Improved CO_2 Flooding for Enhanced Heavy Oil Recovery

BY

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This thesis, written by **Mohammed Abdul-Raheem Mohammed Al-Hakami** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PETROLEUM ENGINEERING**

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Dedication

To my beloved family

This thesis is dedicated to you with the deepest gratitude and love. To **my parents**, whose unwavering support and sacrifices have shaped the man I am today. Your encouragement and belief in my abilities have been the guiding light through my journey. To **my wife** and my son (**Abdul-Raheem**) who have been a pillar of strength and a source of endless inspiration. To my siblings, (**Um Rayan, Ibrahim, Ahmed, Kholoud, and Khaled**) for your countless moments of relief at the most challenging times. To my dear cousins (**Ali Al-Qadri, Bilal Ahmed Al-Ghaithi and Haitham Al-Qadri**) for their endless support, help, and encouragement.

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This thesis stands as a milestone not only in my academic journey but also as a testament to the collective effort and support of all those mentioned above and many others who have contributed in various ways. Many Thanks.

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LIST OF ABBREVIATIONS

CO_2	:	Carbon dioxide
EOR	:	Enhanced oil recovery
MMP	:	Minimum miscibility pressure
IFT	:	Interfacial tension
N_2	:	Nitrogen
API	:	American petroleum industry
MPa	:	Mega Pascal
˚C	:	Celsius degree
˚F	:	Fahrenheit degree
wt.	:	Weight
VIT	:	Vanishing interfacial tension
H_2O	:	Water
ppm	:	Part per million
pH	:	Potential of hydrogen
LPG	:	Liquified petroleum gas
FCM	:	First - contact - miscible process
MCM	:	Multiple – contact – miscible process
PV	:	Pore volume
cP	:	Centipoise
WAG	:	Water – alternating – gas
CH_4	:	Methane
psi	:	Pound per square inch

ft	:	Foot
RBA	:	Rising bubble apparatus
STE	:	Slim tube experiment
PVI	:	Pore volume injected.
RF	:	Recovery Factor
mm	:	millimeter
˚K	:	Kelvin degree
FCMP	:	First – contact – miscibility pressure
σ	:	Interfacial tension
∆p	:	Pressure difference
R	:	Radii of curvature at the vertex
ρ	:	Density
g	:	Gravitational force
z	:	Distance in z direction
Ø	:	Contact angle
Θ	:	Contact angle
x	:	Distance in *x* direction
NIS	:	Non – ionic – surfactants
mN/m	:	millinewton per meter
BL	:	n-butanol
SARA	:	Saturate, aromatic, resin, and asphaltene
CII	:	Asphaltene stability index
CCS	:	Carbon capture and storage
API	:	American petroleum institute
Wt.%	:	Weight percentage
HPHT	:	High pressure high temperature

TLC	:	Thin layer chromatography
FID	:	Flame ionization detection
TAN	:	Total acid number
TBN	:	Total base number
ml	:	millimeter
KOH	:	Potassium hydroxide
mol	:	mole
L	:	Liter
mg	:	milligram
NIS	:	Non-ionic surfactants
XY	:	Xylene
DL	:	Di-limonene
Sx1	:	1-methyl-3-octylimidazolium chloride
Sx4	:	1-decyl-3-methylimidazolium chloride

ABSTRACT

Full Name : [Mohammed Abdul-Raheem Mohammed Al-Hakami]

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In the petroleum industry, innovation and sustainability are crucial, particularly when it comes to enhancing and maximizing the reserves. Usually, heavy oil reservoirs are shallow and therefore are good candidates for thermal-enhanced oil recovery (EOR) methods. However, thermal-EOR methods are not sufficient when it comes to deep heavy oil reservoirs, such as the extensive Burgan field of north Kuwait which is located at approximate depth of 10,000 ft [1]. This conclusion is made due to that is considerable heat is lost during the process of steam injection into deep reservoirs and early steam breakthrough as a subsequent of steam channeling at producing wells might potentially limit oil recovery. For in-situ combustion there are a variety of adverse aspects, including very poor process control that results in poor sweep efficiency and completions that are negatively impacted by the ignition. Also, because the procedure is more sophisticated than other thermal technologies, a larger team of qualified and experienced individuals is needed.

Therefore, there is an urgent need for an alternative and functional EOR method that is sufficient to develop recovery of deep heavy oil reservoirs. CO_2 flooding is the key solution for the development of this category of reservoirs. CO_2 injection is mainly classified into miscible CO_2, and immiscible CO_2 injection depending on whether minimum miscibility

pressure (MMP) is achieved or not. Miscible CO_2 flooding generally leads to higher recovery factors than immiscible CO_2 flooding. Improvement of CO_2 injection can be obtained mainly by the reduction of MMP value in the CO_2-oil system. Our focus is the implementation of various chemicals that are able to reduce the MMP in CO_2-crude oil systems and also, reduce oil viscosity. Moreover, provide a solution for the previously mentioned problems faced in the petroleum industry.

The improvement of CO_2 flooding can be implemented by reducing the value of MMP in the CO_2-crude oil system. This reduction have obtained in the literature by introducing chemicals to the system. In this study we are performing a screening on different substances to adhere their ability to improve CO_2 miscibility in crude oil, also study the effect of some of these chemicals on crude oil viscosity.

Screening is performed on different substances such as micro emulsions, non-ionic surfactants, hydrophilic silica nanoparticles, n-butanol, xylene, di-limonene, 1-methyl-3-octylimidazolium chloride, and 1-decyl-3-methylimidazolium chloride on CO_2-crude oil system. This procedure is performed to select an optimum chemical and concentration that is able to improve the miscibility of CO_2 in five different Saudi crudes. The MMP between Saudi crude oils and CO_2 before and after chemicals addition was determined by the vanishing interfacial tension technique (VIT). The results shows ionic liquids are the optimum chemicals to be used to reduce the values of MMP and FCMP in CO_2-crude 3 system. This chemical behavior on MMP was studied for the other four crudes. The results shows a reduction of 15.5% in MMP in CO_2-extra heavy crude oil, this conclusion plays a key solution to develop deep heavy oil reservoirs.

ملخص الرسالة

الاسم الكامل: محمد عبدالرحيم محمد الحكمي

عنوان الرسالة: تطوير حقن ثاني أكسيد الكربون لتعزيز إنتاجية النفط الثقيل

التخصص: هندسة البترول

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في صناعة البترول ، يعد الابتكار والاستدامة أمرا بالغ الأهمية ، لا سيما عندما يتعلق الأمر بتعزيز الإحتياطيات النفطية. عادة ما تكون مكامن النفط الثقيل ضحلة في العمق وبالتالي فهي مرشحة جيدة لطرق استخلاص النفط المعزز حرارياً. ومع ذلك، فإن طرق الاستخلاص المعزز للنفط الحراري ليست كافية عندما يتعلق الأمر بمكامن النفط الثقيل العميقة، مثل حقل برقان الواسع في شمال الكويت والذي يقع على عمق تقريبي يبلغ 10,000 قدم [1]. تم التوصل إلى هذا الاستنتاج بسبب الفقدان الحراري الكبير أثناء عملية حقن البخار في المكامن العميقة واختراق البخار المبكر في الآبار المنتجة مما قد يحد من استرداد النفط. بالنسبة للإحتراق الداخلي في الموقع ، هناك مجموعة متنوعة من الجوانب الضارة ، بما في ذلك التحكم السيئ للغاية في العملية الذي يؤدي إلى ضعف كفاءة المسح والإكمال الذي يتأثر سلباً بالإشتعال. أيضاً ، نظرا لأن الإجراء أكثر تعقيداً من التقنيات الحرارية الأخرى ، فهناك حاجة إلى فريق أكبر من الأفراد المؤهلين وذوي الخبرات.

ولذلك، هناك حاجة مُلحة إلى طريقة بديلة وعملية للإستخلاص المعزز للنفط تكفي لتطوير إنتاجية مكامن النفط الثقيل العميقة. حقن ثاني أكسيد الكربون هو الحل الرئيسي لتطوير هذه الفئة من المكامن. يصنف حقن ثاني أكسيد الكربون بشكل أساسي إلى قابل للإمتزاج ، وحقن غير قابل للإمتزاج إعتماداً على ما إذا كان الحد الأدنى من ضغط الإمتزاج قد تحقق أم لا. يؤدي حقن ثاني أكسيد الكربون القابل للإمتزاج بشكل عام إلى عوامل إنتاجية أعلى من حقن ثاني أكسيد الكربون الغير القابل للإمتزاج. بالإمكان تحسين حقن ثاني أكسيد الكربون بشكل رئيسي عن طريق تقليل قيمة الحد الأدنى من ضغط الإمتزاج في نظام ثاني أكسيد الكربون- نفط خام. ينصب تركيزنا على إقحام العديد من المواد

الكيميائية القادرة على تقليل الحد الأدنى من ضغط الإمتزاج في أنظمة نظام ثاني أكسيد الكربون- نفط خام تقليل لزوجة النفط. علاوة على ذلك ، توفير حل للمشاكل المذكورة سابقا التي تواجهها صناعة البترول.

يمكن تحسين حقن ثاني أكسيد الكربون عن طريق تقليل قيمة الحد الأدنى من ضغط الإمتزاج في نظام ثاني أكسيد الكربون- نفط خام. وقد تم الحصول على هذا التقليل في دراسات سابقة عن طريق إدخال مواد كيميائية إلى النظام. في هذه الدراسة نقوم بإجراء فحص على مواد مختلفة لإختبار قدرتها على تحسين امتزاج ثاني أكسيد الكربون مع النفط الخام ، كما ندرس تأثير بعض من هذه المواد الكيميائية على لزوجة النفط الخام.

تم إجراء الفحص على مواد مختلفة مثل المستحلبات الدقيقة ، والمواد الخافضة للتوتر السطحي غير الأيونية ، وجسيمات السيليكا النانوية المحبة للماء ، و البوتانول ، و xylene ، و di-limonene ، و 1--3-methyl octylidazolium chloride ، و 1-decyl-3-methylimidazolium chloride على نظام ثاني أكسيد الكربون- نفط خام. تم تحديد الحد الأدنى من ضغط الإمتزاج بين النفط الخام السعودي و ثاني أكسيد الكربون قبل وبعد إضافة المواد الكيميائية بواسطة تقنية التوتر السطحي المتلاشي. تم تنفيذ هذا الإجراء لإختيار المادة الكيميائية المثالية والتركيز القادر على تحسين قابلية إمتزاج ثاني أكسيد الكربون في خمسة من خامات النفط السعودية المختلفة. تم استخدام الخيار الأمثل في تجربة حقن ثاني أكسيد الكربون لتأكيد نجاعة نهجنا.

أظهرت النتائج أن السوائل الأيونية هي المواد الكيميائية المثلى التي يجب استخدامها لتقليل قيم الحد الأدنى من ضغط الإمتزاج و ضغط الإمتزاج من الوهلة الأولى في نظام نظام ثاني أكسيد الكربون- نفط خام 3. تمت دراسة هذا السلوك الكيميائي على الحد الأدنى من ضغط الإمتزاج للخامات الأربعة الأخرى. تظهر النتائج انخفاضا بنسبة 15.5٪ في الحد الأدنى من ضغط الإمتزاج في نظام نظام ثاني أكسيد الكربون- النفط الخام الثقيل الإضافي ، وهذا الإ ستنتاج يلعب كحل رئيسي لتطوير خزانات النفط الثقيل العميقة التي هي محور هذه الدراسة.

CHAPTER 1

INTRODUCTION

Global energy demand along with energy consumption are increasing aggressively worldwide due to the population and economic growth [2]. Therefore, it is crucial to always look forward to unleashing and expanding the hydrocarbon reserves. The oil recovery processes are categorized mainly into primary recovery, secondary recovery, and tertiary recovery (EOR). Contribution of primary and secondary recovery in oil in-place recovery approximately ranges from 40-50% [3]. The leftover oil is considerably high. For that EOR methods have been introduced to enlarge the recovery from a certain reservoir and reduce the residual oil saturation. Based on the type of the utilized methods EOR methods can be classified into (a) thermal methods which include steam stimulation, steam flooding, and in situ combustion. (b) gas injection methods (miscible/ immiscible) depending on the value MMP between the injected gas (CO_2, N_2, or Flue gases) and crude oil. (c) chemical methods injection of (polymer, alkaline, surfactants). (d) biotechnological methods and others. When compared to immiscible flooding, for improving sweep efficiency and reducing CO_2-oil interfacial tension, miscible CO_2 injection appears to be a substantial enhanced oil recovery strategy. which can lead to up to ten percent higher oil recovery [4].

Enhanced heavy oil recovery is mostly achieved by implementation of steam injection or in-situ combustion [5], [6]. However considerable heat is lost during the process of steam injection into deep reservoirs and early steam breakthrough as a subsequent of steam

channeling at producing wells might potentially limit oil recovery. It is not expected to be economically feasible [7]. For in-situ combustion there are a variety of adverse aspects, including very poor process control that results in poor sweep efficiency and completions that are negatively impacted by the ignition. Also, because the procedure is more sophisticated than other thermal technologies, a larger team of qualified and experienced individuals is needed [8]. Due to the previous cons an urgent need for an alternative feasible method has occurred. In this research we are aiming to improve the efficiency of CO_2 flooding in recovering heavy crude oils.

One of the most common procedures in the oil business, known as enhanced oil recovery (EOR) with enormous potential, is gas injection [9]. A successful gas injection application can be influenced by variables like the type of injected gas, the injected gas's minimum miscibility pressure (MMP), reservoir characterization, and fluid properties. CO_2 flooding is introduced to reservoir in two forms miscible injection and immiscible injection [10]. Depending on value of the CO_2 injection pressure whether it is more or less than MMP. In miscible CO_2 injection the injection pressure is atop of MMP between CO_2-oil system and CO_2 become miscible in crude oil. This process is called multi-contact miscibility. It results in increasing the displacement efficiency [11]. However, if the pressure is under MMP the solubility will not be achieved, so the increase of oil recovery will be due to oil swelling [12]. Several studies have compared the efficiency of the two approaches, and it has been approved that miscible is more efficient [13], [14]. From a practical view a reservoir with high temperature and pressure to be developed with CO_2 flooding to reach the miscibility the injection pressure is usually above the MMP value. Escalating the injection pressure to achieve the miscibility would lead to frac the formation [4]. Fracturing a formation always

requires a pressure greater than formation pressure. Because of fracturing a formation several issues occur such as that the invasion fluid damages the formation, lowers oil permeability, and might even shift down production rates [15].

In many reservoirs with high pressure and elevated temperature miscibility of CO_2 in crude oil is not doable [16]. To enhance oil recovery and avoid problems that occur due to formation fracturing. It is crucial to lower MMP during CO_2 flooding. Lowering MMP have been investigated by several studies by utilizing chemicals such as fatty acids, alcohols, and surfactants [4]. Voon & Awang improved the solubility of CO_2 in crude oil by using carboxylic acid (fatty acids) [16]. Qayyimah et al added 5% volume of rubber seed oil methyl ester at 90°C and pressures ranging from 18 to 31 Mpa, on 42.9 API gravity crude oil. Their results were reported by a 4% reduction in MMP values [17]. Despite using a high quantity of fatty acids, however the reported MMP decrease is recognized as insignificant in comparison to other utilized chemical additives such as non-ionic surfactants or alcohols [4].

Alcohol was utilized as chemical to lower MMP in CO_2-oil system. Moradi et al investigated the reduction of MMP between CO_2 and dead crude oil with 37.8 API. The addition of 5 commercial alcohols with different concentrations. Their findings showed that the alcohols undergoing test could lower the IFT between CO_2 and crude oil. Additionally, compared to linear alcohols with the same number of carbons, branched alcohols had a greater IFT reduction [18]. Yang et al studied the reduction of MMP in CO_2–oil system by dissolving five wt.% of monohydric alcohols and five percent of alcohol mixture in crude oil. They concluded that, up to a point, the alcohol's carbon chain length

increases the amount of CO_2 that is soluble in crude oil. The MMP was reduced by 9.21% as compared to the initial example without the addition of alcohols [19].

The reduction of MMP is highly considerable by introducing non-ionic surfactants into CO_2- oil system when compared to other chemicals such as fatty acids and alcohols. Rommerskirchen et al investigated the possibility of lowering the MMP between CO_2 and crude oil by introducing five surfactant-based chemicals [20]. Guo et al synthetic liquid surfactant that is soluble in oil in their slim tube experiment, they used 0.2 weight percent as a pre-slug and reported 22% drop in the MMP in CO_2-oil system [21]. Luo et al used non-ionic surfactant to lower MMP utilizing the pendant drop technique. According to their findings, adding 0.6 weight percent of propoxylated surfactants to CO_2 caused the MMP to drop from 19.1 to 13.8 MPa (27.7% reduction) [22]. Almobarak., et al utilized non-ionic alkoxylated surfactant to reduce CO_2-oil system. The chosen surfactant has a propoxy functional head group, which is soluble in oil, and an alipophilic hydrocarbon chain, which has a poor solubility in water. They came to the conclusion that 1.5 weight percent of surfactant caused the MMP to drop by 9%, from 31.7 to 28.8 MPa. [23].

It entails that improving the miscibility in the CO_2-oil system requires the development of an effective chemical. Where the composition of crude oil and the amount of its heavy components are related to the choice of CO_2-philic and lipophilic (head and tail groups) and optimizing carbon chain length. They arrived at the conclusion from their research that introducing the chemicals as a pre-slug result in a larger recovery factor than incorporating the chemicals with the CO_2 injection stream [4].

In our study we are aiming for the reduction of MMP along with the viscosity of a heavy Saudi crude oils. We are utilizing surfactants along with alcohols and investigating the effect of adding these materials utilizing the vanishing interfacial tension technique (VIT) on the IFT between CO_2 and crude oil. We are aiming to improve heavy oil recovery by CO_2 flooding by concentrating on the reduction of MMP and first contact miscibility pressure (FCMP). These two parameters are crucial in miscible CO_2 flooding and reducing them will increase the CO_2 miscibility in crude oil, which will eventually increase both oil recovery and carbon capture and sequestration (CCS).

1.1 Background of CO_2

An enormous change in human existence was largely based on the first industrial revolution. It caused the economies to shift from being reliant on manual labor and agriculture to being reliant on industry and machinery. Innovations in technology, such the internal combustion engine and the steam engine, made this shift feasible. People became more reliant on fossil fuels as the industrial revolution spread to new areas to strengthen their economies and improve the standard of living in their communities [24], [25]. In general, fuel combustion reactions give energy, CO_2, and water i.e.,

$$\boldsymbol{Fuel + O_2 \xrightarrow{yields} CO_2 + H_2O + Energy} \tag{1.1}$$

Given that CO_2 is a primary byproduct of combustion processes, rising fossil fuel consumption is directly correlated with rising CO_2 emissions into the atmosphere. The global CO_2 concentrations in the atmosphere from 1959 to 2022 are displayed in **Figure 1**.

In 2022, the atmospheric concentration of CO_2 reached 418.58 ppm. Compared to CO_2 levels in preindustrial eras that peaked at 300 ppm, this level is the greatest in the planet's known history. The rate of increase of CO_2 levels is concerning because it is a hundred times quicker than any historical rate increases. If current trends continue, 500 ppm of CO_2 are predicted by 2050 [26]. When considering the atmosphere, CO_2 is classified as a greenhouse gas. It can both emit and absorb radiation from the surface of the Earth. It keeps the earth sufficiently warm for life to exist on it by preventing heat from escaping to space. The greenhouse effect is the name given to these phenomena [27].

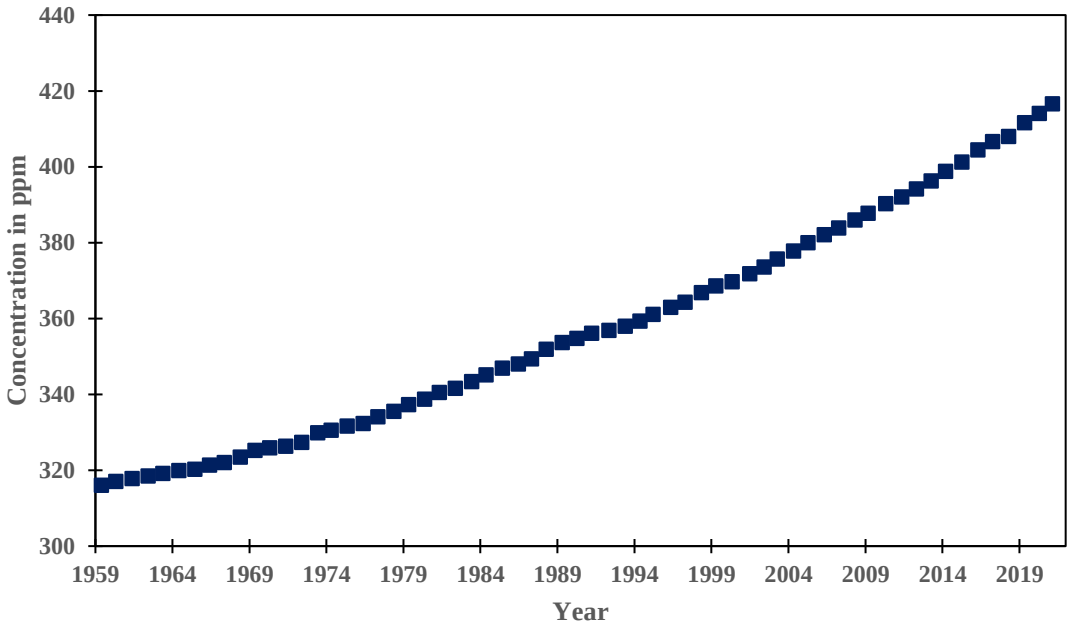

Figure 1 Atmospheric CO_2 concentrations worldwide 1959-2022 modified after [28]

The Earth is experiencing global warming because of the increased concentration of CO_2, a greenhouse gas, in the atmosphere. The planet's overall temperature since 1880 is presented in **Figure 2**. The previous ten years were the warmest in recorded history, with

the warmest years being 2020 and 2016. One degree Celsius is the increase in temperature over the preindustrial period average. Assuming a constant rate of warming, the average increase rate since 1981 has been 0.18 ˚C each decade, meaning that global warming is predicted to surpass 1.5 ˚C by 2050 [29], [30].

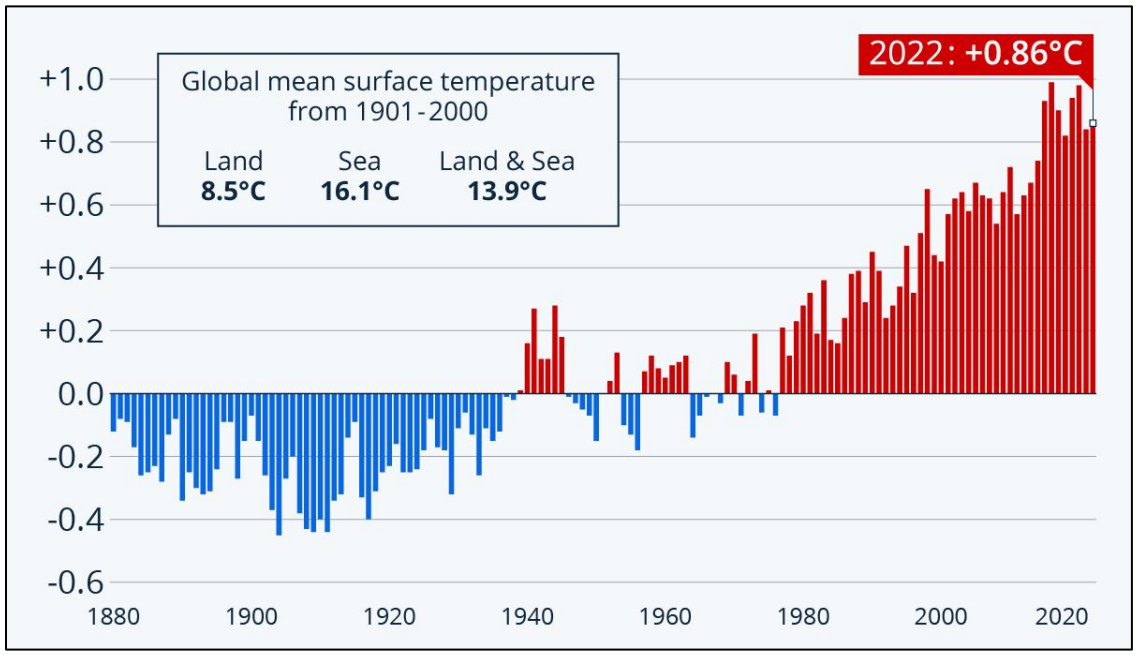

Figure 2 Global Temperature of the Earth Planet since 1880 [31].

Ocean acidification is the result of dissolved CO_2 decreasing the pH of the seas in addition to global warming. The acidity of the ocean's surface waters has grown by about 30%, unbalancing the natural processes [26]. As a result, one of the main causes of the environmental system imbalance on Earth, which is represented by the global climate fluctuations, is the great abundance of CO_2 in the atmosphere. Heat waves, droughts, and floods brought on by melted ice are a few instances of these climate shifts. As a result, significant steps must be taken to minimize CO_2 emissions, and a variety of technologies

are available to do so. While some of these innovations are still in the lab, others have managed to become reality on the ground. Research and development are always being conducted on any to boost their viability and efficiency.

1.2 Summary of CO_2 history in petroleum industry

To participate in preserving the environment from a petroleum engineering point of view. The sufficient implementation of CO_2 in the industry have been proposed. The use of CO_2 as an injection gas for oil recovery was first described in the literature in 1916, but due to the lack of abundant and affordable supplies, it was written off as a laboratory curiosity. Even so, the industry began to seriously consider miscible flooding in the early 1950s. It started with an examination of projects utilizing propane, LPG, and natural gas for first-contact miscible floods. However, because of their low viscosity and density, which could lead to a low volumetric sweep efficiency, these solvents were soon viewed as being too expensive and inappropriate at that time. Since those solvents were rejected, CO_2 was once more on the horizon [32].

1.3 Enhanced oil recovery

Primary, secondary, and tertiary stages have typically been used in dividing up oil recovery procedures. In the historical, these steps provided a chronological description of the production from a reservoir. Primary production, the first stage of production, came about as a result of the displacement energy that an existing reservoir inherently contained. After primary production declines, secondary recovery, the second stage of operations, is typically conducted. While the phrase "secondary recovery" is now essentially exclusively associated with waterflooding, traditional secondary recovery procedures include gas injection, pressure maintenance, and waterflooding. After waterflooding (or another secondary procedure), the third stage of production is known as tertiary recovery. After the secondary recovery process proved unprofitable, tertiary procedures use gases, chemicals, and/or thermal energy to displace extra oil.

In EOR operations, a special type of fluid or fluids are injected into a reservoir. To move oil to the producing wells, the reservoir's intrinsic energy is supplemented by the injected fluids and injection procedures. Additionally, by interacting with the reservoir's rock/oil system, the injected fluids contribute to improving the conditions for oil recovery. For instance, these interactions might lead to lower IFTs, oil swelling, reduced oil viscosity, altered wettability, or favorable phase behavior. The interactions are caused by physical and chemical processes as well as the introduction or generation of thermal energy. The definition excludes waterflooding and injection of dry gas for oil displacement or pressure maintenance. EOR processes are classified into four categorize shown in **Figure 3**. In this

study the main objective is to develop and improve CO_2 flooding for Saudi heavy oils. For that the next section will be describing miscible flooding.

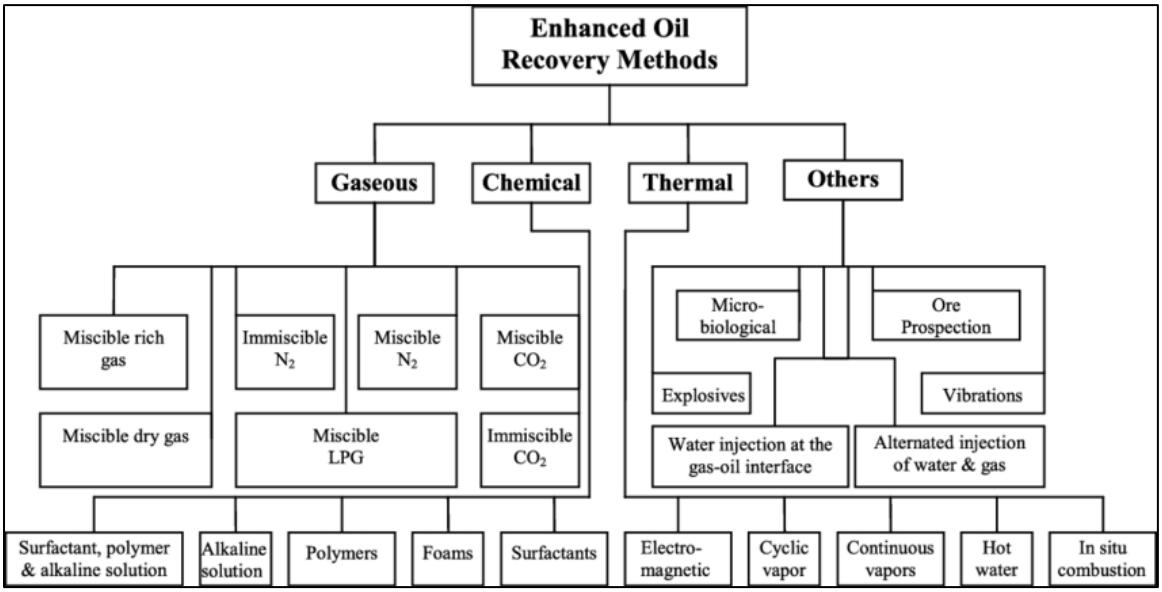

Figure 3 Classification of EOR methods [33]

1.3.1 General description and classification of EOR methods

Five categories exist for EOR processes: miscible, thermal, mobility-control, chemical, and other processes including microbial EOR.

