Effect of Temperature, Phase Change, and Chemical Additive on Interfacial Properties and Performance of Steam Applications

by

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A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in

Petroleum Engineering

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Abstract

When considering the wettability state during steam applications, we find that most issues remain unanswered. The removal of polar groups from the rock surface with increasing temperature improves water wettability; however, other factors, including phase change, play a reverse role. In other words, hot-water or steam show different wettability characteristics, eventually affecting the recovery. Alternatively, wettability can be altered using steam additives. The mechanism of this phenomenon is not yet clear. The objective of this work is to quantitatively evaluate the steam-induced wettability alteration in different rock systems and analyze the mechanism of wettability change caused by the phase change of water and chemical additives.

Heavy-oil from a field in Alberta (27,780 cP at 25°C) was used in contact angle measurements conducted on quartz and calcite plates. All measurements were conducted at a temperature ranging up to 200°C using a high-temperature high-pressure IFT device. To obtain a comprehensive understanding of this process, different factors, including the phase of water, pressure, rock-type, and contact sequence were considered and studied separately.

To study the effect of pressure on wettability, we started with maintaining the water in liquid phase and measured the contact angles between the oil and water at different pressures. Next, the contact angle was measured in pure steam by keeping the pressure lower than saturation pressure. The influence of contact sequence was investigated by reversing the sequence of generating steam and introducing oil during measurement; these measurements were repeated on different substrates. Different temperature resistant chemical additives including conventional chemicals additives—alkalis, surfactants, ionic liquid—and novel chemicals additives—biodiesel, Switchable-Hydrophilicity Tertiary Amines (SHTA), nanofluids (dispersed SiO2 and ZrO2), ethers, alcohols, and chelating agents—were added to the steam during contact angle to test the wettability alteration characteristics at different temperature and pressure conditions (steam or hot-water phase). In addition to these wettability state observations, surface tension experiments to evaluate the performance of additives in reducing surface tension for the oil/steam system were conducted. The results showed that wettability of tested substrates is not sensitive to pressure as long as the phase has not been changed. The system, however, was observed to be more oil-wet in steam than in water at the same temperature in the calcite test. The wettability state could be altered by utilizing chemical additives in certain ranges of concentration; moreover, the optimum chemical additive concentration was also observed from both contact angle and surface tension measurements.

Even though they reveal useful information, contact angle measurements are limited in accounting for the importance of the wettability alteration effect on the phase distribution/entrapment and oil recovery. Micromodel studies are then preferred to assess these characteristics. All observations and measurements in this micromodel research were conducted at temperatures up to 200°C on glass bead micromodels. The models were initially saturated with brine solution and displaced with the oil phase to maintain initial water and oil saturation. Hot-water was then constantly injected into the micromodels to evaluate the impact of phase change and wettability status on residual saturation development. Similar parameters were also evaluated in pure steam injection by elevating the temperature to match the steam temperature and

maintaining pressure below saturation pressure. Next, several chemical additives screened from the previous contact angle and thermal stability measurements were introduced during both hot-water and steam applications to observe their ability in modifying phase distribution, wettability state, and oil recovery at different pressures and temperatures.

The result of the experiments in the glass bead micromodel presented that phase distribution and wettability state were sensitive to steam phase (vapor yielded oil-wet or condensate yielded water-wet case). This phenomenon also aligned with the previous hypotheses indicating that phase change has an impact on wettability state and residual oil saturation. At any circumstances, wettability alteration with chemicals was possible. The shape and characteristics of the trapped oil with and without chemicals were identified through micromodel images and suggestions were made as to the conditions (pressure, temperature, and time to apply during the injection application) at which these chemicals show optimal performance.

Analysis of the degree of wettability alteration induced by steam (or hot-water) and temperature was helpful to further understand the interfacial properties of the steam/bitumen/rock system, as well as proving useful in the recovery performance estimation of the steam injection process in carbonate and sand reservoirs, specifically in chemically enhanced heavy-oil recovery. According to this research, conventional steam additives can be altered by these novel chemicals that are both cheaper and more thermally stable, thus showing potential and appearing promising for steam wettability improvement and surface tension reduction in steam applications. In addition, the study and analysis of phase distribution and wettability change in micromodels during hot-water and steam applications provides useful data and understanding of interfacial

properties, oil trapping mechanism, and the recovery performance of rock/bitumen/hot-water or steam system in the reservoirs. For practitioners, chemical additives were recommended, validated by visual images and thermal stability tests.

Acknowledgements

Every single phase in my Master of Science program journey truly provided me with countless precious moments and experiences; from sitting in classes to investigating in the laboratory, these experiences augmented my knowledge in petroleum engineering. Therefore, first and foremost, I would like to thank Almighty Allah *Subhanallahu Wa Ta'ala* for the blessings and strength throughout my journey in accomplishing this graduate study.

I would like to deliver my sincere gratitude to my supervisor, Professor Tayfun Babadagli, for his devotion, patience, generous guidance, inspiration, and encouragement throughout the entire phase upon the completion of my degree. He taught me everything I needed to fulfill my gap of knowledge and to gain the essential values to be an outstanding academic. Without his supervision, I would not have been able to achieve and complete my degree and master thesis.

I would also like to deeply appreciate our technicians Georgeta Istratescu and Lixing Lin for their unlimited supports. Moreover, my appreciation also goes to Pam Keegan and Lindsey Gauthier for editing and amending my papers and thesis, and also to my research group workfellows both for their contribution to my research and in building a collaborative teamwork environment.

I would like to gratefully acknowledge our sponsorships under Professor Babadagli's NSERC Industrial Research Chair in Unconventional Oil Recovery: Petroleum Development Oman, Total E&P Recherche Development, SiGNa Oilfield Canada, Husky Energy, Saudi Aramco, Devon, and BASF) and an NSERC Discovery Grant (No: RES0033730). I am also thankful to Indonesia Endowment Fund for Education (LPDP) and Ministry of Finance of The Republic of Indonesia for providing the financial support for my graduate study at the University of Alberta.

Last but not least, I have to express my profound gratitude to my beloved wife who was always there for me days and nights, together with my parents and sisters who always provided me with never-ending encouragement and prayers throughout my graduate study. Thank you.

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Chapter 1: Introduction

1.1 Introduction

Total worldwide energy consumption coming from crude oil was documented to be as high as 32% (Enerdata 2017). Around two-thirds of its production originates from heavy-oil reserves (Færgestad 2016). In fact, there is more than 500 billion barrels of heavy-oil in potential globally including both proved and unproved reserves in heavy-oil, extra heavy-oil, and bitumen (Meyer 1998). The complexity of the heavy-oil characteristics generates even more challenging processes in heavy-oil recovery. There are two recognized recovery methods utilized in heavy-oil and bitumen extractions which can be defined as surface mining and in-situ recovery (Masliyah et al. 2011). The surface mining method is commonly used to recover the heavy-oil or bitumen contained in the shallow formations, usually less than 75 m deep. When the formations containing heavy-oil or bitumen are too deep—more than 75 m—the in-situ recovery technique is preferable because of the mining operation economics concern. Since this research focuses on steam applications, further explanations will be emphasizing more on in-situ recovery.

One of the most well-known enhanced oil recovery methods in heavy oil production is thermal recovery, mostly applied by injecting steam into the reservoir. The steam injection allows heat transfer to the rock formation, yielding oil viscosity reduction (Sheng 2013). Furthermore, this mechanism increases oil mobility resulting in substantial oil recovery improvement. In general, thermal oil recovery consists of six techniques: cyclic steam stimulation (CSS), continuous steam injection, in-situ combustion, steam-assisted gravity drainage (SAGD), vapor extraction (VAPEX), and expanding solvent-steam-assisted gravity drainage (ES-SAGD) (Ghoodjani et al. 2011). The most common thermal recovery techniques are SAGD and CSS. However, the utilization of preferable technique depends on several factors including reservoir fluids and reservoir characteristics. Furthermore, this thermal oil recovery can also be combined with chemicals as additives, for instance, in the case of tertiary recovery. In combining the chemicals with thermal recovery, a selective screening process should be established when finding the most suitable and cost-effective chemical additives for field applications.

In the late 1950s, the first study on the relationship between pH and wettability was conducted by Wagner and Leach (1959). This study encouraged latter scientific publications regarding alkaline injection—particularly for steam applications (Haas et al. 2013). Some other chemicals including ionic liquids and surfactants were also studied. Favorable results from these chemicals were evidenced leading to desirable incremental oil recovery in steam applications (Shah et al. 1977; Hanamertani et al. 2015; Wei and Babadagli 2017). Recently, due to the cost-effective concerns, research and applications in new generation chemical additives have received more consideration as the alternatives to conventional chemical additives. Evidences of these new generation chemicals—nanoparticles, ethers, alcohols, chelating agents, biodiesel, switchable-hydrophilicity tertiary amines (SHTA)—have proved to deliver promising results in enhancing oil recovery (Babadagli et al. 2010; Karimi et al. 2012; Maghzi et al. 2012; Alkindi et al. 2016; Chahardowli et al. 2016; Nwidee et al. 2016; Sui et al 2016; Almubarak et al 2017; Wei and Babadagli 2017). However, some of these new generation chemicals are not suitable for thermal oil recovery (Gatlin and Slobod 1960; Holm and Csaszar 1962).

This research intends to achieve a comprehensive understanding of steam-induced wettability alteration, interfacial properties, and phase distribution or oil entrapment mechanisms. Involvement of both conventional and novel chemical additives is also part of this research to further investigate the performance in improving the mentioned parameters.

1.2 Statement of the Problem

Enhanced oil recovery (EOR) is believed to be a reliable methodology in unlocking potential oil reserves. Nonetheless, this technique could be a very challenging process in oil field operations—specifically when it is related to thermal recovery processes in heavy-oil production. Steam usage, operational costs, and energy utilization are several factors that remain challenging with the thermal recovery technique. Furthermore, several factors impacting wettability characteristics and phase distribution/entrapment are still undefined eventually affecting heavy-oil recovery. Addition of chemical additives is able to improve the oil recovery, but the mechanism is still unclear. A limited number of published research honoring the steam condition increases the challenges in heavy-oil thermal recovery processes. Finding the suitable formulation of steam additive is the key problem to solve. The chemical additive has to be acquiring its component stability at high pressure and temperature in particular. Crucial parameters affecting the petrophysical behaviors need to be defined in order to achieve successful field implementation. Detailed challenges on the thermal recovery methodology are summarized as follows:

1.2.1 Irreversible Wettability Alteration

Thermal recovery technique is an effective methodology in improving heavy-oil recovery. In the aspect of petrophysics, introduction of thermal technique—particularly steam injection—is proved to restore the wettability. However, this mechanism is possible to achieve if the impairment of the wettability is caused by the polar components interaction, as also previously concluded by Roosta et al. (2009). When it arises to the phase change, the mechanism of the wettability alteration is totally different. Previous hypothesis stated that changing the liquid phase to a steam phase could alter the wettability state from a water-wet to an oil-wet state (Bennion et al. 1992). However, this hypothesis still needs further study and verification about the mechanism of this phenomenon.

1.2.2 Undesirable Impact of Brine Chemistry

Hydrocarbon reservoirs contain formations of water having different levels of salinity and brine chemistry. The wettability of the reservoir rocks is possible to modify by the presence of the brine chemistry leading to unfavorable wettability alteration (Anderson 1986; Haagh 2017). Thus, comprehensive understanding regarding this brine chemistry effect is essential to implement appropriate thermal recovery technique and suitable chemical additive formulation.

1.2.3 Chemical Additives Thermal Stability

Thermal stability is a very important parameter when using the chemical as an additive in thermal recovery applications. This parameter can be defined by performing a thermal stability test to the preferred chemical additive. The most reliable and commonly used methodology in evaluating chemical thermal stability is thermogravimetric analysis (TGA). Fundamentally, this

TGA measures the mass of the chemical constantly by progressively elevating the temperature. This measurement presents the decomposition degree of the chemicals in a high temperature environment. The thermal stability from this TGA measurement might be overestimated due to short-term steadiness during rapid temperature jumps (Cao and Mu 2014). By conducting this thermal stability test, chemical additives can be screened for suitable use in steam applications.

1.2.4 Phase Distribution/Entrapment in Porous Media

Contact angle measurements in representing wettability degree are not sufficient enough to comprehend the phase distribution or residual oil saturation in the reservoir rocks. Residual oil saturation does not have any direct correlation with the wettability state of the reservoirs and obviously has further impact in the heavy-oil recovery. Furthermore, oil blobs and snap-off phenomena are accountable for the residual oil saturation (Roof 1970; Ng et al. 1978). Thus, representative pore-scale visualization is necessary to observe the phase distribution and residual oil behavior in porous media.

1.3 Aims and Objectives

This research aims to investigate the irreversible steam-induced wettability alteration triggered by phase change and its influence on phase distribution/entrapment and oil recovery. Performance of both conventional chemical additives—high pH solution, ionic liquid, surfactants—and novel chemical additives comprising dispersed nanoparticles, alcohol, ethers, chelating agents, biodiesel, and switchable-hydrophilicity tertiary amines (SHTA) are also evaluated regarding their ability in promoting favorable wettability alteration. Several detailed objectives of this research include:

- Quantitative analyses of irrevocable wettability alteration promoted by the phase change. This investigation is performed by conducting contact angle experiments with two different solid plates—quartz and calcite—at liquid phase and steam phase.

- Analyses of brine chemistry and polar components interaction effects on wettability alteration at elevated and steam pressure and temperature. Investigation of these phenomena is quantitatively performed through streaming potential surface charge and contact angle measurements.
- Quantifying the interfacial properties behavior of heavy-oil at steam condition by conducting the experimental study with a surface/interfacial tension (IFT) device using pendant drop methodology.
- Screening and testing the steam additives including conventional and novel chemicals regarding the potential performance in restoring wettability state, reducing surface/interfacial properties, and improving residual oil saturation.
- Sensitivity of chemical additive concentration to further analyze the optimum chemical concentration yielding to the maximum degree of wettability alteration and surface/interfacial tension reduction.
- Visualizing the wettability alteration and phase distribution/entrapment in porous media through a glass bead micromodel at hot-water and steam conditions with and without chemical additives.

1.4 Structure of the Thesis

This paper-based thesis encompasses five chapters. Chapter 2 contains two papers which were previously presented at a technical conference and accepted for publication in a research journal. Chapters 3 and 4 consist of two conference papers which were presented at two different conferences in September and October 2019. One of said papers has been submitted to a research journal and is currently under review for publication.

Chapter 1. This chapter provides a general overview of this thesis describing the fundamentals of thermal recovery methodology and several challenges regarding the use of chemical additives in steam applications. Aims and objectives of this research are also stated in this chapter.

Chapter 2. Phase change plays an essential role in unfavorable wettability alteration. Water or steam phase presents dissimilar wettability characteristics. Wettability state is able to be restored by introducing chemical additives. The mechanism of this phenomenon is still not well-defined yet. This chapter provides further verification regarding the earlier proposed hypothesis about phase change. Quantitative analyses of wettability degree and interfacial properties were performed by conducting contact angle and surface/interfacial tension measurements. Phase change was then applied to the system to further investigate the steam-induced wettability alteration. Furthermore, conventional chemical additives—high pH solution, ionic liquid, and surfactants—were also introduced to further investigate the performance of restoring the wettability state, done by first performing a thermal stability test to each chemical additive. Effects of brine chemistry and polar compounds interaction were also investigated. In addition, sensitivity of chemical concentration was also performed and explained in this chapter.

Chapter 3. In continuation of the previous study in Chapter 2, this chapter presents and explains the performance of novel chemical additives—nanofluids, alcohol, ethers, chelating agents, biodiesel oil-in-water emulsion, and switchable-hydrophilicity tertiary amines (SHTA)—on favorable wettability alteration and surface/interfacial tension reduction. Similar quantitative analyses were performed including thermal stability tests, contact angle, and surface/interfacial tension measurements. Brine chemistry effect on solid surface charge modification was further investigated by performing streaming potential measurement.

Chapter 4. Quantitative analyses of wettability alteration proved to reveal beneficial information. However, the analyses are still inadequate to further comprehend the wettability alteration effect on the phase distribution and residual oil saturation in porous media. This chapter elaborates the results perceived from pore-scale visualization using a glass bead micromodel. Phase change was conducted during the visualization. Wettability alteration and phase distribution in hot-water and steam conditions were then evaluated. Moreover, chemical additives such as anionic surfactant and SiO_2 dispersed nanoparticles were introduced to the system. The behavior of the phase distribution with and without chemical additives was then compared to further investigate the effect of chemical additives.

Chapter 2: Effect of Temperature, Phase Change, and Chemical Additive on Wettability Alteration during Steam Applications in Sands and Carbonates

This chapter of the thesis is a modified version of a published research paper SPE 191188. The conference paper version SPE-191188-MS was presented at SPE Trinidad and Tobago Section Energy Resources Conference held in Port-of-Spain, Trinidad and Tobago, 25-26 June 2018. The journal version of this research paper SPE-191188-PA has been published in SPE Reservoir Evaluation & Engineering Journal.

2.1 Preface

One unanswered issue with steam applications regards wettability state during the recovery process. Removal of polar groups from the rock surface with increasing temperature improves water wettability; however, other factors, including phase change, play a reverse role. In other words, hot water or steam will show different wettability characteristics, eventually affecting the recovery. Alternatively, wettability can be altered using steam additives. The mechanism of these phenomena is not yet clear. The objective of this work is to quantitatively evaluate the steam-induced wettability alteration in different rock systems and analyze the mechanism of wettability change caused by the change of the phase of water and chemical additives.

Heavy-oil from a field in Alberta (27,780 cP at 25°C) was used in contact angle measurements conducted on quartz, mica, calcite plates, and rock pieces obtained from a bitumen containing carbonate reservoir (Grosmont). All measurements were conducted at a temperature range up to 200°C using a high-temperature high-pressure IFT device. To obtain a comprehensive understanding of this process, different factors, including the phase of water, pressure, rock-type, and contact sequence were considered and studied separately.

Initially, the contact angles between oil and water were measured at different pressures to study the effect of pressure on wettability by maintaining water in liquid phase. Secondly, the contact angle was measured in pure steam by keeping the pressure lower than saturation pressure. The influence of contact sequence was investigated by reversing the sequence of generating steam and introducing oil during measurement. These measurements were repeated on different substrates. Different temperature resistant chemical additives (alkalis, surfactants, ionic liquid) were added to steam during contact angle to test wettability alteration characteristics at different temperature and pressure conditions (steam or hot-water phase). In addition to these wettability state observations, surface tension experiments for the oil/steam system were conducted by introducing chemical additives to evaluate the performance in regards to reduction of surface tension. The results showed that wettability of tested substrates is not sensitive to pressure as long as the phase has not been changed. The system, however, was observed to be more oil-wet in steam than in water at the same temperature, for example, in the case of calcite. The wettability state could be altered by utilizing chemical additives in certain ranges of concentration; moreover, the optimum chemical additive concentration was also observed from both contact angle and surface tension measurements.

Analysis of the degree of the wettability alteration induced by steam (or hot-water) and temperature was helpful to further understand the interfacial properties of the steam/bitumen/rock system and useful in the recovery performance estimation of the steam injection process in carbonate and sand reservoirs, specifically in chemically enhanced heavy-oil recovery.

Key words: Wettability alteration, steam injection, phase change, chemical additive, Grosmont carbonates, oil sands, nano materials.

2.2 Introduction

Injection of steam for longer periods of time may lead to a wettability alteration of the reservoir rock surface, leading to a rapid production decline. Blevins (1990) reported that steep declining production occurred in the major steam flood fields in the United States 10-20 years after steam applications. Furthermore, the Oil-to-Steam Ratio (OSR) was declining at that period confirming the fields have reached the maturity stage. Other evidence was reported by Jones et al. (1995) regarding this declining period in Kern River steam flood field. In addition, similar behavior was observed in Duri steam flood field in Indonesia (Winderasta et al. 2018). The team reported that the field production plummeted from approximately 290,000 barrels of oil per day to currently 100,000 barrels of oil per day after achieving its maturity stage. These evidences are substantiated by previous lab scale research concluding that the introduction of steam to an oil drop placed on the quartz surface leads to a wettability reduction by declining the contact angle relative to the oil drop (Naser et al. 2014). This wettability alteration is driven by the phase change of water from liquid phase to steam phase (Bennion et al. 1992) as illustrated in **Figure 1**.

