of OC play needs to be optimized based on the concentration of HCL acid in the system.

9. The results of the 20% HCl-PEAS are similar to the 15% HCl-PEAS, there is a minor alteration in the pressure drop or drag reduction due to an increase in the concentration of HCl.

5.5.8 Recommendation

It recommended conducting core flooding experiments, as well as microfluidic utilizing the PEAS with different HCl, and OC concentrations.

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Academic Background :Petroleum Engineering

EDUCATION	
2023	Ph. D. , Petroleum Engineering Department, College of Petroleum Engineering and Geosciences, KFUPM, Dhahran, KSA. Dissertation: “Drag Reduction of Emulsified Acid System in Pipes”, Graduation: December 2023.
2018	MSc. , Petroleum Engineering Department, College of Petroleum Engineering and Geosciences, KFUPM, Dhahran, KSA. Thesis: “Evaluating the Effects of Density, Viscosity, and Surface Tension on Two-Phase Flow in Horizontal Pipes”, Graduation: May 2018.
2012	B.Sc. , Petroleum Engineering Department, Hadhramout University, Mukalla, Yemen. First honor, Graduation: August 2012.
ACADEMIC EXPERIENCE	
09/2014–01/2024	Teaching Assistant , Petroleum Engineering Department, College of Petroleum Engineering and Geosciences, KFUPM, Dhahran, KSA (Part-Time), Courses: Well Completion, Production Engineering, Well Performance, Surface Production Facilities. Responsibilities include assisting grading and conducting research experiments.
12/2012–08/2014	Teaching Assistant , Petroleum Engineering Department, College of Engineering and Petroleum, Hadhramout University, Yemen (Full Time). Courses: Petroleum Introduction, Reservoir Rock properties, Reservoir Fluid Properties, Reservoir Engineering, Well logging, and Geophysics.
PROJECTS and GRANTS (Team Member)	

09/2023-Ongoing	Online mixer for stable emulsion generation, (CIPR2363), Funded by Saudi Aramco Saudi Arabia (529,624 SAR).
01/2021-10/2023	Development of an Emulsified Acid System for Production Enhancement in Carbonate Reservoirs, (DTV21101), Funded by Halliburton Saudi Arabia (282000 USD).
02/2021-01/2022	Gas-Oil Separation Plant-Operation Advisory System (GOSP-OAS), (CIPR 2342), Funded by YOKOGAWA Saudi Arabia (77,000SAR).
11/2018-10/2019	GOSP Operation Decision Support System (GOSP-ODSS), (CIPR 2328), Funded by YOKOGAWA Saudi Arabia (130,000SAR).
04/2018-04/2019	Evaluating the Effects of Density, Viscosity, and Surface Tension on Two-Phase Flow in Horizontal Pipes (SB 171012), Small Basic Research Grant (106,590 SAR) Sponsored by Deanship of Research, KFUPM.
CERTIFICATIONS	
2016	TECHLOG Formation Evaluation, King Fahd University of Petroleum and Minerals.
2015	CMG-IMEX modeling with BUILDER, King Fahd University of Petroleum and Minerals.
2014	Exploration Methods (Geophysics and Geology), Hadhramout University-Yemen.
2012	Summer Training Program, Assistant Production Engineer, PETRO MASILA company-Hadhramout-Yemen.
CURRENT MEMBERSHIP IN PROFESSIONAL ORGANIZATIONS	
	▪ Society of Petroleum Engineers (SPE) ▪ American Rock Mechanics (ARMA) ▪ Dhahran Geoscience Society (DGS) ▪ Society of Petrophysicists and Well Log Analysts (SPWLA) ▪ Society of Exploration Geophysicists (SEG)
HONORS AND AWARDS	
2012	▪ B.Sc. First honor, Petroleum Engineering Department, Hadhramout University-Yemen.
PUBLICATION	
Master Thesis:	
■ Al-Dogail, A. S. A. (2018). <i>Evaluating the Effects of Density, Viscosity and Surface Tension on Two-Phase Flow in Horizontal Pipes</i> (Doctoral dissertation, King Fahd University of Petroleum and Minerals (Saudi Arabia)).	

Patents:	
■ Gajbhiye, R., Ala, A. D., Badr, A. D., Al-Naser, M., & Mahmoud, M. (2023). <i>U.S. Patent No. 11,827,858</i>. Washington, DC: U.S. Patent and Trademark Office. ■ https://patents.google.com/patent/JP2022053374A/ja (JP2022053374A).	
Journals:	
■ AL-Dogail, A., Gajbhiye, R., Solling, T. I., Sultan, A. S., Patil, S., & Alsarkhi, A. (2023). Novel Environmentally Friendly Nanomaterials for Drag Reduction of the Emulsified Acid System. <i>ACS omega</i>. ■ Ala, A. D., Gajbhiye, R., Sultan, A., Solling, T., Patil, S., & Alsarkhi, A. (2023). Development of emulsified acid system (EAS) using organoclays (OC): Rheology and implication to the acidizing. <i>Geoenergy Science and Engineering</i>, 212022. ■ AL-Dogail, A., Gajbhiye, R., & Patil, S. (2023). A Review of Drag-Reducing Agents (DRAs) in Petroleum Industry. <i>Arabian Journal for Science and Engineering</i>, 48(7), 8287-8305. ■ AL-Dogail, A., Gajbhiye, R., Al-Shammari, H., Alnaser, M., & Kamerkar, T. (2023). Maximization of Gas-Oil Separation Plant Oil Recovery by Operation Parameter Optimization. <i>SPE Production & Operations</i>, 1-12. ■ AL-Dogail, A., Gajbhiye, R., AlNaser, M., AlNajim, A., & Mahmoud, M. (2022). Intelligent approach for gas-oil separation plant oil recovery enhancement. <i>SPE Production & Operations</i>, 37(04), 632-653. ■ AL-Dogail, A., Gajbhiye, R., AlNajim, A., & AlNaser, M. (2022). Dimensionless artificial intelligence-based model for multiphase flow pattern recognition in horizontal pipe. <i>SPE Production & Operations</i>, 37(02), 244-262. ■ AL-Dogail, A. S., & Gajbhiye, R. N. (2021). Effects of density, viscosity and surface tension on flow regimes and pressure drop of two-phase flow in horizontal pipes. <i>Journal of Petroleum Science and Engineering</i>, 205, 108719. ■ AL-Dogail, A. S., & Gajbhiye, R. N. (2021). Dataset of flow experiment: effects of density, viscosity and surface tension on flow regimes and pressure drop of two-phase flow in horizontal pipes. Data in Brief,107396.	
Conferences:	
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Patents Filed:	
■ Inv2023-190 A Novel Drag Reducing Agent For Emulsified Acid System ■ Inv2023-211 Pickering Emulsified Acid Systems (PEAS): A Novel Approach With Reduced Drag For Enhanced Matrix Acidizing	
Papers under Publications:	
■ Pickering Emulsified Acid Systems (PEAS): A Promising Approach for Reduced Drag in Matrix Acidizing (Geoenergy Science and Engineering). ■ Machine Learning Approach To Optimize Gas-Oil Separation Plant (GOSP) For Maximizing Oil Recovery.	
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