1.3.1.1 Mobility-control procedures

As the name suggests, mobility-control procedures are those that rely mostly on preserving advantageous mobility ratios to increase the magnitude of macroscopic (volumetric)

displacement efficiency (E_V). Examples include using foams to reduce gas mobility and polymers to thicken water.

1.3.1.2 Chemical processes

Chemical processes are ones in which specific chemicals are introduced, like alkaline or surfactant agents, to improve microscopic displacement efficiency (E_D) by displacing oil through a combination of phase behavior and IFT reduction. There are scenarios where the chemical process includes mobility control as well, which could lead to improvements in both E_V and E_D.

1.3.1.3 Miscible processes

The aim of miscible procedures is to introduce fluids that either directly mix with the oil or create miscibility in the reservoir by changing its composition. Injections of CO_2 or hydrocarbon solvents are two examples. Phase behavior has a key role in how these processes are applied.

1.3.1.4 Thermal processes

To enhance oil recovery, thermal methods rely on the in-situ creation of heat or the transfer of thermal energy. Examples include in-situ combustion using oxygen or air injection and steam injection. Improved oil recovery is mostly caused by favorable phase behavior, altered oil viscosity, and occasionally chemical reactions.

1.3.1.5 Other EOR processes

A general category called "Other processes" is used. Microbial-based methods, immiscible CO_2 injection, and shallow depth resource mining are a few examples of processes falling

under this category. The classification scheme is not completely satisfactory because some terms are employed with a certain lack of specificity. Chemical processes, for instance, fall under one category, even though they are undoubtedly utilized in all of them. Furthermore, there is some overlap in the mechanisms among the classifications. For instance, the chemical processes are comparable to the miscible processes in that they depend on phase behavior and/or limited solubility across the various fluids.

1.3.2 Screening criteria of EOR processes

General, or rule-of-thumb, technical screening criteria of EOR processes were utilized in the process evaluations of the US national studies (Energy Research and Development Administration 1976; National Petroleum Council 1976, 1984; US Office of Technology Assessment 1978; US DOE 1989, 1990). Current estimations of the range of oil and reservoir qualities that the various processes can be applied to are reflected in these criteria. **Table 1** gives an overview on the screening criteria for EOR methods modified after [34]. As it can be inferred that CO_2-EOR is utilized for medium to light crude oils with low crudes viscosities. Based on the screening criteria given in the literature, CO_2-EOR is not applicable for heavy crudes. However, this study aims to improve CO_2 flooding by optimizing CO_2 miscibility in crude oil. This phenomenon could be inferred from the reduction of the value of MMP in CO_2-oil system. Various types of crudes are being investigated ranging from light Saudi crude up to ultra-heavy Saudi crude oil.

Table 1 Overview of the EOR method's screening criteria modified after [34], [35].

Oil Properties				Reservoir Characteristics					
EOR method	Gravity, °API	Viscosity, cP	Composition	Oil saturation, %	Formation type	Net thickness, ft	K_a, mD	Depth, ft	Temperature, °F
Miscible gas injection methods									
CO_2	>22 ↗ 36 ↗	<10 ↘ 1.4 ↘	High % of C_5 – C_{12}	>20 ↗ 55 ↗	Sandstone or Carbonate	Wide range	Not critical	>2,500	Not critical
Hydrocarbon	>23 ↗ 41 ↗	< 3 ↘ 0.5 ↘	High % of C_2 – C_7	>30 ↗ 80 ↗	Sandstone or Carbonate	Thin unless dipping	Not critical	>4,000	Not critical
N_2	>35↗ 48 ↗	< 0.4↘ 0.2 ↘	High % of C_1 – C_7	>40 ↗ 75 ↗	Sandstone or Carbonate	Thin unless dipping	Not critical	>2,500	Not critical
Chemical methods									
Micellar, polymer, Alkaline-polymer, and	>20↗ 35 ↗	< 35 ↘ 13 ↘	Light, intermediate, some organic acids for	>35 ↗ 53 ↗	Sandstone is preferable	Not critical	< 10 ↗ 450 ↗	< 9,000 ↘3250	< 200 ↘ 80

alkaline flooding			alkaline floodings						
Polymer flooding	>15, ≤ 40	<150, >10	Not Critical	>70 ↗ 80 ↗	Sandstone is preferable	Not critical	< 1,000 ↗ 800 ↗	< 9,000	< 200 ↘ 140
Thermal methods									
Combustion	>10↗, ↗16	< 5,000 to 1,200	Some asphaltic components	>50 ↗ 72 ↗	High porosity sand/ sandstone	>10	>50,000	<11,500 ↘3,500	< 100 ↗ 135
Steam	>8 ↗, 13.5 ↗	< 200,000 to 4,700	Not critical	>40 ↗ 66 ↗	High porosity sand/ sandstone	>20	>200,000	<4,500 ↘1,500	Not critical

1.4Miscible Processes

In a miscible procedure, the main goal is to swap out oil with a fluid that is miscible with oil (i.e., forms a single phase when mixed with oil in all proportions) under the circumstances present at the interface between the injected fluid and the oil bank being replaced. There are two major variations in this process [36]:

1.4.1 First-contact-miscible (FCM) process

At the pressure and temperature conditions present in the reservoir, the injected fluid is immediately miscible with the reservoir oil. **Figure 4** illustrates the FCM process. To extract the oil, a relatively limited quantity of hydrocarbon fluid, such as liquefied petroleum gas (LPG), is injected. The main slug size would be in the range of 10 to 15% PV. The LPG slug is then replaced by a bigger amount of a less expensive gas with a high proportion of methane (dry gas). In some cases, water may be used as the secondary displacing fluid.

The key reason the method works so well is that the primary slug and oil phase mix well together. Primary slug/oil interfaces are eliminated, and oil drops are mobilized and moved ahead of the primary slug. It is also preferable for the primary slug and the secondary displacing (dry gas in **Figure 4**) fluid to be miscible together. Otherwise, the primary slug would be trapped as a residual phase as the process progresses.

1.4.2 Multiple-contact-miscible (MCM) process

On initial contact, the injected fluid in this procedure does not mix with the reservoir oil. Instead, the process relies on mass transfer of components between the phases in the reservoir and repeated interactions between the phases to change the composition of the injected phase, or oil phase. In situ miscibility between the displacing and displaced phases will result from this composition alteration under suitable pressure, temperature, and composition conditions.

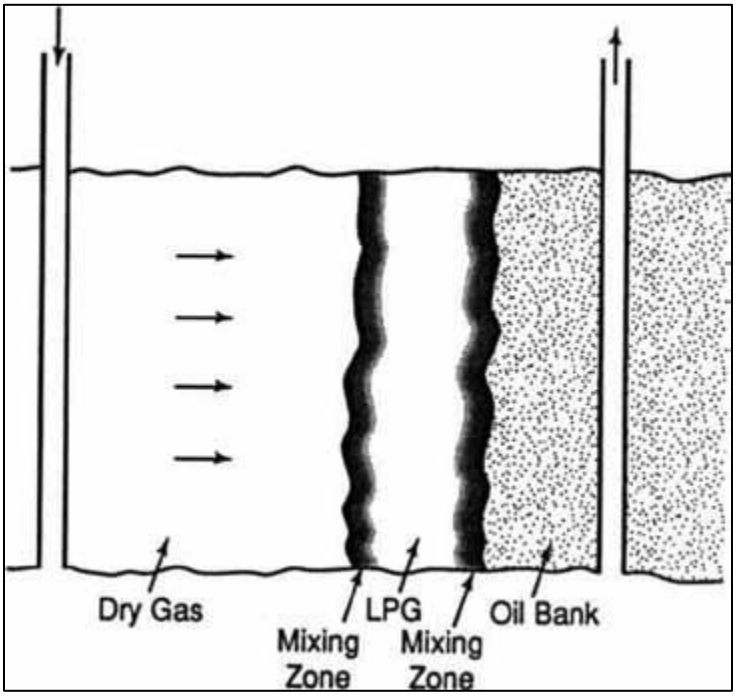

Figure 4 First-contact-miscibility process with LPG and dry gas [36]

1.5 Miscible CO_2 flooding

The CO_2 miscible process illustrated in **Figure 5** is a multi-contact-miscible process. To mobilize and remove leftover oil, a quantity of relatively pure CO_2 is injected. Intermediate- and higher-molecular weight hydrocarbons are removed into the CO_2-rich phase via many interactions between the CO_2 and oil phases. This CO_2-rich phase will become miscible with the original reservoir oil under suitable circumstances. From that time situations exist at the displaced front interface that are miscible or almost miscible. The distance needed to initially create multiple-contact miscibility is low in comparison to the distance between wells, and that will happen under ideal circumstances, this miscibility state will be established in the reservoir very rapidly. The typical percentage of PV for CO_2 amounts injected during a process is around 25%.

The critical temperature of CO_2 is 31.1° C which is equal to 87.8° F, and thus, most of the time, it is injected as a fluid at a temperature above its critical point. Depending on reservoir temperature and pressure, the viscosity of CO_2 during injection circumstances ranges from 0.06 to 0.10 cP.

Oil and water are displaced by CO_2 under unfavorable-mobility-ratio conditions in most cases due to low viscosity value of CO_2 when compared with oil and water. Due to this, the CO_2 is fingered through the oil phase, which results in low macroscopic displacement efficiency.

Injecting slugs of CO_2 and water alternately has been one strategy for overcoming this challenge. This method is called the water-alternating-gas (WAG) process. The water

injection's goal is to minimize CO_2's relative permeability and, as a result, its mobility. The WAG process also spreads out the demand for CO_2 over time, which is a benefit.

Other methods of mobility control are being assessed. These involve injecting CO_2 while utilizing foams and polymers. The difference in density between CO_2 and water, and occasionally between CO_2 and oil, is another issue with the CO_2 method. Depending once more on the reservoir conditions, CO_2 has a specific gravity at injection conditions of roughly 0.4. Depending on the density of the oil, CO_2 may rise to the top of the formation and supplant the displaced fluids. This gravity effect is occasionally taken advantage of by flooding the reservoir from the top and pushing fluids downdip, although this is only possible in situations when the reservoir structure is appropriate.

In a similar way to how CO_2 was mentioned, other gases can be used as MCM displacement fluids. Flue gases, nitrogen, and moderately dry hydrocarbon gases with a high CH_4 content are a few examples. The difference is that these gases often need much higher pressures than CO_2 to become miscible. In deep reservoirs where high pressures can be reached without fracturing the reservoir rock, these other gases are more appropriate. 0.6 psi/ft of depth is a general rule of thumb for fracturing pressures. The reservoir rock will collapse if fracture pressure is surpassed during the operation, and injected fluids will channel via the fractures, skipping most of the oil. Thus, operating pressure, which in turn depends on reservoir depth, determines the process design and the choice of displacing fluid.

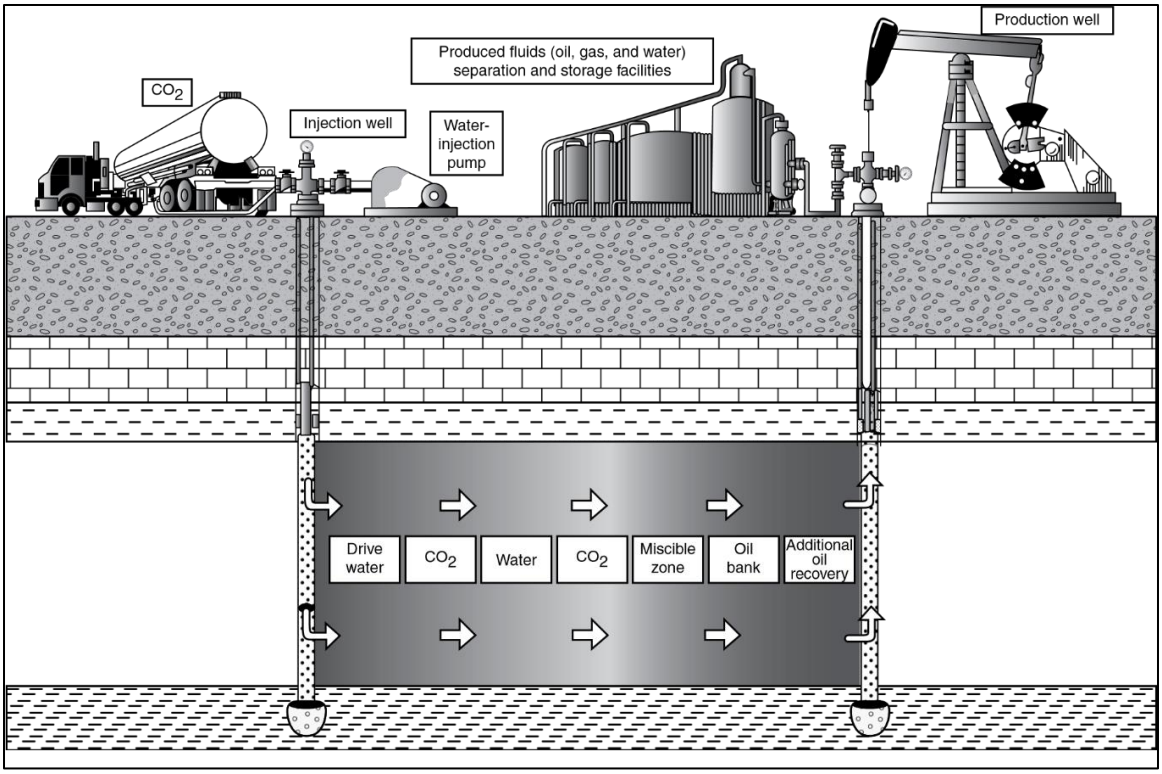

Figure 5 CO_2 miscible process [36]

A different MCM modification makes use of a hydrocarbon fluid that is plentiful in substances like ethane and propane. These injected materials condense into the oil phase during this process, enriching the oil with the lighter elements. Once more, under the right circumstances, the composition of the oil-phase can be changed to make it miscible with the injected fluid and in-situ creation of miscibility happens.

The issues with the miscible processes are mostly those that have been mentioned for the CO_2 MCM method. Because the miscible fluids typically have low viscosities, fingering and insufficient volumetric sweeps occur. Heterogeneities in the reservoir make this issue worse. It has shown to be difficult to create strategies to control movement. Insufficient

volumetric contact is also a result of density disparities due to gravity override, unless dipping reservoirs can make use of these variances to their advantage. Finally, the fluids useful at modest reservoir pressures are costly and occasionally in short supply.

1.5.1 Ternary phase diagram

Ternary diagrams are used to visually represent the phase behavior of displacement processes involving liquid/liquid or liquid/vapor equilibrium. Ternary, or triangular, phase diagrams can be used to depict the phase behavior of three-component systems. In rare circumstances, for systems with more than three components, specific components can be grouped to form pseudo components. The degradation of crude oil into CH_4, C_2C_6 components, and C_{7+} molecules is a common example. At constant pressure and temperature, the phase behavior of a ternary diagram is depicted.

1.5.2 Phase diagram of CO_2-oil system

indicates the ternary diagram of phase behavior of reservoir oil and CO_2. The light component (CO_2) are represented by the J dots, while I dots represent the heavy components (crude oil). As long as the dilution line is intersecting the two-phase region the process will remain immiscible process. The target is to achieve a ternary phase diagram, where the dilution line is outside the two-phase region such as I_2-J_3.

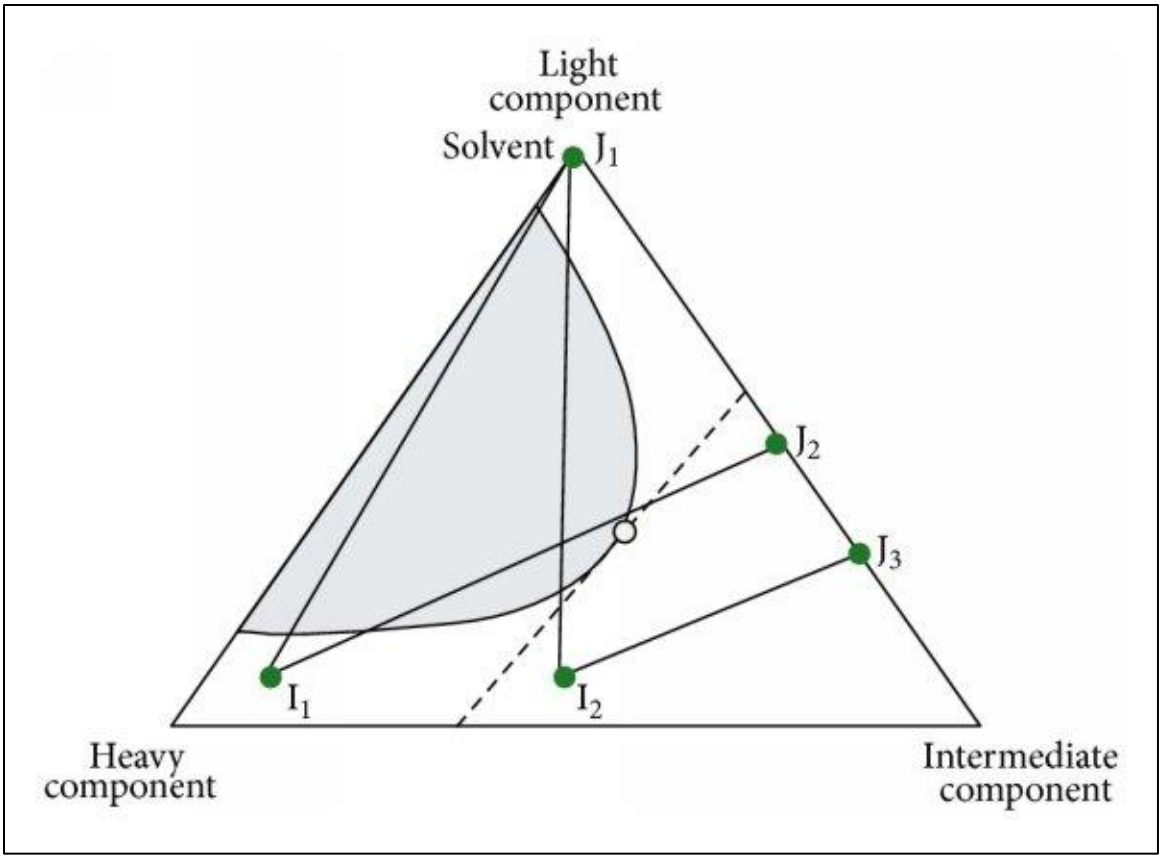

Figure 6 Typical ternary diagram for a CO_2-oil system [34]

1.6 Immiscible CO_2 Flooding

Oil recovery can be improved by the immiscible CO_2 displacement method, particularly in low pressure reservoirs or when recovering heavy oils. CO_2 is injected during immiscible displacement to increase and maintain reservoir pressure. Additionally, CO_2 can partially dissolve in oil, causing considerable swelling and a tenfold fall in viscosity, even though it is not miscible with the reservoir fluids. In a small number of projects, immiscible CO_2 flooding is used to increase reservoir pressure when rock permeability is too poor, or the

geologic environment is unfavorable to the use of the more common water flooding method. In a small number of projects, immiscible CO_2 flooding is used to increase reservoir pressure when rock permeability is too poor, or the geologic environment is unfavorable to the use of the more common water flooding method. To produce an artificial gas cap at the reservoir crest and shift oil downward toward the production wells, CO_2-GSGI is normally injected at slow rates. If this procedure is used after a large flood or when there is water in the reservoir, it could not be effective [37].

Due to the unattainable economics, the immiscible displacement process has only had a few uses thus far. Significant amounts of CO_2 are pumped into the entire reservoir during an immiscible project, which restricts the possibility of small-scale implementation to slowly recover additional oil. However, projects using immiscible displacement may store more CO_2 than projects using miscible displacement, making this method more desirable for CO_2 capture and storage. Observation has shown that the immiscible displacement is preferred by the following conditions:

1. A high reservoir permeability vertically.
2. The existence of an oil column that is sufficiently thick.
3. The reservoir has steep dipping and good lateral and vertical communication.
4. The lack of cracks that can lower the sweep efficiency.

1.7 Demand for improved CO_2-EOR

Enhanced heavy oil recovery is mostly achieved by implementation of steam injection or in-situ combustion [5], [6]. However considerable heat is lost during the process of steam injection into deep reservoirs and early steam breakthrough as a subsequent of steam channeling at producing wells might potentially limit oil recovery. It is not expected to be economically feasible [7]. For in-situ combustion there are a variety of adverse aspects, including very poor process control that results in poor sweep efficiency and completions that are negatively impacted by the ignition. Also, because the procedure is more sophisticated than other thermal technologies, a larger team of qualified and experienced individuals is needed [8].

Usually heavy oil reservoirs are shallow, as consequence thermal methods are preferred to increase the recovery. However, there are deep heavy oil reservoirs which can reach up to 10,000 ft, such as Burgan reservoir located in Kuwait. The tertiary recovery for such reservoirs cannot be attained by thermal processes. Due to the extreme loss of heat. Due to the previous cons an urgent need for an alternative feasible method has occurred. In this research we are aiming to improve the efficiency of CO_2 flooding in recovering heavy crude oils.

In this study the focus is to improve CO_2-EOR for different kinds of Saudi crudes by improving CO_2 miscibility in crude oil. This improvement is identified by achieving a reduction in the value of MMP in the CO_2-oil system. Reduction of the MMP was measured by vanishing interfacial-tension technique (VIT) before and after the addition of different

kinds and concentrations of chemicals to the CO_2-oil system. This process is obtained to define the optimum chemical along with the optimum concentration to maximize the MMP value in CO_2-oil system.

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CHAPTER 2

LITERATURE REVIEW

Global energy demand along with energy consumption are increasing aggressively worldwide due to the population and economic growth [2]. Therefore, it is crucial to always look forward to unleashing and expanding the hydrocarbon reserves. The oil recovery processes are categorized mainly into primary recovery, secondary recovery, and tertiary recovery (EOR). Contribution of primary and secondary recovery in oil in-place recovery approximately ranges from 40-50% [3]. The leftover oil is considerably high. For that EOR methods have been introduced to enlarge the recovery from a certain reservoir and reduce the residual oil saturation. Based on the type of the utilized methods EOR methods can be classified into (a) thermal methods which include steam stimulation, steam flooding, and in situ combustion. (b) gas injection methods (miscible/ immiscible) depending on the value MMP between the injected gas (CO_2, N_2, or Flue gases) and crude oil. (c) chemical methods injection of (polymer, alkaline, surfactants). (d) biotechnological methods and others. When compared to immiscible flooding, for improving sweep efficiency and reducing CO_2-oil interfacial tension, miscible CO_2 injection appears to be a substantial enhanced oil recovery strategy. which can lead to up to ten percent higher oil recovery [4].

In many reservoirs with high pressure and elevated temperature miscibility of CO_2 in crude oil is not doable [16]. To enhance oil recovery and avoid problems that occur due to formation fracturing. It is crucial to lower MMP during CO_2 flooding. Lowering MMP

have been investigated by several studies by utilizing chemicals such as fatty acids, alcohols, and surfactants [4].

The two primary areas of the literature review for this study are (1) chemicals used to lower the minimum miscibility pressure (MMP) in CO_2-oil systems and (2) techniques for determining out MMP in these systems.

2.1 Chemicals utilized to reduce MMP in CO_2 -oil system.

According to published research, adding a little amount of certain chemical additives can improve miscibility behavior at reservoir conditions by lowering the MMP in the CO_2-crude oil system. The tested substances are evaluated and discussed in the ensuing subsections in terms of crude oil properties, utilized chemicals, utilized methods, and the results.

2.1.1 Fatty acids

Saturated, mono-unsaturated, polyunsaturated, and trans fats are the four subgroups of fatty acids, which are long-chain hydrocarbons. Several studies used fatty acids to lower MMP in CO_2-oil system and enhance oil recovery. These studies are summarized in **Table 2**. Despite the high fatty acid concentration, the reported MMP decrease is deemed small in comparison to other chemical additions such as surfactants or alcohols.

Voon & Awang improved the solubility of CO_2 in crude oil by using carboxylic acid (fatty acids) [16]. Qayyimah et al added 5% volume of rubber seed oil methyl ester at 90°C and pressures ranging from 18 to 31 Mpa, on 42.9 API gravity crude oil. Their results were reported by a 4% reduction in MMP values [17]. Despite using a high quantity of fatty acids, however the reported MMP decrease is recognized as insignificant in comparison to other utilized chemical additives such as non-ionic surfactants or alcohols [4].

Table 2 MMP reduction in CO_2-oil system by utilizing fatty acids.

Reference	Crude Oil Properties	Utilized Chemicals	Utilized Method	Results
[16]	-	Oleophilic Chemicals	VIT	MMP is reduced, but no clear trend with increasing the saturation
[17]	42.90 API at 90°C	5 % volume of rubber seed oil methyl ester	VIT	Four percent MMP reduction

2.1.2 Alcohols

Due to their capacity to dissolve nonpolar compounds, semi-polar solvents like alcohols have been utilized in the petroleum industry. Alcohols are added to the CO_2-oil system, which changes the viscosity and density of the displacing fluid (CO_2) while decreasing those of the displaced fluid (crude oil), lowering the interfacial tension between the two fluids and improving miscibility. When alcohol is added to a CO_2-oil system, the non-polar ends of CO_2 and crude oil connect to the alcohol. This procedure would make gas more

soluble, lowering the friction at the interface between gas and crude oil. Several studies used alcohols to lower MMP in CO_2-oil system and enhance oil recovery. These studies are summarized in **Table 3**.

Alcohol was utilized as chemical to lower MMP in CO_2-oil system. Moradi et al investigated the reduction of MMP between CO_2 and dead crude oil with 37.8 API. The addition of 5 commercial alcohols with different concentrations. Their findings showed that the alcohols undergoing test could lower the IFT between CO_2 and crude oil. Additionally, compared to linear alcohols with the same number of carbons, branched alcohols had a greater IFT reduction [18]. Yang et al studied the reduction of MMP in CO_2–oil system by dissolving five wt.% of monohydric alcohols and five percent of alcohol mixture in crude oil. They concluded that, up to a point, the alcohol's carbon chain length increases the amount of CO_2 that is soluble in crude oil. The MMP was reduced by 9.21% as compared to the initial example without the addition of alcohols [19].

Table 3 MMP reduction in CO_2-oil system by utilizing alcohols.

Reference	Crude Oil Properties	Utilized Chemicals	Utilized Method	Results
[19]	16.68 API at 343.16 ˚K	5 wt.% of monohydric alcohols and 5% of alcohol mixture.	VIT	a 9.21% reduction in the MMP.
[18]	37.8 API	Five commercial alcohols with different concentrations.	VIT	Reduction of IFT between the crude oil and CO_2. Branched alcohols had a greater drop in IFT than linear alcohols.

2.1.3 Non-ionic surfactants

Surfactant molecules have an amphiphilic character, where two functional groups - the hydrophilic head and hydrophobic tail-define it. The capacity of surfactants to reduce interfacial tension and change reservoir wettability justifies their use in various EOR applications. By becoming adsorbent at the interface of two liquids or a liquid and a gas, a surfactant can lower the interfacial tension force, which lowers capillary pressure and allows water to transport the trapped oil. Depending on the type of hydrophilic head group, diverse types of surfactants, divided into anionic, non-ionic, cationic, and zwitterionic surfactants, are employed in EOR applications.

Since cationic surfactants may convert carbonate rock from an oil-wet to a water-wet nature, they are favored for use with carbonate rock, where the positively charged minerals on the surface of the carbonate rock absorb the negatively charged components of the crude oil. The introduction of the surfactant results in an ion pair formation interaction between its monomers and the anionic components of the oil, which absorbs the oil phase from the rock surface and modifies the rock's wettability. The use of anionic surfactants, in contrast, is favored in sandstone reservoirs due to their similar charge, which makes them effective for the rock system.

The reduction of MMP is highly considerable by introducing non-ionic surfactants into CO_2- oil system when compared to other chemicals such as fatty acids and alcohols. Rommerskirchen et al investigated the possibility of lowering the MMP between CO_2 and crude oil by introducing five surfactant-based chemicals [20]. Guo et al synthetic liquid surfactant that is soluble in oil in their slim tube experiment, they used 0.2 weight percent as a pre-slug and reported 22% drop in the MMP in CO_2-oil system [21]. Luo et al used non-ionic surfactant to lower MMP utilizing the pendant drop technique. According to their findings, adding 0.6 weight percent of propoxylated surfactants to CO_2 caused the MMP to drop from 19.1 to 13.8 MPa (27.7% reduction) [22]. Almobarak., et al utilized non-ionic alkoxylated surfactant to reduce CO_2-oil system. The chosen surfactant has a propoxy functional head group, which is soluble in oil, and an alipophilic hydrocarbon chain, which has a poor solubility in water. They came to the conclusion that 1.5 weight percent of surfactant caused the MMP to drop by 9%, from 31.7 to 28.8 MPa. [23].

It can be established that developing an effective chemical is required to improve the miscibility of the CO_2-oil system. Whereas the choice of head and tail groups (CO_2-philic and lipophilic) and optimizing carbon chain length is affected by the crude oil composition and heavy component content. According to their findings, introducing the chemical as a pre-slug result in a larger recovery factor than mixing the chemical with the CO_2 injection stream. Several studies used alcohols to lower MMP in CO_2-oil system and enhance oil recovery. These studies are summarized in **Table 4**.

Table 4 MMP reduction in CO_2-oil system by utilizing non-ionic surfactants.

Reference	Crude Oil Properties	Utilized Chemicals	Utilized Method	Results
[20]	38 API at 65°C.	2 wt.% of five surfactant-based chemicals.	Visual observation cell	Reduction of MMP ranging from 16 to 22 %
[21]	29 API 10.8 cP at 85° C	Synthesized oil-soluble liquid surfactant (CAE)	STE	22 % reduction in the MMP using 0.2 wt.%
[22]	18 API at 20° C	Propoxylated surfactants	VIT	MMP was reduced from 19.1 to 13.8 MPa (a 27.7% drop).
[23]	35 API 5.23 cP	1.5 wt.% alkoxylated surfactant	VIT	MMP was reduced from 31.7 to 28.8 MPa (a 9% drop).