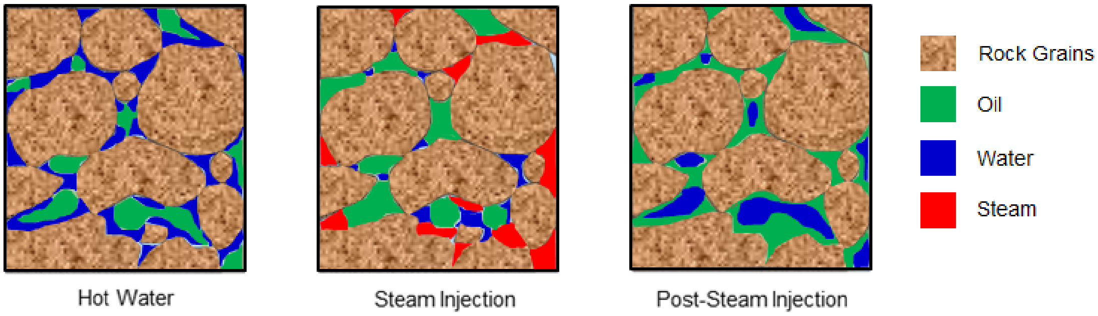


Figure 1—Theoretical wettability alteration (modified after Bennion et al. 1992).

Earlier research also claimed that wettability alteration was induced by an adsorption mechanism (Bennion et al. 1992). However, this hypothesis still needs proved research in evaluating the most influencing parameters through qualitative and quantitative analyses. To further evaluate the wettability characteristic, carbonate reservoirs must be taken into account in petrophysical evaluation and analysis. The distinct oil-wet behavior of carbonate inhibits the displacement of heavy-oil from water injection. This behavior is driven by negative capillary forces in the rock matrix (Mohammed and Babadagli 2016). Natural oil-wet behavior of carbonate is caused by its total surface charge which is much less negatively-charged compared to sandstone. This characteristic was also observed by Lee et al. (2016) and Moulin and Roques (2003). Furthermore, this behavior initiates more attractive forces between carbonate rock surface and heavy-oil yielding to oil-wet state. Hence, the oil-wet state leads to the negative capillary forces of carbonate rocks.

High temperature thermal induction was reported to be more effective in shifting wettability to be more water-wet in carbonate reservoirs. Al-Hadhrami and Blunt (2001) concluded that the application of steam injection in carbonate reservoirs could lead to a better wettability state, yielding in satisfactory oil recovery. This phenomenon was also observed by Zhang and Austad (2005). However, this effect of temperature in carbonate wettability is still not clear and remains challenging due to the difference of several affecting parameters, such as salinity, physical properties of the surface and oil, and the drop size of tested oil phase (Sohal et al. 2017). In addition to this particular case, Modaresghazani et al. (2016) concluded that wettability alteration being more water-wet is impossibly achieved even after elevating the temperature for the carbonate samples from the Grosmont reservoir as well as in calcite substrates (Wei and Babadagli 2016). Wettability alteration from an oil-wet to a more water-wet state was unlikely to occur for those rock samples even at a high temperature because of the adsorption of polar compounds from heavy-oil to the rock samples (natural-state cores or aged substrates) according to their observations.

Another essential factor impacting wettability state is brine chemistry; the presence of brine in the rock/oil system as an external phase could shift the wettability state to become more oil-wet. The impact of surface charge on the rock and fluid system will be given by certain salinity level contained in the brine (Anderson 1986). Haagh et al. (2017) showed that, generally, applying a higher concentration of salt in the rock/oil/brine system alters the wettability state to be more oil-wet. This wettability state was demonstrated by the declining contact angle between oil phase and substrate. The change in wettability state also depends on the composition of the brine. Higher divalent ion concentration could lead to a decreased oil/substrate contact angle (Haagh et al. 2017). This mechanism was also observed in the previous research. Yang et al. (2015) concluded that lower oil recovery is obtained as the divalent (Ca^{2+}) ion concentration is elevated. Sharma and Mohanty (2013) also demonstrated that the introduction of formation brine to a rock/oil system results in a more oil-wet state at higher temperatures. Furthermore, introducing chemical additives to steam injection could lead to a favorable wettability alteration. Modifying the pH of the rock/oil/steam (or hot water) system is one of several common methodologies in shifting wettability state to be more water-wet. An earlier study by Wagner and Leach (1959) concluded that changing the pH of the displacing phase to be a higher pH level could drive to a less oil-wet state by involving the reaction with surface-active materials in the oil adsorbed on the rock system. The advantage of pH modification in altering the wettability state was also observed by Cao et al. (2017) for heavy-oil reservoirs. Wettability alteration to be more water-wet is obtained by introducing $NaBO_2$ to the rock/oil/water system, which is shown in a declining contact angle of oil relative to the surface. This phenomenon was also observed by Wei and Babadagli (2017), even at steam temperature conditions. In addition, improvement of bitumen drainage was achieved 35-67% faster in alkaline, leading to higher oil recovery compared to the regular steam injection (Haas et al. 2013).

Other promising methodology in altering the wettability state is the involvement of surfactant to the rock/oil/steam (or hot water) system. Shah et al. (1977) concluded that this technique involving surfactant could be very effective in reducing residual oil saturation and a greater oil recovery. In general, the main objective of surfactant addition is to reduce the interfacial tension between oil and water phase and altering the wettability to more preferable state. A wide-range selection of surfactants (cationic, anionic, and nonionic) is available to be applied in altering wettability of both sandstone and carbonate type of rock systems, even for heavy oils (Mohammed and Babadagli 2015). This evidence was also confirmed by a previous experimental study on surfactants in steam application. Bruns and Babadagli (2017, 2018, 2019a-b) also observed that anionic and nonionic surfactants presented great thermal stability and good incremental oil recovery under a steam environment through core flood and Hele-Shaw experimental studies. However, not all types of surfactants are thermally stable in steam applications; the thermal stability of the cationic surfactant, for example, remains challenging in elevated temperatures (Wei and Babadagli 2017).

In addition to these types of chemical additives, a substantial amount of research was conducted on ionic liquids for enhancing heavy-oil recovery. Ionic liquids are basically mixture of components containing cationic and anionic-type of salts. These ionic liquids are also thermally resistant, meaning it is able to be applied at a very high temperature—more than 100°C (MacFarlane et al. 2017). According to their observations and studies, these ionic liquids delivered promising results. Hanamertani et al. (2015) conducted both a study and review in the area of ionic liquids, claiming that ionic liquids are effective in reducing the interfacial tension high salinity solution due to charges interaction amongst ions.

In summary, phase change is an essential parameter affecting wettability state, specifically in steam injection. Wettability state will show different behavior in hot water and steam environments even though higher temperatures may result in the removal of polar groups on the rock surface, eventually resulting in wettability alteration to be more water-wet. Under these circumstances, introducing chemicals as steam additives in altering wettability could be an option to change the wettability condition to be less oil-wet. This option still needs further research to obtain a stronger understanding about its mechanism in different rock systems. Studies on phase change and application of chemical additives in steam environments in interfacial properties are still limited. This research also continues from previous hot-water phase research by Wei and Babadagli (2017) and obtains a better understanding of phase change and chemical additive behaviors to the wettability alteration in steam environment. Result and analysis of this research on the wettability alteration degree induced by steam and temperature will lead to further understanding of interfacial properties of the steam-bitumen-rock system.

2.3 Materials and Experimental Setup

Crude Oil Sample. The crude oil sample that was used in this research was obtained from a heavy-oil field in Alberta. **Figure 2** presents the oil viscosity plot with temperature. The viscosity of this crude oil sample was recorded as 27,780 cP at 25°C. The recorded density of this oil sample was 0.97 g/cm^3 at 25°C. Saturate, aromatic, resin, and asphaltene (SARA) analysis was also conducted for this heavy-oil with the results presented in **Table 1**.

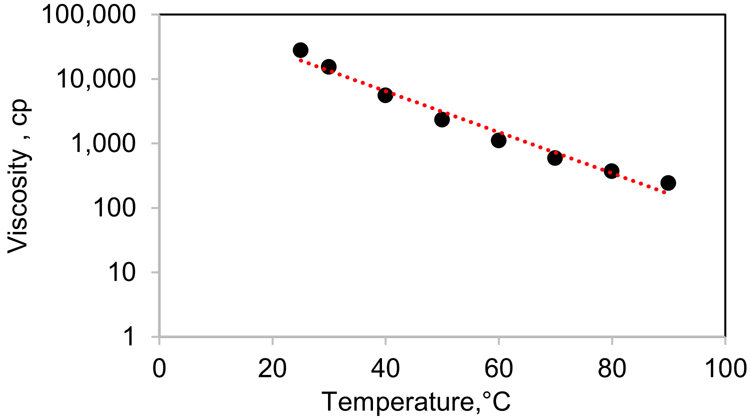


Figure 2—Oil viscosity profile with temperature.

Table 1—SARA analysis table for utilized heavy-oil.

Saturate	**Aromatic**	**Resin**	**Asphaltene**
26.36%	24.85%	25.74%	22.39%

Substrates. Quartz, mica, calcite, and Grosmont (carbonate reservoir containing bitumen in Canada) plates were used in this research. This research was more focused on quartz and calcite substrates to represent sandstones and carbonates. Mica and limestone (obtained from the

Grosmont formation in Canada) substrates were used as comparisons of wettability degree and surface flatness. Untreated and treated samples of substrates were also part of this research; untreated substrates reflected no treatment to the substrates before conducting each experiment. These substrates were utilized as is. Alternatively, untreated substrates reflected saturated substrates with crude oil. These substrates were aged in the crude oil sample minimum one week at 70°C, followed by the extra oil from this process being carefully treated with toluene. This procedure was performed with the objective of establishing the natural wettability state of the substrates.

External Phase. External phase used in this research is summarized in **Table 2**. Brine was also part of this research to both observe and investigate its influence to the wettability state. The chemical additives selected for this research were based on the previous research conducted by Wei and Babadagli (2017) to observe and evaluate their consistency in phase change and steam environments. Vacuumed tap water was used as base case to evaluate other chemical additive performances. Brine and chemical additive solutions were produced by mixing chloride type of salts and specific chemical with deionized water (DI). The concentration of each chemical additive referred to the previous research performed by Wei and Babadagli (2017) and Cao et al. (2017) as a base case. A varied range of chemical additive concentrations were also considered to observe and evaluate the correlation between chemical additive concentration and wettability state. In addition to this external phase, pH level was also measured.

Table 2—List of chemical additives.

Chemical Classification	Chemical Name	Concentration
Base case	Vacuumed tap water	-
Brine solution	NaCl; $CaCl_2$; $MgCl_2$	30,000 ppm; 1,000 ppm; 100 ppm
High pH solution	$NaBO_2$	1-5 wt%
Cationic surfactant	$C_{12}TAB$	1 wt%
Anionic surfactant	Linear-alkyl toluene sulfonate (LTS) Internal olefin sulfonate (IOS)	1-5 wt%
Nonionic surfactant	Sodium monooleat	1-5 wt%

Contact Angle Measurement. To evaluate the wettability alteration, a contact angle measurement was performed. Rame-Hart Goniometer/Tensiometer and DROPimage Advanced software were utilized for this contact angle measurement in a hot water/steam environment. The experimental equipment setup is shown in **Figure 3**. In measuring the contact angle, the oil drop was created on the different substrates inside the cell by also filling the IFT cell with vacuumed tap water, brine solution, and several chemical additives as external phase. Contact angle was measured by considering the oil drop phase as a reference. In this research, a contact angle greater than 90° indicates water or steam as a wetting phase whereas a contact angle less than 90° indicates oil as a wetting phase. Each chemical additive has its own mechanism and behavior when it interacts with the rock/oil system, specifically in steam applications.

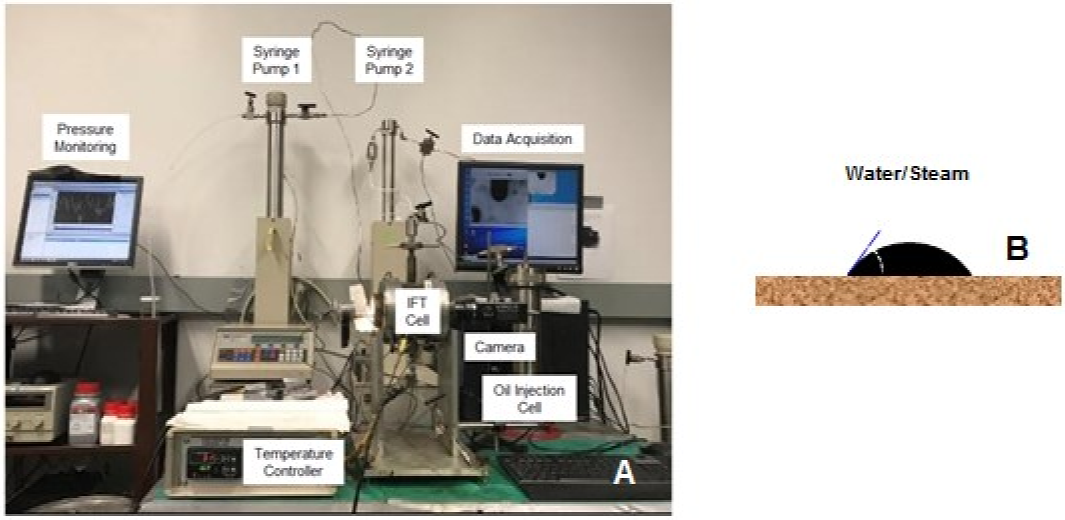


Figure 3—(a) IFT device and (b) contact angle.

2.4 Results and Discussion

2.4.1 Effect of Untreated and Treated Surface of the Substrates

In assessing the impact of oil film attachment on substrates to the wettability, untreated and treated substrates were included in this research. Untreated substrates are a group of substrates in their natural condition without any treatment conducted, whereas treated substrates are a group of substrates that are aged in crude oil at 70°C for minimum one week. **Figures 4** and **5** show the effect of substrate treatment in wettability for each substrate in 90°C hot-water phase at 30-40 psi. It was observed that there was a consistency of wettability alteration in each substrate after aging it in crude oil.

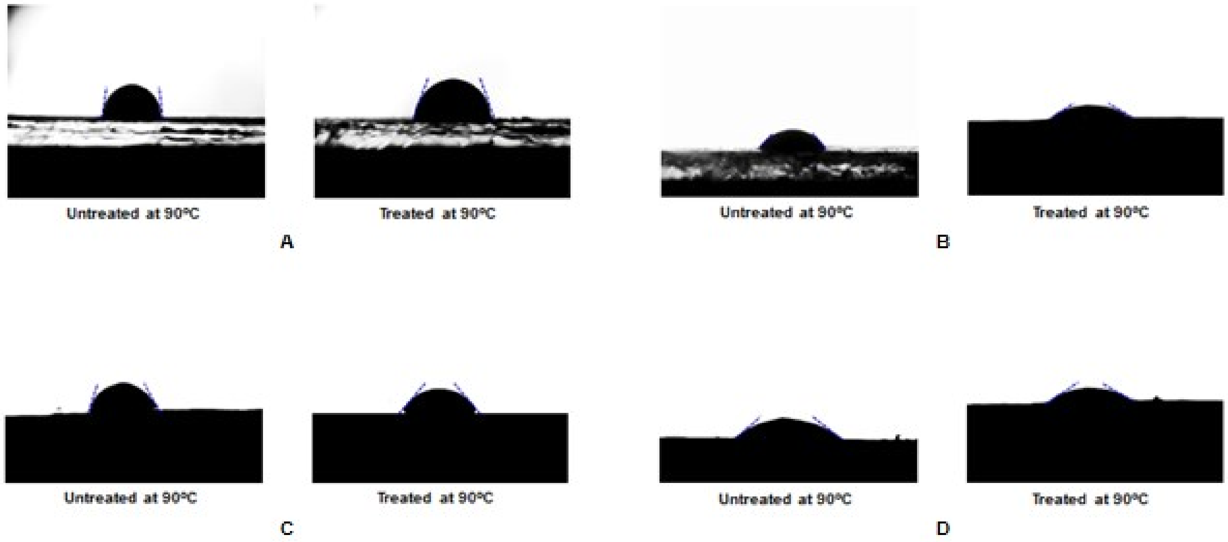


Figure 4—Untreated and treated (a) quartz, (b) calcite, (c) mica, and (d) Grosmont in hot-water.

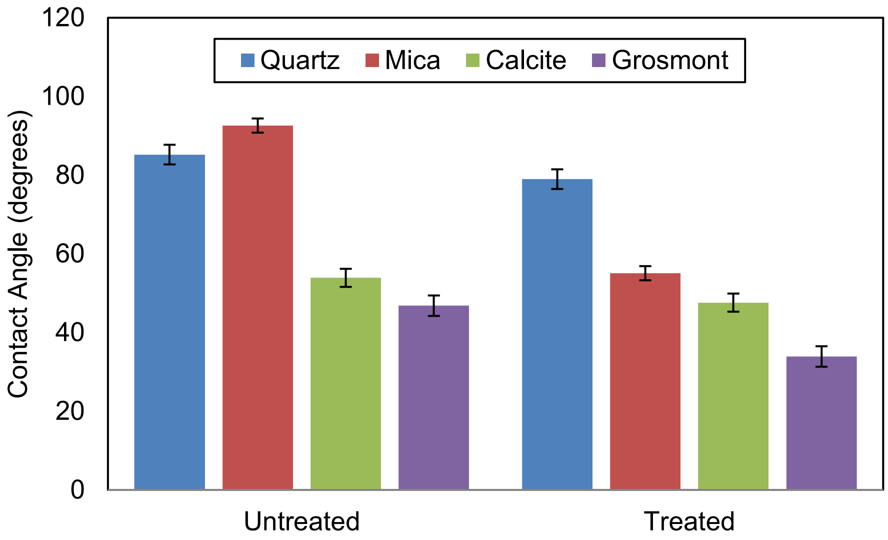
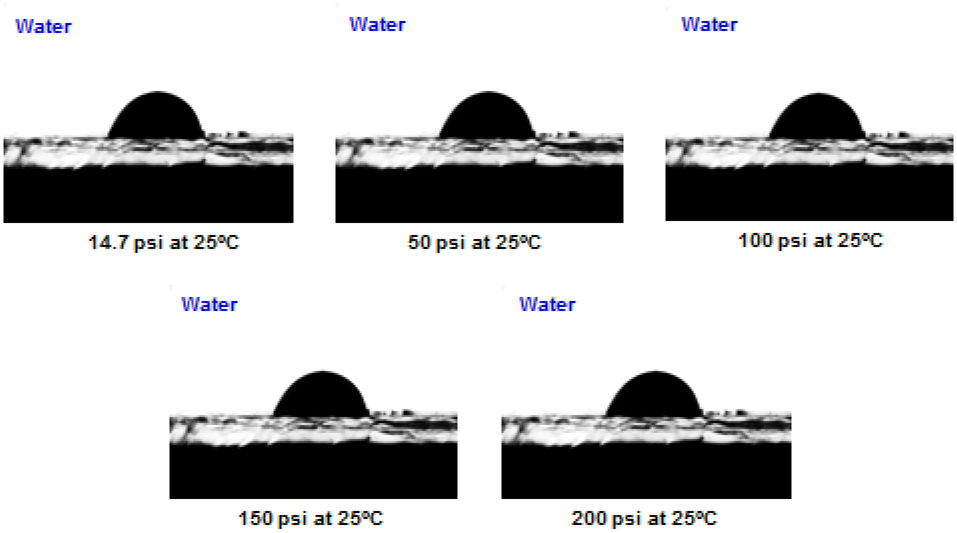


Figure 5—Effect of substrates treatment in contact angle at 90°C hot-water phase.

According to observations made from **Figures 4** and **5**, there is quite a significant change in wettability state as an effect of substrates treatment. Reduction of contact angle was observed in quartz substrate lowering the contact angle from 85° to 79°. The contact angle of calcite substrate dropped from 60° to 48°. Similar behavior was also identified in the Grosmont plate. The contact angle of this Grosmont plate also plummeted from 47° to 34°. A substantial drop of contact angle was also observed on mica substrates and the contact angle of oil drop on mica surface decreased from 93° to 55°. The attachment of oil film to the solid phase surface could alter the wettability state because this mechanism enables interaction among polar compounds in the oil phase (Abdallah et al. 2007). This polar interaction could lead the wettability state to be more oil-wet. In addition to this mechanism, treated substrates were applied to all experiments. At initial reservoir saturation, hydrocarbon—specifically heavy-oil—is present in the pores after its migration. Furthermore, this condition lets the reservoir rocks to be in contact with heavy-oil allowing the adsorption of mostly polar fractions of heavy-oil. In summary, treating the substrates with heavy-oil is a good practice to represent saturation history in the reservoir condition.