2.2 Experimental methods used to determine MMP in CO_2-oil system.

In this section we reviewed the most used experimental procedures to determine MMP in the petroleum industry. According to the preformed studies on MMP in gas-oil system, the most used experimental procedures are STE, RBA, and VIT [38]–[43]. These techniques will be discussed in the following subsections historically, experimental setup, and procedures obtained to measure MMP value.

2.2.1 Slim tube experiment (STE)

Background of STE

Originally, the slim tube was designed with a long inner diameter (ID) of 0.53 in and an initial length of 8.97 ft by [44]. At a slim tube experiment, [45] put forth the initial alteration suggestion. They made the narrow ID of the slim tube 0.18 inches and 21.98 feet long. Numerous research led to changes in the lengths and inner diameter of equipment with slim tubes such as [46], [47]. However, [48] provided the "standard" method, which involved a slim tube with a 40-foot length and an ID of 0.25 inches.

STE setup design

In the petroleum industry, the STE is a commonly employed laboratory procedure [49], [50] to assess the reservoir fluids' flow characteristics and how they behave in porous media. It demands the use of a lengthy tube with a small diameter (often less than 1 inch). To represent the flow of reservoir fluids through the rock matrix, it is referred to as a slim tube.

The STE (**Figure 7)** consists primarily of a 40–80 foot long, 1/4 inch inner diameter, coiled tube filled with Ottawa sands or glass beads (commonly in the 100 mesh range). Oil is originally pumped into the tube at a pressure greater than its saturation pressure [51], [52]. After that the injection of gas at one end at different sets of temperatures and pressures to model the fluid flow of a gas-oil system in porous medium is obtained. The slim-tube tests were generally divided into three periods, which included the pre-experimental preparation, experimental execution, and post-experimental clean-up [53].

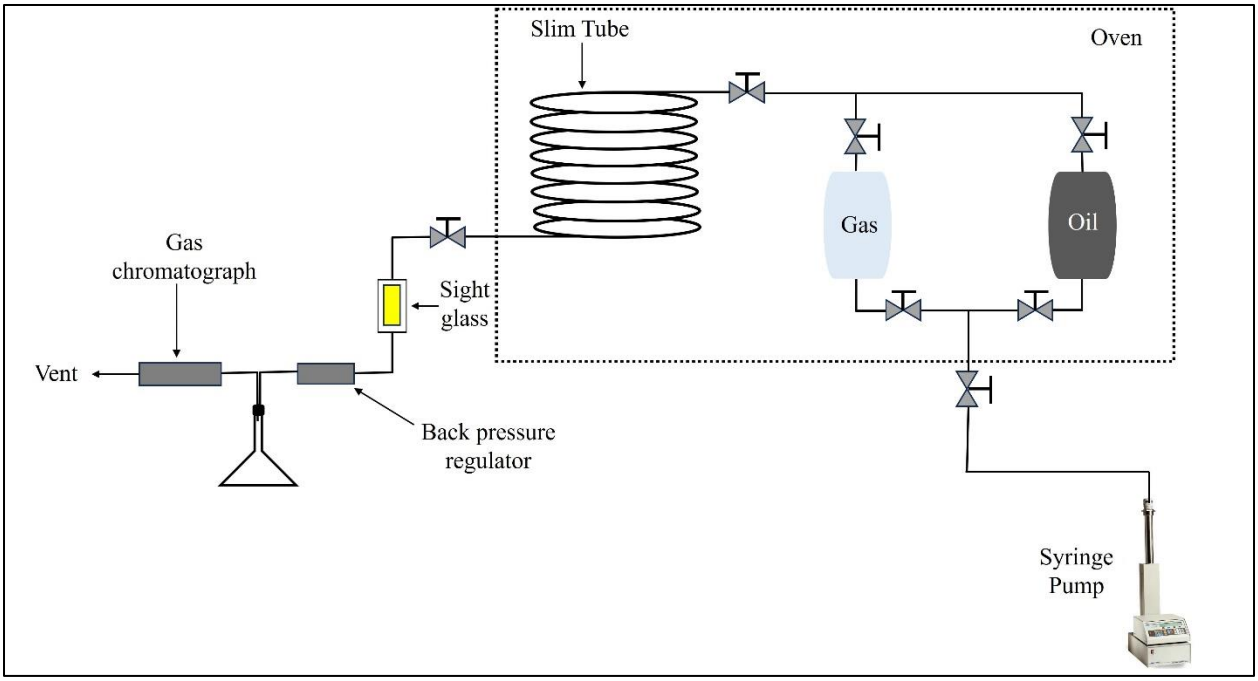


Figure 7 Slim tube experiment (STE) schematic diagram.

Determination of MMP from STE

When the oil recovery factor (RF) was 90 up to 95 % or greater at 1.0 up to 1.5 pore-volumes of injected gas (PV), it was believed that the MMP of the gas-oil system had been reached. Although different high RFs might be thought of as having different cutoff points for determining the MMP utilizing the RF criterion. The threshold RF, which is used as an indicator of the dynamic MCM process, is generally recognized to be 90% or greater at 1.2 PV of injected gas. [42], [54].

After 1.2 PV of the injected gas, the final RF is computed. Plotting the RF at 1.2 and different of PVI vs pressure is possible since each displacement is carried out at a precise

pressure and temperature [55]. The estimation of MMP in a gas-oil system from STE can be inferred from **Figure 8** [54]. The extrapolation of immiscible dots recognized as square dots along with extrapolation of miscible dots recognized as circle dots would intersect at pressure point. This point is referred to as the MMP value for the current gas-oil system at the specified temperature.

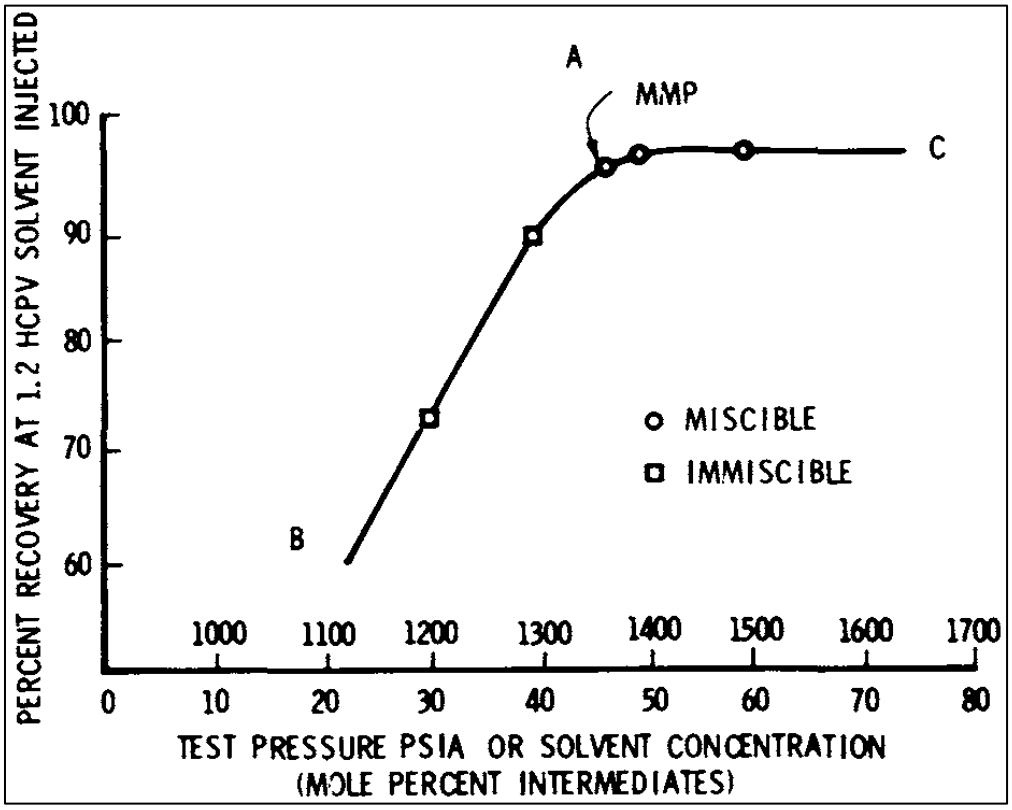


Figure 8 Determination of MMP in a gas-oil system utilizing STE [54].

2.2.2 Rising bubble apparatus (RBA)

RBA background

It is acknowledged that the RBA was the first totally visual experiment used to determine MMP in a gas-oil system. [56] developed RBA as a swift replacement for the slim tube, and numerous researchers have since used it extensively [57]–[60].

RBA setup design

The idea of the RBA (**Figure 9**) is to allow gas bubbles to make their way through a small glass tube (usually rectangular in shape, size 1x5x200 mm) loaded with oil at various pressures. A camera records the rising bubbles and their shapes, as well as the lowest pressure at which the bubble disappears during its rise (i.e., dissolves) which is considered as the MMP.

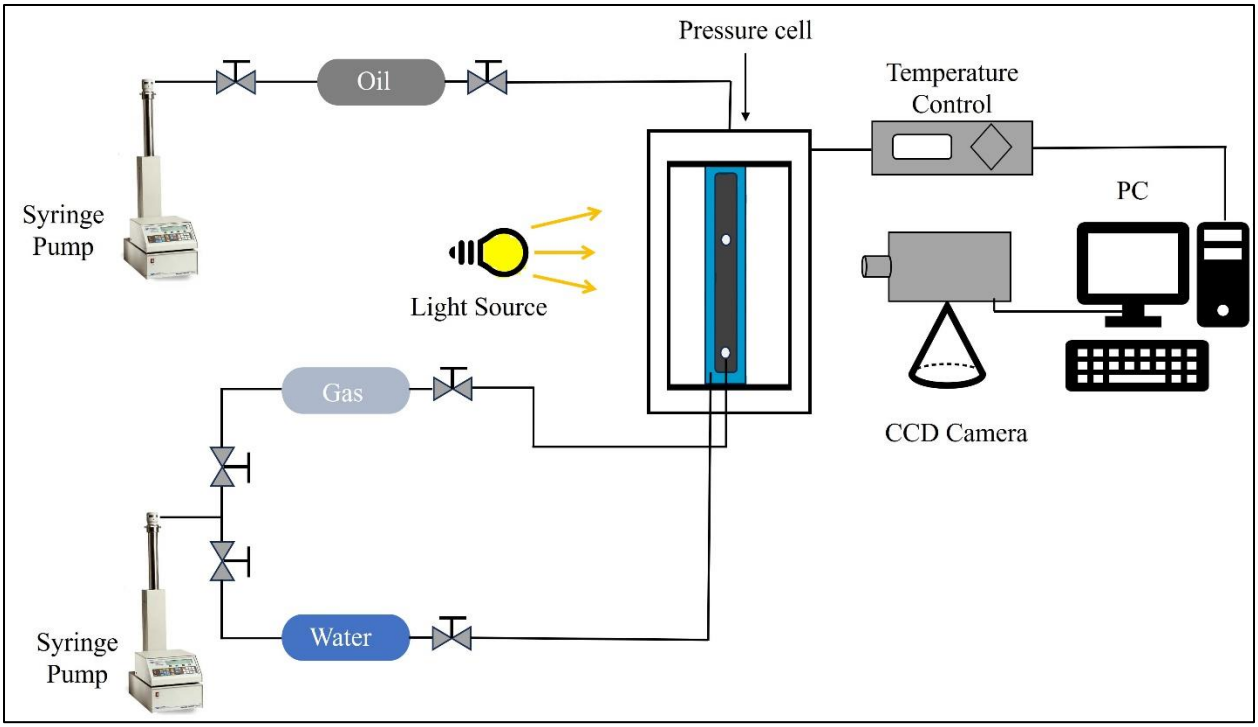


Figure 9 Rising bubble apparatus (RBA) schematic diagram.

Determination of MMP from RBA

RBA is used in the petroleum industry as a method for measuring interfacial tension between two immiscible fluids. The RBA technique involves injecting a small amount of gas into an oil-water mixture and measuring the rate of rise of the bubbles. The rate of bubble rise is influenced by the interfacial tension between the gas and the liquid phases and can be related to the interfacial tension through well-established models. By measuring the rate of bubble rise and applying these models, the interfacial tension between the two fluids can be calculated. **Figure 10** shows the procedures to obtain MMP from RBA. The maximum rising bubble height is plotted against the pressure of gas-oil system. Two straight lines can be identified out of this plot. The extrapolation of these two lines will

result in an intersection point. The reflection of this point on the pressure axis represents the MMP for the gas-oil system at the system temperature.

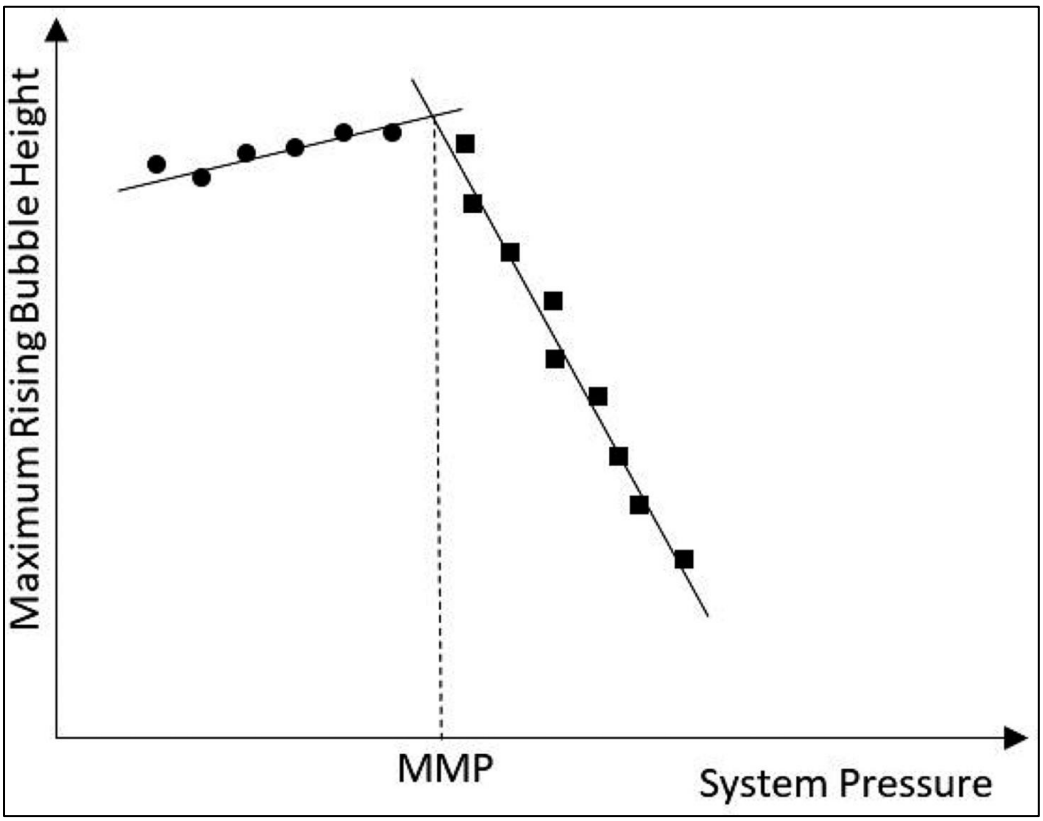


Figure 10 Determination of MMP in a gas-oil system utilizing RBA [61]

2.2.3 Vanishing interfacial tension (VIT)

VIT background

The VIT has several applications in the petroleum industry, particularly in the evaluation of interfacial tension (IFT) between immiscible fluids, which is a critical parameter that affects the efficiency of various oil recovery techniques. Rao invented the VIT for the same

goal as the RBA which is to acquire MMP readings more quickly than with the STE [62]. VIT technique is also used in the evaluation of the wettability of reservoir rocks. Wettability is a critical parameter that affects the efficiency of EOR processes.

VIT setup design

The idea of VIT experiment (**Figure 11**) is to use a transparent cell that is initially charged with injection gas and reservoir oil (usually with slightly under ten percent volume of oil). Oil droplets are introduced into the cell by a capillary tube at the top of the cell, and gas is injected into the cell to keep the pressure at a set value. Before the first oil droplet is delivered through the capillary tube, the initial volume of gas and oil in the cell is given time to equilibrate for around an hour. The Young-Laplace equation is used to estimate the IFT based on the droplet's physical shape after photographing its shape [63]. Until the droplet vanishes, this is done repeatedly at higher pressures.

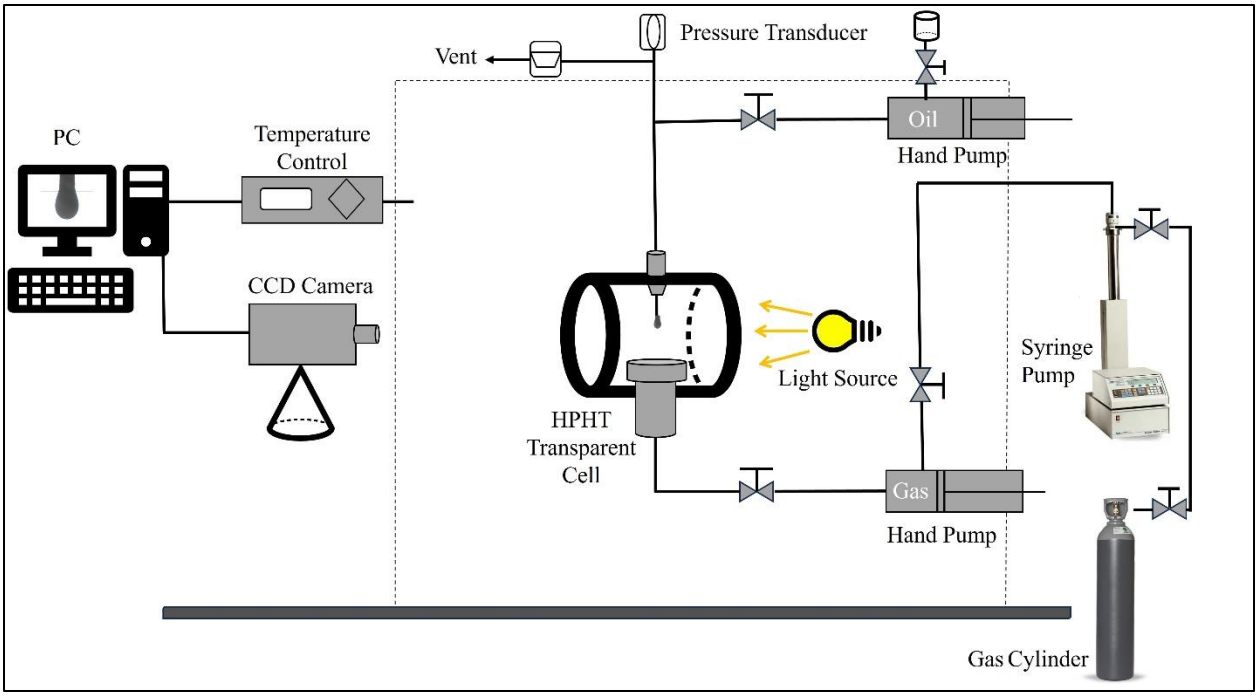


Figure 11 Schematic diagram of VIT equipment.

Determination of MMP

Two ranges can be identified when plotting IFT vs pressure in a cartesian coordinates. **Figure 12** shows a plot of IFT vs pressure is created, with the points fitted with the proper function. The curve is then extrapolated to the pressure that gives zero IFT, and this is deemed the MMP from VIT.

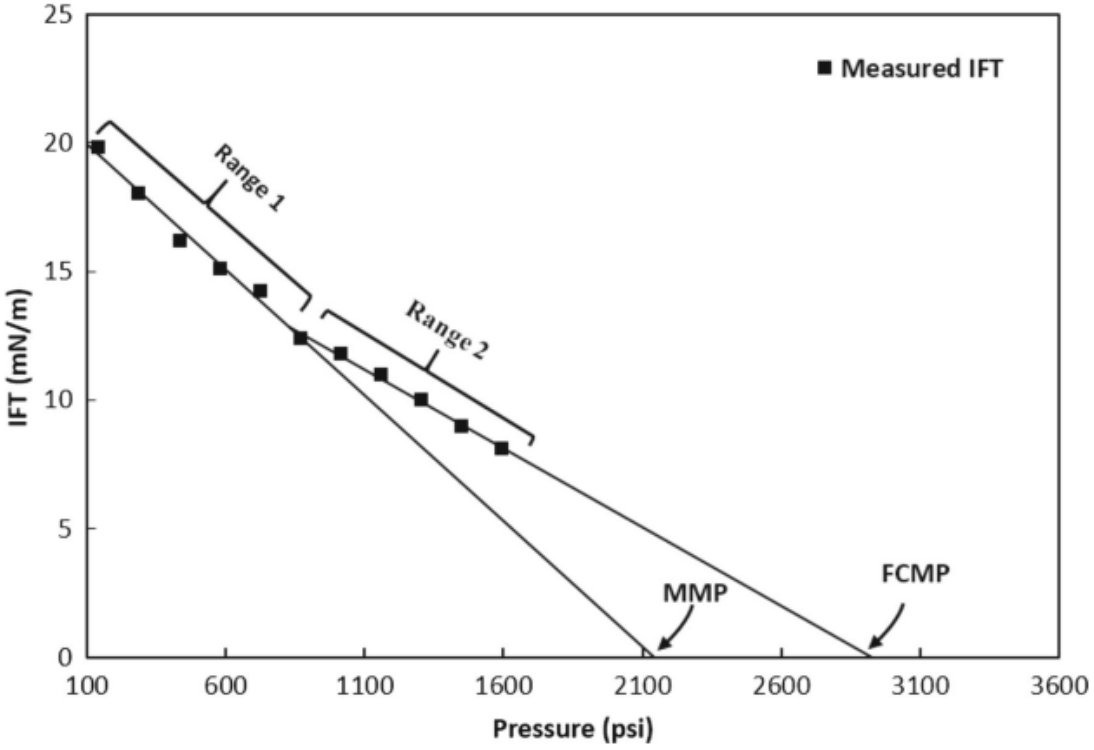


Figure 12 MMP and FCMP values from a VIT [64].

CHAPTER 3

PROBLEM STATEMENT & METHODOLOGY

In this chapter two main points will be addressed, which are (1) problem statement of this study and (2) the methodology that is obtained to provide a solution for the previous problem.

3.1 Problem statement

Usually, heavy oil reservoirs are shallow and therefore are good candidates for thermal-enhanced oil recovery (EOR) methods. Enhanced heavy oil recovery is mostly achieved by implementation of steam injection or in-situ combustion [5], [6]. However considerable heat is lost during the process of steam injection into deep reservoirs and early steam breakthrough as a subsequent of steam channeling at producing wells might potentially limit oil recovery. It is not expected to be economically feasible [7]. For in-situ combustion there are a variety of adverse aspects, including very poor process control that results in poor sweep efficiency and completions that are negatively impacted by the ignition. Also, because the procedure is more sophisticated than other thermal technologies, a larger team of qualified and experienced individuals is needed [8].

One of the most common procedures in the oil business, known as enhanced oil recovery (EOR) with enormous potential, is gas injection [9]. A successful gas injection application can be influenced by variables like the type of injected gas, the injected gas's minimum

miscibility pressure (MMP), reservoir characterization, and fluid properties. CO_2 flooding is introduced to reservoir in two forms miscible injection and immiscible injection [10]. Depending on value of the CO_2 injection pressure whether it is more or less than MMP. In miscible CO_2 injection the injection pressure is atop of MMP between CO_2-oil system and CO_2 become miscible in crude oil. This process is called multi-contact miscibility. It results in increasing the displacement efficiency [11]. However, if the pressure is under MMP the solubility will not be achieved, so the increase of oil recovery will be due to oil swelling [12]. Several studies have compared the efficiency of the two approaches, and it has been approved that miscible is more efficient [13], [14]. From a practical view a reservoir with high temperature and pressure to be developed with CO_2 flooding to reach the miscibility the injection pressure is usually above the MMP value. Escalating the injection pressure to achieve the miscibility would lead to frac the formation [4]. Fracturing a formation always requires a pressure greater than formation pressure. Because of fracturing a formation several issues occur such as that the invasion fluid damages the formation, lowers oil permeability, and might even shift down production rates [15].

Thermal-EOR methods are not sufficient when it comes to deep heavy oil reservoirs, such as the extensive Burgan field of north Kuwait which is located at approximate depth of 10,000 ft [1]. Thermal-EOR methods are not functional due to the severe heat losses which is a result of heavy-oil reservoir depth. Due to the previous cons an urgent need for an alternative feasible method has occurred.

In this research we are aiming to improve the efficiency of CO_2 flooding in recovering heavy crude oils.

From the obtained literature review the following gaps can be inferred:

- The focus was on reduction of MMP in the CO_2- oil system. The effect of the chemicals on reservoir crude oil viscosity were not considered.
- The majority of the preformed studies were obtained on light oils. Also, heavy oil was not considered that much.

3.2 Objectives of the study

The main objectives of this study are as follows:

- Evaluate the capability of several chemicals to reduce MMP in CO_2 – oil systems to enhance the heavy oil recovery, along with their effect on crude oil viscosity.
- Investigate the effect of crude oil composition, temperature, and chemical concentrations on the CO_2 miscibility.

3.3 Methodology

In this part an overview of the procedures that will be conducted to evaluate the potential of our approach. We are tackling the improvement of heavy oil recovery by CO_2 flooding through utilization of chemicals., so a pre-slug of the optimum chemical will be introduced first to lower viscosity of heavy oil and IFT in CO_2-oil system. To achieve the proposed objectives of this study, the following procedures will be conducted **Figure 13**. The

procedures of this study are categorized as screening procedures and comparison procedures. The screening procedures include MMP measurement and viscosity measurement. These procedures will be conducted utilizing various kinds of chemicals and concentrations.

After screening criteria are obtained the optimum chemical and its concentration will be moving to the next step. This step is studying the effect of the proposed chemical in different types of crudes. These crudes will cover wide range of properties. These properties include density, viscosity, total acid number (TAN), and asphaltene content.

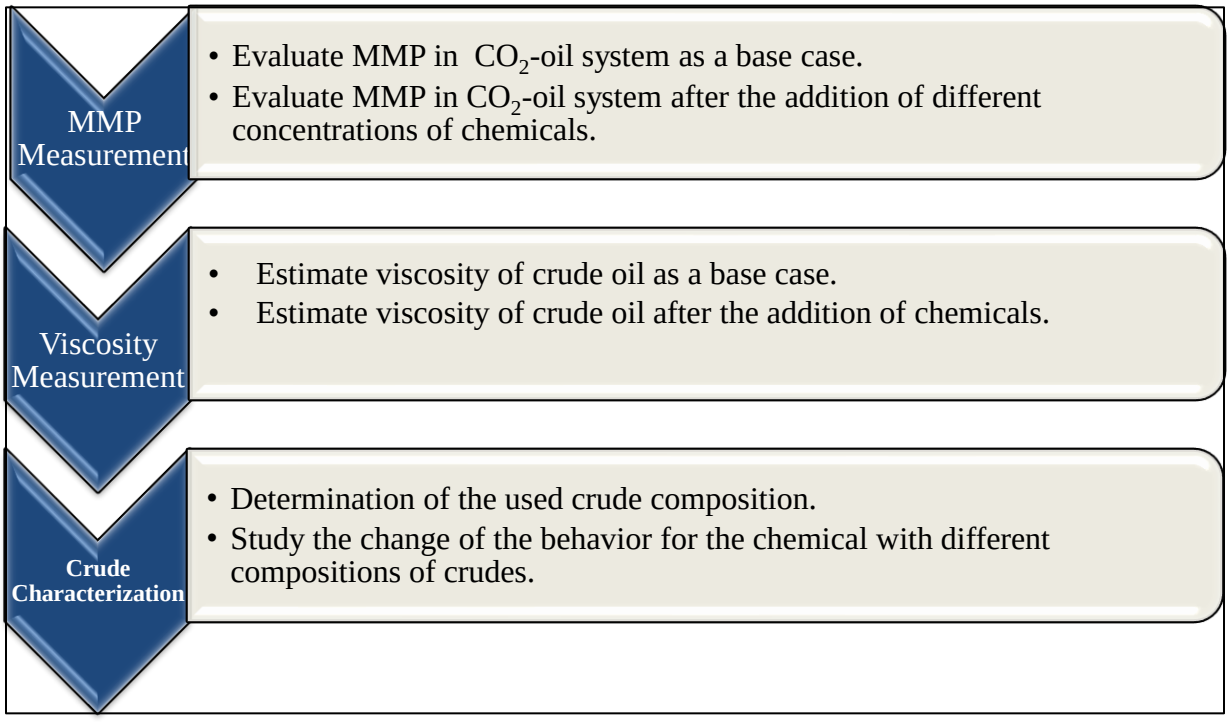


Figure 13 Methodology and workflow of this study.

CHAPTER 4

EXPERIMENTAL WORK

In this chapter all the experiments that were fulfilled in this study will be discussed in terms of concept, setup, procedures, and outcomes. Moreover, the materials utilized in this study will be presented in this chapter. First, we start with the materials used in this study:

4.1 Materials

4.1.1 Carbon dioxide

In this study the focus is on a CO_2-oil system, so it is fundamental to acquire high purity CO_2. For that CO_2 was supplied by Air Liquide Al Khafrain Ind Gases (ALKIG), the purity of the utilized CO_2 is 99.9 %.

CO_2 molecular structure is made up of two oxygen (O_2) atoms bonded to one carbon (C) atom. Molecular structure of CO2 is presented in **Figure 14**.

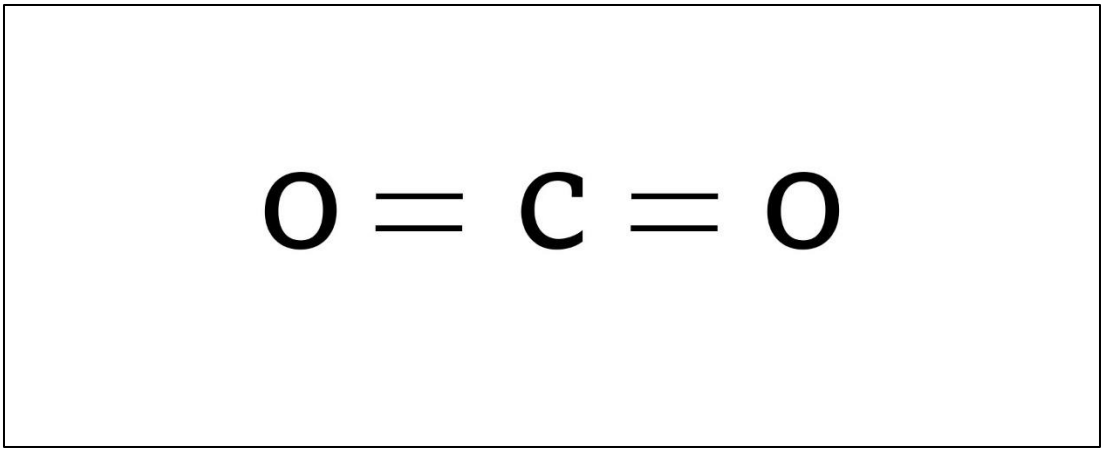


Figure 14 Molecular structure of CO_2.

4.1.2 Saudi Crude oils

Five Saudi crudes were utilized in this study with wide range of difference in their properties. Densities of these crudes ranges from 0.862 up to 1.15 g/cm^3 at ambient conditions, while asphaltene content ranges from 6.41 up 35.96 wt.%. These properties along with total acid number (TAN) for these crudes are shown in **Table 5**. It can be inferred from the table that a wide range is covered in order to do a sensitivity analysis and screening for these crudes.

Table 5 Saudi crudes utilized in the study along with their properties at ambient conditions.

Crude	Density, g/cm^3	TAN, mgKOH/g	Asphaltene Content, %
Crude 1	0.862	0.05	6.41
Crude 2	0.87	0.22	10.17
Crude 3	0.907	0.58	18.69
Crude 4	1.067	1.358	26.27
Crude 5	1.15	3.2	35.96

4.1.3 Chemicals utilized to reduce MMP in CO_2-oil system.

1. **Non-ionic surfactant**

In the literature non-ionic surfactants were used to reduce the MMP, so non-ionic surfactant (NIS) was used to reduce MMP in CO_2-oil system. Moreover, the effect of the addition of this chemical on the crude dynamic viscosity were investigated at different concentrations and temperatures. This chemical was supplied by Sunita Hydrocolloids Inc (SHI). The used micro-emulsion is mainly composed of non-ionic surfactant, limon oil, and water. The percentage of each element is shown in **Table 6**.

Table 6 Composition of the used micro-emulsion.

Element	Wt.%
Non-ionic surfactant	1-5
Limon oil	5-20
Water	30-50

2. Silica nanoparticles

Hydrophilic silica nanoparticles (NPs) were utilized in combination with ME to study their effect on MMP value of CO_2-oil system.

3. n-butanol

In the literature alcohol was used to reduce the MMP in CO_2-oil system. In this study we are tackling the use of n-butanol (BL) with different concentrations to reduce crude viscosity and MMP in CO_2-oil system. BL was supplied also by SHI with a purity of 99%. The molecular structure of BL is presented in **Figure** 15.

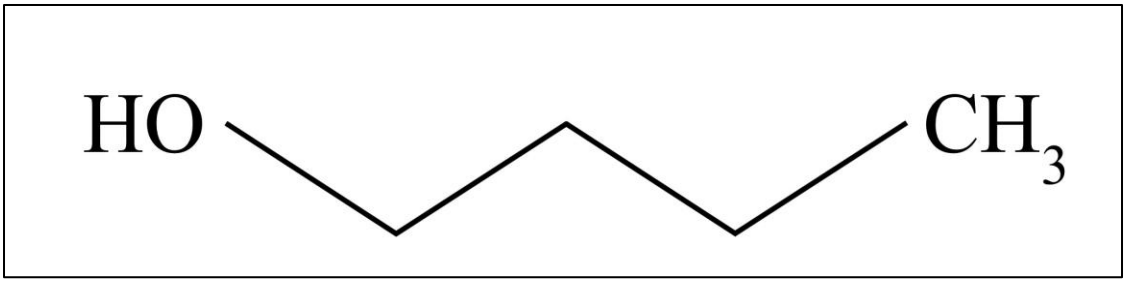


Figure 15 Molecular structure of BL.

4. Xylene

Xylene (XY) is a hydro-carbonic (aromatic) flammable liquid, where two groups of methyl replaces two hydrogens (H_2) atoms which are bonded to a benzene cycle. In this study XY was supplied by SHI. XY was used in different concentrations to lower the value of MMP in CO_2-oil system. The average weight percent of the utilized XY ranges between 25 and 75 %.

5. D-limonene

Limonene is an aliphatic hydrocarbon liquid. D-limonene (DL) was used in different concentrations in order to adhere the effect of DL on the value of MMP. In this study DL was supplied by SHI and the average weight percent of the utilized DL ranges between 25 and 75 %.

6. Ionic liquids (green chemicals)

Green chemicals have more pros than most chemicals. Green chemicals are less toxic, biodegradable, sustainable sourcing, energy efficiency in production, reduce waste, safer synthesis & processing, and improve life cycle chemicals.

I. 1-methyl-3-octylimidazolium chloride

1-methyl-3-octylimidazolium chloride (Sx1) is an ionic liquid, which can also be introduced as a green chemical. This chemical (**Figure 16**) was supplied by Sigma-Aldrich. It have a purity of 97% that were determined by high performance liquid chromatography (HPLC). Different concentrations were utilized on the different crudes and their effect on MMP value in CO_2-oil systems were investigated.

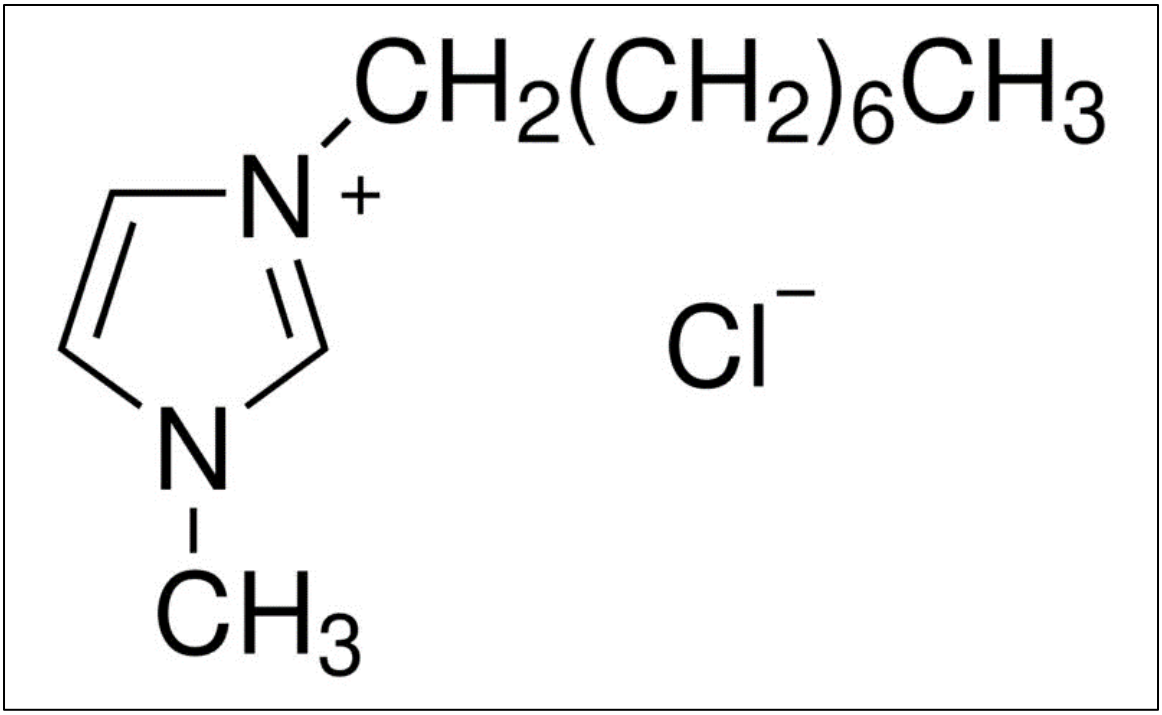


Figure 16 Chemical structure of Sx1.

II. 1-decyl-3-methylimidazolium chloride

1-decyl-3-methylimidazolium chloride (Sx4) is an ionic surfactant, which can also be introduced as a green chemical. This chemical (**Figure 17**) was supplied by Sigma-Aldrich. It have a purity of 97% that were determined by high performance liquid chromatography (HPLC). Different concentrations were utilized on the different crudes and their effect on MMP value in CO_2-oil systems were investigated.

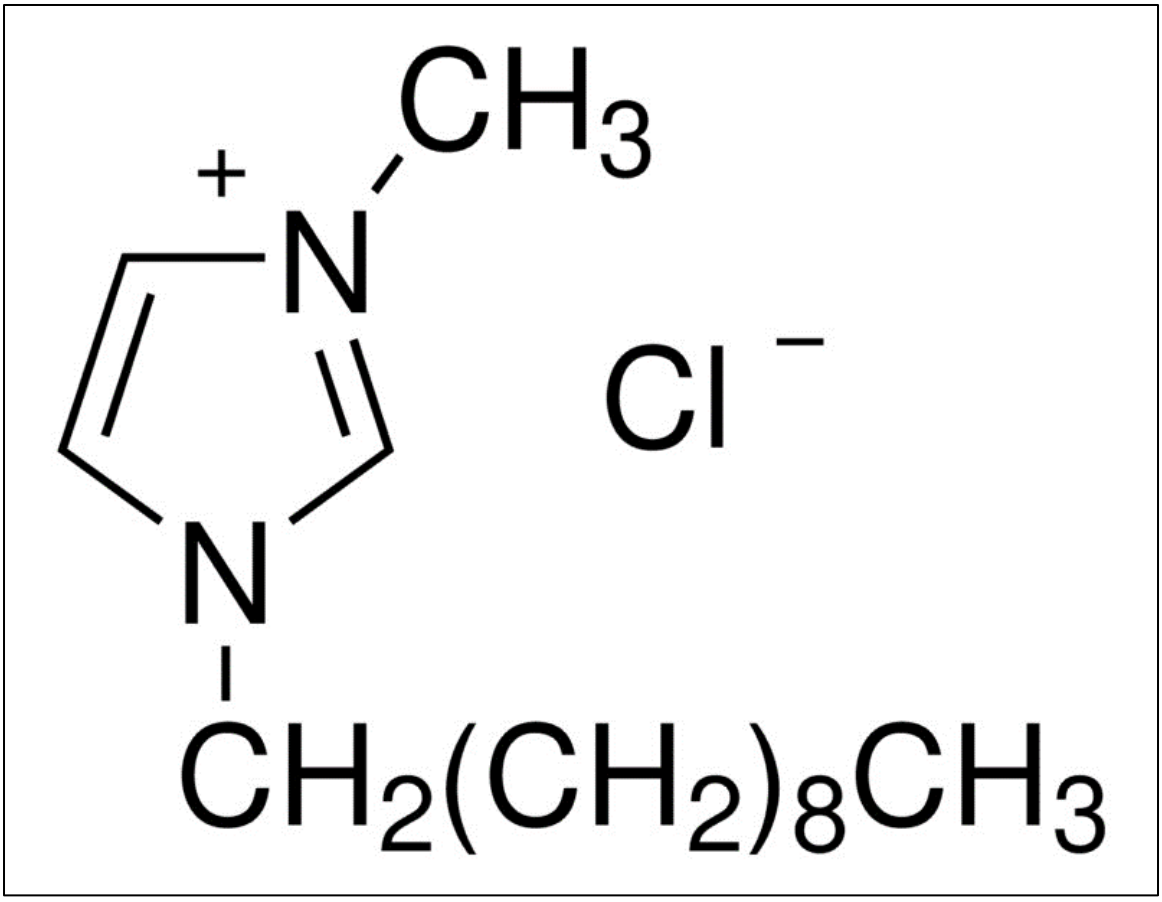


Figure 17 Chemical structure of Sx4.

4.2 Experimental procedures

Experimental procedures that were obtained in this study will be discussed in terms of principle, experimental setup, workflow, and outcomes. Mainly these procedures are used to characterize the crudes used in this study, determine the MMP for the CO_2-oil system, and establish a recovery factor (RF) out of the core flooding experiment. These procedures are density measurement, viscosity measurement, (saturate, aromatic, resin, and

asphaltene) SARA analysis, TAN, VIT, porosity measurement, permeability measurement, computed tomography (CT scan), nuclear magnetic resonance (NMR), and core flooding.

4.2.1 Density measurement

The density of the crudes were measured at atmospheric pressure and elevated temperatures. This procedure is obtained by the utilization of densitometer for liquids (ambient and HT). The model of the instrument is Anton Paar DMA 4500M, which is founded on in-depth understanding of oscillation properties. Take back control of your filling with the help of the automatic bubble detection technology and make viscosity correction across the entire viscosity ranges. **Figure 18** shows the instrument used to determine the density of the Saudi crudes.

To specify the density of a liquid using this instrument. First, the instrument shall be calibrated to air density by using an air pump, which is part of the device. Then the liquid is injected utilizing a syringe and through the screen that gives visual details of the sample. There should be no bubbles to determine the density correctly. The temperature is set to the desired value and the instrument starts to measure the density at the specified conditions.

Figure 18 Anton Parr DMA 4500 M utilized for density measurement.

4.2.2 Viscosity measurement

Dynamic viscosity of the five Saudi crude oil samples were determined by the utilization modular compact rheometer (MCR 702) at atmospheric pressure and different temperatures. This instrument measures the dynamic viscosity at different shear stress values. Light to medium and even heavy crude oils and BL are recognized as Newtonian fluids [65][66], which means at a constant temperature viscosity will exhibit a linear relationship with shear stress [67].

To operate the device about 20 ml of the sample is inserted into the cup, the temperature is set to the desired value. After that the cone is lowered into the sample and a torque is applied on the sample. Finally, the shear stress along with the shear strain are recorded and plotted and from the graph obtained, value of the viscosity can be inferred from the slope of the straight line. **Figure 19** shows a picture of the instrument used to measure the viscosity.

Figure 19 Modular compact rheometer that is used to determine the viscosity.

4.2.3 SARA analysis

SARA analysis provides information regarding the total chemical composition of the sample, without going into its molecular detail. It allows separation of the mixtures under examination into (a) saturates; (b) aromatics; (c) resins; and (d) asphaltenes. The experimental procedure involves the utilization of the thin layer chromatography (TLC) and flame ionization detection (FID) using Iatroscan MK-7 according to standard method IP 469/01. The SARA analysis is carried out in three stages: (1) spotting one microliter of the sample diluted in dichloromethane in chromo-rod (quartz rod covered with silica), (2) elution of the spotted samples using TLC, (3) detection of the diverse groups along the chromo-rods using FID [68]–[70]. **Figure 20** shows the setup used to preform SARA analysis on the five Saudi crudes.

Figure 20 Experimental setup used to obtain SARA analysis.

4.2.4 Total acid number (TAN)

All the measurements were done at ambient pressure and temperature for the five dead Saudi oil samples. Total acid number (TAN) is measured by the potentiometric titration using Metrohm Ti-touch 916 titrator according to ASTM D664-18, respectively.

For TAN determination, a crude oil sample of ten grams was dissolved in 60 ml of titration solvent (50% toluene, 49.5% isopropanol, and 0.5% water) and a dosing rate of 0.1 ml of the titrant (0.1 molar KOH in 2-propanol) was set. Before any titration, the pH electrode was preconditioned until a stable pH was obtained. All the measurements were done at ambient pressure and temperature for the dead oil samples.

$$TAN = \frac{M_{KOH} \times MW_{KOH} \times (A-B)}{W} \quad (4.1)$$

Where M_{KOH} is the molar concentration of KOH titrant (mol/L), MW_{KOH} is the molecular weight of KOH (56.1 g/mol), A is the volume of titrant at the sample inflection point (ml) and B is the blank titration volume (ml).

Figure 21 shows the instrument that is used to determine TAN for the five Saudi crudes.

Figure 21 Metrohm Ti-touch 916 titrator used to determine TAN for the five Saudi crudes.

4.2.5 Vanishing interfacial-tension technique (VIT)

In 1997 Rao invented the VIT for the same goal as the rising bubble apparatus (RBA) which is to acquire MMP readings more quickly than with the slim tube test [62]. VIT technique, (which relies on pendant drop technique) has several applications in the petroleum industry, particularly in the evaluation of IFT between immiscible fluids, which

is a critical parameter that affects the efficiency of various oil recovery techniques. VIT technique is also used in the evaluation of the wettability of reservoir rocks. Wettability is a critical parameter that affects the efficiency of EOR processes.

The idea of VIT experiment **Figure 22** that was utilized in this study is to use a transparent cell that is initially charged with CO_2 and reservoir oil (usually with slightly under ten percent volume of oil). Oil droplets are introduced into the cell by a capillary tube at the top of the cell. CO_2 is injected into the cell to keep the pressure at a set value. Before the first oil droplet is delivered through the capillary tube, the initial volume of CO_2 and oil in the cell is given time to equilibrate for around an hour. The Young-Laplace equation is used to estimate the IFT based on the droplet's physical shape after photographing its shape [63]. Young-Laplace equation is used to analyze the drop shape. The pressure difference (Laplace pressure) between the areas within and outside of a curved liquid surface/interface with the primary radii of curvature Ri is described by this equation [71] :

$$\Delta \boldsymbol{p} = \boldsymbol{\sigma}\left(\frac{\mathbf{1}}{\boldsymbol{R_1}} + \frac{\mathbf{1}}{\boldsymbol{R_2}}\right) \tag{4.2}$$

Where $\Delta \boldsymbol{p}$ is Laplace pressure which is the difference in pressure between the areas outside and inside of a curved liquid surface with the principal of radii curvature which are $\boldsymbol{R_1}$and $\boldsymbol{R_2}$. $\boldsymbol{\sigma}$ is interfacial tension between the immiscible fluids.

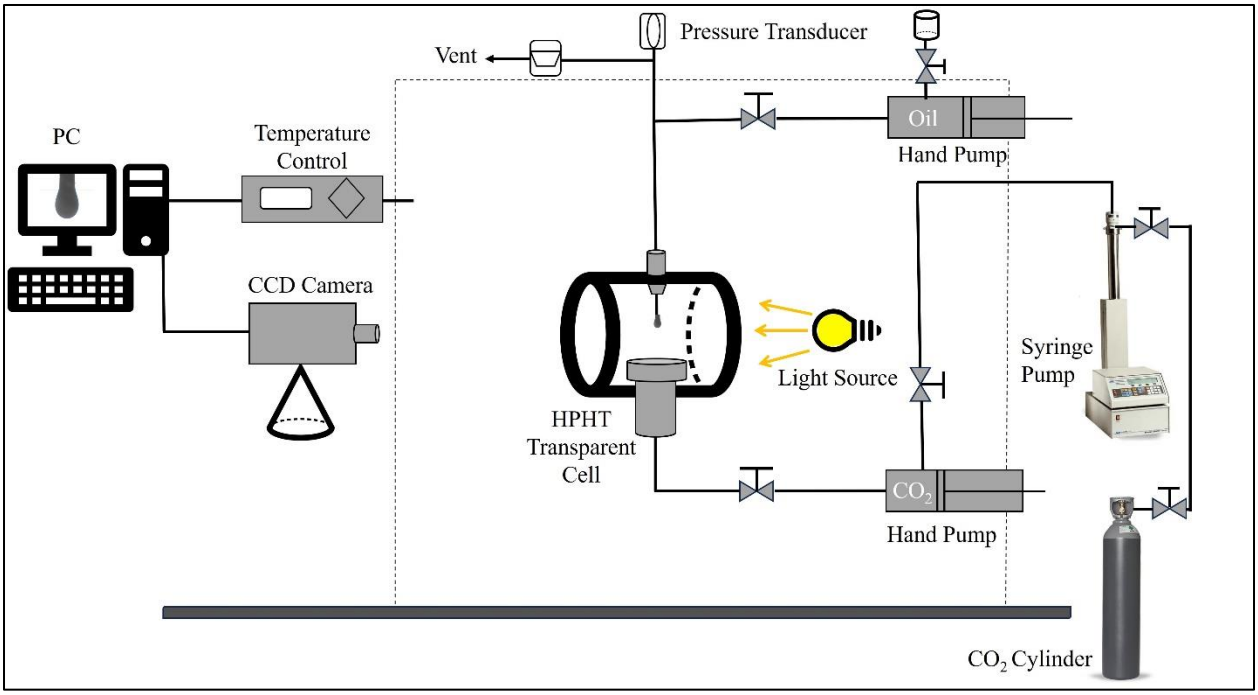


Figure 22 Schematic diagram of VIT utilized in the study.

Until the droplet vanishes, this is done repeatedly at higher pressures. A plot of IFT vs pressure is created, with the points fitted with the proper function. The curve is then extrapolated to the pressure that gives zero IFT, and this is deemed the MMP value, while another set of linear points is extrapolated to the pressure that gives zero IFT, and this value is deemed as the first contact miscibility pressure (FCMP).

4.2.6 MMP measurement

Measurement of MMP in a gas-system can be obtained by plotting pressure versus IFT **Figure 23**. From the obtained plot two linear trend lines can be recognized.

Extrapolation of the first line will result in an MMP value at zero IFT, while extrapolation of the second line would result FCMP value at zero IFT.

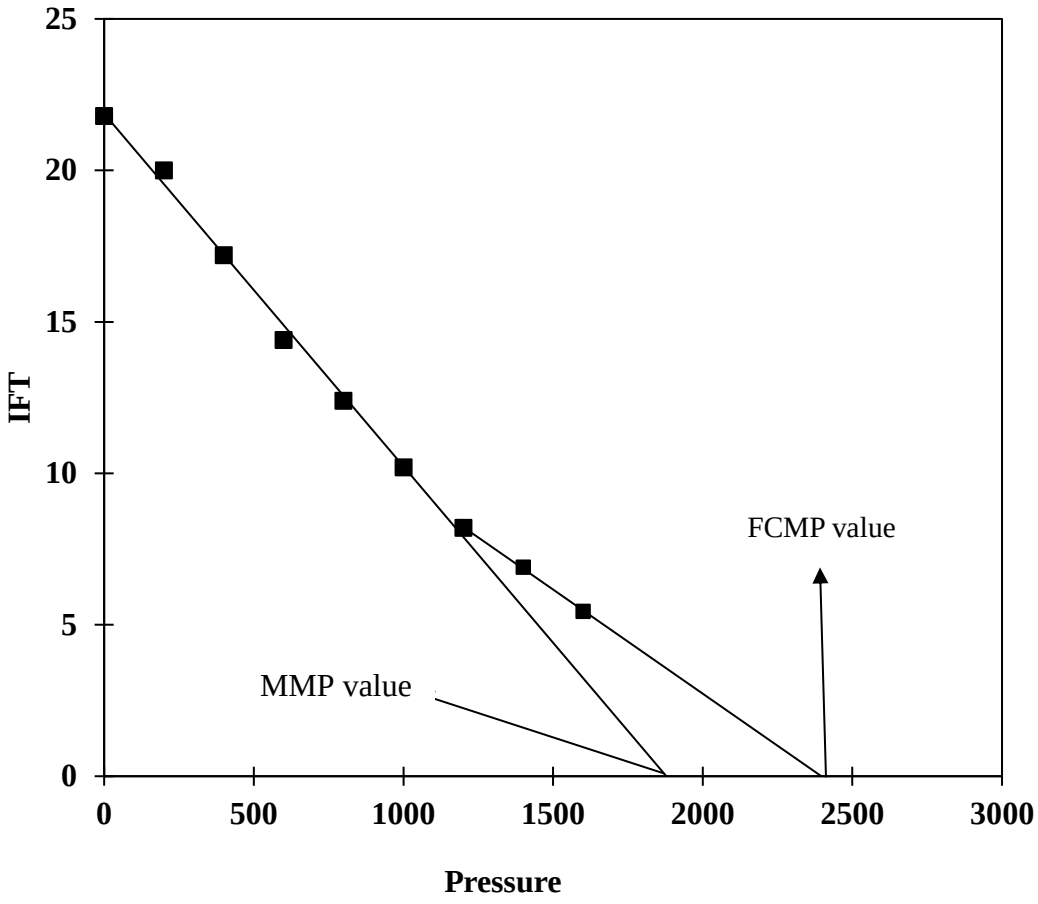


Figure 23 MMP and FCMP values from a plot of pressure versus IFT modified after [72].

An optical contact angle measuring, and contour analysis device can be used to determine the surface tension of a liquid as well as the interfacial tension of two liquids. The setup drafted in **Figure 24** is used to capture an image of a liquid drop that hangs

on a dosing needle and to then analyze it using the Instruments program. The corresponding assessment approach is known as the pendant drop method.

The Young-Laplace equation is used to analyze the drop shape. The pressure difference (Laplace pressure) between the areas within and outside of a curved liquid surface/interface with the primary radii of curvature Ri is described by this equation:

$$\Delta \boldsymbol{p} = \boldsymbol{\sigma}\left(\frac{\mathbf{1}}{\boldsymbol{R_1}} + \frac{\mathbf{1}}{\boldsymbol{R_2}}\right) \tag{4.3}$$

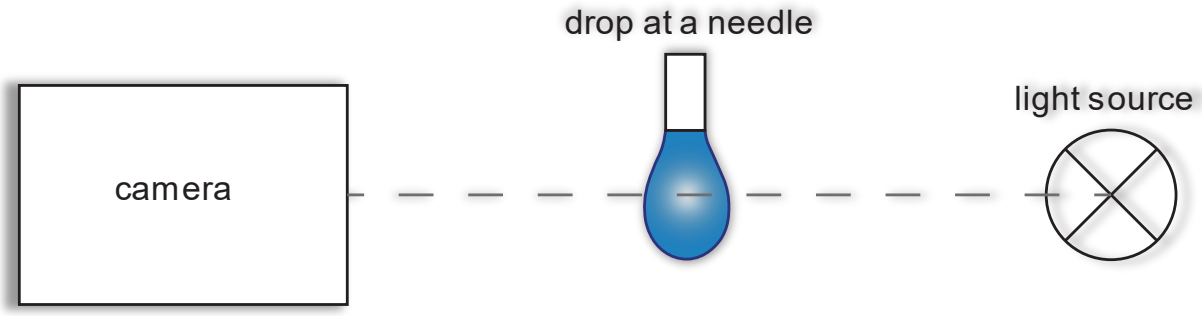


Figure 24 Diagram of the pendant-drop technique's setup [73].

The surface tension and gravitational forces, in particular, define the shape of the pendant drop. Surface tension aims to reduce surface area and shape the drop into a spherical shape. Gravitation, on the other hand, stretches the drop from its spherical shape, resulting in the classic pear-like shape.

According to Pascal's law (hydrostatic pressure), gravity generates a pressure difference across the z-axis. As a result, the Laplace pressure $\Delta p_{(z)}$ at a distance z from an arbitrary reference plane with Laplace pressure Δp_0 is:

$$\Delta \boldsymbol{p}_{(\boldsymbol{z})} = \Delta \boldsymbol{p_0} \pm \Delta \boldsymbol{\rho g z} \tag{4.4}$$

The major radii of curvature at the vertex (lowest point of the drop) of a pendant drop are: R1=R2=R. As a result, it is convenient to locate the reference plane at this location. For every point above it holds R_2=x/sin Φ (**Figure 25**). The mentioned equations lead to:

$$\frac{\mathbf{1}}{\boldsymbol{R_1}} + \frac{\boldsymbol{sin\emptyset}}{\boldsymbol{x}} = \frac{\mathbf{2}}{\boldsymbol{R}} \pm \frac{\boldsymbol{\Delta\rho gz}}{\boldsymbol{\sigma}} \tag{4.5}$$

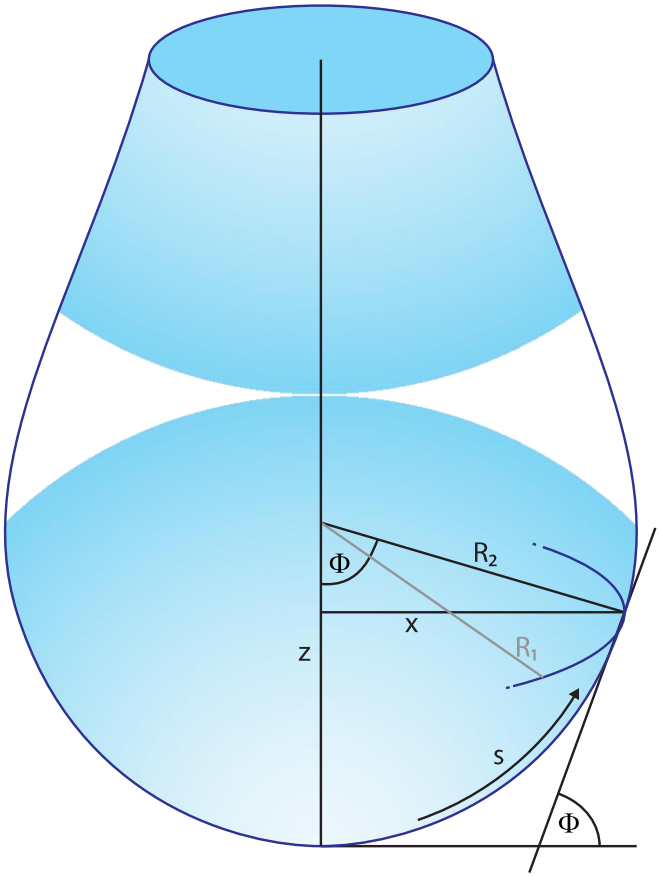


Figure 25 Young-Laplace fit deviation on a pendant drop [73].