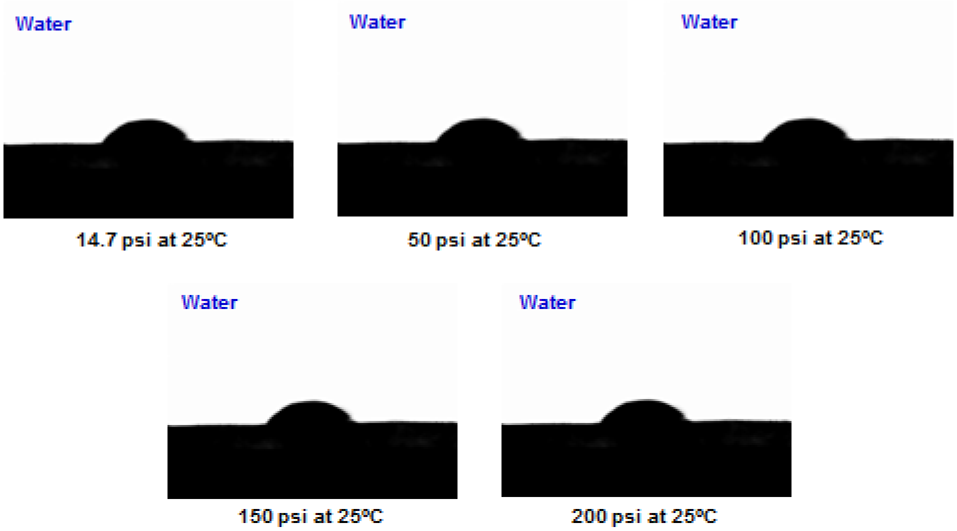
2.4.2 Effect of Pressure

The effect of pressure was studied first, as pressure variations were applied to maintain the certain phase of water (hot water or steam) while changing the temperature. A range of pressure was applied from atmospheric pressure of up to 200 psi together with a constant temperature of 25°C for each substrate. Vacuumed tap water was used as external phase in this experiment. The temperature in this experiment was maintained constantly to suppress the further effect of thermal induced wettability alteration, of which is also a scope of this research. The response of this elevated pressure to the wettability is presented in **Figures 6-10**. It was observed that pressure did not show a significant impact on the wettability state. This behavior was observed in all substrates; thus, any changes in wettability can be attributed to temperature or phase change.



14.7 psi at 25°C
50 psi at 25°C
100 psi at 25°C
150 psi at 25°C
200 psi at 25°C

Figure 6—Contact angle of treated quartz substrate in elevated pressure.



14.7 psi at 25°C
50 psi at 25°C
100 psi at 25°C
150 psi at 25°C
200 psi at 25°C

Figure 7—Contact angle of treated calcite substrate in elevated pressure.

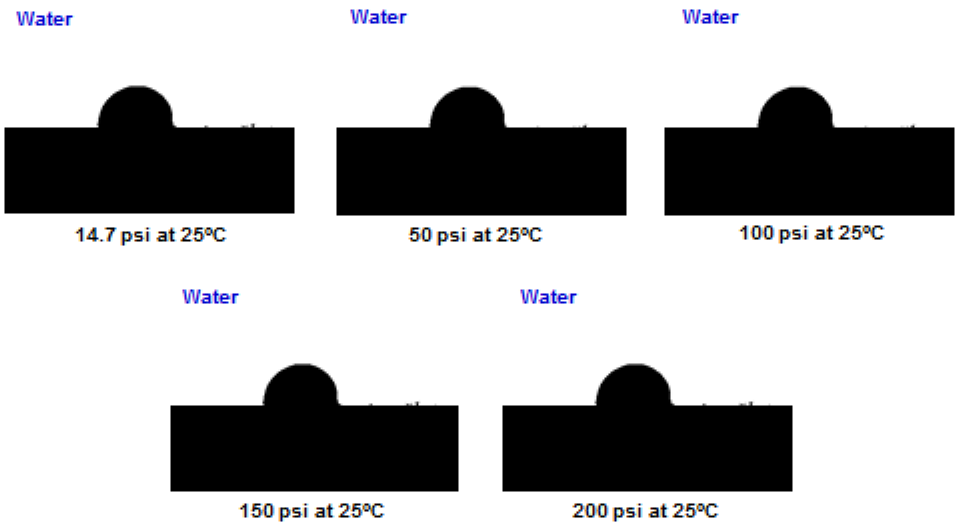


Figure 8—Contact angle of treated mica substrate in elevated pressure.

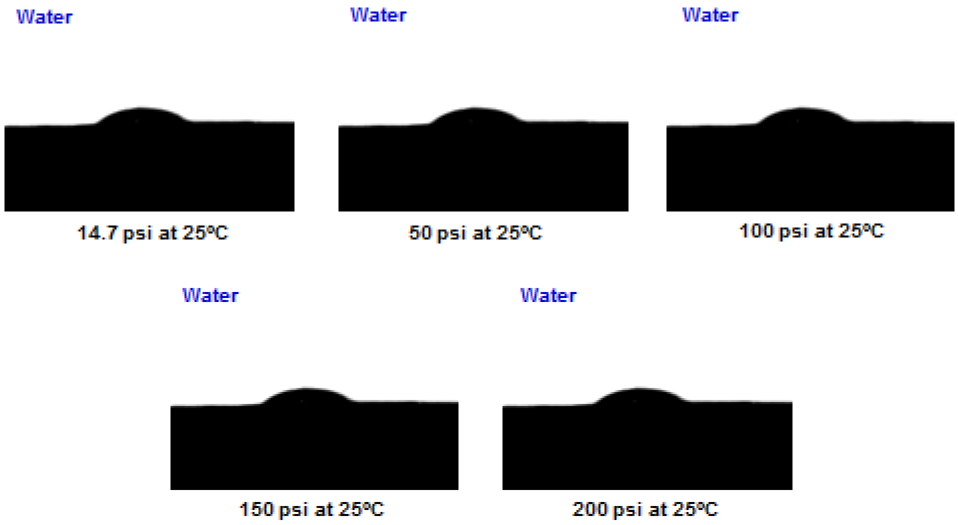


Figure 9—Contact angle of treated Grosmont substrate in elevated pressure.

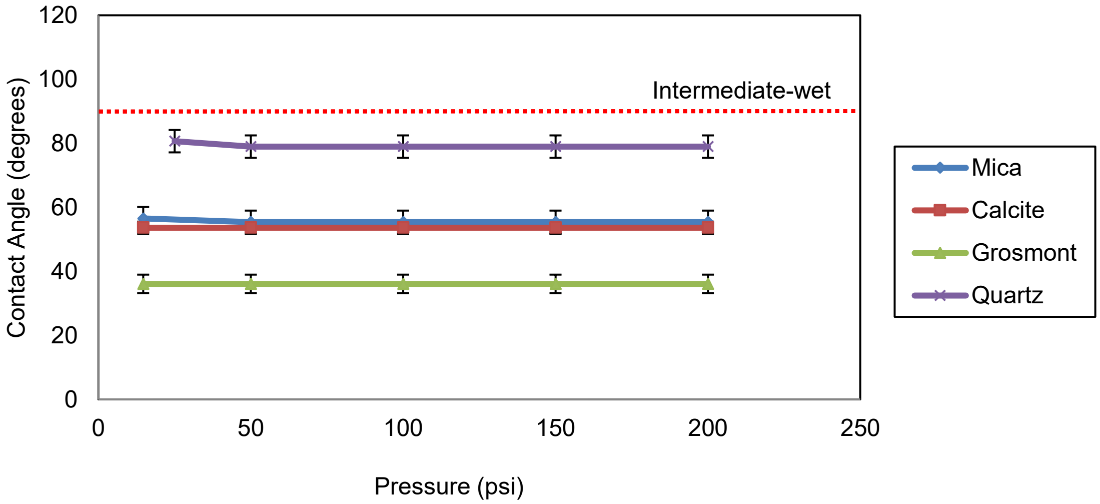
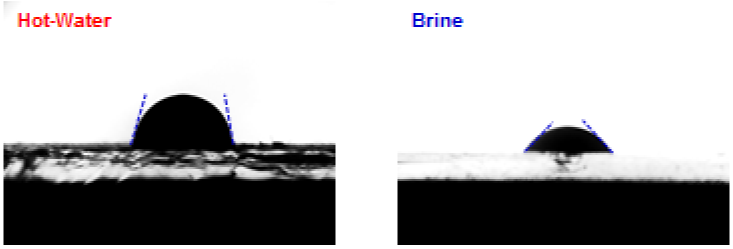


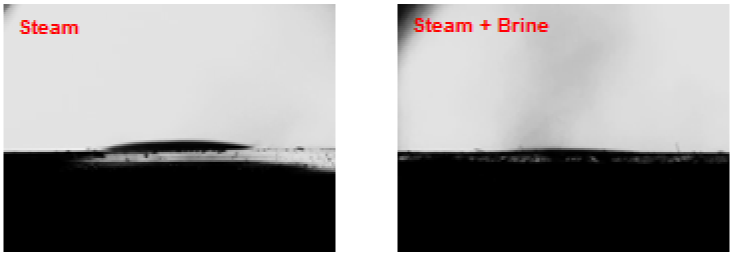
Figure 10—Elevated pressure response to contact angle in all treated substrates.

2.4.3 Effect of Brine Chemistry

Wettability is also impacted by brine chemistry. The introduction of high salinity solution to the rock/oil system as an external phase could lead the wettability state to be more oil-wet. In this research, brine solution was created by mixing 30,000 ppm NaCl, 1,000 ppm $CaCl_2$, and 100 ppm $MgCl_2$ with deionized water. This is a typical low formation water salinity in Alberta. Note that the measured pH of this brine solution was 7.55, which was not substantially different from the vacuumed tap water pH. **Figures 11-14** demonstrate the wettability behavior of oil drop on quartz, calcite, mica, and Grosmont surfaces. Furthermore, the declining contact angles were observed amongst three substrates. Mica substrate contact angle dropped from 55^o to 47^o, and similar wettability behavior was also identified in the calcite substrate. The contact angle of this calcite substrate was observed to decline from 48^o to 39^o. The Grosmont plate had a similar phenomenon as well. The contact angle of the Grosmont plate changed from 34^o to 17^o. Wettability state reduction was also notified in quartz, giving values from 79^o to 59^o.

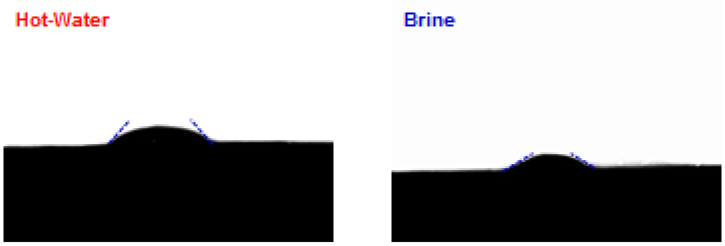


Treated at 90°C and 30-40 psi

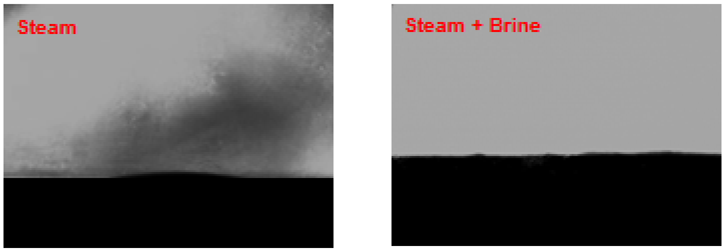


Treated at 150-160°C and 60-70 psi

Figure 11—Treated quartz in liquid and steam phase.

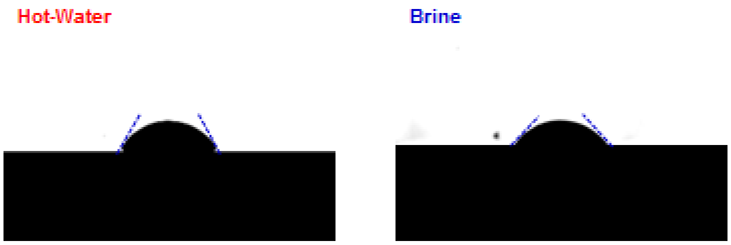


Treated at 90°C and 30-40 psi

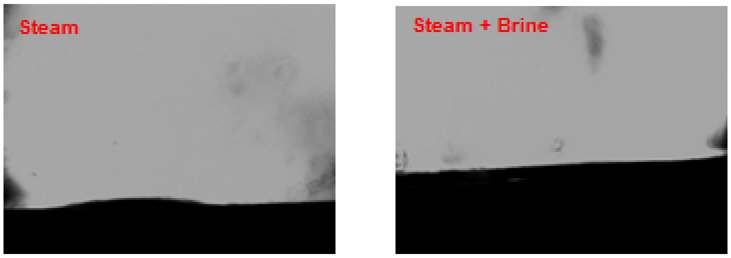


Treated at 150-160°C and 60-70 psi

Figure 12—Treated calcite in liquid and steam phase.

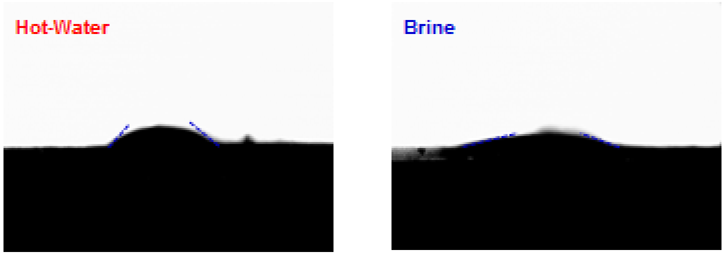


Treated at 90°C and 30-40 psi

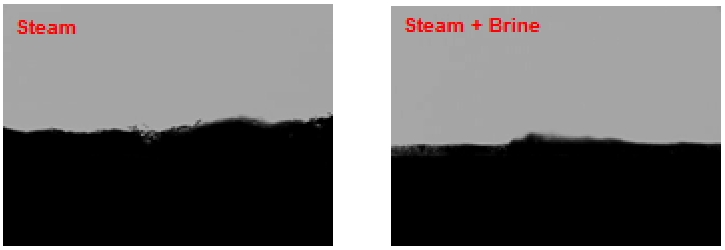


Treated at 150-160°C and 60-70 psi

Figure 13—Treated mica in liquid and steam phase.



Treated at 90°C and 30-40 psi



Treated at 150-160°C and 60-70 psi

Figure 14—Treated Grosmont in liquid and steam phase.

Physically, quartz (SiO_2) is identified as a negatively-charged material having negative zeta potential at pH value around 7.0 (Masliyah et al. 2011). When heavy-oil drop containing negative surface charge is introduced to the quartz surface, repulsive forces occur between the heavy-oil drop and the quartz surface. This mechanism causes the wettability state to be more water-wet. Adding the brine solution to the rock/heavy-oil system could lead to wettability alteration because there is a dynamic change in total surface charge of the rock samples. Furthermore, brine chemistry modifies the total surface charge of the rock samples to be more positively-charged (calcium-activated) and hydrophobic because cations—specifically divalent Ca^{2+}—are attracted to the negatively-charged rock samples (Masliyah et al. 2011).

Wettability alteration triggered by brine chemistry is also presented in **Figure 15**. A similar phenomenon also occurred in calcite and Grosmont samples. Calcite and Grosmont samples also have negatively-charged surfaces. These characteristics were observed in earlier research. Lee et al. (2016) identified negative zeta potential in calcite. Moulin and Roques (2003) also concluded that calcium carbonate plate was observed to be negatively-charged according to the zeta potential measurement. However, these calcite and Grosmont samples are much less negatively-charged compared to quartz leading the wettability state to be more oil-wet initially.

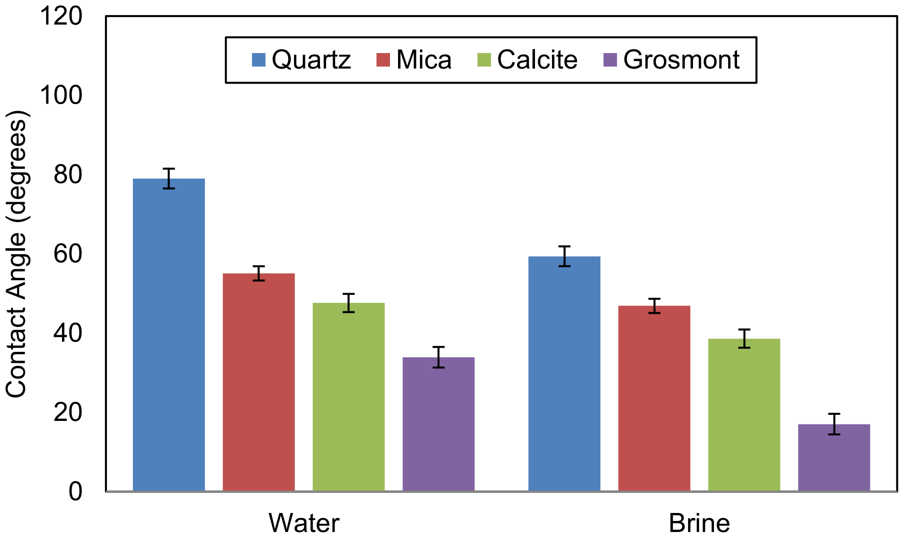


Figure 15—Effect of brine chemistry in contact angle at 90ºC liquid phase.

Numerous published research stated that divalent cation—specifically Ca^{2+}—is more attracted to the negatively-charged solid surface. This conclusion is still valid when the concentrations of cations—monovalent and divalent—are exactly the same. On the other hand, this experimental study involved a mixture of cations with various concentrations. Furthermore, Electrical Double Layer (EDL) is introduced to mentioned cases. This EDL concept is a dependable approach to evaluate the interactions between charged solid surface and ions or charged particles. Fundamentally, this theory is a function of electric potential to the distance of the surface or interface having a charge. In this theory, Debye parameter (κ) is the essential value in further determining the charged particles distance (Debye Length) which is a reciprocal value of κ involving elementary charge (e), permittivity of medium (ε), Boltzmann constant (k), absolute temperature (T), ion concentration (c_i), ion valency (z_i), and Avogadro number (N_A). Debye Length satisfies the following equation:

$$\kappa^{-1} = \left[\sqrt{\left(\frac{e^2}{\varepsilon\, k\, T}\right) \sum z_i{}^2 c_i N_A}\right]^{-1} \tag{1}$$

According to the Electrical Double Layer theory, it was confirmed that divalent cations present the least Debye Length value when the ions concentrations are exactly the same. On the contrary, monovalent cations—Na^+ ions—present the least Debye Length value with various ions concentrations used in this experimental study (30,000 ppm NaCl, 1,000 ppm $CaCl_2$, and 100 ppm $MgCl_2$) in both liquid and steam phase as shown in **Figure 16**. In this particular case, monovalent cations are more dominantly attracted and adsorbed to the negatively-charged solid surfaces because it has the least Debye Length value. Along with this EDL concept, we believe that ions concentrations play important role in intermolecular forces (attractive or repulsive forces). However, this still remains hypothetical and needs further evaluations and validations.

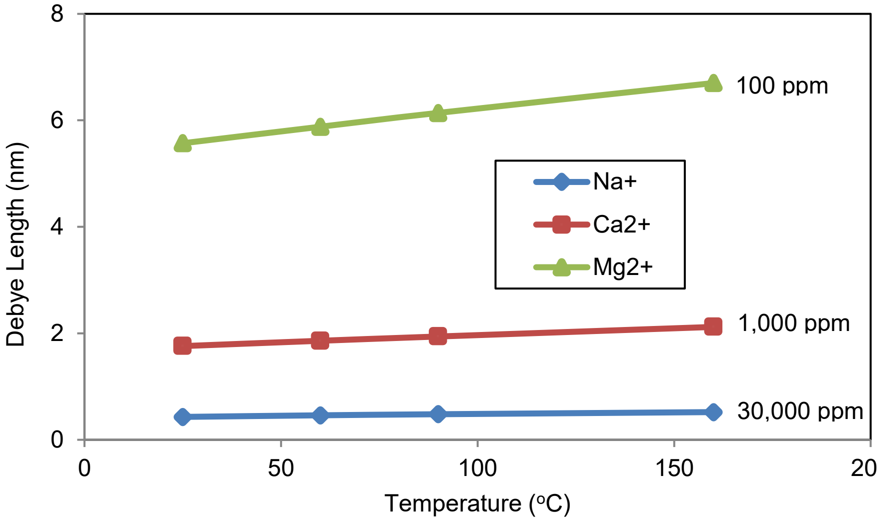


Figure 16—Electrical double layer distance between charged surfaces and cations.