Interfacial tension (IFT) between the immiscible fluids (oil and CO_2) measurement at 50 and 90°C and different pressures were preformed utilizing drop shape analyzer

manufactured by KRÜSS (DSA 100 HP) **Figure 26**. The experiment were performed on crude oil and CO_2 as a reference for this study. The experiment is repeated frequently with different chemicals and different concentrations. Each chemical and its concentration represents a single case at which MMP and FCMP were conducted by the interpolation of the measured IFT values vs pressure. MMP and FCMP values were estimated for each case, individually and comparison with the base case along with other cases is performed. MMP of different Saudi crude oils have been determined by [55] utilizing slim tube experiment (STE). They reported that MMP increase with the increment of temperature value. IFT values of the five Saudi crudes along with the different chemicals and different concentrations of chemicals at pressures ranging from 10 up to 210 bar. The IFT values recorded by the instrument assumes constant densities for the crude used along with CO_2, due to that a correction must be obtained using the following equation.

$$Corrected\ IFT = \ IFT\ reading \times \frac{(Oil\ density - CO_2 density)}{(DSA\ oil\ density - DSA\ CO_2 density)} \quad (4.6)$$

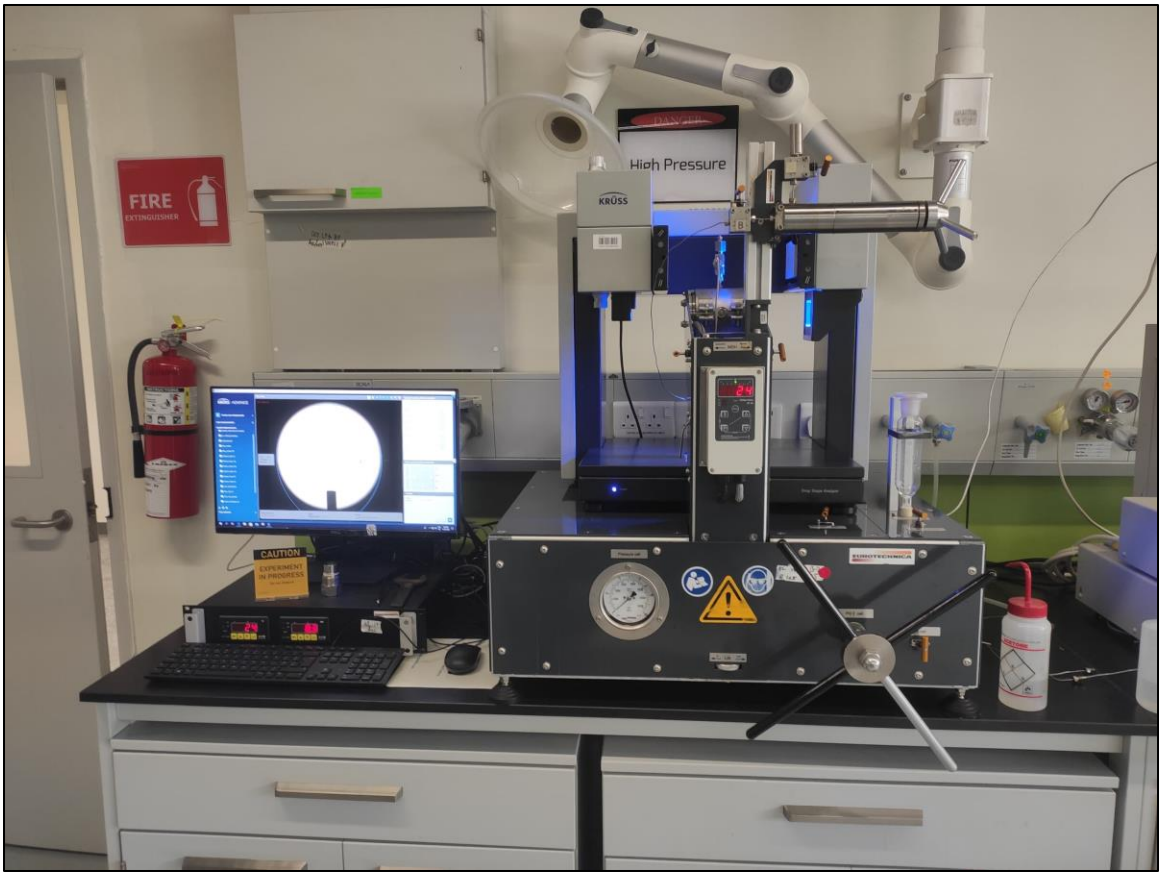


Figure 26 Drop shape analyzer (DSA 100 HP)

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Density and viscosity measurements

Density of the five Saudi crudes are measured at atmospheric pressure and wide ranges temperatures. These values of temperatures includes the values at which VIT is conducted and at which CO_2 core flooding is conducted. These temperatures ranges from 20 up to 90° C. Densities of the five Saudi crudes are presented in **Table 7.**

In order to start the screening criteria one of the crudes is selected to examine the effect of different chemicals with different concentrations on it. Crude 3 represents the average when compared to other crudes in terms of density, viscosity, TAN, and asphaltene content. Due to the previously specified reasons, crude 3 is taken to perform the screening on it. In this part we will discuss the introduced chemicals and their effect on crude 3 viscosity.

Table 7 Densities of the five Saudi crudes at different temperatures and atmospheric pressure.

Temperature, ° C	Crude 1 Density, g/cm^3	Crude 2 Density, g/cm^3	Crude 3 Density, g/cm^3	Crude 4 Density, g/cm^3	Crude 5 Density, g/cm^3
20	0.866	0.873	0.908	-	-
25			-	1.067	1.150
30	0.862	-	0.901	-	-
40	-	-	0.894	1.060	1.142
50	0.845	0.836	0.888	-	-
60	-	-	-	1.050	1.132
65	-	-	0.877	-	-
75	0.827	0.834	0.869	-	-
90	0.817	0.823	-	1.032	1.117

The viscosity of the three of the crudes is measured without any additions of chemicals. The dynamic viscosities of these crudes are shown in **Table 8**. The unit used to describe the dynamic viscosity is centipoise which is equivalent to one millipascal-second 1 cP = 1 mPa.s.

Table 8 Dynamic viscosities of the heavier crudes used in the study.

Temperature, ° C	μ of Crude 3, cP	μ of Crude 4, cP	μ of Crude 3, cP
20	91.4	-	0.908
25	-	2,220	47,700
40	-	473	9,260
50	23.5	-	-
60	-	173	1,450
75	11.16	-	-
90	0.817	26	123
100	-	15	60

Also, kinematic viscosity (v) can be determined from the previously mentioned values of viscosities and densities. Kinematic viscosities of these crude can be obtained by dividing the dynamic viscosity over density of the crude at the same conditions of temperature and pressure. Kinematic viscosity is measured by the unit of centistokes (cSt).

To test the effect of chemicals on crude 3 viscosity, NIS were introduced to the crude, this introduction is obtained by stirring and heating of the sample. Mainly, two concentrations of NIS were considered, which are 0.6 and 0.75 wt.% of NIS into crude 3. The viscosities of these crudes were measured at similar conditions of temperature and pressure. **Table 9** shows the results after the addition of NIS to crude 3.

Table 9 Dynamic and kinematic viscosities after the addition of 0.6 and 0.75 wt.% to crude 3.

Crude oil type	Temperature, °C	μ, cP	v, cSt
Crude 3	20	91.43	100.69
	50	23.49	26.45
	75	11.16	12.83
Crude 3 + 0.6 wt.% NIS	20	127.73	140.67
	50	26.74	30.11
	75	11.24	12.93
Crude 3 + 0.75 wt.% NIS	20	142.86	157.34
	50	29.09	32.75

From the previously mentioned data, it can be inferred that negative impact on crude 3 is induced. With increasing NIS concentration, the value of crude 3 viscosity increases. However, this is not the case when the MMP is measured for CO2-oil system with the addition of NIS.

Due to the increase of the values of viscosity with NIS, an alternative chemical that was used in the literature to reduce MMP on CO_2-oil system. This chemical is BL. Light to medium crude oils and BL are recognized as Newtonian fluids(Wong et al., 2015; Sharma et al., 2016), which means at a constant temperature viscosity will exhibit a linear relationship with shear stress [67]. Due to the high solubility of BL in crude oil [75], different concentrations which are 2.5,5,7.5, and 10 wt.% of BL were solubilized in crude oil and the viscosity of these samples were measured.

Crude 3 viscosity is taken as a base case, nevertheless that crude oil and BL are Newtonian fluids [76]. The viscosity of the prepared crude oil samples with different concentrations

2.5,5,7.5, and 10 wt.% of BL, along with crude 3 oil sample were measured at different shear rates. Shear rates ranging from 1 to 1000 sec^{-1} were applied on the samples to examine the Newtonian behavior of these samples. Also, the measurements were obtained at 25 and 50°C.

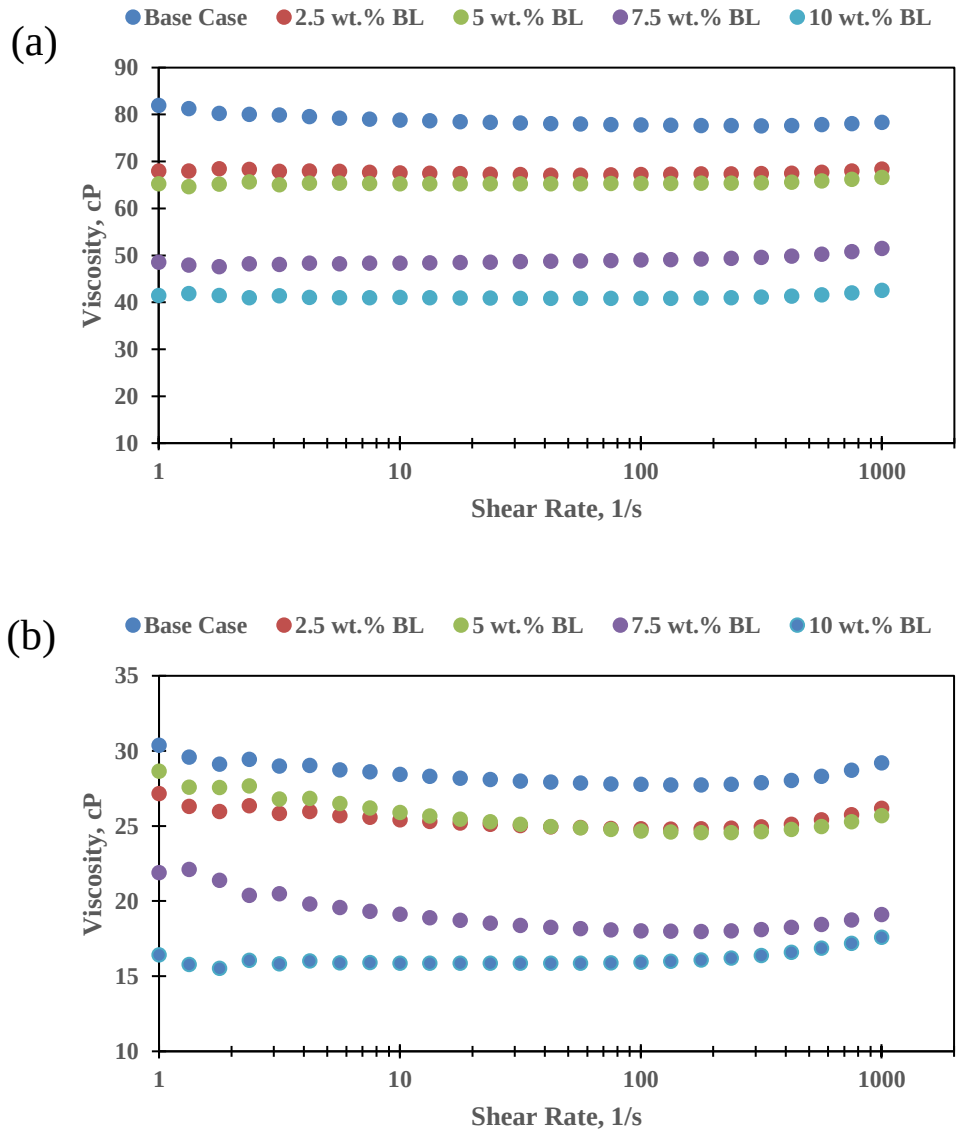


Figure 27 Viscosity measurement at different shear rates and at (a) 25 and (b) 50°C.

Viscosity measurements at the previously specified conditions are presented in **Figure 27** At temperature of 25°C crude oil viscosity is 80 cP, while at 2.5,5,7.5, and 10 wt.% of BL the values of viscosity were 67, 65.4, 48.7, and 40.1 cP, respectively. These reductions in viscosity values can be described in percentages of 16.25, 18.25, 39.1, and 49.8%, respectively. A clear trend of viscosity reduction with increasing the concentration of BL with approximate reduction at 2.5 and 5 wt.%. In the other hand at temperature of 50°C crude oil viscosity is 29.2 cP, while at 2.5,5,7.5, and 10 wt.% of BL the values of viscosity were 26.2, 25.7, 18.7, and 16 cP, respectively. These reductions in viscosity values can be described in percentages of 10.4, 12, 35.8, and 44.9 %, respectively. A clear trend of viscosity reduction with increasing the concentration of BL with approximate reduction at 2.5 and 5 wt.%.

It can be inferred from the values obtained that the maximum reduction is obtained at highest concentration. However, that's not the case for optimum concentration. In order to choose the optimum concentration, it should preserve the maximum reduction with the use of minimum BL concentration. As a consequence of that, the optimum reduction in oil viscosity is achieved at 7.5 wt.% BL, due to the shift in reduction values at both temperature sets. Also, the difference in reduction between 7.5 and 10 wt.% can be considered as minor. From the outcomes of the viscosity measurements, it can be inferred that NIS are not sufficient to reduce the viscosity of crude 3, despite the use of higher concentrations of NIS. This behavior can be attributed to the presence of lemon oil and water in the micro-emulsion (ME), indeed while we are using ME viscosity of the crude will increase. For that the use of BL to reduce both viscosity of the crude along with the MMP in CO_2-oil system. BL can be identified as a viscosity reducer.

5.2 SARA analysis and TAN

Determining the components of the five Saudi crudes into saturate, aromatic, resin, and asphaltene (SARA analysis), along with knowing of total acid number (TAN) is crucial, to have a comprehensive understanding of the behavior of these crudes with addition of different chemicals with different of concentrations. For a start the results of SARA analysis for the five Saudi crudes are presented in Table 10.

Table 10 SARA analysis of the five Saudi crudes utilized in this study.

	Saturate, %	Aromatic, %	Resin, %	Asphaltene, %
Crude 1	22.86	64.56	6.17	6.41
Crude 2	18.17	50.69	20.98	10.17
Crude 3	18.69	50.66	12.6	18.05
Crude 4	8.27	43.1	22.4	26.27
Crude 5	3.79	45.1	15.1	35.96

SARA analysis is preformed to magnify the asphaltene stability index (CII), as a result judge the efficiency of BL with different concentrations to reduce or increase CII. [77] proposed CII from the composition of crude obtained by SARA analysis. CII is calculated by dividing the summation of saturates and asphaltene fractions to the summation of aromatics and resins. Severe precipitation of asphaltene can be recognized when the CII exceeds a critical value of 0.9 [78].

Table 11 Comparison of SARA analysis of the base case and crudes of different concentrations of BL.

	Saturate, %	Aromatic, %	Resin, %	Asphaltene, %
Crude 3	18.69	50.66	12.6	18.05
2.5 % BL	14.64	49.36	22.62	13.38
5 % BL	14.92	49.40	22.32	13.36
7.5 % BL	14.51	49.79	14.48	21.22
10 % BL	14.43	49.78	15.02	20.77

When it comes to interactions between BL with asphaltene and resin, it's important to understand the nature of these components and how they interact with solvents. Asphaltene and resin are complex, high molecular weight compounds found in crude oil [79]. The interactions between BL and asphaltenes can involve physical dispersion, hydrogen bonding, and Van Der Waals forces [80]. The polar nature of BL allows it to form hydrogen bonds with polar functional groups present in asphaltene, such as oxygen, nitrogen, and sulfur, this can lead to the partial dissolution of asphaltenes in BL. When it comes to resin, BL can have a better solvency due to its polarity. The polar functional groups in resin, such as hydroxyl and carboxyl groups, can form hydrogen bonds with BL, facilitating their dissolution.

It is important to note that the interactions between BL with asphaltene and resin are complex and can vary depending on the specific properties of the crude oil and the experimental conditions. Therefore, a thorough understanding of the composition and behavior of the crude oil system is crucial for studying these interactions effectively. The

hydroxyl group in BL plays a crucial role in the interaction with resin and asphaltene which are recognized as the polar components that exists in crude oil composition.

The composition of the crude 3 along with the crudes of different concentrations of BL were investigated. **Table 11** shows the SARA analysis of the utilized crude oil along with crudes of different concentrations of BL. At lower concentrations of BL, a sharp reduction of asphaltene content is observed, this reduction is followed up with an increase in resin content. This behavior will result in lower CII, as a result less asphaltene precipitation is achieved in concentrations of 2.5, and 5 % of BL. However, that's not the case with higher BL concentrations. An increment of asphaltene content is observed which will lead to higher values of CII, which implies that more precipitation of asphaltene is likely to happen. **Table 12** illustrates the values of CII for the crude oil as a base case, along with different concentrations of BL. The lower concentration of BL results in the lowest value of CII when compared to other cases. Clear indication that lower concentration resulted in better performance in terms of asphaltene precipitation and vice versa for higher concentrations. It can be inferred that the optimum concentration is the one resulting in maximum reduction which is 2.5 wt.% of BL.

Table 12 Asphaltene precipitation index for crude 3 and different concentrations of BL.

	Crude 3	**2.5 % BL**	**5 % BL**	**7.5 % BL**	**10 % BL**
CII	0.581	0.389	0.394	0.556	0.543

5.3 Screening Results using VIT.

Properties of the five Saudi crudes are shown in **Figure 28.** The properties are asphaltene content, TAN, and density. Diversity can be inferred from the properties of these crudes. To start doing the screening a crude is selected to examine the effect of chemicals and different concentrations. The median crude is taken to do so, due to the average values of asphaltene content, TAN, and crude oil density. This crude is crude 3.

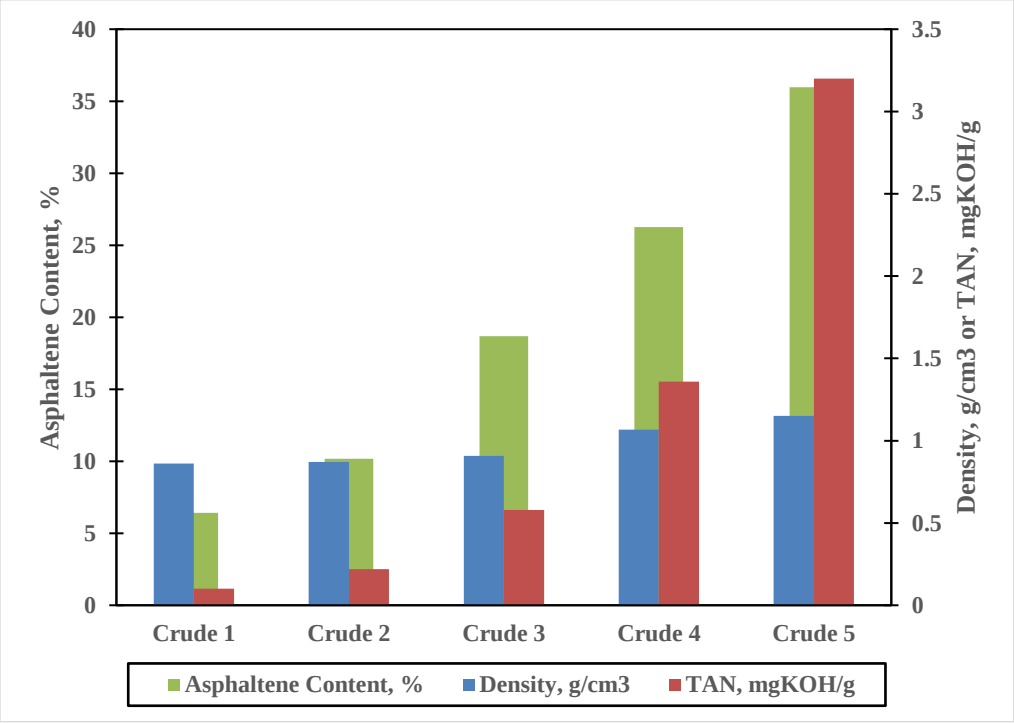


Figure 28 Properties of the five Saudi Crudes.

5.3.1 NIS and NPs, MMP and FCMP Results

As a start we introduced two concentrations of NIS, which are 0.6 and 0.75 wt.%. The MMP and FCMP values are taken for the CO_2-crude 3 system as a reference case. After

the addition of 0.6 and 0.75 wt.% of NIS, MMP and FCMP were determined. Reduction in MMP and FCMP is recorded as percentiles when compared to base case. These values are taken at 50° C and are shown in **Figure 29** and **Table 13**.

Table 13 MMP and FCMP values of crude 3, 0.6, and 0.75 wt.% of NIS at 50° C.

Crude type	MMP, psi	Reduction, %	FCMP, psi	Reduction, %
Crude 3	1785	-	2584.3	-
Crude 3 + 0.6 NIS	1617.5	9.38	2532.4	2
Crude 3 + 0.75 NIS	1460.8	18.16	2253.4	12.8

A clear reduction in the values of MMP and FCMP these are reported in the table earlier. This conclusion allies with what is found in literature. However, when it comes to the effect of NIS which is dispersed in ME on crude 3 viscosity, as reported earlier more NIS resulted on the viscosity increment of crude 3. For that we moved on to examine the effect of NIS with hydrophilic silica nanoparticles (NPs) on either the reduction or increment of MMP and FCMP. However, negative impact of NPs with 0.6 NIS on the value of MMP where it increased up to 2229.84 psi, which indicates an increment of 24.9 %. This combination of NIS and NPs resulted in an increment of MMP, which is not recommended in the petroleum industry.

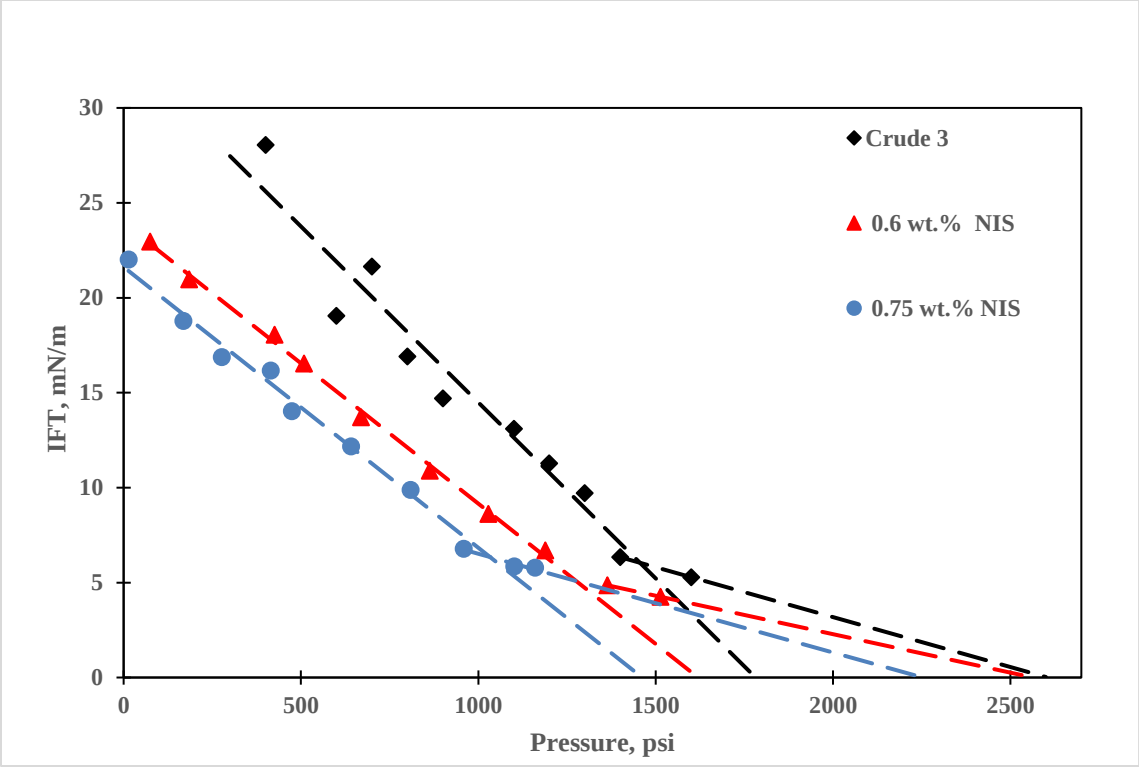


Figure 29 MMP and FCMP values of crude 3, 0.6, and 0.75 wt.% of NIS at 50° C.

The obtained results are not sufficient in preforming reduction in the viscosity of crude oil, MMP, and FCMP in CO_2-crude 3 system. So, the behavior of BL on crude 3 viscosity, MMP, and FCMP with different concentrations of BL.

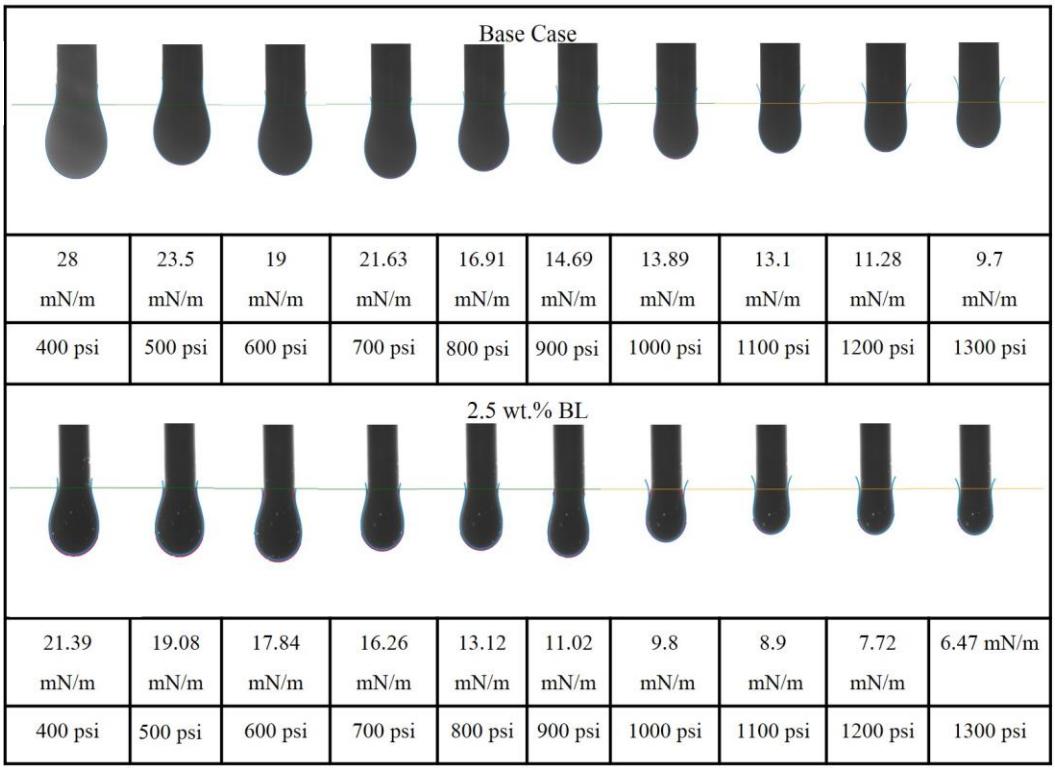
5.3.2 BL MMP and FCMP Results

Interfacial tension between the immiscible fluids (oil and CO_2) measurement at 50°C and different pressures were preformed utilizing drop shape analyzer manufactured by KRÜSS (DSA 100 HP). The experiment were performed on crude 3 and CO_2 as a reference for this study. The experiment is repeated frequently with different concentrations of viscosity reducer BL. Each concentration represents a single case at which MMP and FCMP were

conducted by the interpolation of the measured IFT values vs pressure. MMP and FCMP values were estimated for each case, individually and comparison with the base case along with other cases is performed.

MMP of different Saudi crude oils have been determined by [55] utilizing slim tube experiment (STE). They reported that MMP increase with the increment of temperature value. IFT values of the base case along with the four different concentrations of BL at pressures ranging from 400 up to 1300 psi are shown, individually. **Figure 30** (a) shows the IFT values for the CO_2-oil system for base case and 2.5 wt.% BL. Significant reduction is observed in IFT values when compared with the base case. This reduction will be significant when it comes to estimation of MMP and FCMP values for these cases as shown in **Figure 30** (b). By extrapolation of the IFT values until reaching the zero IFT value, MMP and FCMP for the base case are 1785 and 2584.3 psi, respectively. While MMP and FCMP for 2.5 wt.% BL are 1543.5 and 1824.3 psi, respectively. Clear reduction can be inferred, this reduction can be described in percentage as 12.33 % in MMP and 29.4 % in FCMP.

(a)



(b)

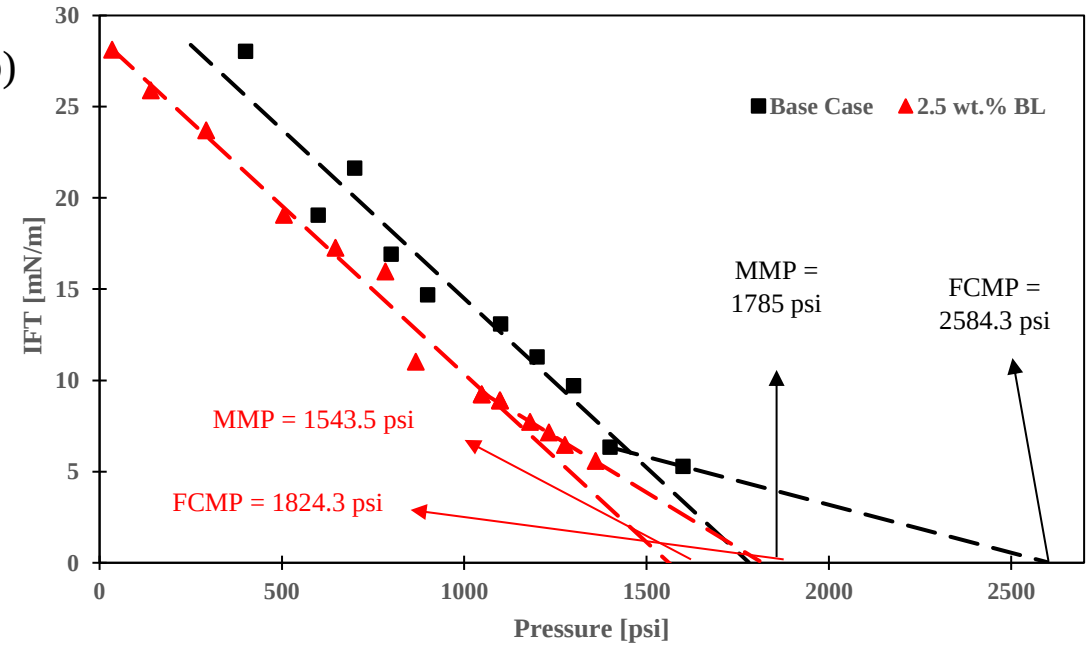
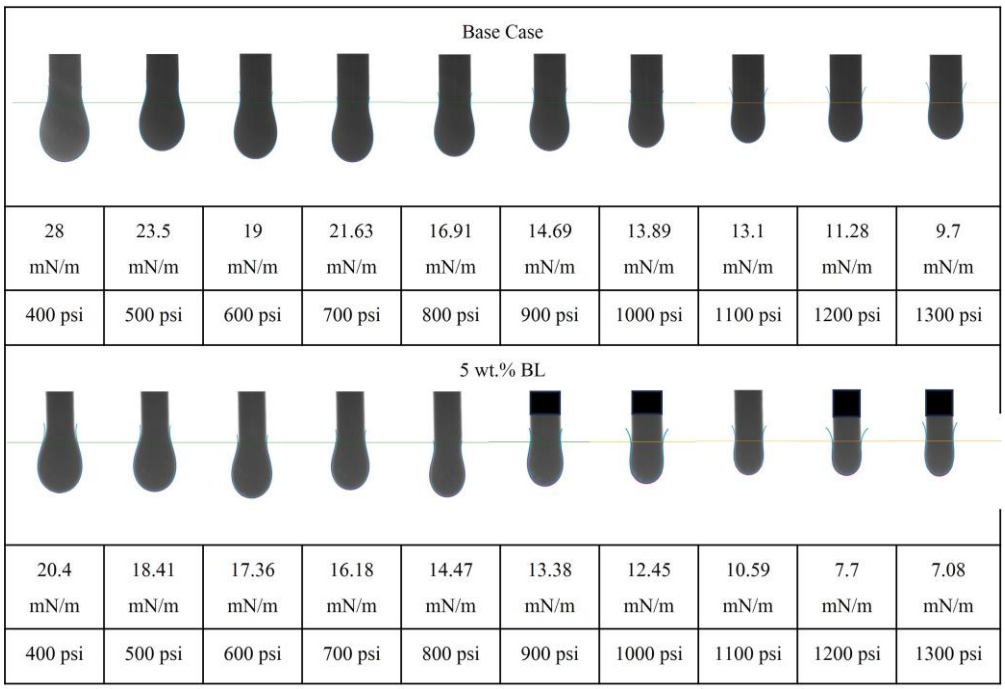


Figure 30 (a) Drops shape along with IFT values at different pressures for the base case and 2.5 wt. % BL. (b) MMP and FCMP values for the base case and 2.5 wt.% BL.

Figure 31 (a) shows the IFT values for the CO_2-oil system for base case and 5 wt.% BL. Significant reduction is observed in IFT values when compared with the base case. This reduction will be significant when it comes to estimation of MMP and FCMP values for these cases as shown in **Figure 31** (b). By extrapolation of the IFT values until reaching the zero IFT value, MMP and FCMP for the base case are 1785 and 2584.3 psi, respectively. While MMP and FCMP for 5 wt.% BL are 1672.5 and 2134.1 psi, respectively. Clear reduction can be inferred, this reduction can be described in percentage as 6.3 % in MMP and 17.4 % in FCMP.

(a)



28 mN/m	23.5 mN/m	19 mN/m	21.63 mN/m	16.91 mN/m	14.69 mN/m	13.89 mN/m	13.1 mN/m	11.28 mN/m	9.7 mN/m
400 psi	500 psi	600 psi	700 psi	800 psi	900 psi	1000 psi	1100 psi	1200 psi	1300 psi

20.4 mN/m	18.41 mN/m	17.36 mN/m	16.18 mN/m	14.47 mN/m	13.38 mN/m	12.45 mN/m	10.59 mN/m	7.7 mN/m	7.08 mN/m
400 psi	500 psi	600 psi	700 psi	800 psi	900 psi	1000 psi	1100 psi	1200 psi	1300 psi

(b)

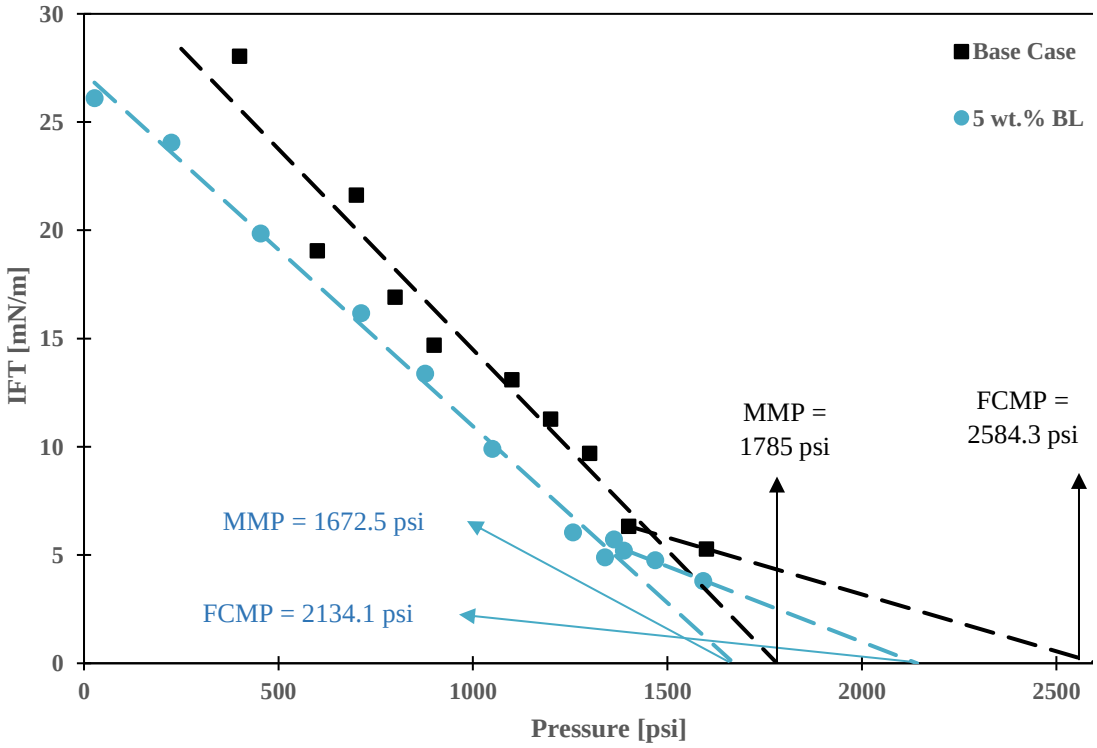
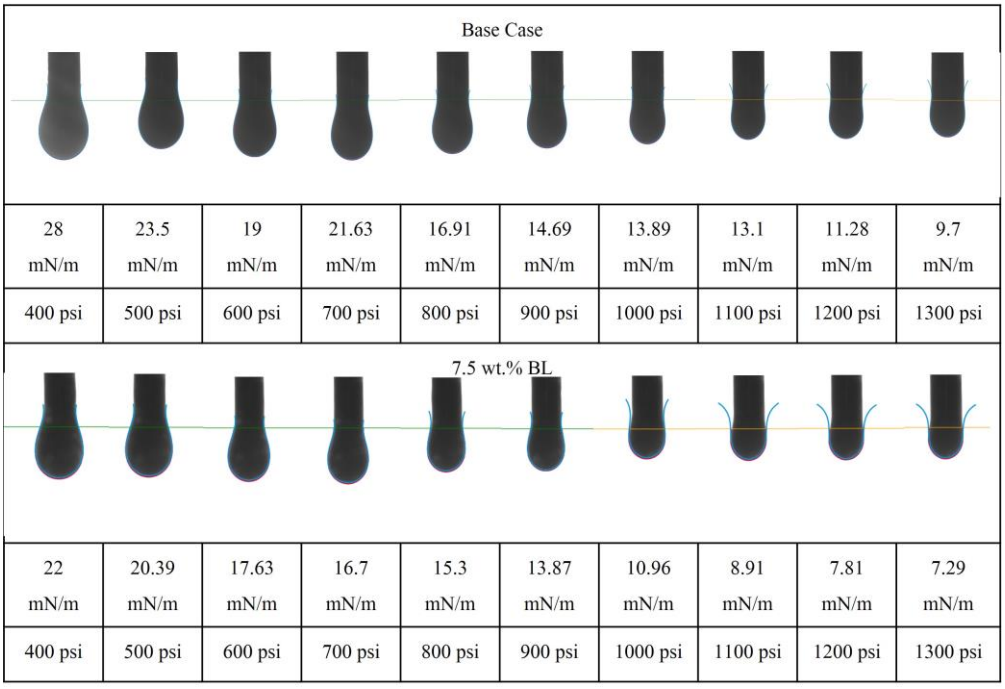


Figure 31 (a) Drops shape along with IFT values at different pressures for the base case and 5 wt. % BL. (b) MMP and FCMP values for the base case and 5 wt.% BL.

Figure 32 (a) shows the IFT values for the CO_2-oil system for base case and 7.5 wt.% BL. Significant reduction is observed in IFT values when compared with the base case. This reduction will be significant when it comes to estimation of MMP and FCMP values for these cases as shown in **Figure 32** (b). By extrapolation of the IFT values until reaching the zero IFT value, MMP and FCMP for the base case are 1785 and 2584.3 psi, respectively. While MMP and FCMP for 5 wt.% BL are 1638 and 2394 psi, respectively. Clear reduction can be inferred, this reduction can be described in percentage as 8.24 % in MMP and 6.67 % in FCMP.

(a)



28 mN/m	23.5 mN/m	19 mN/m	21.63 mN/m	16.91 mN/m	14.69 mN/m	13.89 mN/m	13.1 mN/m	11.28 mN/m	9.7 mN/m
400 psi	500 psi	600 psi	700 psi	800 psi	900 psi	1000 psi	1100 psi	1200 psi	1300 psi

22 mN/m	20.39 mN/m	17.63 mN/m	16.7 mN/m	15.3 mN/m	13.87 mN/m	10.96 mN/m	8.91 mN/m	7.81 mN/m	7.29 mN/m
400 psi	500 psi	600 psi	700 psi	800 psi	900 psi	1000 psi	1100 psi	1200 psi	1300 psi

(b)

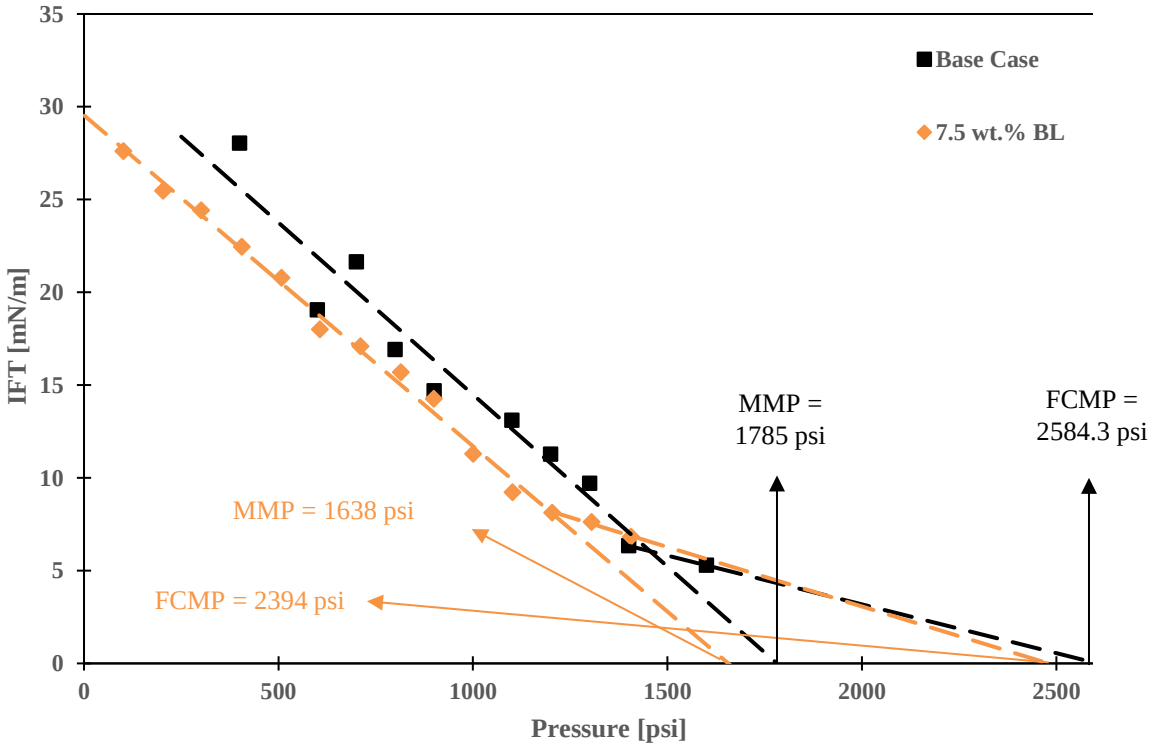
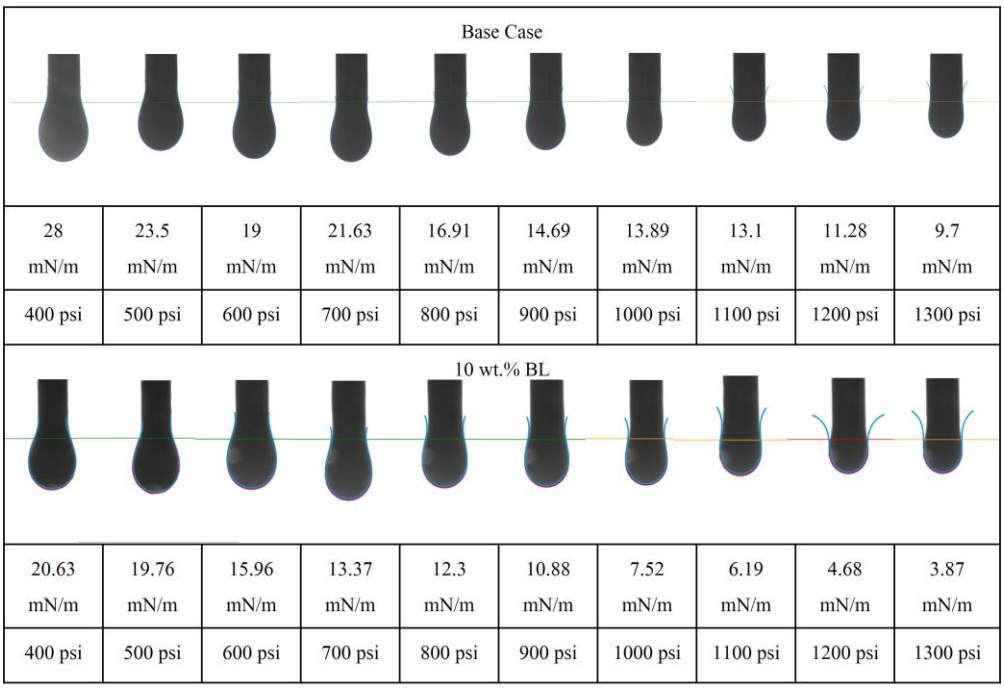


Figure 32 (a) Drops shape along with IFT values at different pressures for the base case and 7.5 wt. % BL. (b) MMP and FCMP values for the base case and 7.5 wt.% BL.

Figure 33 (a) shows the IFT values for the CO_2-oil system for base case and 7.5 wt.% BL. Significant reduction is observed in IFT values when compared with the base case. This reduction will be significant when it comes to estimation of MMP and FCMP values for these cases as shown in **Figure 33** (b). By extrapolation of the IFT values until reaching the zero IFT value, MMP and FCMP for the base case are 1785 and 2584.3 psi, respectively. While MMP and FCMP for 5 wt.% BL are 1353.3 and 1945.3 psi, respectively. Clear reduction can be inferred, this reduction can be described in percentage as 24.2 % in MMP and 24.7 % in FCMP.

(a)



28 mN/m	23.5 mN/m	19 mN/m	21.63 mN/m	16.91 mN/m	14.69 mN/m	13.89 mN/m	13.1 mN/m	11.28 mN/m	9.7 mN/m
400 psi	500 psi	600 psi	700 psi	800 psi	900 psi	1000 psi	1100 psi	1200 psi	1300 psi

20.63 mN/m	19.76 mN/m	15.96 mN/m	13.37 mN/m	12.3 mN/m	10.88 mN/m	7.52 mN/m	6.19 mN/m	4.68 mN/m	3.87 mN/m
400 psi	500 psi	600 psi	700 psi	800 psi	900 psi	1000 psi	1100 psi	1200 psi	1300 psi

(b)

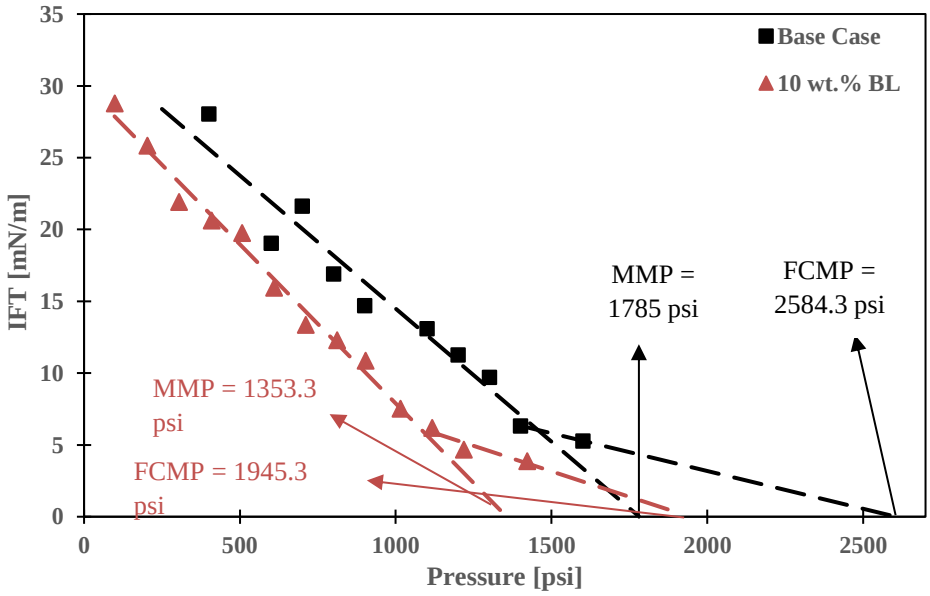


Figure 33 (a) Drops shape along with IFT values at different pressures for the base case and 10 wt. % BL. (b) MMP and FCMP values for the base case and 10 wt.% BL.

The results of using BL of different concentrations along with the reductions in the values of MMP and FCMP are shown in **Table 14**.

Table 14 Values of MMP and FCMP of crude 3 and different concentrations of BL.

Crude type	MMP, psi	Reduction, %	FCMP, psi	Reduction, %
Crude 3	1784.5	-	2584.34	-
2.5 % BL	1543.5	13.5	1824.3	29.4
5 % BL	1672.5	6.3	2134.1	17.42
7.5 % BL	1638	8.23	2394	7.36
10 % BL	1353.3	24.18	1945.9	24.7

In this study the VIT is used to determine the MMP and FCMP with different concentrations of viscosity reducer to determine the optimum concentration. This concentration shall function optimum reduction of MMP and viscosity along. This concentration shall result in improving the efficiency of CO_2 flooding and increase the recovery factor. For each individual case a clear reduction of IFT with increasing the pressure. However, the reduction of IFT is highly observed with increasing the viscosity reducer concentration. This behavior is recognized until reaching the concentration of 7.5 wt.% of BL. At this concentration the IFT start to increase slightly for this particular case. The reduction trend of IFT continuous as an increase in concentration to 10 wt.% of BL.

The obtained IFT values are plotted versus pressure, and the extrapolation of these trendlines is performed to estimate MMP and FCMP. This process have been repeated for each case which are base case, 2.5, 5, 7.5, and 10 wt.% of BL. The case in which MMP is

minimum is recognized as the optimum concentration required for a CO_2-EOR. It can be inferred that maximum reduction of MMP and FCMP are obtained by utilization of 10 wt.% of viscosity reducer. In the other hand minimum reduction of MMP and FCMP are obtained by the utilization of 5 and 7.5 wt.% of viscosity reducer. While 2.5 wt.% of viscosity reducer attained the optimum reduction in MMP. In this study we are aiming to use a viscosity reducer to improve CO_2 miscibility in crude oil and choose the optimum concentration of viscosity reducer to improve CO_2-EOR.

Optimum Concentration to Reduce Oil Viscosity and MMP in CO_2-Oil System using BL.

Optimum concentration should preserve the usage of minimum concentration of viscosity reducer. This concentration shall be sufficient to give preferable effect on the reduction of both crude oil viscosity and MMP in CO_2-oil system. Moreover, the effect of that concentration on crude oil composition to be preferable, which is recognized in this study by ensuring minimum CII. Determining the optimum concentration depend on MMP values along with viscosity values which are shown in **Figure 34**, also the value of asphaltene stability index. Depending on the crude oil characteristic optimum concentration is estimated.

When it comes to CII, different behaviors are observed with each concentration. Generally lower concentrations (2.5 and 5 wt.% BL) reduced the CII by reduction of both asphaltene and saturates content, moreover, increasing aromatic, and resins content. This reduction is preferable when compared to the original CII. However, in higher concentrations (7.5 and 10 wt.% BL) opposite behavior is recognized by increment of asphaltene content which

will eventually results in higher values of CII. As a result of that more asphaltene precipitation is anticipated with higher concentrations.

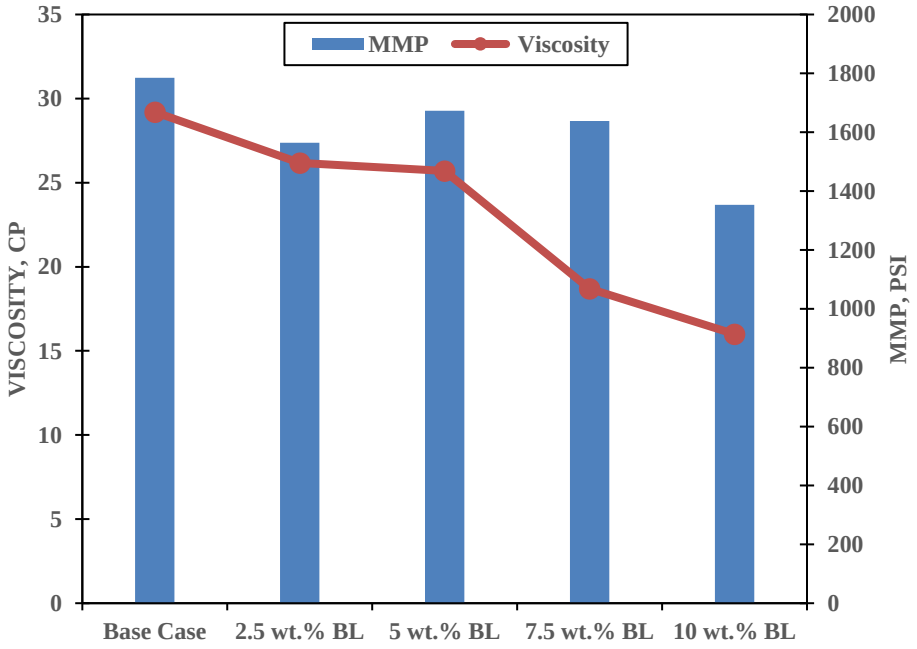


Figure 34 MMP values and viscosity values for each case at 50° C.

In terms of viscosity, it keeps decreasing with increasing the concentration of BL, while MMP gives maximum reduction at a concentration of 10 wt.% of BL. MMP value decreases with decreasing concentration to 5 wt.% of BL. Furthermore, decreasing the concentration to 2.5 wt.% of BL will reduce the MMP when compared to 5 wt.% of BL. Figure 35 shows the MMP values along with the FCMP values versus viscosity for each case at 50° C. From the previous observations it can be inferred that the optimum concentration that would result in optimum reduction of oil viscosity, asphaltene precipitation index, and improve CO_2 miscibility in crude oil depends on crude oil characteristics. For example, if the oil being dealt with is heavy and viscous, the optimum

concentration is 10 wt.% of BL. In the other hand if the oil being dealt with is not very viscous, the optimum concentration is 2.5 wt.% of BL. In conclusion the optimum concentration for the crude used in this study is 2.5 wt.% of BL based on the achieved reduction on MMP, CII, and viscosity of crude oil.

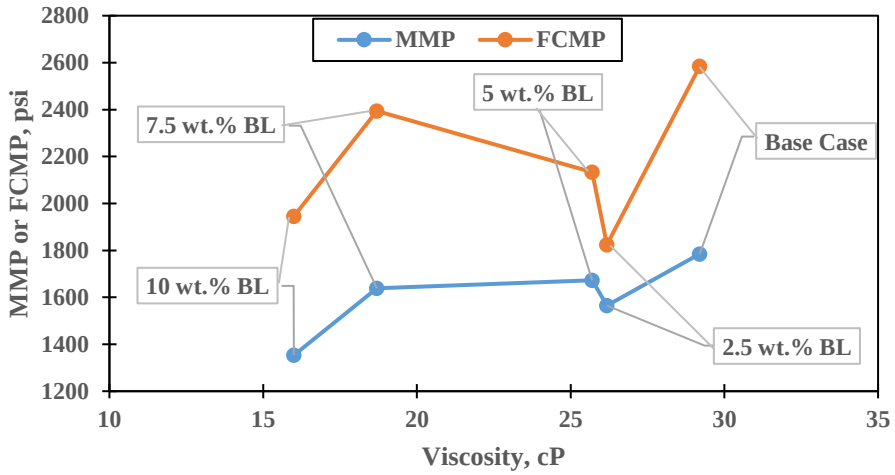


Figure 35 MMP values and FCMP values versus viscosity for each case at 50° C.

5.3.3 XY and DL, MMP and FCMP Results

To further examine, aromatic liquid (XY) and aliphatic hydrocarbon liquid (DL), effect on MMP value were investigated. Two concentrations of each chemical were considered. These concentrations are 1 and 10 wt.% of each. The values of MMP and FCMP after the addition of the previously specified concentrations are compared with the values of CO_2-crude 3 oil system.

Addition of 10 wt.% of XY achieved a significant impact on the reduction of MMP and FCMP **Figure 36**. The values are as follows 1450.4 and 1772.2 psi, respectively. These values can be presented as percentages as 18.74 and 31.42, respectively. However, the addition of 10 wt.% of DL resulted in more reduction in terms of MMP values and approximate values in terms of FCMP. The values are as follows 1421.8 and 1826.51 psi, respectively. These values can be presented as percentages as 20.34 and 29.32, respectively.

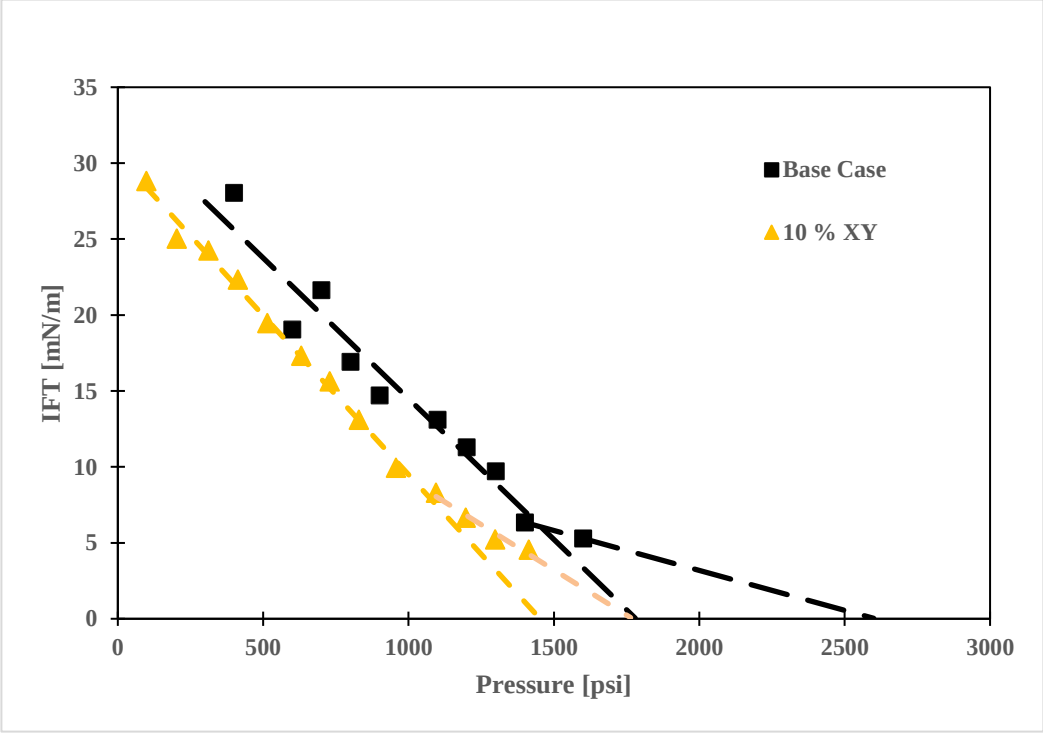
Addition of 1 wt.% of XY achieved a significant impact on the reduction of MMP and FCMP **Figure 37**. The values are as follows 1563.74 and 2249.66 psi, respectively. These values can be presented as percentages as 12.39 and 12.95, respectively. Moreover, the addition of 1 wt.% of DL resulted in an approximate reduction in terms of MMP values and much more reduction values in terms of FCMP. The values are as follows 1572.15 and 1701.84 psi, respectively. These values can be presented as percentages as 11.92 and 34.14, respectively.