2.4.4 Effect of Phase Change and Temperature

Phase change is a critical factor that must be taken care of, as this mechanism could lead to a wettability alteration in the rock/oil system. Observing phase change impact in wettability alteration was conducted for this research. Observation on the effect of phase change and temperature to the wettability was conducted using vacuumed tap water as an external phase with a measured pH of 7.15. **Figure 17** exhibits the observation of steam-induced wettability alteration in quartz substrate, identifying the contact angle as significantly declining due to phase change. Similarly, **Figure 18** presents the wettability alteration behavior in mica due to phase change occurrence from liquid phase to steam phase; it was observed that the contact angle dropped significantly whenever the external phase was changed from hot water phase to steam phase. This mechanism led to shift the wettability state to be fully oil-wet in steam phase. This phenomenon was observed on the calcite and Grosmont as well, of which is presented in **Figures 19** and **20**. Additionally, it was observed that the contact angle has fallen significantly during this phase change. The supporting contact angle measurements and its hysteresis from the IFT device are exhibited in **Figure 21**.

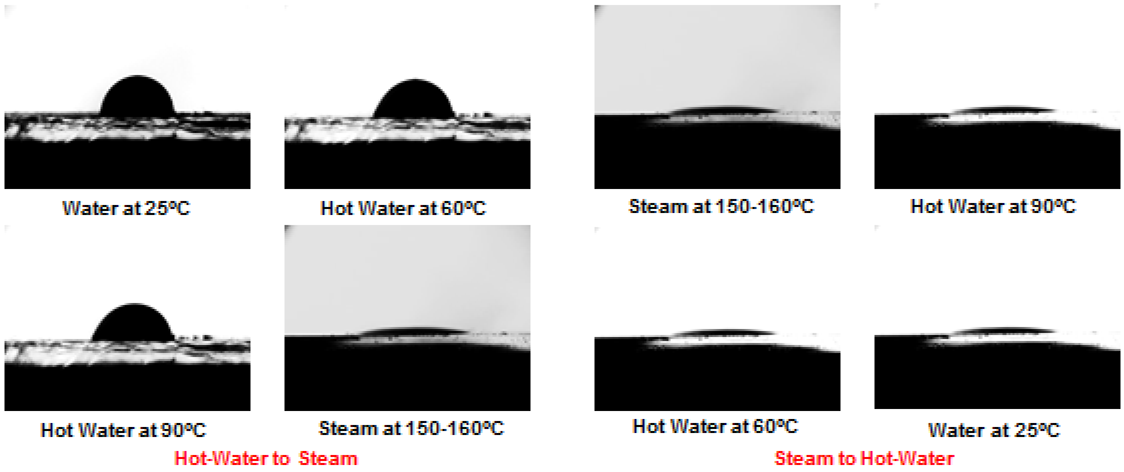


Figure 17—Phase change effect in wettability alteration on treated quartz at pressure range 25-70 psi.

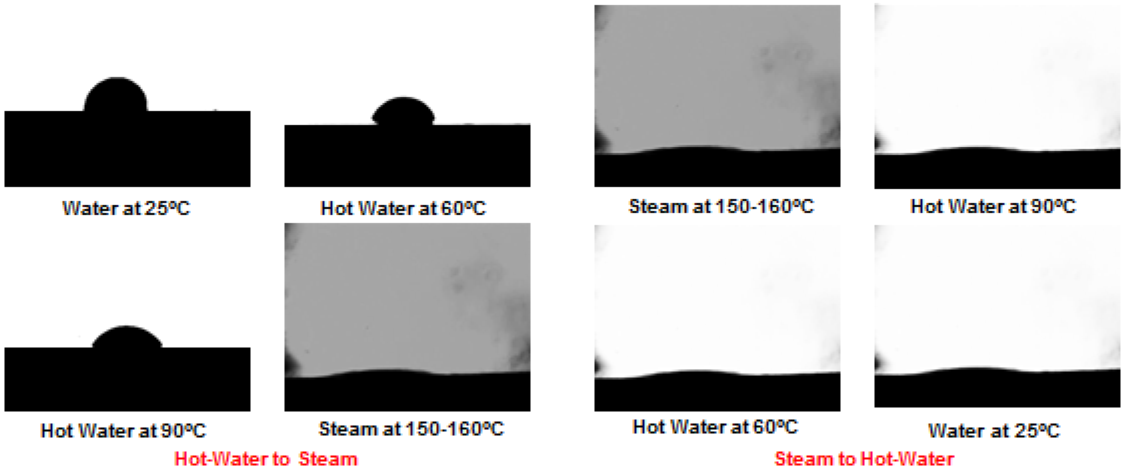


Figure 18—Phase change effect in wettability alteration on treated mica at pressure range 25-70 psi.

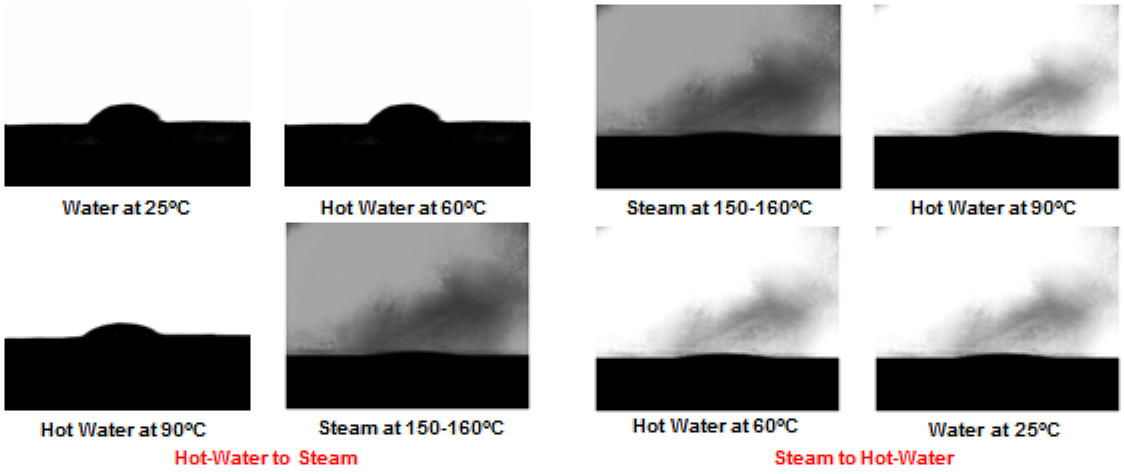


Figure 19—Phase change effect in wettability alteration on treated calcite at pressure range 25-70 psi.

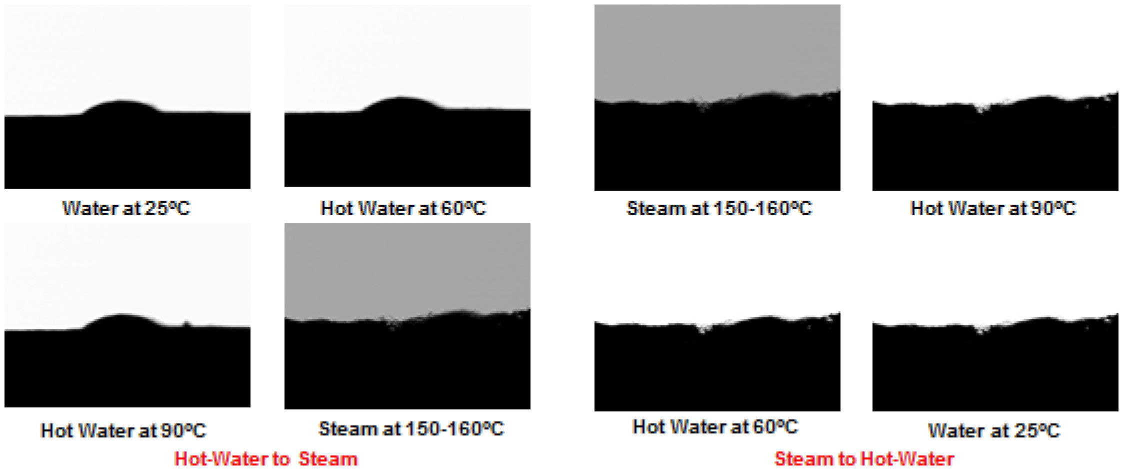


Figure 20—Phase change effect in wettability alteration on treated Grosmont at pressure range 25-70 psi.

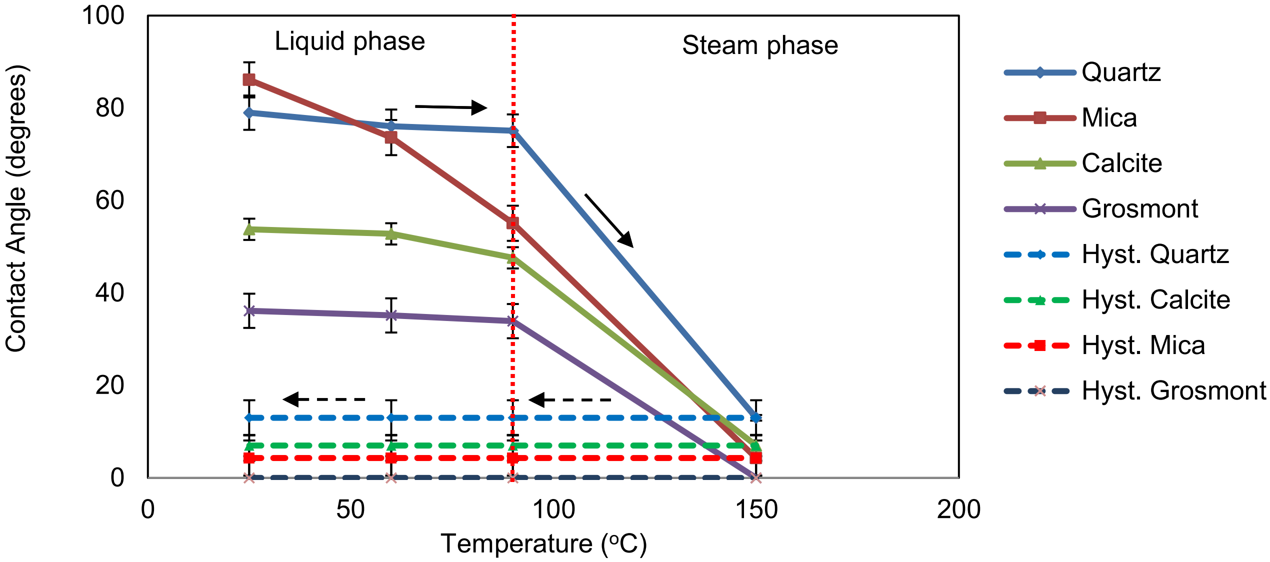


Figure 21—Comparison of contact angle measurement during phase change.

Observation from this experiment showed that the calcite substrate contact angle dropped from averagely 54° to 7° (almost 0°). Similarly, Grosmont plate also experienced a decreasing contact angle from averagely 36° to almost 0°; moreover, the same phenomenon was also observed in quartz and mica substrate when the contact angle plummeted from 79° to 13° and from 86° to 4°, respectively, in steam condition. This research result also confirms and proves the previous hypothesis brought by Bennion et al. (1992) that states when the steam is introduced to the rock/oil/hot water system, the surrounding hot water will evaporate. This circumstance enables more adsorption between the rock surface and oil molecules, shifting the wettability to be more oil-wet, or even fully oil-wet. **Figures 17-21** also explain that original wettability state could not be restored whenever reverse phase change occurred from steam phase to hot water phase. This phenomenon most likely occurred due to polar interaction (Roosta et al. 2009) and the possibility of imbibition occurrence particularly at steam condition due to the negative capillary forces.

2.4.5 Effect of Chemical Additives

High pH solutions, ionic liquid, and surfactants (anionic and nonionic) as chemical additives were used as a wettability alteration agent. Additionally, observation of cationic surfactant was also conducted as our earlier experiment. All experiments were conducted under the presence of brine in the time range of 90 minutes, except cationic surfactant which was exposed to a high steam temperature for a short period of time; the steam injection pressure in each experiment was recorded as 60-70 psi. Sensitivity of each chemical additive concentration is also in the scope of this research. Moreover, this experimental study utilized quartz and calcite as solid samples for each chemical additive experiment. These rock minerals are suitable enough to represent sandstones and carbonates behaviors. Additionally, we also observed that cloudy images are present in almost all steam or elevated temperature experiments. This is a very common and normal behavior when steam was generated in the system, particularly when chemical additives were applied. However, the equipment could still capture and calculate the contact angle for quantitative analysis.

In supporting this experiment, Thermogravimetric Analysis (TGA) was performed to investigate the thermal stability of each chemical additive. **Figure 22** presents the result of TGA for each chemical additive in term of its thermal stability. It was observed that decomposition of high pH solution and anionic surfactants occurred at temperatures above 120°C, of which can be considered medium thermal stability. On the other hand, ionic liquid, nonionic, and cationic surfactant could deliver great thermal stability at extremely high temperatures, but the thermal stability from this TGA measurement might be overrated due to short-term stability during rapid temperature jumps as explained by Cao and Mu (2014) in their previous research in thermal stability analysis. In addition to this experimental study, chemical concentration was also taken into consideration in evaluating the optimum concentration for both contact angle and surface tension quantitative analysis.

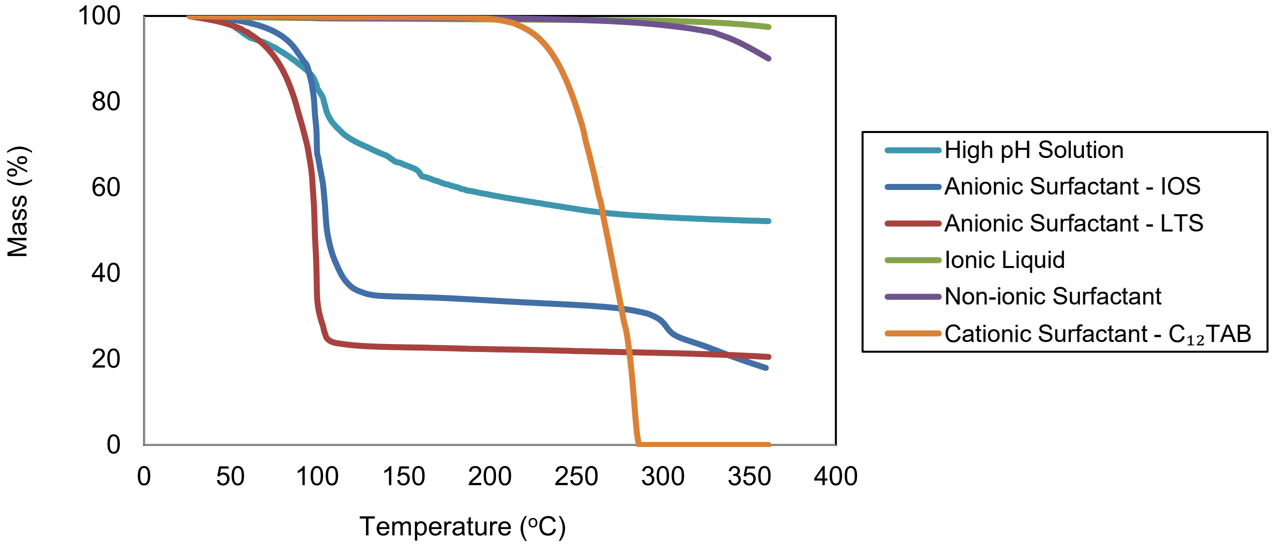
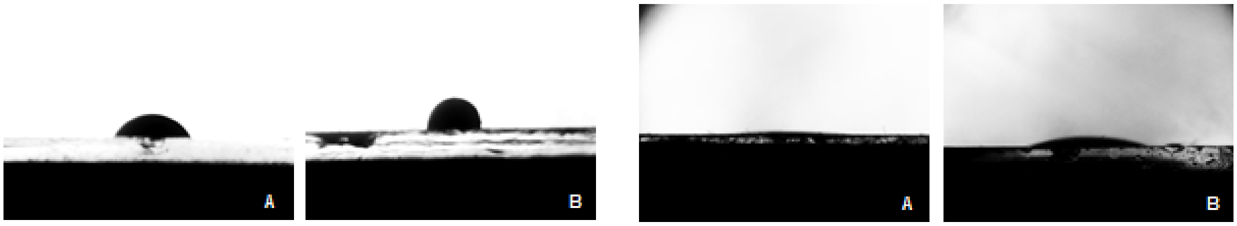


Figure 22—Thermogravimetric Analysis (TGA) of tested chemical additives.

High pH Solution. In this research, sodium metaborate ($NaBO_2$) was utilized as the high pH solution, the utilization of this type of high pH solution being applied in our previous research as well. In liquid phase, both incremental contact angle improvement and reduction of IFT were observed by Wei and Babadagli (2016). According to this research, the high pH solution was identified to give wettability improvement in both liquid and steam phase on quartz and calcite. Improvement in contact angle was observed about 18-21° on both substrates. These measurements together with brine presence in steam phase are represented by **Figures 23** and **24**. Additionally, **Figure 25** exhibits the wettability state of mica after applying the high pH solution to the system; wettability alteration was observed on mica substrate, but the wettability alteration was reduced with brine chemistry. Wettability alteration in phase change with the high pH solution for each substrate is also presented in **Figure 26**. The optimum chemical concentration was also identified in the range of 1-2 wt% as shown in **Figure 27**. In core flood experiments, favorable incremental oil recovery was obtained with this high pH solution (Bruns and Babadagli 2017). Adding this type of high pH solution into steam led to wettability improvement as this mechanism could modify the surface charge of the substrates and particles interaction in the solid/oil system (Masliyah et al. 2011). Furthermore, incremental pH value could lead the surface charge of the substrates to be more negatively-charged, which also triggered higher repulsive forces between the solid surface and oil drop.



Liquid Phase at 90°C and 30-40 psi

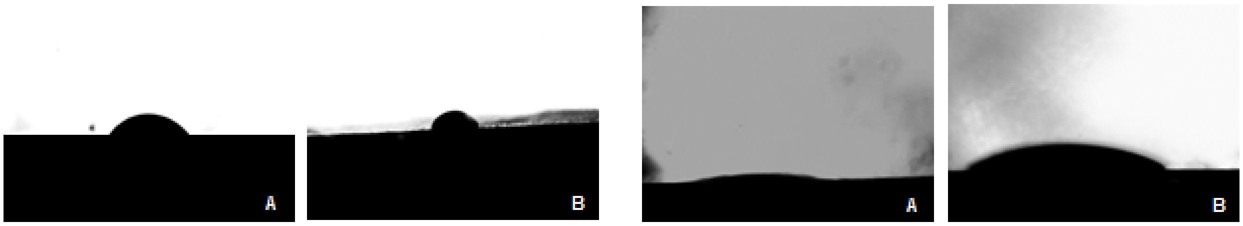
Steam Phase at 150-160°C and 60-70 psi

Figure 23—Contact angle observation of quartz (a) before and (b) after adding high pH solution.

Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 24—Contact angle observation of calcite (a) before and (b) after adding high pH solution.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 25—Contact angle observation of mica (a) before and (b) after adding high pH solution without brine chemistry.