A summary of the impact of the addition of XY and DL into CO_2-crude 3 oil system is illustrated in table 17.

Table 15 MMP and FCMP for 1 and 10 wt.% of XY and DL compared to the base case.

Crude type	MMP, psi	Reduction, %	FCMP, psi	Reduction, %
Crude 3	1784.5	-	2584.34	-
10 % XY	1450.42	18.74	1772.27	31.42
10 % DL	1421.8	20.34	1826.51	29.32
1 % XY	1563.74	12.39	2249.66	12.95
1 % DL	1572.15	11.92	1701.84	34.14

(a)



(b)

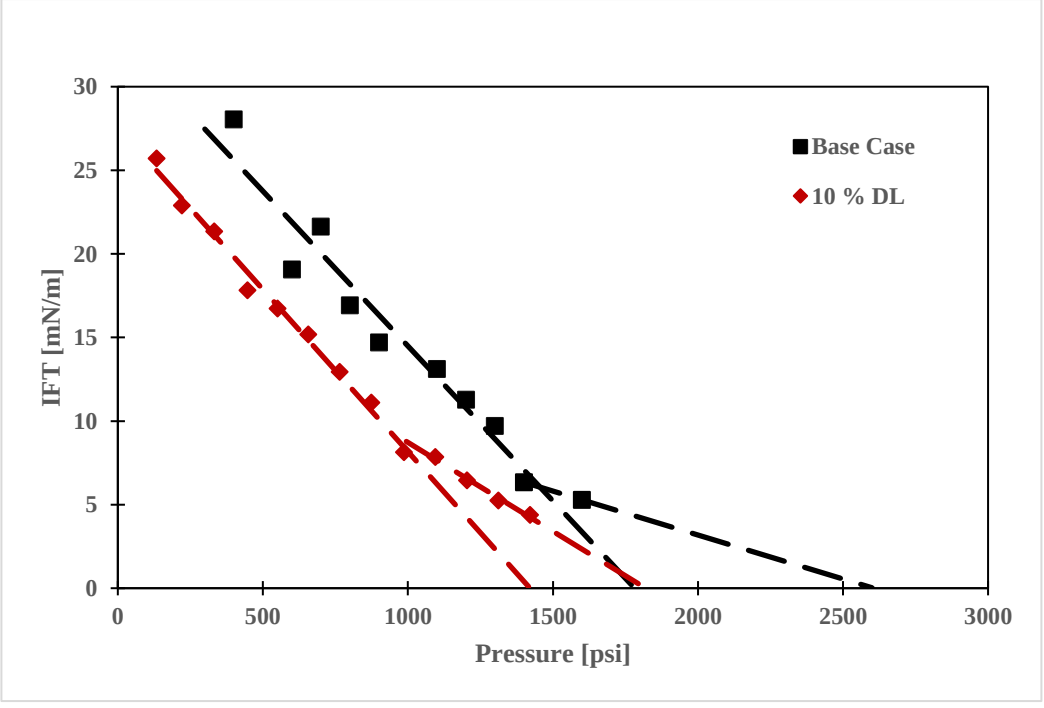
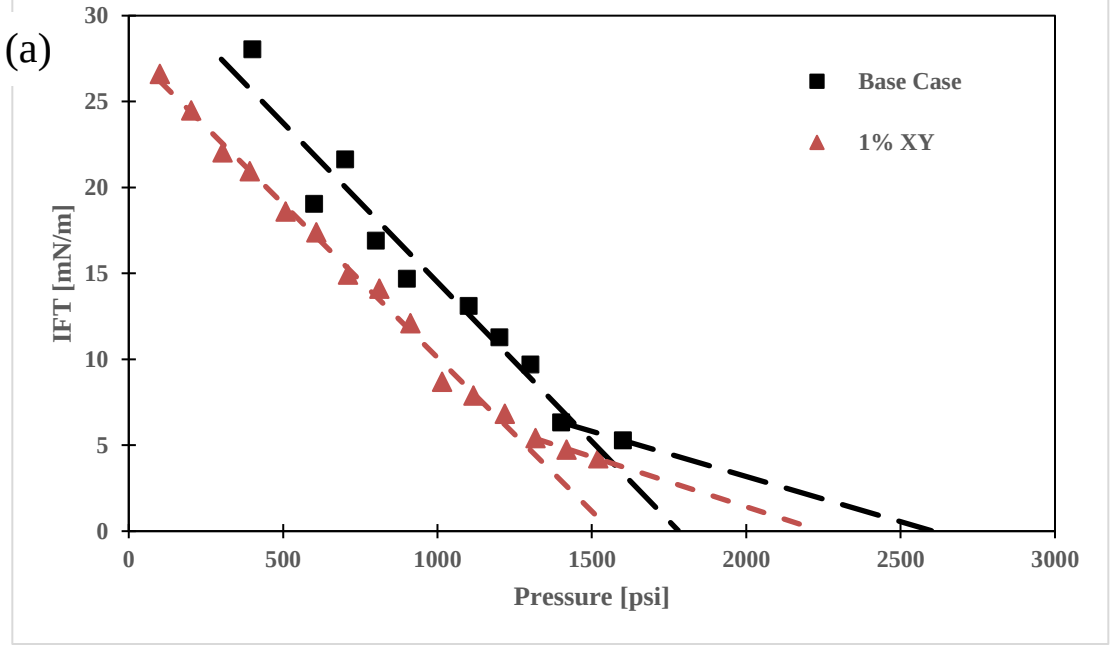


Figure 36 MMP and FCMP for 10 wt.% of (a) XY and (b) DL compared to the base case (crude 3).



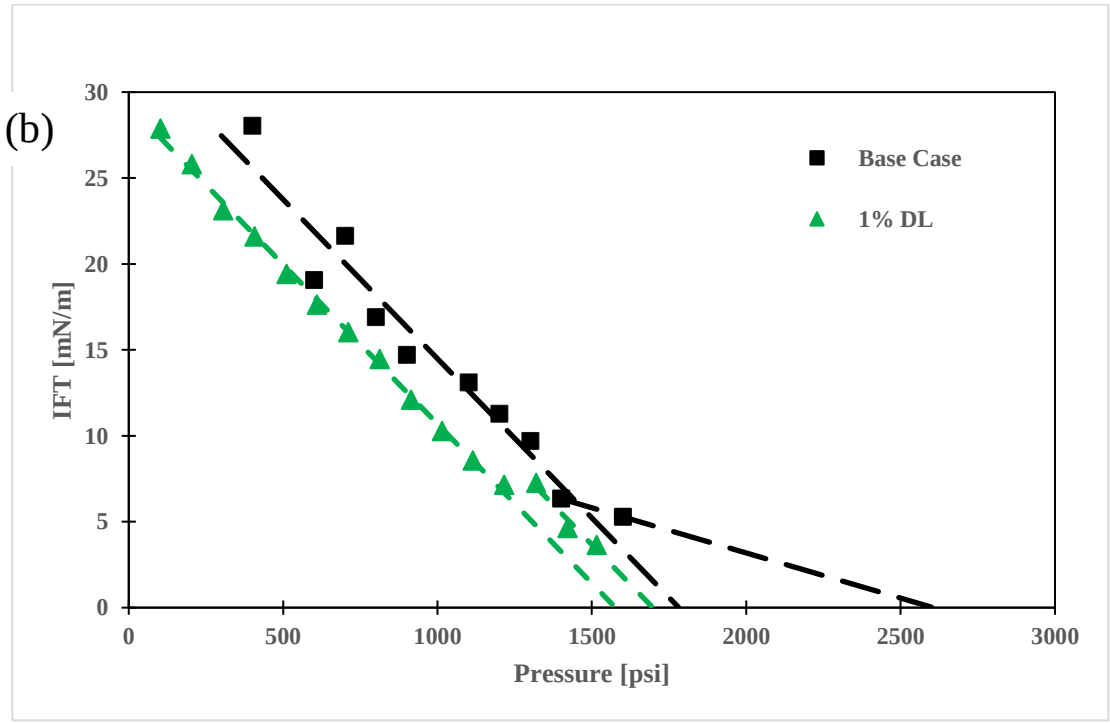


Figure 37 MMP and FCMP for 1 wt.% of (a) XY and (b) DL compared to the base case (crude 3).

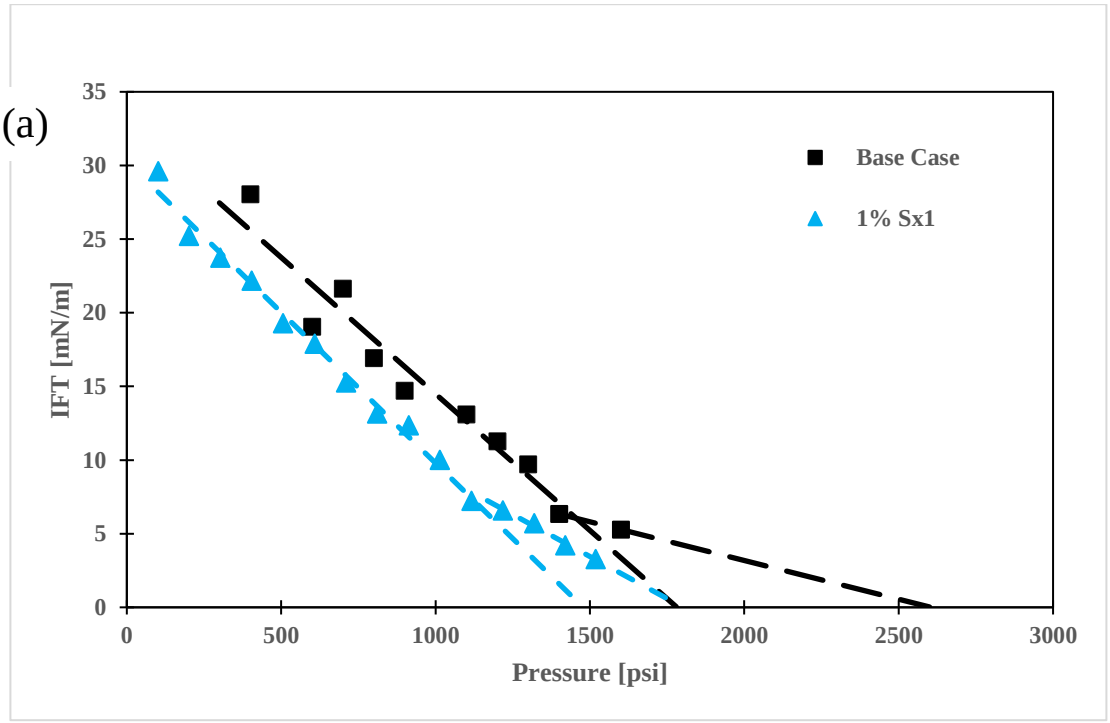
5.3.4 Sx1 and Sx4, MMP and FCMP Results

For further examination, ionic liquids (green chemicals) were investigated. Two chemicals are used, which are 1-methyl-3-octylimidazolium chloride (Sx1) and 1-decyl-3-methylimidazolium chloride (Sx4). The effect of these chemicals on MMP value were examined. Two concentrations of each chemical were considered. These concentrations are 0.1 and 1 wt.% of each. The values of MMP and FCMP after the addition of the previously specified concentrations are compared with the values of CO_2-crude 3 oil system.

Addition of 1 wt.% of Sx1 achieved a significant impact on the reduction of MMP and FCMP **Figure 38**. The values are as follows 1476.63 and 1805.26 psi, respectively. These values can be presented as percentages as 17.27 and 30.14, respectively. Moreover, the addition of 1 wt.% of Sx4 resulted in a lower reduction in terms of MMP values and higher reduction values in terms of FCMP. The values are as follows 1544.48 and 1741.4 psi, respectively. These values can be presented as percentages as 13.47 and 32.61, respectively.

Addition of 0.1 wt.% of Sx1 achieved a significant impact on the reduction of MMP and FCMP **Figure 39**. The values are as follows 1528.95 and 2200.6 psi, respectively. These values can be presented as percentages as 14.34 and 14.84, respectively. Moreover, the addition of 0.1 wt.% of Sx4 resulted in a lower reduction in terms of MMP values and much more reduction values in terms of FCMP. The values are as follows 1567.74 and

2017.72 psi, respectively. These values can be presented as percentages as 12.16 and 21.92, respectively.



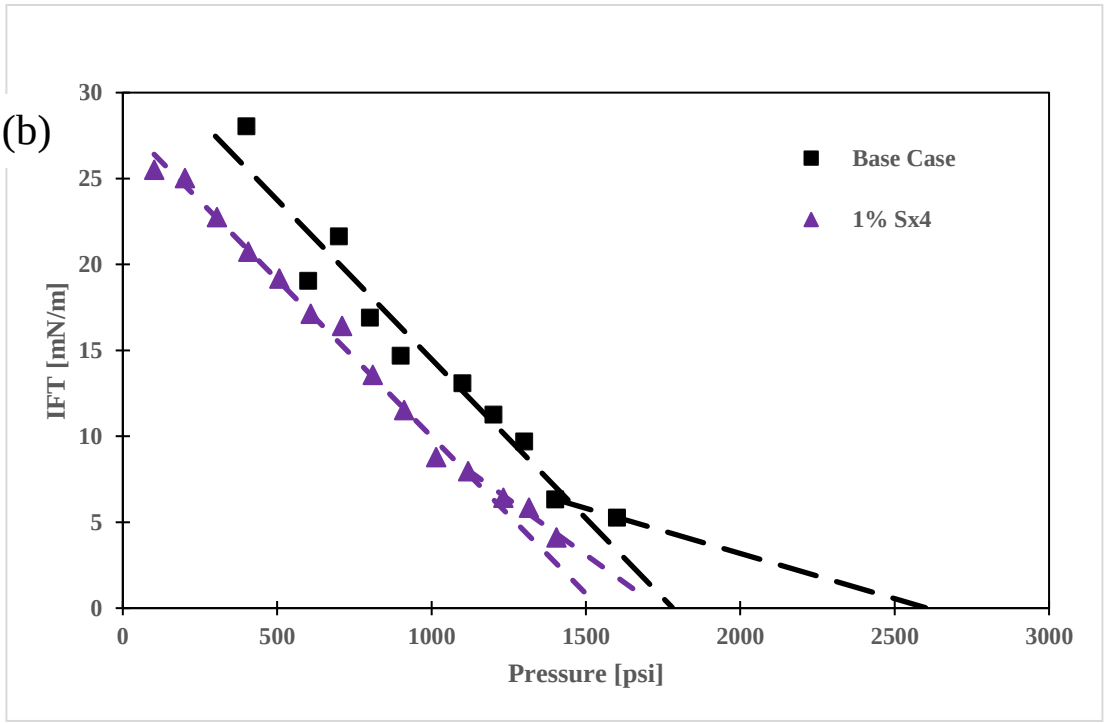


Figure 38 MMP and FCMP for 1 wt.% of (a) Sx1 and (b) Sx4 compared to the base case (crude 3).

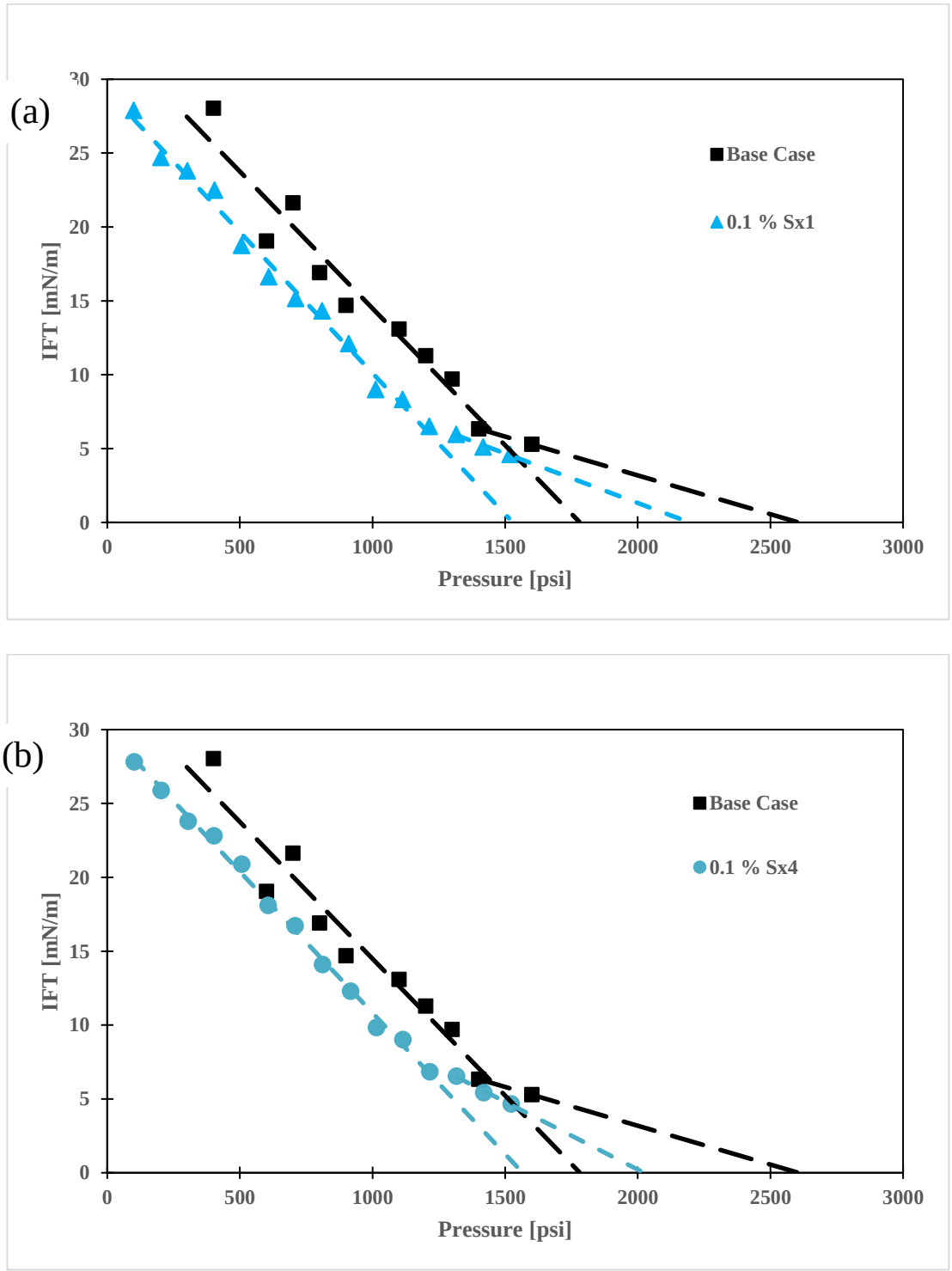


Figure 39 MMP and FCMP for 0.1 wt.% of (a) Sx1 and (b) Sx4 compared to the base case (crude 3).

A summary of the impact of the addition of Sx1 and Sx4 into CO_2-crude 3 oil system is illustrated in Table 16.

Table 16 MMP and FCMP for 0.1 and 1 wt.% of Sx1 and Sx4 compared to the base case.

Crude type	MMP, psi	Reduction, %	FCMP, psi	Reduction, %
Crude 3	1784.5	-	2584.34	-
1 % Sx1	1476.63	17.27	1805.26	30.14
1 % Sx4	1544.48	13.47	1741.4	32.61
0.1 % Sx1	1528.95	14.34	2200.6	14.84
0.1 % Sx4	1567.74	12.16	2017.72	21.92

5.4 Optimum concentration obtained from the screening.

After obtaining the screening on different types of chemicals on CO_2-crude oil 3 system with various concentrations. Most of the used chemicals implemented an impact on the reduction of MMP and FCMP. The results are reported as follows: testing the effect of NIS on CO_2-crude 3 system gave a good reduction, these results allies with the ones obtained in the literature. However, NIS is mixed with huge amount of lemon oil and water in mixture is ME. Introducing this chemical obtained an increment in terms of crude 3 viscosity.

NPs were tested in a combination with ME, value of MMP increased into a much higher values which is recognized as con and for that this mixture of ME and NPs is not recommended. Different chemicals are used with different concentrations. These chemicals and their subsequent effect on the reduction of MMP and FCMP are shown in

Figure 40. It can be inferred that the optimum chemicals and concentrations are ionic liquids with much lower concentrations than other chemicals used. When Sx1 and Sx4 are compared, it is observed that Sx1 resulted in a higher reduction in MMP values. By that we can conclude the screening process, by selecting Sx1 is to further examine on other crudes and proceed on obtaining the core flooding.

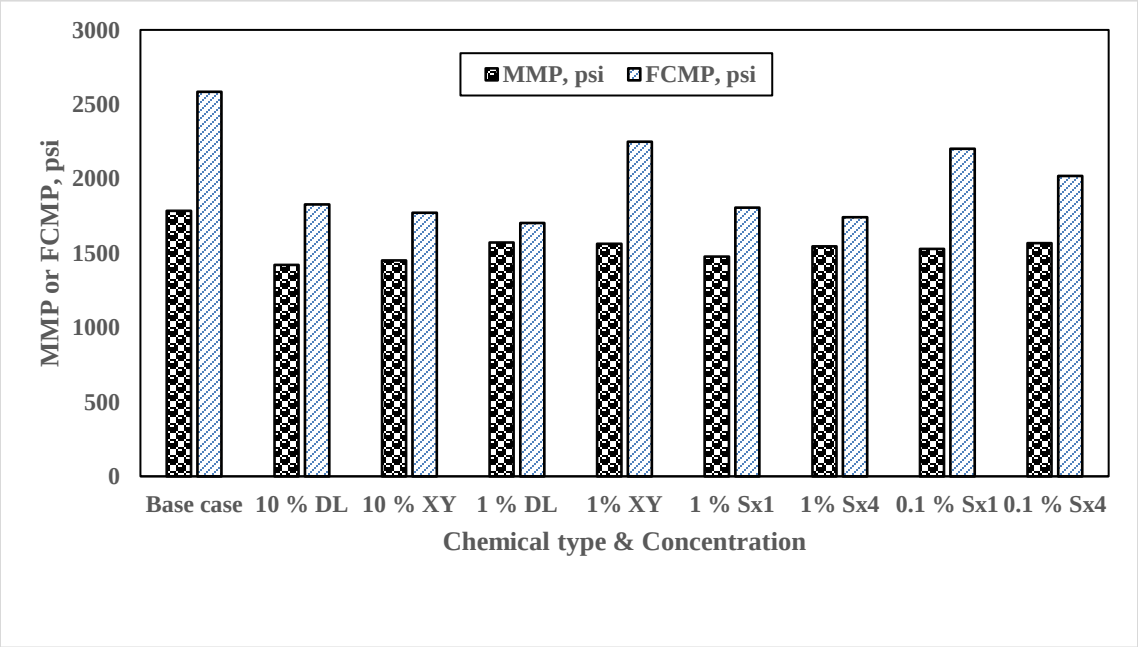


Figure 40 MMP and FCMP values of crude 3 and different chemicals and concentrations.

5.5 MMP and FCMP Results on Crude 1,2,4, and 5.

Sx1 proved that it is the optimum chemical by implementing the optimum reduction in MMP at the lowest concentration, when compared to other chemicals. That's why in this section an investigation is carried out to examine the effect of Sx1 on the remaining four crudes. The VIT were obtained at different temperatures of 50 and 90° C. In the screening

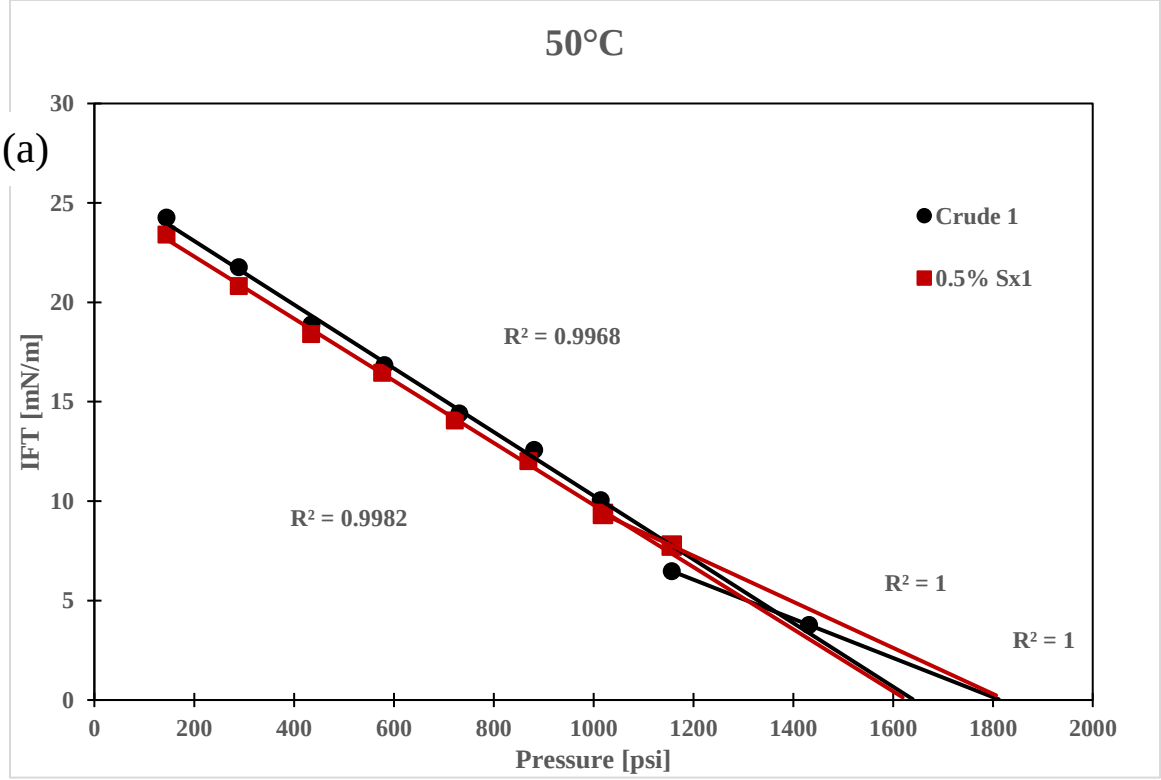
part two concentrations are investigated, which are 0.1 and 1 wt.% of Sx1. To further verify our conclusions, two concentrations were considered, which are 0.5 and 1 wt.% on the four crudes -CO_2 systems.

5.5.1 MMP and FCMP results of Sx1 in crude 1.

Crude1 is categorized as a light Saudi crude, due to its density and low asphaltene content. As a consequence, 0.5 wt.% of Sx1 were added to the crude and the results of MMP and FCMP at 50 and 90° C were estimated. As a start both MMP and FCMP are estimated at the previously specified conditions. The values at 50° C are as follows 1643.1 and 1823.7 psi, respectively. Moreover, the values at 90° C are as follows 2571.8 and 3513.9 psi, respectively.

Addition of 0.5 wt.% of Sx1 achieved a minor impact on the reduction of MMP and FCMP **Figure 41** at temperatures of 50 and 90° C. The values at 50° C are as follows 1630 and 1823.4 psi, respectively. These values can be presented as percentages as 0.8 and 0, respectively. Moreover, the addition of 0.5 wt.% of Sx1 at 90° C resulted in a more reduction in terms of MMP and FCMP values. The values are as follows 2523.8 and 3400 psi, respectively. These values can be presented as percentages as 1.9 and 3.2, respectively.

This reduction is minor and recommended to be implemented in the industry. However, it can be inferred that Sx1 performs better at higher temperatures.