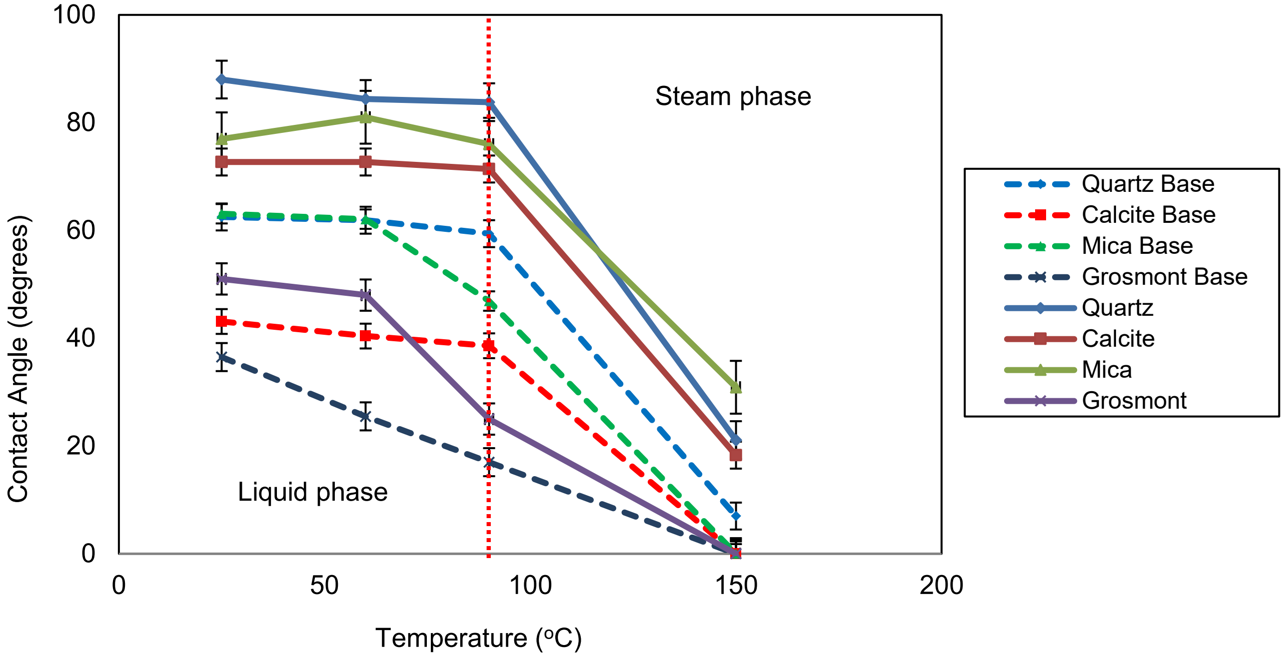


Figure 26—Comparison of contact angle measurement during phase change with high pH solution.

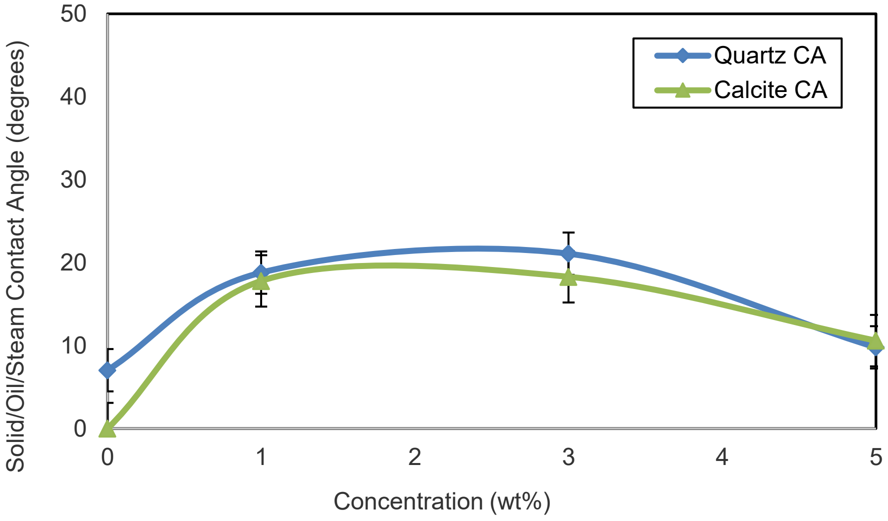
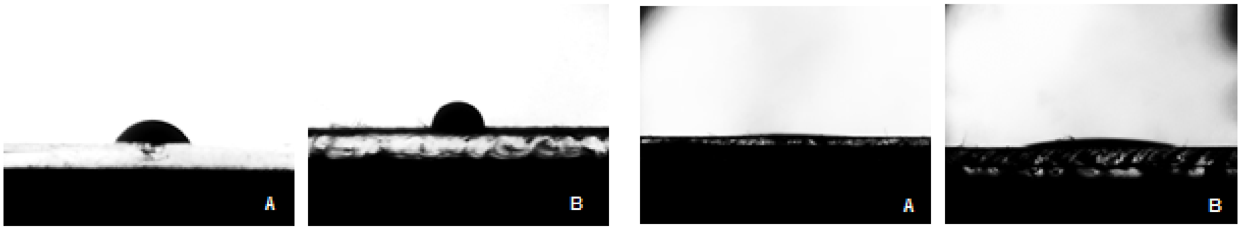


Figure 27—Contact angle and surface tension profile in steam phase with high pH solution.

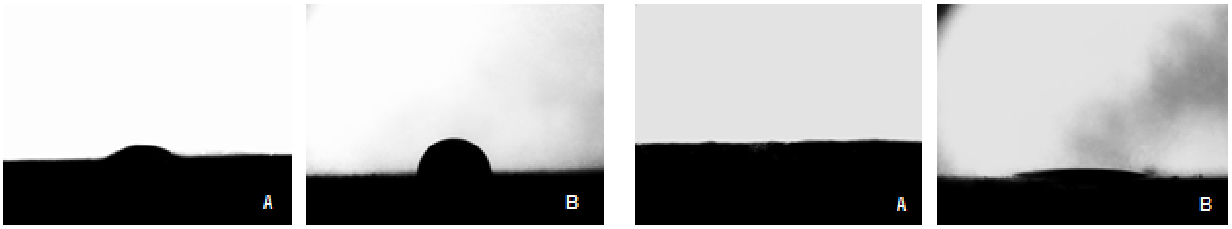
Ionic Liquid. There are many types of ionic liquids beneficial to enhanced oil recovery. The resistance to a high temperature and high salinity environment has made this chemical even more renowned in thermal recovery. Cao and Mu (2014) tested sixty-six ionic liquids when researching great thermal stability in extremely high temperatures. This experimental study focuses on using 1-butyl-3-methyl-imidazolium (cation) and tetrafluoroborate (anion) as a chemical additive. **Figures 28-30** exhibit the wettability alteration on quartz and calcite after adding the ionic liquid. Contact angle improved from 7° to 17° for quartz substrate and from 0° to 15° for calcite substrate in steam condition. According to information presented in **Figure 31**, the optimum contact angle was observed at 1 wt% of ionic liquid concentration. Alternatively, a higher ionic liquid concentration of at least 3 wt% was required to attain the optimum contact angle in shifting the wettability to be less oil-wet. This mechanism of wettability alteration is also aligned with the previous research performed by Bruns and Babadagli (2017) of which exposed the incremental oil recovery to more than 40% through steam core flooding with ionic liquid.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 28—Contact angle observation of quartz (a) before and (b) after adding ionic liquid.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 29—Contact angle observation of calcite (a) before and (b) after adding ionic liquid.

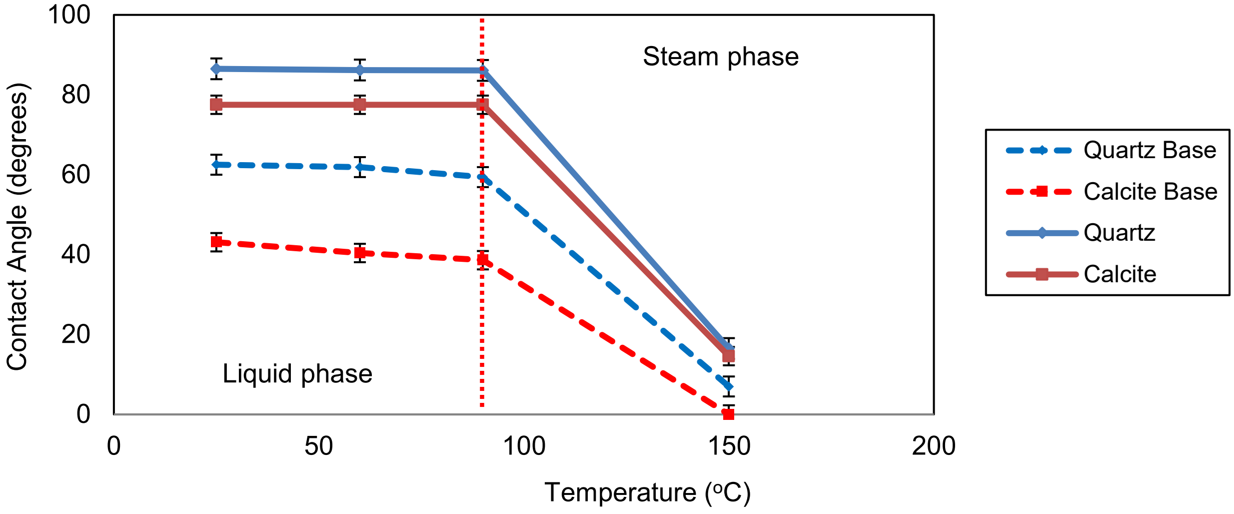


Figure 30—Comparison of contact angle measurement during phase change with ionic liquid.

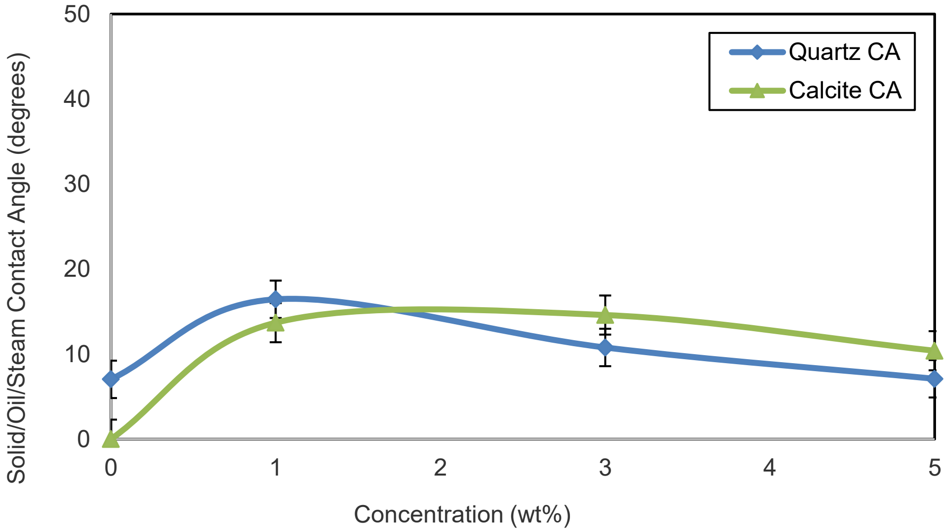


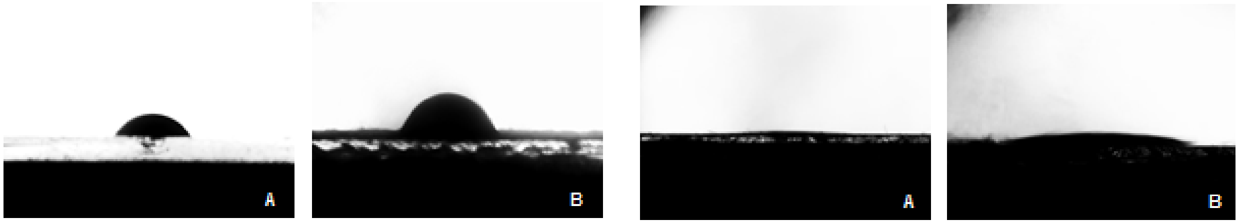
Figure 31—Contact angle and surface tension profile in steam phase with ionic liquid.

Anionic Surfactants. Two types of anionic surfactants were applied in this wettability alteration research: Internal Olefin Sulfonate (IOS) and Linear-alkyl Toluene Sulfonate (LTS). Both surfactants presented very favorable results under steam condition. **Figures 32-34** present the promising wettability alteration of quartz and calcite substrates after adding IOS surfactant.

Contact angle improvement was observed as 34° on a quartz substrate and 21° on calcite substrate. Optimum IOS surfactant concentration was also perceived at 3 wt% as presented in **Figure 35**, yielding to the maximum degree of wettability alteration.

Moreover, the experimental study of using LTS type surfactant in steam condition presents a very promising outcome in wettability alteration on both quartz and calcite substrates. Unfortunately, the wettability state could not be observed in liquid phase due to its cloudy behavior. LTS surfactant led to the improvement of the contact angle to 34° and 28° on quartz and calcite substrates, correspondingly leading to be more steam-wet as exhibited in **Figures 36** and **37**. According to this experimental study, optimum surfactant concentration was achieved around 3 wt% as shown in **Figure 38**.

In addition to this wettability alteration, the adsorption mechanism of this surfactant was very essential in modifying the surface charge of the solid phase. At the very beginning, both solid surfaces were more positively-charged under the effect of brine presence. In summary, optimum chemical concentration in this steam application research was observed at around 2-3 wt% for IOS and 1-2 wt% for LTS resulting the maximum wettability alteration degree. By adding anionic surfactants, it will fundamentally modify the surface charge of the solid surface by allowing the adsorption of anionic part in surfactant onto the solid surface. This adsorption process causes the solid surface to be more negatively-charged creating repulsive forces between the solid surface and the oil phase. This phenomenon was also observed by Moulin and Roques (2003) through the zeta potential measurement of calcite with anionic surfactants. Furthermore, Bruns and Babadagli (2017) concluded that anionic surfactants provided the highest oil recovery through steam core flooding.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 32—Contact angle observation of quartz (a) before and (b) after adding IOS.

Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 33—Contact angle observation of calcite (a) before and (b) after adding IOS.

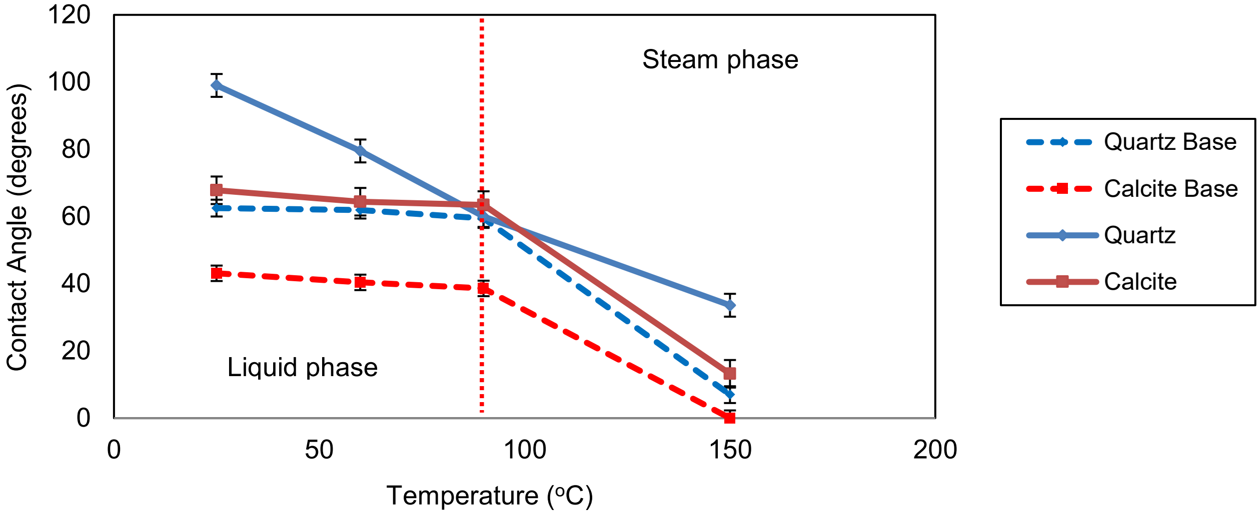


Figure 34—Comparison of contact angle measurement during phase change with IOS.

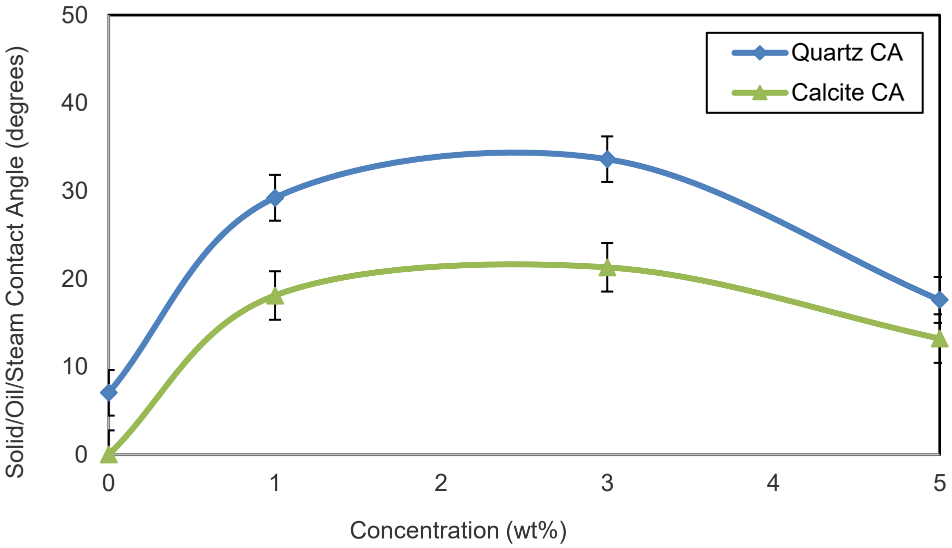


Figure 35—Contact angle and surface tension profile in steam phase with IOS.

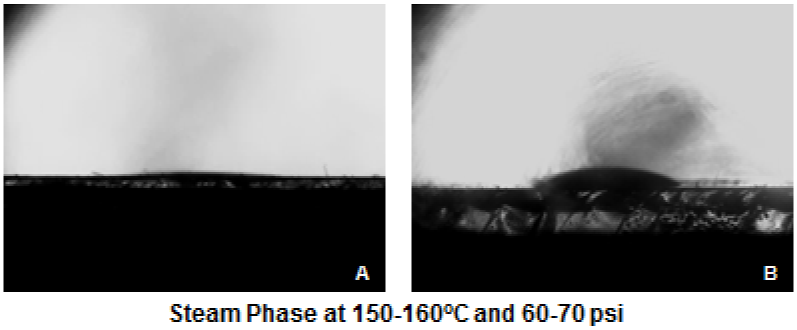


Figure 36—Contact angle observation of quartz (a) before and (b) after adding LTS.

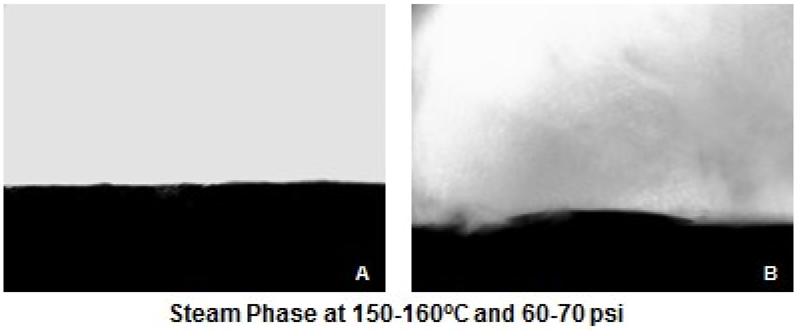


Figure 37—Contact angle observation of calcite (a) before and (b) after adding LTS.

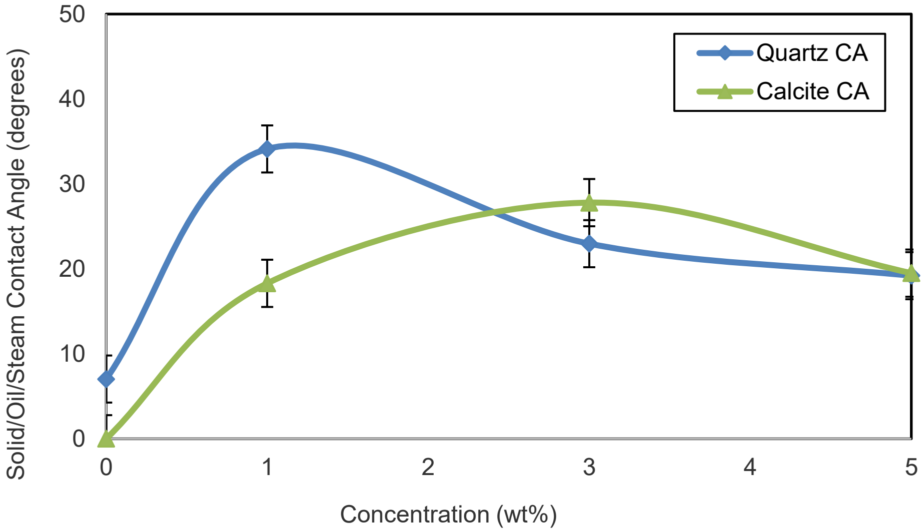


Figure 38—Contact angle and surface tension profile in steam phase with LTS.

Nonionic Surfactant. According to this research, nonionic surfactant also delivers favorable results in terms of wettability alteration in steam application—specifically in calcite substrate. Sorbitan monooleat (Span 80) was selected as nonionic surfactant in this wettability alteration research. **Figures 39** and **40** present the wettability state of both quartz and calcite substrates, but wettability state in liquid phase could not be observed due to its cloudy behavior. Wettability alteration was achieved and represented by contact angles as 17° on a quartz substrate and 25° on a calcite substrate. Furthermore, **Figure 41** presents both contact angle and surface tension profiles in different ranges of chemical concentrations for nonionic surfactant. Based on this result, optimum nonionic surfactant concentration was observed for both substrates. Around 1 wt% of surfactant concentration will give the maximum contact angle for quartz substrate; meanwhile, a higher nonionic surfactant concentration of about 3 wt% was needed to achieve the maximum contact angle on a calcite substrate. In summary, the wettability alteration is not really favorable for quartz substrate by using this type of nonionic surfactant, but very favorable wettability alteration was observed on calcite surface with the nonionic surfactant. Wu et al. (2006) also reported that applying nonionic surfactant could lead to very promising oil recovery in carbonates.

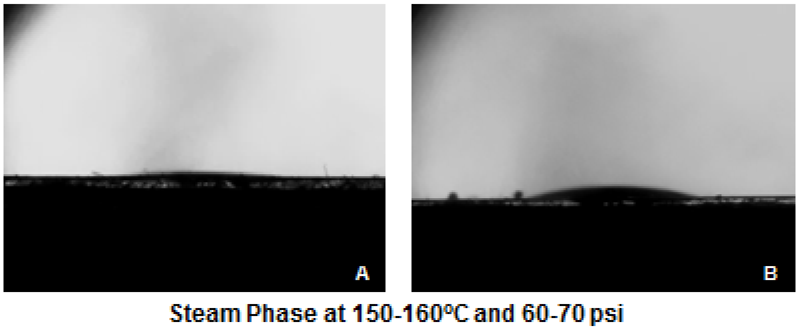


Figure 39—Contact angle observation of quartz (a) before and (b) after adding nonionic surfactant.

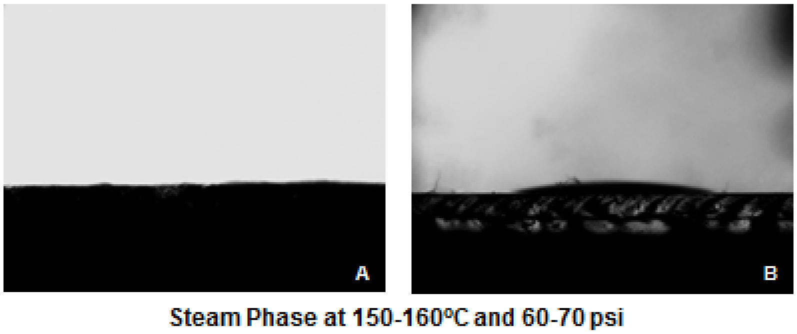


Figure 40—Contact angle observation of calcite (a) before and (b) after adding nonionic surfactant.

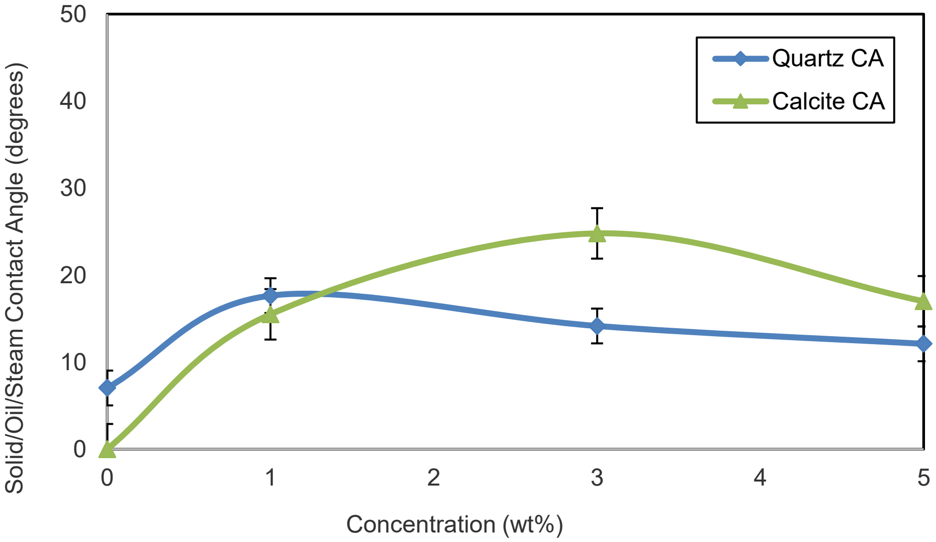


Figure 41—Contact angle and surface tension profile in steam phase with nonionic surfactant.

Cationic Surfactant. This type of surfactant was also included according to the previous experiment. C_{12}TAB was utilized for this cationic surfactant as it was noticed that this cationic surfactant was more effective in low temperatures. When the temperature increased, this surfactant performed much less effective, which can be attributed to thermal instability of this chemical. This mechanism was also observed on a mica substrate by Wei and Babadagli (2017). **Figure 42** shows the trend of wettability state on mica substrate before and after adding cationic surfactant without brine presence. However, the result was obtained from the very early part of this experimental study, not conducted for the long exposure of the high steam temperature, and after only using one concentration it was considered to be a less representative result. Moreover, effect of brine chemistry might also be affecting this wettability alteration mechanism. An experimental study with cationic surfactant was not continued in this research due to thermal stability issues observed in the earlier experience.

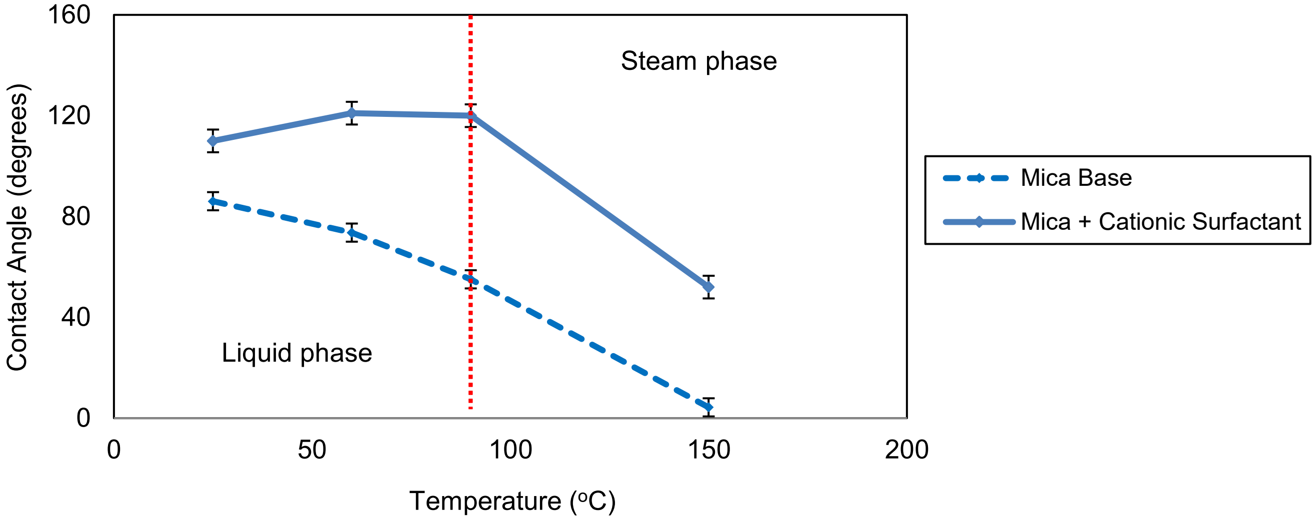


Figure 42—Contact angle observation in mica and cationic surfactant without brine presence.

2.5 Conclusions

1. Pressure is not a significant parameter impacting wettability state, of which is also represented by stable contact angle value in elevated pressure.

2. Substrate treatment is also an essential factor that has to be considered in steam-wettability alteration mechanisms. It is proven that aged substrates were giving lower contact angle values compared to non-treated substrates; furthermore, the Wenzel model also confirmed that solid surface roughness plays an essential role in the wettability state of the substrates. However, it is also recommended to age the substrates in every interfacial property experiment when representing reservoir natural wettability state.
3. Phase change at an elevated temperature is the most critical and dominant factor affecting steam-induced wettability alteration in steam injection. Previous hypothesis about this phase change have been proven and confirmed by this research. During phase change from liquid phase to steam phase, wettability alteration occurred which caused the drop in contact angle magnitude to be in the fully oil-wet state; therefore, chemical additives must be applied in shifting the wettability to be a more water or steam-wet state.
4. Steam-wettability state is also affected by salinity. A higher salinity environment leads to the declining wettability state, of which is a more oil-wet state, especially when divalent ions are present in exactly similar salt concentrations. The presence of the brine chemistry led the substrates to be more positively-charged. Furthermore, this surface interaction turned the substrates to a more hydrophobic state and created more attractive forces between the substrates and the oil drop.
5. Almost all chemical additives presented good thermal stability. Only anionic surfactants show medium thermal stability levels through TGA testing. The selection of these chemicals for hot-waterflooding or steam injection can be determined by their temperature limitations.
6. Despite the medium thermal stability from TGA testing, anionic surfactants showed the most favorable wettability alteration under steam application amongst all tested chemical additives, according to this research. The adsorption of anionic chain from these types of surfactants was very beneficial in modifying the solid surface charge to be way more negatively-charged, resulting in more repulsive forces in the rock/heavy-oil system. As well, additional favorable surface tension reduction was also achieved by utilizing these anionic surfactants.

7. Nonionic surfactant is also very promising when applied to carbonates in steam. According to this research, wettability alteration was achieved at the maximum degree of wettability state represented by maximum contact angle.
8. Cationic surfactant was more effective in low temperatures. Brine presence might also impact the wettability alteration mechanism. Higher concentrations of this cationic surfactant might also improve its performance in brine environment; however, longer heat exposure is still a challenge and requires further investigation in steam condition.
9. Optimum chemical additives concentration is also very essential in obtaining maximum wettability alteration degree, as a higher chemical additive concentration does not mean that higher wettability alteration degree will be achieved. According to this research, lower concentration is sufficient for some chemical additives to obtain maximum wettability alteration degree, specifically in steam condition.

Chapter 3: Reconsideration of Steam Additives to Improve Displacement Efficiency: Can New Generation Chemicals be Solution for Steam Induced Unfavorable Wettability Alteration?

This chapter of thesis is a modified version of a published research paper SPE 195833. The conference paper version SPE-195833-MS was presented at SPE Annual Technical Conference & Exhibition held in Calgary, Canada, 30 September-2 October 2019. The journal version of this research paper was submitted to SPE Journal.

3.1 Preface

In this paper, contact angles in a rock/heavy-oil/steam system were measured to observe the degree of wettability alteration when unconventional chemicals were added to steam. A heavy-crude-oil obtained from a field in Alberta (27,780 cP at 25ºC) was used in all contact angle measurements and the measurements were repeated on different types of substrates (quartz and calcite). In addition to this observation, surface tension tests between heavy-oil and steam were also conducted to study the change in interfacial properties. All measurements in this research were conducted at a range of temperatures up to 200ºC in a high-temperature-high-pressure IFT device. In gaining a comprehensive evaluation of this mechanism, several impacting factors such as pressure, phase change, and type of rock were taken into consideration and evaluated separately. Different types of novel chemical additives—biodiesel, Switchable-Hydrophilicity Tertiary Amines (SHTA), nanofluids (dispersed SiO_2 and ZrO_2), ethers, alcohols, and chelating agents—were ere applied to the steam with a range of concentrations throughout surface tension and contact angle measurements to evaluate wettability alteration performance at steam temperature and pressure.

The observation presented that pressure does not contribute substantially to the wettability state and was perceived to be more oil-wet in steam conditions—as also confirmed by our previous research. The irreversible mechanism of wettability state was the result when phase change occurred with the presence of brine. Wettability alteration and surface tension reduction in steam condition were achieved after involving these unconventional chemicals, an example being in the steam with biodiesel application. In addition, optimum chemical concentration was also observed through surface tension and contact angle measurements.

The study and analysis of chemical additives applications provides a stronger understanding of steam-induced wettability alteration mechanisms in a rock/heavy-oil/steam system. In summary, conventional steam additives can be altered by these novel chemicals that are both cheaper and more thermally stable, thus showing potential and appearing promising for steam wettability improvement and surface tension reduction in steam applications.

Key words: Steam injection efficiency, phase change, wettability alteration, chemical and nanofluid additives, interfacial tension, contact angle.

3.2 Introduction

Thermal recovery has been largely developed for decades to unlock this heavy oil potential; specifically, steam injection is the most renowned thermal recovery technology for heavy-oil production. This methodology has been widely applied throughout the world in the form of Steam-Assisted Gravity Drainage (SAGD) and Cyclic Steam Stimulation (CSS). These steam applications are proven to be effective in recuperating heavy-oil production as shown by Sheng (2013) in his literature review of field case studies.

On the other hand, steam injection has been a challenging process due to excess cost, huge amounts of steam and energy needs, as well as environmental concerns. Thus, any attempt to improve the efficiency by recovery improvement or reducing steam needs is valuable. Chemical additives for this purpose have been tested since the 80s but high cost and thermal stability have restricted the use of them in practice. Steam applications (SAGD and CSS) have gained more attention over the last decade due to the number of steam applications made available in the world increasing (SAGD and CSS in Canada and Venezuela, steam flooding and CSS in China, Kuwait, and Indonesia). In parallel to this and with advancements in the chemical industry and nano sciences, research on new types of chemicals as additives is being conducted for use in steam applications.

Recently, the innovation of unconventional (or new generation) chemicals has presented the capability to reconsider conventional chemical additives in improving oil recovery; however, the wettability alteration mechanism, specifically in steam applications, remains inconspicuous. Bruns and Babadagli (2018) recently tested both the conventional and non-conventional (new generation) chemicals for recovery improvement using core tests. They also investigated the recovery mechanisms of these materials using visual experiments (Bruns and Babadagli 2018). It was observed that conventional surfactants and alkalis (IOS, LTS, Span 80, and $NaBO_2$) can be used to reduce wettability and IFT (Pratama and Babadagli 2018, 2019) but the cost and thermal stability of those materials could be a limiting factor to use in steam applications; therefore, new types of materials should be initially tested before core flooding experiments.

Wettability state is one of the unsolved issues occurring during steam injection applications. Increasing temperature in a rock/heavy-oil/water system leads to the detachment of polar groups from the rock surface area leading to the improvement of water wettability. On the other hand, phase change in a rock/heavy-oil/water system performs conversely in terms of the wettability state behavior. Furthermore, the phase change process from hot-water phase to steam phase will affect the reduction of wettability, undoubtedly influencing oil recovery performance. Earlier research by Pratama and Babadagli (2018, 2019) concluded that the wettability of the rock surface became more or even fully oil-wet when the phase of injected fluid was transformed from hot-water phase to steam phase. The observed phenomenon also aligned with the experimental study brought by Naser et al. (2014) concluding that the contact angle between the heavy-oil drop and quartz surface was reduced substantially after applying steam to the system. This mechanism plays the most important role in wettability alteration according to the experimental study. These findings also confirm the previous hypothesis about wettability alteration being affected by phase change as promoted by Bennion et al. (1992).

Figure 43 illustrates the phase change mechanism in reservoir rocks. Initially, most of the reservoir rocks are most-likely water-wet, particularly sandstones. At this state, most of the oil phase is typically surrounded by water phase. This circumstance prevents the oil phase from being in contact with the rock surface in the reservoir. Moreover, when steam is injected into the reservoir, the encapsulating water phase will be transformed from liquid phase to steam phase. This phase change—at saturated steam pressure and temperature—leads to direct contact between the oil phase and the surface of the rock in the reservoir. In summary, wettability alteration from an initially water-wet to an oil-wet state occurred due to this phase change mechanism (Bennion et al. 1992), leading to the declining of heavy-oil recovery.

In addition to this phenomenon, a steep production decline was reported from the producing steam flood fields. Winderasta et al. (2018) documented the Duri heavy-oil steam flood field production performance in Indonesia; the field has experienced a rapid production decline after reaching its stage of maturity from initially 290,000 barrels of oil per day to 100,000 barrels of oil per day presently. Similar behavior was also perceived in most of steam flood fields in the

United States reported by Jones et al. (1995) and Blevins (1990). This evidence has substantiated that phase change involves an essential role in wettability alteration yielding to the diminishing oil recovery.

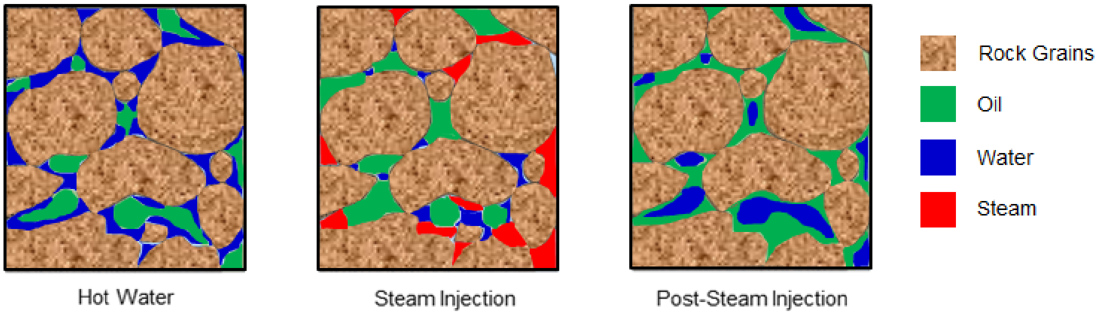


Figure 43—Wettability alteration in phase change mechanism (after Pratama and Babadagli 2019).

Efforts in chemical-induced wettability alteration have been established for decades. These conventional chemicals—alkalis, surfactants, and ionic liquids—are considered to present a favorable outcome in restoring wettability alteration from an oil-wet to more water-wet state. Numerous published researches have also demonstrated this promising chemical-induced wettability alteration, including steam applications. Furthermore, our recent research efforts in these conventional chemicals as steam additives also presented auspicious results in steam-wettability alteration. Pratama and Babadagli (2018, 2019) concluded that some chemical additives exhibited favorable performance in wettability alteration and surface tension reduction in steam condition, particularly anionic and nonionic surfactants. Additionally, optimum chemical additive concentration was also observed yielding to the maximum wettability alteration degree and the minimum surface tension. This observation also aligned with our previous steam core flooding and Hele-Shaw visualization conducted by Bruns and Babadagli (2017, 2018, 2019a-b). According to the experimental studies, some of these conventional chemicals—anionic and nonionic surfactants—presented favorable thermal stability and oil recovery.

Recently, research in novel chemical additives has received more attention as it is believed to be more economical and promising in altering wettability state to be more of a water-wet state. Therefore, novel chemical additives are presently taken into consideration in alternating conventional chemicals. One of the most commonly investigated novel chemical additives for enhanced oil recovery is metal nanoparticles, since their introduction and subsequent promotion in nanoscience starting in the late 1950s. Feynman (1960)—in his first publication regarding nanoscience—stated that human eyes can only accommodate the smallest object with the dimension about 1/120 of an inch. Nanoparticles, by definition, are particles having a size of approximately 1 to 100 nanometers; thus conveying that these nanoparticles are impossible to observe with bare eyes. This novel discovery in nanotechnology was then applied to petroleum technology due to its potential to enhance oil recovery.

Numerous research about these nanoparticles—silicon oxide (SiO_2) and zirconium oxide (ZrO_2)—presents very promising performance in wettability alteration and interfacial tension reduction. Maghzi et al. (2012), through a glass-etched micromodel experimental study, concluded that dispersed silica nanoparticles could improve the wettability state from originally oil-wet to a strongly water-wet state, yielding to incremental oil recovery and areal sweep efficiency improvements during waterflood. A similar behavior of this wettability alteration was also observed by Cao et al. (2017), Wei and Babadagli (2017), and Mohammed and Babadagli (2016) in a high-temperature environment. The use of zirconium oxide was also reported to be effective in altering the wettability of the rocks; Karimi et al. (2012) and Nwidee et al. (2016) concluded that zirconia nanofluids could shift the wettability of the carbonates to a more water-wet state. Fundamentally, adding this chemical additive leads to adsorption of nanoparticles on the rock surface yielding to the wettability shifting. This evidence presents the favorable potential of nanofluids for wettability alteration.