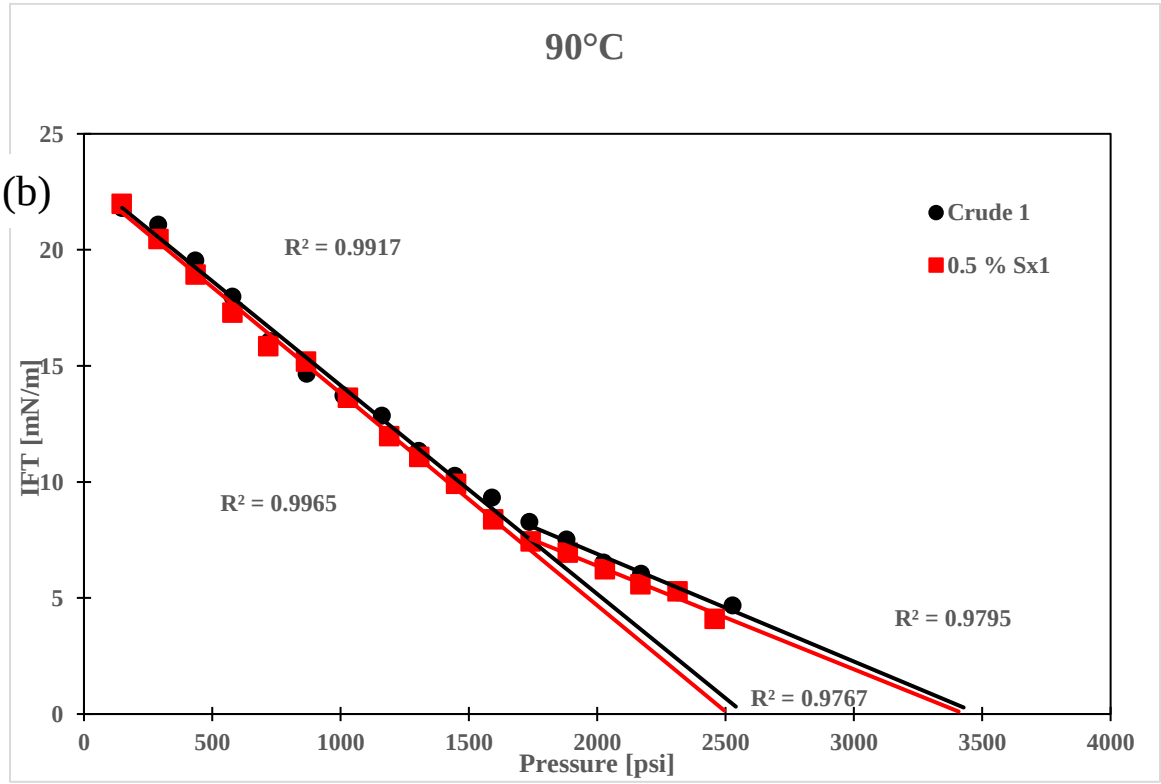


Figure 41 MMP and FCMP for crude 1 and 0.5 wt.% of Sx1 at (a) 50 and (b) 90°C.

5.5.2 MMP and FCMP results of Sx1 in crude 2.

Crude 2 is categorized as a medium Saudi crude, due to its density and moderate asphaltene content. As a consequence, 0.5 wt.% of Sx1 were added to the crude and the results of MMP and FCMP at 50 and 90° C were estimated. As a start both MMP and FCMP are estimated at the previously specified conditions. The values at 50° C are as follows 1762.8 and 2004.4 psi, respectively. Moreover, the values at 90° C are as follows 2477.5 and 2973.5 psi, respectively.

Addition of 0.5 wt.% of Sx1 achieved a minor impact on the reduction of MMP and FCMP **Figure 42** at temperatures of 50 and 90° C. The values at 50° C are as follows 1609.4 and 1869.4 psi, respectively. These values can be presented as percentages as 8.7 and 6.7, respectively. However, the addition of 0.5 wt.% of Sx1 at 90° C resulted in a minor reduction in terms of MMP and more reduction in terms of FCMP values. The values are as follows 2443.1 and 2674.9 psi, respectively. These values can be presented as percentages as 1.4 and 10.04, respectively. This reduction is minor and recommended to be implemented in the industry. However, it can be inferred that Sx1 performs better at higher temperatures in lowering the FCMP.

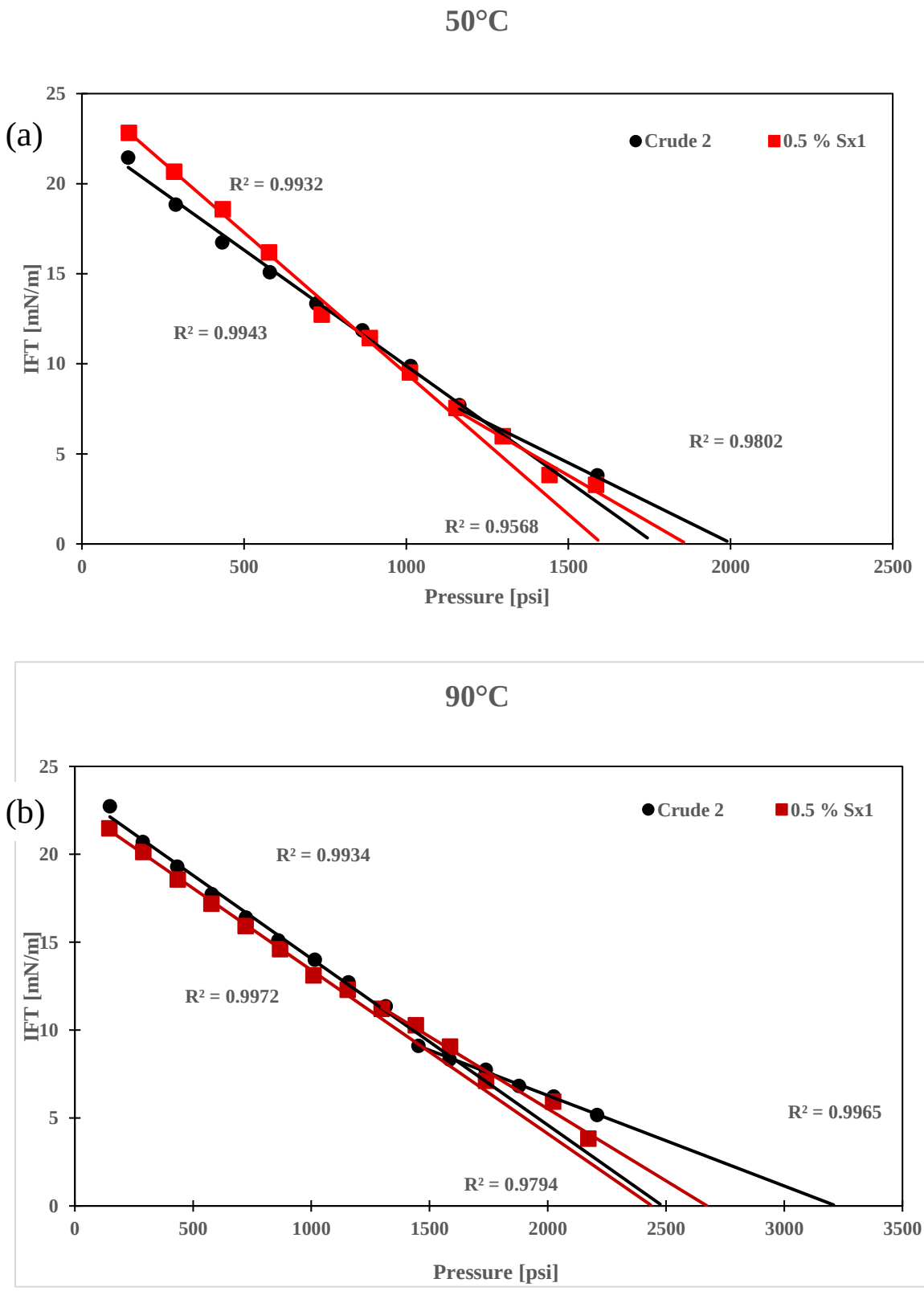


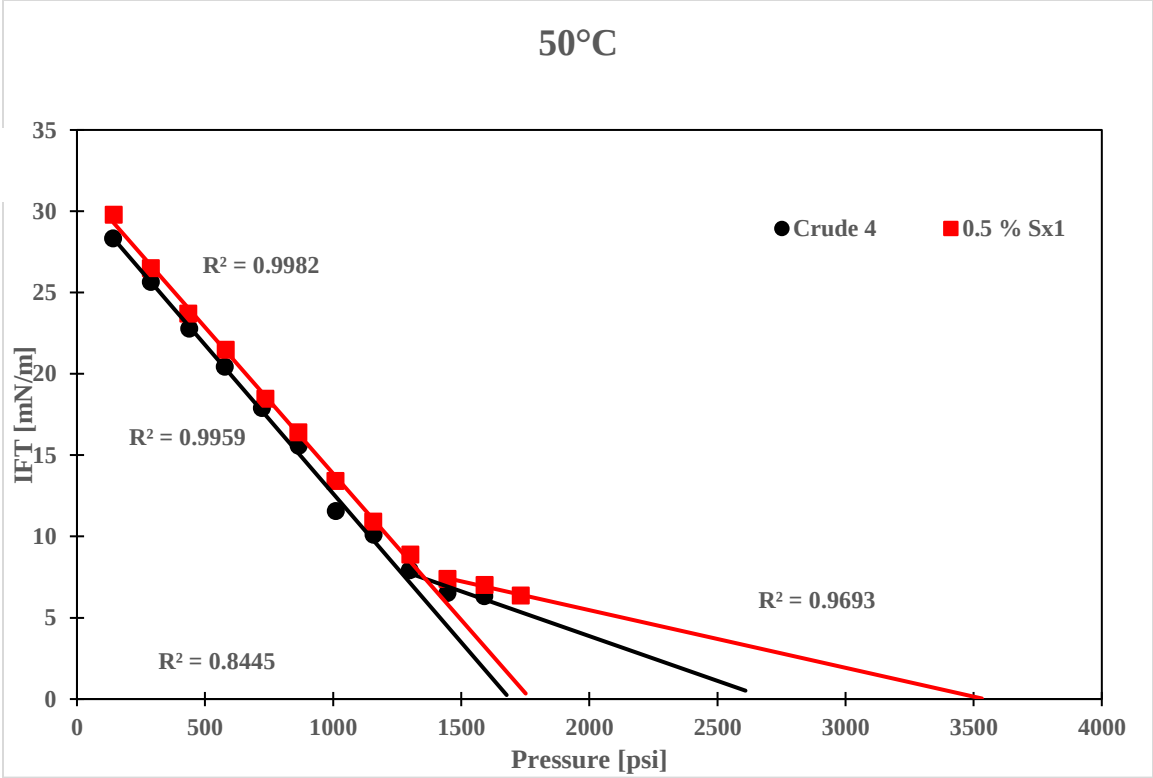
Figure 42 MMP and FCMP for crude 2 and 0.5 wt.% of Sx1 at (a) 50 and (b) 90°C.

5.5.3 MMP and FCMP results of Sx1 in crude 4.

Crude 4 is categorized as an extra-heavy Saudi crude, due to its high density and high asphaltene content. As a consequence, 0.5 wt.% of Sx1 were added to the crude and the results of MMP and FCMP at 50 and 90° C were estimated. As a start both MMP and FCMP are estimated at the previously specified conditions. The values at 50° C are as follows 1690 and 2705.8 psi, respectively. Moreover, the values at 90° C are as follows 2783.9 and 4183.9 psi, respectively.

Addition of 0.5 wt.% of Sx1 achieved a negative impact on the reduction of MMP and FCMP at temperature of 50° C, However, that's not the case at 90° C **Figure 43**. The values at 50° C are as follows 1749.7 and 2869.5 psi, respectively. These values can be presented as percentages as 3.53 and 6.05, respectively. However, the addition of 0.5 wt.% of Sx1 at 90° C resulted in a significant reduction in terms of MMP and good reduction in terms of FCMP values. The values are as follows 2351.7 and 37561.1 psi, respectively. These values can be presented as percentages as 15.5 and 10.2, respectively. This reduction is superb and is strongly recommended to be implemented in the industry. Moreover, it can be inferred that Sx1 performs better for crudes with higher polarity content at higher temperatures. In other words, at higher asphaltene content and high temperatures Sx1 is performing very well in the reduction of MMP and FCMP.

(a)



(b)

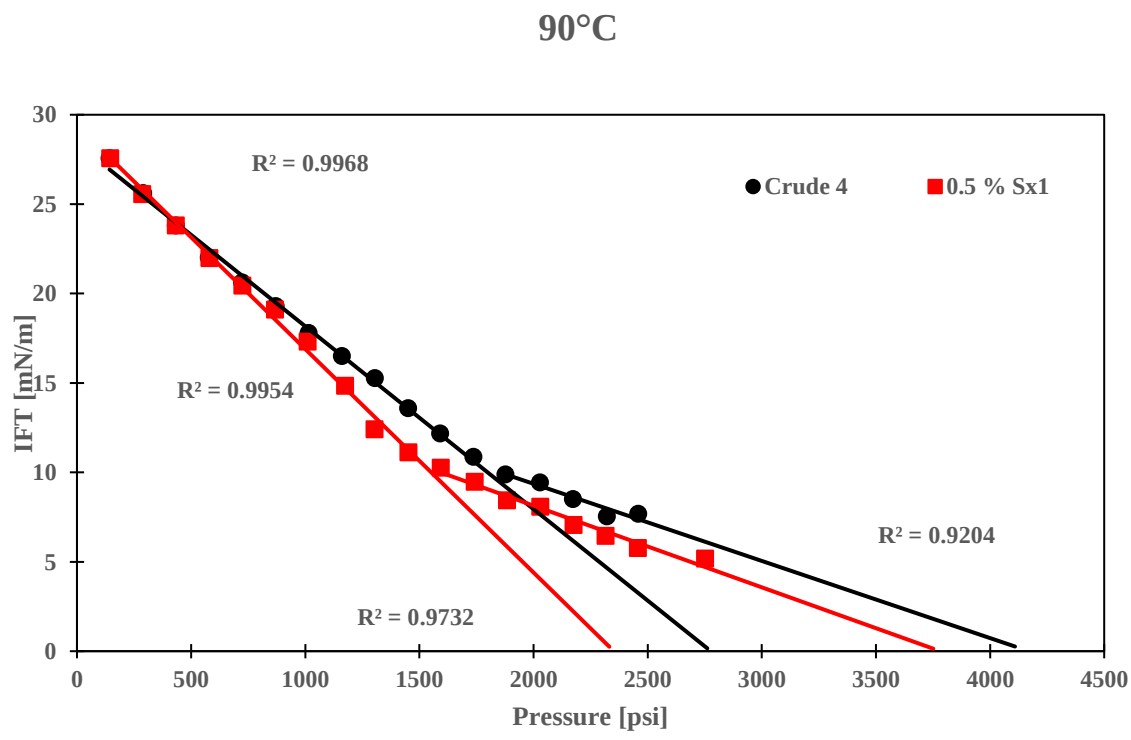
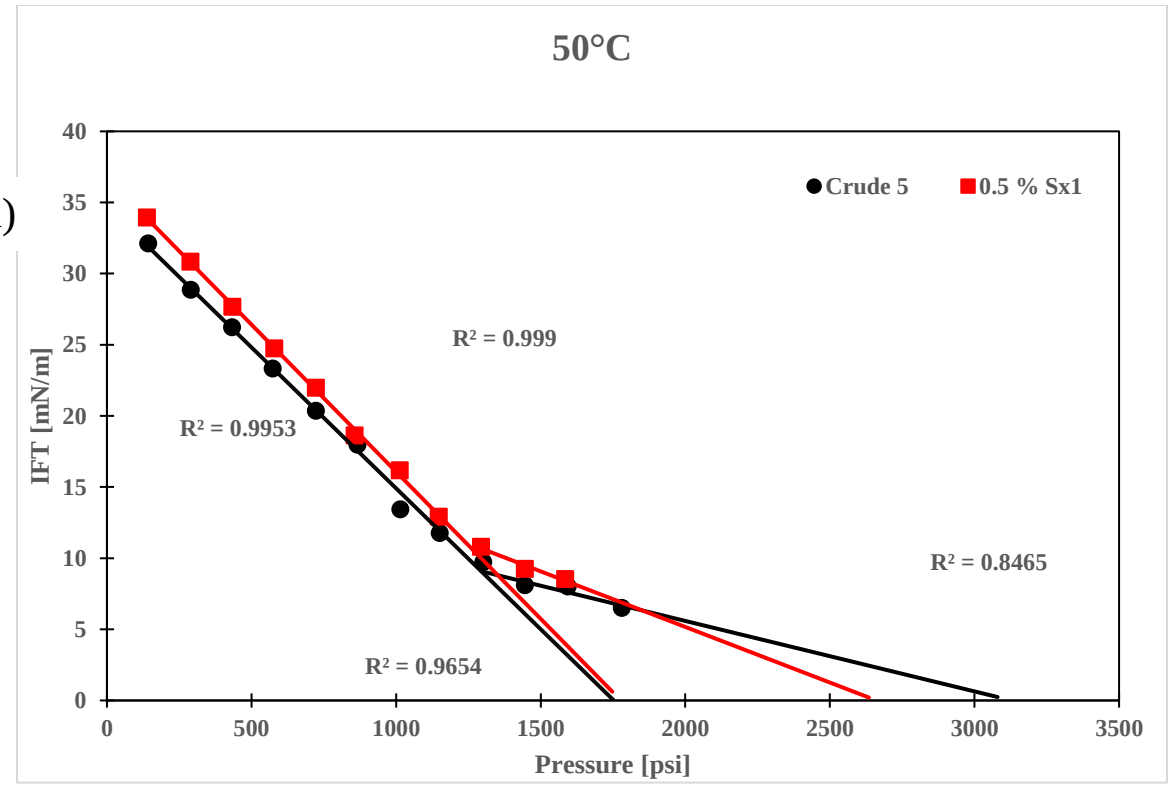


Figure 43 MMP and FCMP for crude 4 and 0.5 wt.% of Sx1 at (a) 50 and (b) 90°C.

5.5.4 MMP and FCMP results of Sx1 in crude 5.

Crude 5 is categorized as an ultra-heavy Saudi crude, due to its very high density and very high asphaltene content. As a consequence, 0.5 wt.% of Sx1 were added to the crude and the results of MMP and FCMP at 50 and 90° C were estimated. As a start both MMP and FCMP are estimated at the previously specified conditions. The values at 50° C are as follows 1753.4 and 3098.4 psi, respectively. Moreover, the values at 90° C are as follows 2856.1 and 4124.1 psi, respectively.

Addition of 0.5 wt.% of Sx1 achieved a negative impact on the reduction of MMP and not the FCMP at temperature of 50° C, Moreover, that is the same case at 90° **Figure 44**. The values at 50° C are as follows 1775.4 and 2665.9 psi, respectively. These values can be presented as percentages as -1.25 and 13.96, respectively. However, the addition of 0.5 wt.% of Sx1 at 90° C resulted in a reduction in terms of MMP and poor reduction in terms of FCMP values. The values are as follows 2741.8 and 4078.4 psi, respectively. These values can be presented as percentages as 4 and 1.125, respectively. This reduction is not recommended to be implemented in the industry. Moreover, it can be inferred that Sx1 performs better for crudes with higher polarity content at higher temperatures. In other words, at higher asphaltene content and high temperatures Sx1 is performing very well in the reduction of MMP and FCMP.



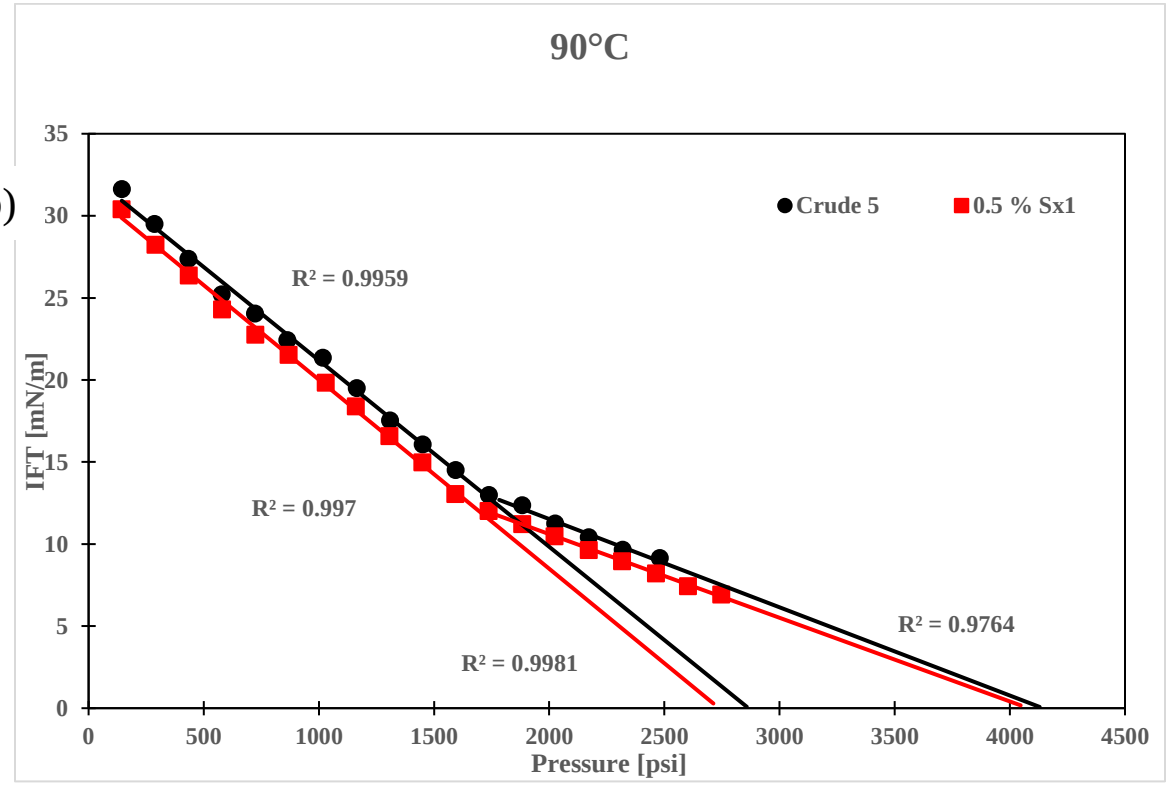
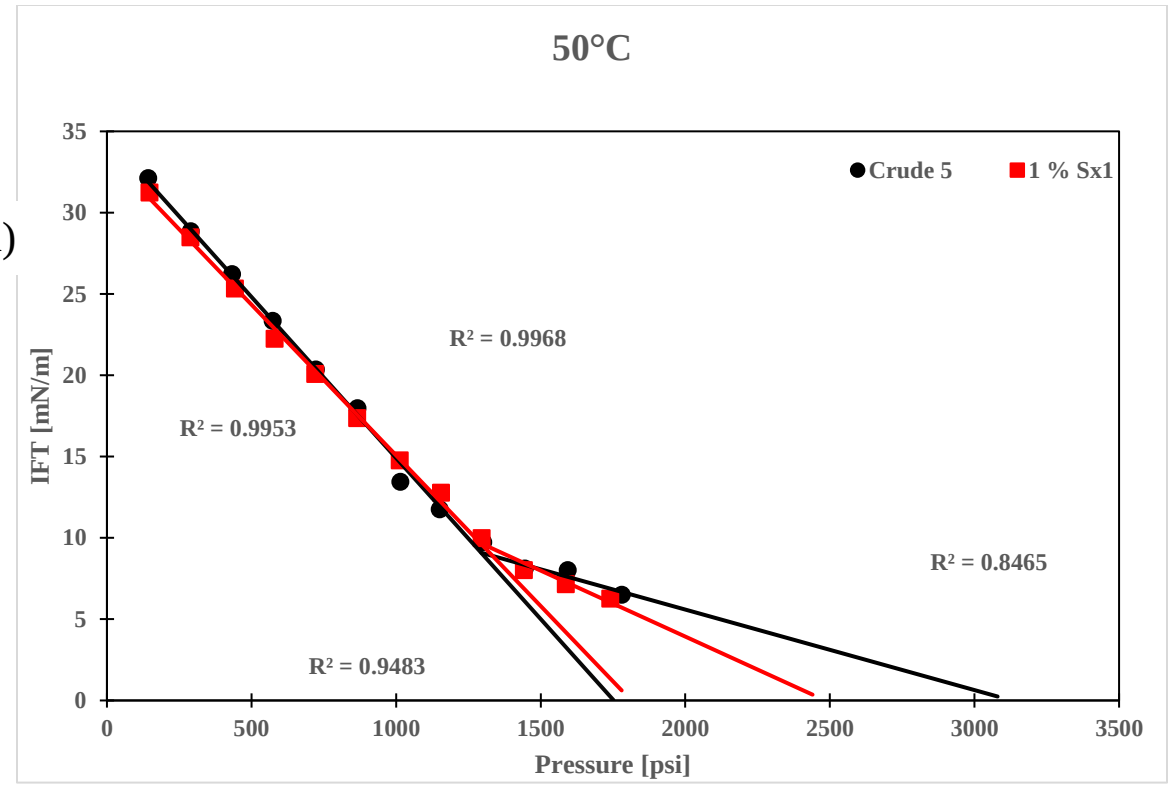


Figure 44 MMP and FCMP for crude 5 and 0.5 wt.% of Sx1 at (a) 50 and (b) 90°C.

Addition of 1 wt.% of Sx1 achieved a negative impact on the reduction of MMP and not the FCMP at temperature of 50° C, Moreover, that is the same case at 90° C **Figure 45**. The values at 50° C are as follows 1816.5 and 2488.7 psi, respectively. These values can be presented as percentages as -3.6 and 19.67, respectively. However, the addition of 1 wt.% of Sx1 at 90° C resulted in a reduction in terms of MMP and reduction in terms of FCMP values. The values are as follows 2672.5 and 3902.4 psi, respectively. These values can be presented as percentages as 6.4 and 5.4, respectively. This reduction is highly recommended to be implemented in industry, especially the deep heavy oil reservoirs. Moreover, it can be inferred that Sx1 performs better for crudes with higher polarity content at higher temperatures. In other words, at higher asphaltene content and high temperatures Sx1 is performing very well in the reduction of MMP and FCMP.

(a)



(b)

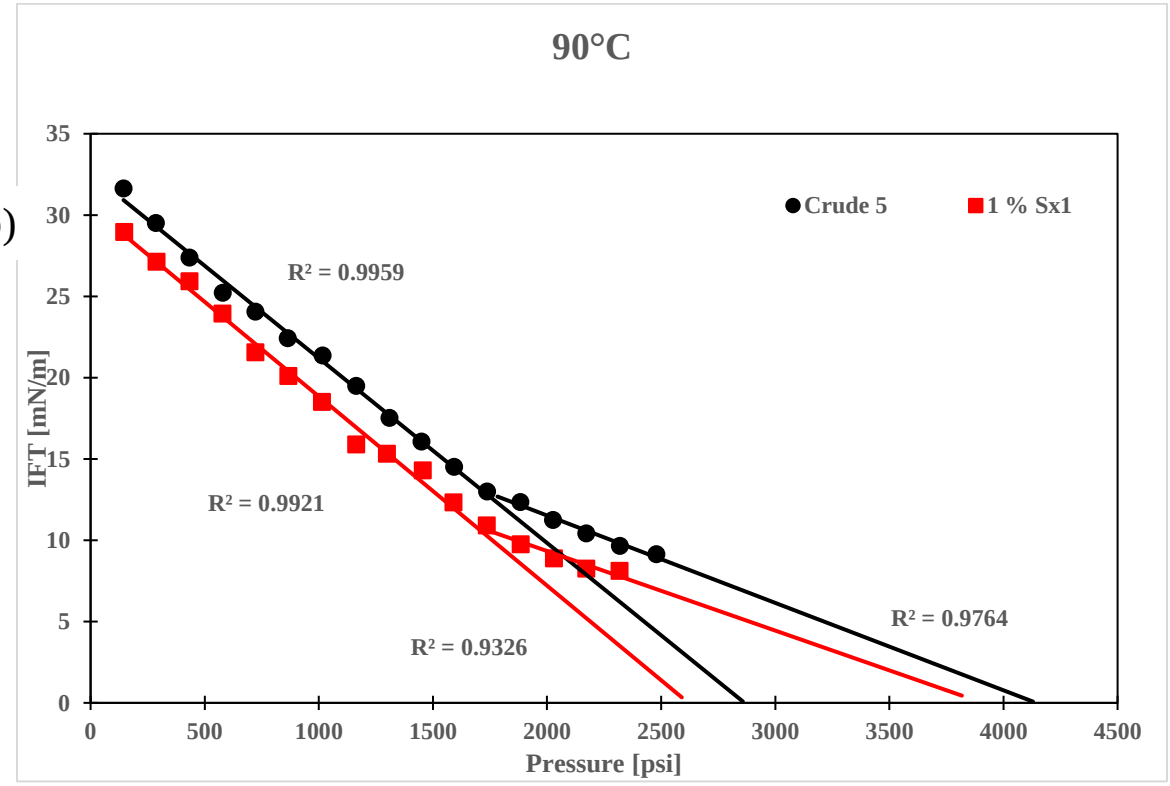


Figure 45 MMP and FCMP for crude 5 and 1 wt.% of Sx1 at (a) 50 and (b) 90°C.

CHAPTER 6

CONCLUSION AND RECOMMENATIONS

6.1 Conclusion

In this study different chemicals were utilized to reduce the MMP and FCMP in CO_2-oil system. Based on the findings obtained, the following conclusions are declared:

- Chemicals used in the literature (BL and NIS) proved to have significant impact on the reduction of MMP and FCMP. However, each of them has its cons.
  - BL concentrations are too high.
  - NIS works as an emulsifier, as a result it increases the oil viscosity.
- Commercial chemicals (XY and DL) achieved a reduction in both MMP and FCMP. However, they have their cons.
  - XY and DL are volatile and flammable chemicals.
  - Their capability to enhance CO_2 miscibility is lower than ionic liquids.
- From the screening obtained, ionic liquids proved to be the optimum chemicals to reduce MMP and FCMP with the lowest concentrations, when compared to others.
- Sx1 and Sx4 represents the two optimum chemicals, where both have remarkable impact on the reduction of MMP and FCMP, moreover Sx1 resulted in more reduction in MMP the Sx4.

- Sx1 effect on MMP and FCMP of four different crudes and CO_2 was studied.
- Sx1 performs very well in terms of reduction of MMP and FCMP at higher temperatures. This is attributed to the increase of kinetic energy of ionic liquid cations, which would increase dynamic diffusion and interfacial adsorption.
- Sx1 reduction of the MMP and FCMP increase with the increment of asphaltene content. Due to the high polarity of asphaltene, which interact with ionic liquid cations.
- The optimum reduction occurs where asphaltene content ranges between 18 and 26 wt.%, at higher temperatures.

6.2 Recommendations for Future Work

- Solubility of chemicals in scCO_2 shall be tested utilizing the PVT system.
- MMP and FCMP shall be measured between crude oil and CO_2, at which chemicals are solubilized in.
- CO_2 flooding shall be performed in the early stages of the production of deep heavy oil reservoirs.

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