Other potential novel chemicals in restoring the wettability state are solvent-based chemical additives. These solvent-based chemicals—dimethyl ether (DME) and diethyl ether (DEE)—have been gaining more consideration in enhanced oil recovery applications. Several published researches have confirmed the advantage of these solvent-based chemicals in altering wettability and improving oil recovery. A successful core flood experimental study of DME was reported by Alkindi et al. (2016) through solvent-based waterflood. This integrated enhanced oil recovery process delivered up to 20% additional oil recovery from carbonates core samples after water injection. Moreover, Chahardowli et al. (2016) presented that auspicious oil recovery up to 60% was achieved by combining waterflood and DME throughout an imbibition experimental study of sandstones and carbonates. Additionally, the use of another solvent-based type—DEE—was also evidenced to have favorable performance in exhibiting incremental oil recovery.

Published research about the application of DEE done by Chahardowli et al. (2013) stated that more than 20% additional oil recovery was attainable after implementing DEE during spontaneous imbibition. Another novel chemical additive that has also been considered for improving oil recovery is isopropyl alcohol, one of several types of alcohols. Isopropyl alcohol was also identified as 2-propanol and miscible when mixed with water. Gatlin and Slobod (1960) conducted an experimental study on the unconsolidated porous medium core by utilizing this isopropyl alcohol as the alcohol slug. They reached the conclusion that miscible displacement to both oil and water was achieved because the isopropyl alcohol slug behaved as a piston. Another favorable result coming from this isopropyl alcohol application was presented by Holm and Csaszar (1962) through sandstone core flooding. Nearly 30% incremental oil recovery was accomplished after applying this isopropyl alcohol compared to conventional waterflood; however, this type of alcohol still needs further investigation into its thermal stability.

In addition to these novel chemical additives, numerous experimental studies have been conducted on chelating agents for enhancing oil recovery. Fundamentally, chelating agents are materials which are able to initiate some bonds to an ion of a metal. The most common chelating agents utilized in enhanced oil recovery are aminopolycarboxylic acids which are hydroxyethylethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), and ethylenediaminetetraacetic acid (EDTA). Applying chelating agents could lead to the additional oil recovery up to 25% through sandstone core flooding experimental studies, and lower the IFT value (Mahmoud et al. 2017). Similar behavior was also perceived by Mahmoud and Abdelgawad (2015) on carbonates. According to their core flood experimental study, more than 80% total oil recovery was obtained from carbonate cores after injecting these chelating agents. Furthermore, these chelating agents were also reported to be effective at high temperature (Almubarak et al. 2017).

Another promising novel chemical additive for favorable wettability alteration is biodiesel. This type of chemical additive yielded auspicious surface/interfacial tension reduction, wettability alteration, and incremental oil recovery. Babadagli et al. (2010) and Babadagli and Ozum (2010) applied this biodiesel in their experimental studies with bitumen from Canada. The studies concluded that more than 80% bitumen recovery was achieved after adding biodiesel along with thermal recovery. Moreover, the addition of the biodiesel could favorably reduce the IFT between the bitumen and process water (Argüelles-Vivas et al. 2012). This evidence leads to the conclusion that the use of biodiesel as a chemical additive can potentially boost up the incremental oil recovery, particularly for heavy-oil thermal recovery.

In addition to above summarized novel chemical additives, switchable-hydrophilicity tertiary amines (SHTA) has also been taken into consideration for chemical enhanced oil recovery. SHTA is basically a solvent that can be reversibly switched between hydrophobic and hydrophilic forms by establishing a reversible chemical reaction. This reversible chemical reaction can be triggered by involving carbon dioxide (CO_2). Jessop et al. (2010) conducted the initial research on switchable-hydrophilicity solvent in soybeans to extract the soybean oil, presenting the conclusion that this switchable-hydrophilicity solvent is very effective in extracting the organic components. Research in this specific SHTA has been expanded to the solvent-assisted bitumen recovery; a recent experimental study discovered that the use of SHTA led to the bitumen extraction from the oil sands to be up to 98% total recovery (Holland et al. 2012; Sui et al. 2016). As well, the reversible chemical reaction of this SHTA is able to make this chemical additive retrievable for future use, making this SHTA even more economical.

Essentially, steam applications in thermal oil recovery could lead to unfavorable wettability alteration predominantly due to the phase change phenomenon as concluded in our previous research. Involving novel chemical additives in a rock/heavy-oil/steam system could be the alternative to conventional chemical additives. These novel chemical additives have substantiated to present favorable wettability alteration to a less oil-wet state and incremental oil recovery. Through comprehensive research, it is essential to comprehend the mechanism of wettability alteration yielded by these novel chemical additives in various reservoir rocks, i.e sandstones and carbonates. Therefore, one of the objectives of this paper quantitatively investigates steam-induced wettability alteration in a rock/heavy-oil/steam system and evaluates the wettability alteration mechanism impacted by unconventional chemical additives. Analyses and outcomes from this research concerning the degree of wettability alteration and surface tension reduction in high-temperature steam applications will be beneficial to acquire a comprehensive understanding of the wettability alteration mechanism and interfacial properties.

3.3 Materials and Experimental Setup

Heavy-Oil Sample. This research utilized a heavy-oil sample of which was obtained from a heavy-oil field in Alberta, Canada. **Tables 3** and **4** present the oil properties and saturate, aromatic, resin, and asphaltene (SARA) analysis and measurement conducted in our research lab.

Table 3—Heavy-oil properties at measured temperature.

Parameter	Value	Temperature
Viscosity, cP	27,780	25°C
Density, g/cm^3	0.97	25°C

Table 4—Heavy-oil analysis of SARA.

Saturate	Aromatic	Resin	Asphaltene
26.36%	24.85%	25.74%	22.39%

Rock Samples. In this research, quartz and calcite were used as substrates. These kinds of minerals are good representatives of most sandstone and carbonate reservoirs. Each substrate was aged in the heavy-oil sample for about one week at a 70°C environment. The extra oil produced from this aging process was treated with toluene carefully. This aging process is good enough to embody the original wettability of the solid samples.

Chemical Additives. The list of the chemical additives applied in experiments is given in **Table 5**. The brine chemistry was encompassed in this research to further comprehend the impact on total solid surface charge and the degree of wettability, and for the base case this research utilized vacuumed tap water as a comparison to the effect of chemical additives on surface tension and wettability state. When synthesizing the brine solution and chemical additives, three types of chloride salts were used and mixed with deionized (DI) water. In addition, a specific chemical additive concentration range was applied in this experimental study to further analyze the relationship amongst chemical concentration, surface tension, and wettability condition.

Table 5—Tested novel chemical additives.

Chemical Type	Specific Name	Concentration
Base Case	Vacuumed tap water	-
Brine Solution	NaCl, $CaCl_2$, $MgCl_2$	30,000 ppm, 1,000 ppm, 100 ppm
Nanofluids	SiO_2	1-5 wt%
	ZrO_2	1-5 wt%
Ethers	Dimethyl ether (DME)	1-5 wt%
	Diethyl ether (DEE)	
Alcohol	Isopropyl alcohol	1-5 wt%
Chelating Agents	Hydroxyethylethylenediamninetriacetic acid (HEDTA)	1-5 wt%
	Diethylenetriaminepentaacetic acid (DTPA)	
Biodiesel	Biodiesel-in-water emulsion	0.25-1 wt%
SHTA	N, N-dimethylcyclohexylamine	1-5 wt%

Contact Angle and Surface Tension Measurements. Since wettability alteration and interfacial properties are the main objectives in this research, contact angle and surface tension measurements were implemented. In observing and quantitatively measuring those parameters, a Rame-Hart Goniometer/Tensiometer was used for each experimental study at elevated pressure and temperature. Additionally, the measurement data were generated and interpreted through DROPimage Advanced software. The whole experimental setup is presented in **Figure 44**.

When observing the contact angle, a drop from the heavy-oil was produced from a needle and placed on the rock samples. The contact angle was measured between the oil drop and the solid surface referring to an oil phase. Water or steam-wet is indicated by a contact angle $>90^o$ while oil-wet is specified by a contact angle $<90^o$. In addition to this contact angle observation, a surface tension measurement was also performed to comprehend the contribution of each chemical additive to the interfacial properties. Methodology of contact angle and surface tension measurements are depicted in **Figure 45**. This study is envisioned to evaluate the performance of chemical additives in both wettability alteration and surface tension reduction.

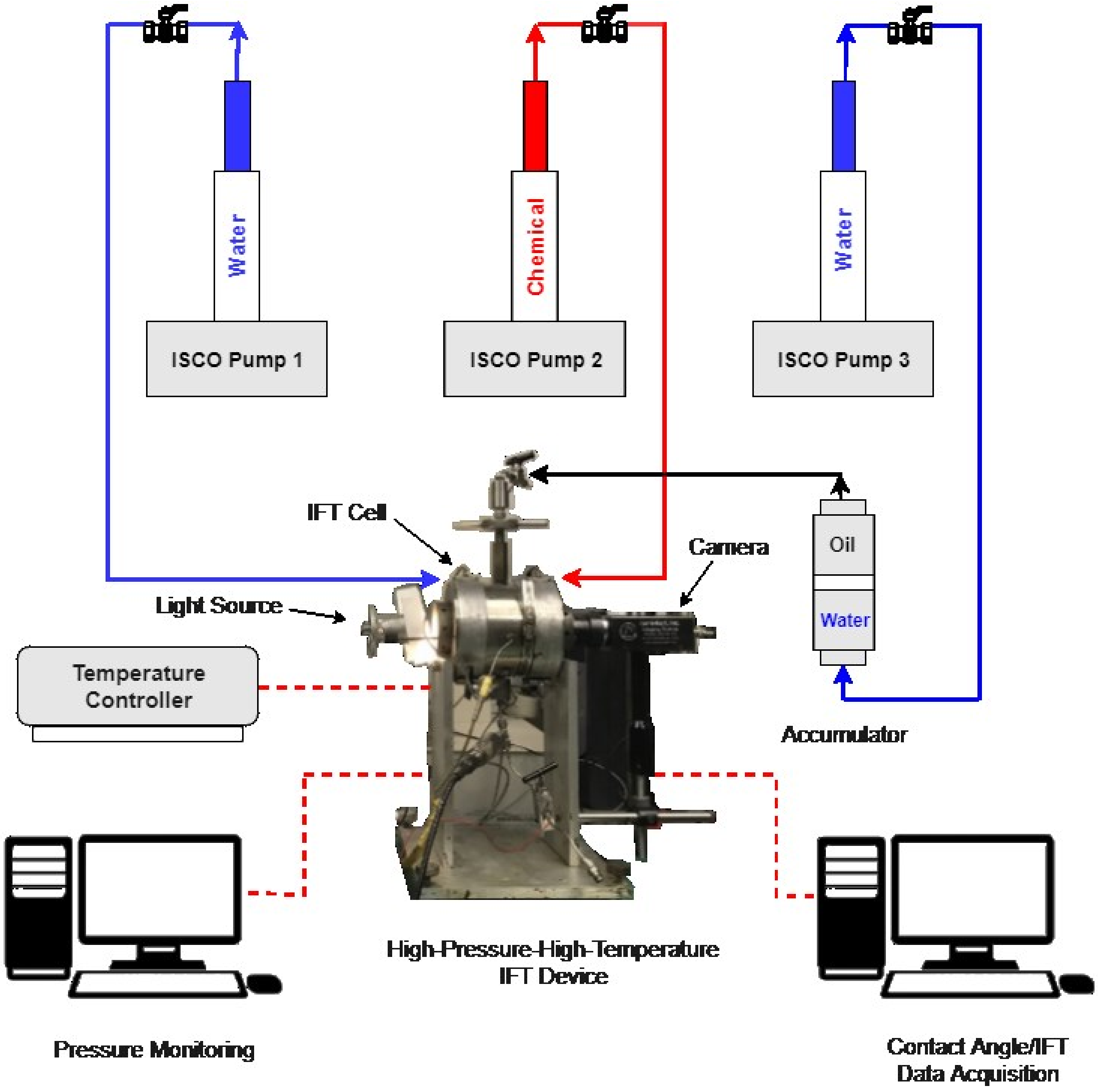


Figure 44—Contact angle and surface tension experimental setup.

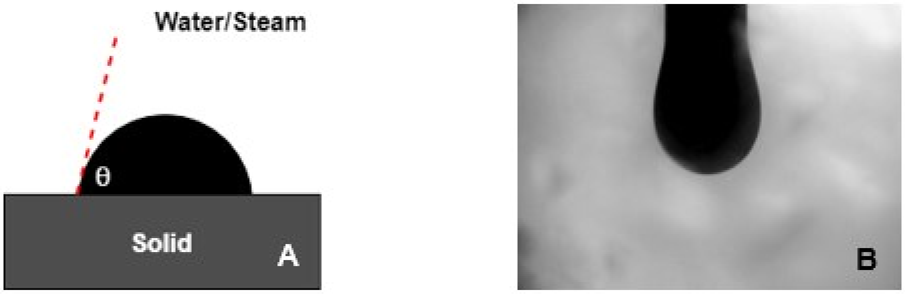


Figure 45—(a) contact angle and (b) pendant drop methodology.

3.4 Results and Discussion

3.4.1 Effect of Aging the Substrates

In this research, each experiment applied treated substrate to exemplify the natural reservoir condition, particularly in its wettability behavior. Our previous research (Pratama and Babadagli 2019) concluded that aging the substrates in the heavy-oil could alter the wettability to a more oil-wet state. When aging the substrates, the temperature was set to 70ºC for one week of aging time. **Figure 46** depicts the change of wettability state after treating the substrates with the heavy-oil for both quartz and calcite. The wettability alteration at this condition is predominantly triggered by the polar interaction. Fundamentally, polar interaction specifies the interaction amongst the polar components—asphaltenes and resins—contained in most heavy-oils. Abdallah et al. (2007) and Roosta et al. (2009) have also evidenced through their research that the change in wettability state was influenced by this polar interaction. Aging the solid phase in the heavy-oil lets an adsorption of those polar components to the surface of the solid phase. The mechanism of this interaction will then occur when the oil is introduced to the solid surface leading to be a more oil-wet surface. The process of aging the substrates in the heavy-oil is very favorable in representing the initial condition of the reservoir rocks.

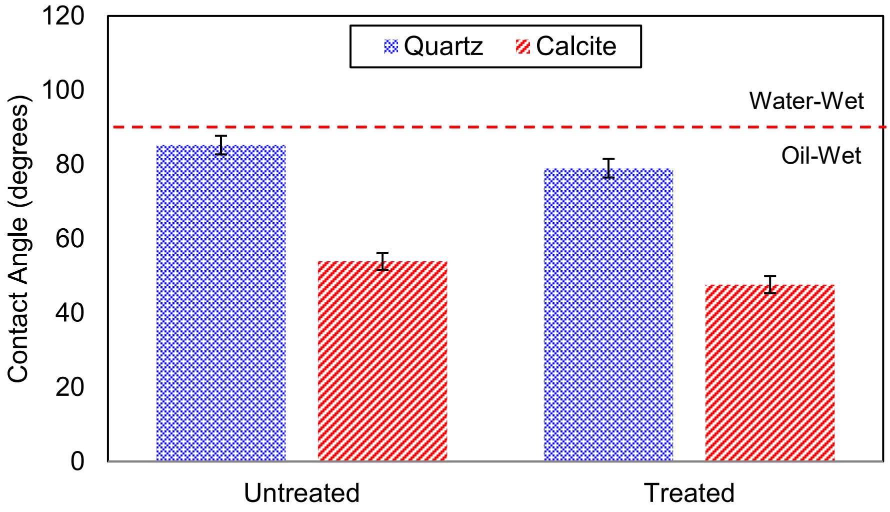


Figure 46—Wettability alteration at 90ºC after aging the substrates (modified after Pratama and Babadagli 2019).

3.4.2 Effect of Pressure and Brine Chemistry

One of the several factors impacting wettability state is the brine chemistry yielding to a more oil-wet state. In our series of experiments, the exact formulation of 30,000 ppm NaCl, 1,000 ppm $CaCl_2$, and 100 ppm $MgCl_2$ was combined with DI water to synthesize the brine solution. These brine concentrations were selected to replicate a typical formation water salinity in Alberta, Canada. The brine chemistry effect on solid surface wettability state was previously studied by Pratama and Babadagli (2018, 2019), their research confirming, through contact angle observation, that the wettability of the quartz and calcite changed to a more oil-wet state.

Figures 47-49 present the change in wettability state after introducing the brine chemistry to both quartz and calcite. According to this research, contact angle between the oil drop and quartz surface decreased from averagely 60° to 50° after applying brine solution to the system. Similarly, the contact angle between the oil drop and the calcite surface was also observed to be declining from averagely 50° to 40° after introducing brine solution to the rock/heavy-oil system. A similar behavior was also observed in steam condition. The quartz and calcite surfaces turned to be fully oil-wet after introducing the brine chemistry to the system.

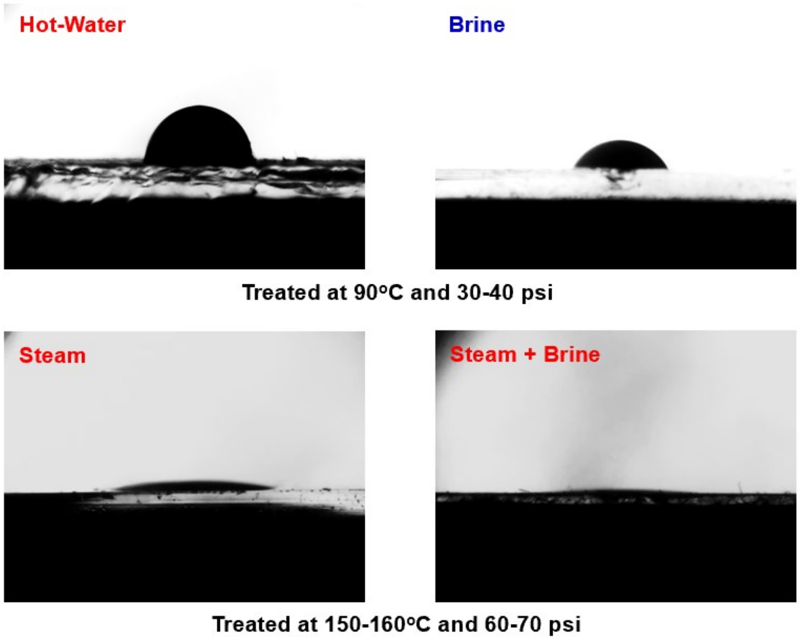


Figure 47—Contact angle of quartz under the brine chemistry (after Pratama and Babadagli 2019).

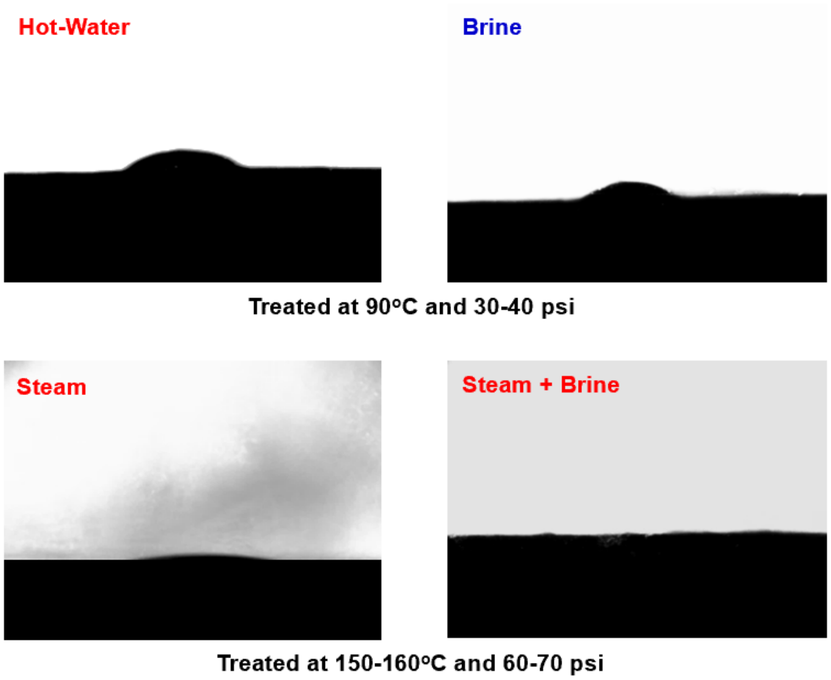


Figure 48—Contact angle of calcite under the brine chemistry (after Pratama and Babadagli 2019).

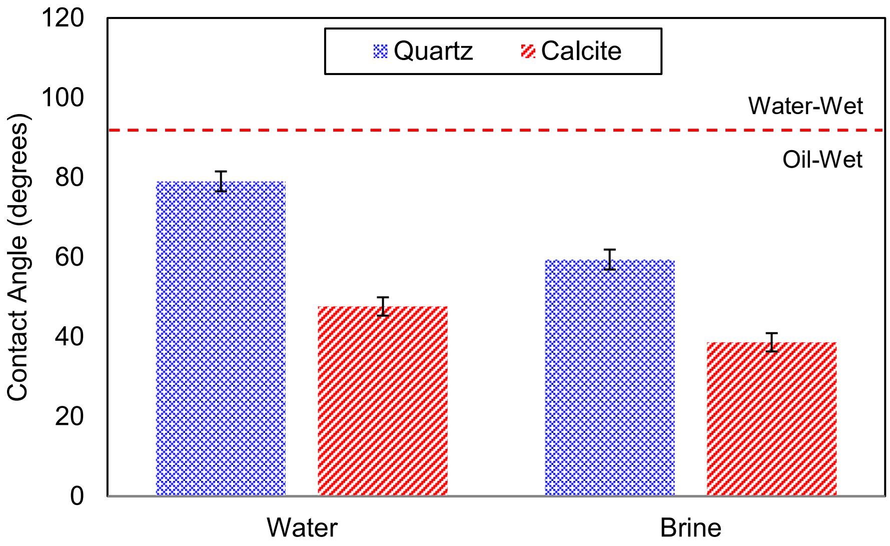


Figure 49—Wettability alteration after introducing brine chemistry at 90°C (modified after Pratama and Babadagli 2019).

Naturally, quartz is recognized as acquiring a negative surface charge. This evidence was verified through previous research on intermolecular interaction demonstrated by Masliyah et al.

(2011), their research concluding that quartz presented to have a negative zeta potential when the pH was adjusted to 7.0. Similarly, Moulin and Roques (2003) and Lee et al. (2016) perceived that calcium carbonate and calcite plates were identified to have negatively-charged surfaces. However, much less negative zeta potential values were observed on calcium carbonate and calcite plates compared to the zeta potential value of quartz. This condition leads the wettability of carbonates and calcites to be more oil-wet naturally.

Introducing brine chemistry to the rock/heavy-oil system allows an adsorption mechanism of the positively-charged cations—particularly divalent cations—to the solid surface. This adsorption mechanism leads to the total solid surface charge modification to be more positively-charged. To further verify and comprehend this hypothesis, an electrokinetic analysis through streaming potential measurement was conducted. Fundamentally, streaming potential measurement has the objective to obtain zeta potential value representing the total solid surface charge through the flow of electrolyte solution. **Figure 50** describes the total solid surface charge on quartz in different brine concentration ranging from 0.001–0.1 M.

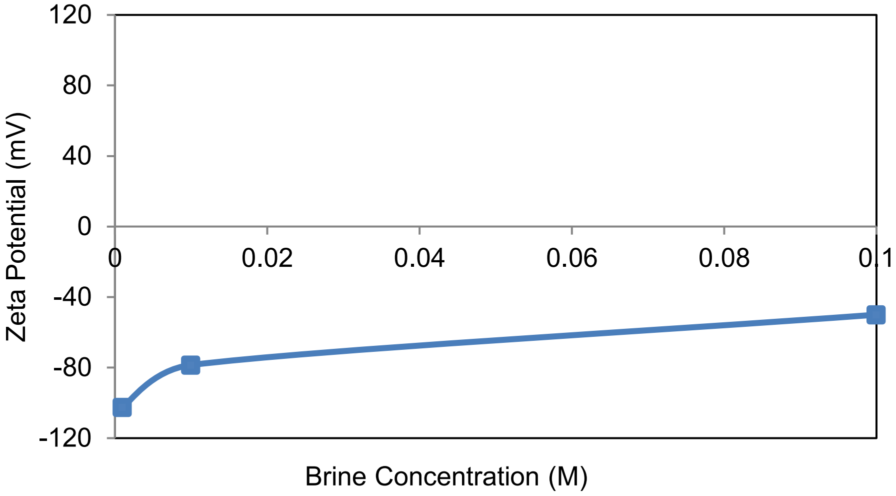
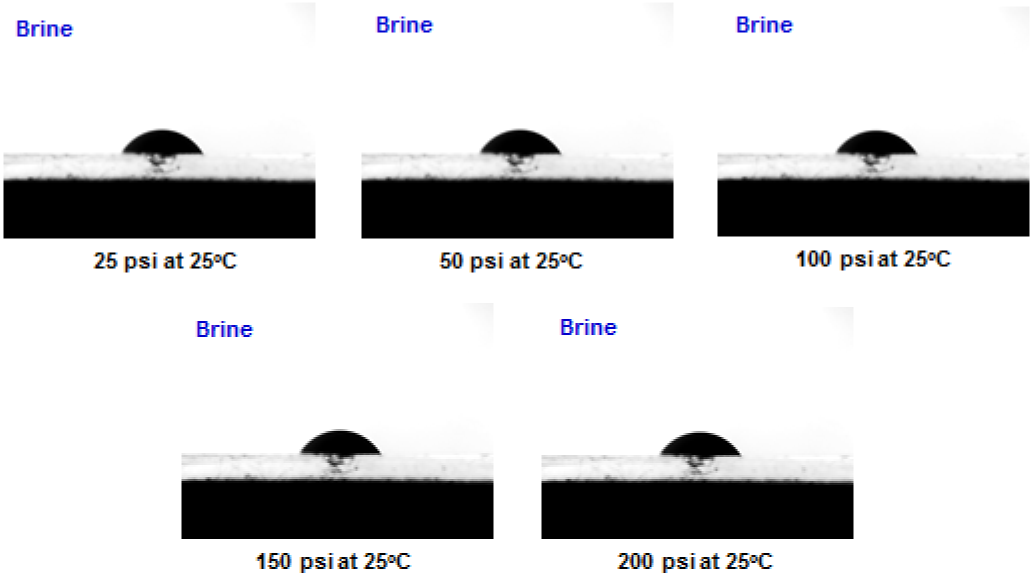


Figure 50—Total solid surface charge on quartz in different brine concentration.

It was observed that the total solid surface charge moved towards the positive value when the brine concentration was increased. The total solid surface charge jumped from averagely -130 mV to -50 mV. Increasing brine concentration could potentially lead to an even more positively-charged solid surface. When the heavy-oil drop—acquiring a negative charge naturally—is introduced to the more positively-charged solid surface, the attractive forces are then initiated. The attractive forces trigger the wettability alteration from initially water or steam-wet to be more oil-wet.

Additionally, a study of pressure sensitivity effect was also conducted to evaluate its impact to the wettability state. The temperature of the system was upheld at 25ºC continuously to evade the thermal-induced wettability alteration effect. Then, the pressure of the rock/heavy-oil/brine system was elevated from 25 psi to 200 psi progressively. **Figures 51-53** exhibit the wettability state of both quartz and calcite as a response of pressure. According to this research, elevated pressure was not presenting any substantial influence on the wettability of both quartz and calcite.



25 psi at 25°C

50 psi at 25°C

100 psi at 25°C

150 psi at 25°C

200 psi at 25°C

Figure 51—Wettability state of aged quartz under brine chemistry at elevated pressure.

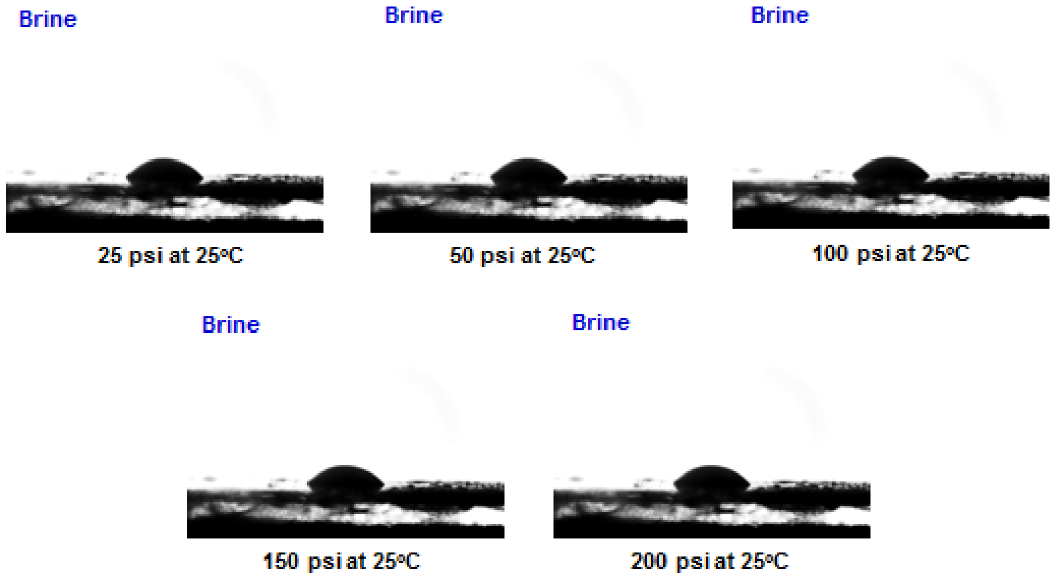


Figure 52—Wettability state of aged calcite under brine chemistry at elevated pressure.

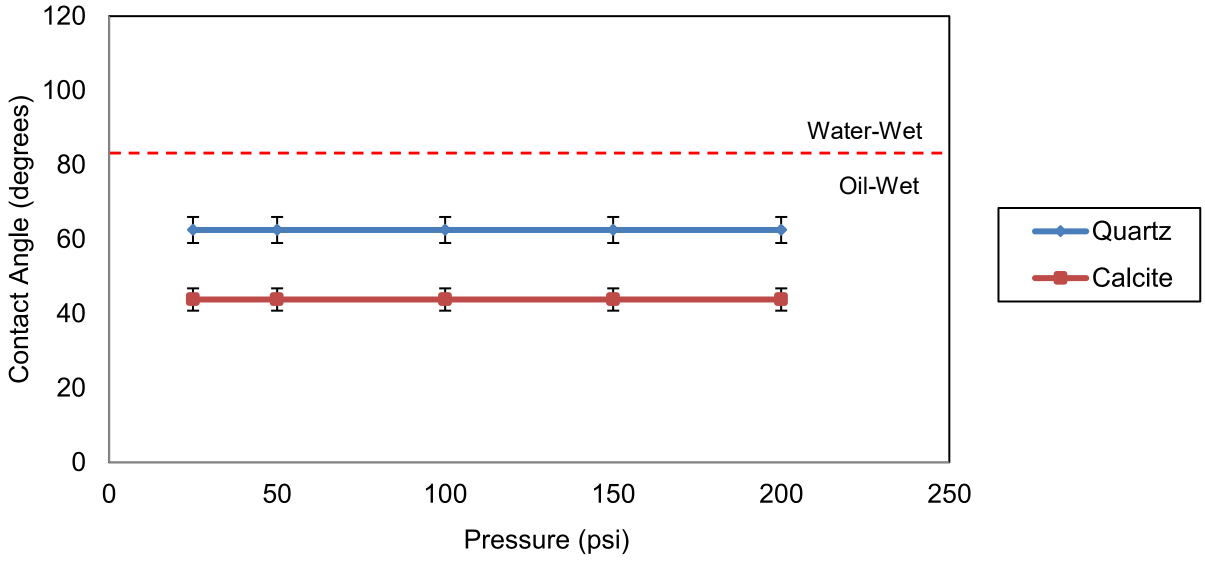
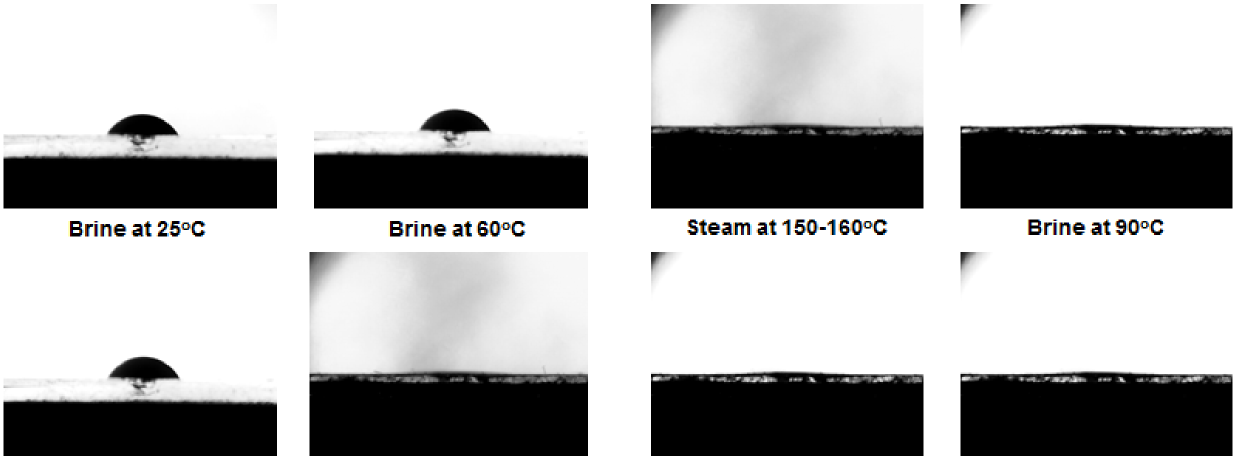


Figure 53—Contact angle profiles of quartz and calcite at elevated pressure.

3.4.3 Effect of Phase Change

As previously noted by Pratama and Babadagli (2018, 2019), phase change plays an essential role in unfavorable wettability alteration. In this paper, a study of phase change was also conducted to further understand its impact to wettability state. Moreover, the experimental study of the phase change effect was performed under the presence of the brine chemistry. **Figures 54** and **55** show the substantial declining contact angle due to the steam-induced wettability alteration caused by the phase change on quartz and calcite substrates. It was clearly observed that the wettability state of quartz and calcite substrates had been altered to a completely oil-wet state after the fluid phase was transformed from initial liquid phase to steam phase. Furthermore, when the external fluid phase was retransformed from steam phase to liquid phase, the wettability state of both quartz and calcite was not restored. This evidence undoubtedly presents that steam-induced wettability alteration behaves irreversibly.



Brine at 25°C

Brine at 60°C

Steam at 150-160°C

Brine at 90°C

Brine at 90°C

Steam at 150-160°C

Brine at 60°C

Brine at 25°C

Liquid Phase to Steam Phase

Steam Phase to Liquid Phase

Figure 54—Irreversible steam-wettability alteration on quartz triggered by phase change at pressure 25-70 psi.

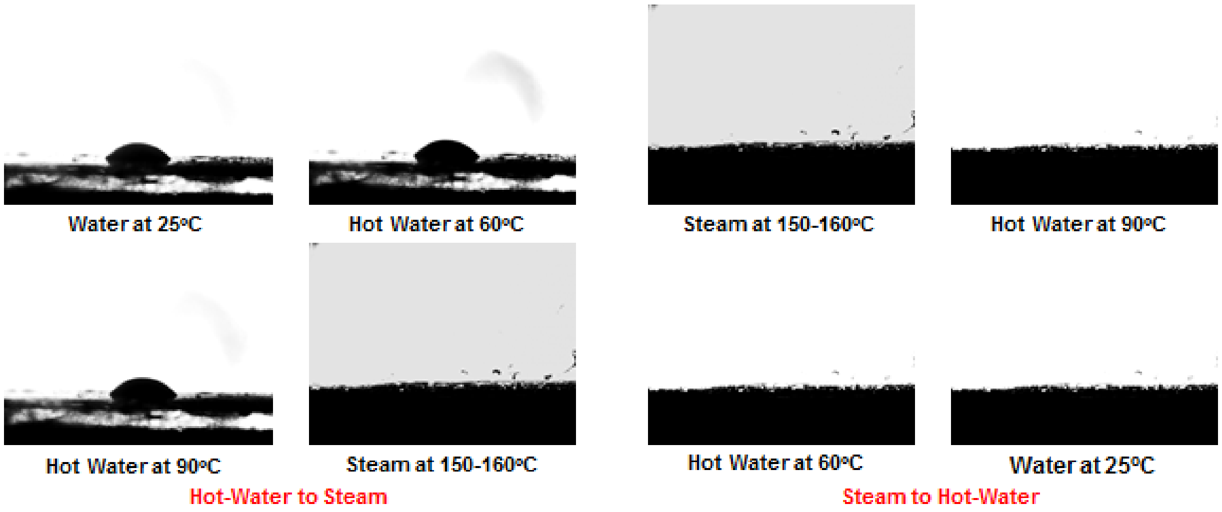


Figure 55—Irreversible steam-wettability alteration on calcite triggered by phase change at pressure 25-70 psi.

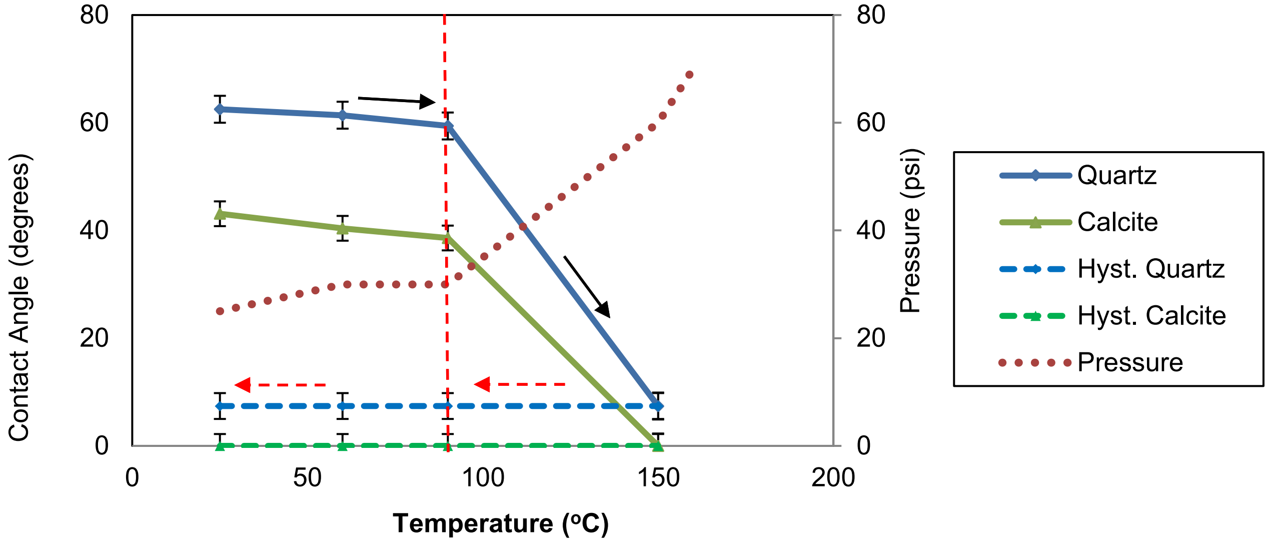


Figure 56—Contact angle and hysteresis observation during phase change.

This phenomenon is shown graphically in **Figure 56** through contact angle and hysteresis plots during phase change. As seen, the contact angle of quartz declined from averagely 62.5° to 7° after phase change occurred. Correspondingly, the contact angle of the calcite substrate was also observed to plummet after the external fluid phase was changed from liquid phase to steam phase. The contact angle of the calcite substrate fell down from 39° to nearly 0° showing the surface to be completely oil-wet.

3.4.4 Effect of Chemical Additives

The performance of each novel chemical additive—nanofluids, ethers, alcohol, chelating agents, biodiesel, and SHTA—was evaluated for its effect in altering the wettability state of both quartz and calcite at steam condition. Each experimental study was performed at steam pressure and temperature for 1.5 hours. Steam injection pressure and temperature were documented as 60-70 psi and 150-160°C.

This research covered the chemical concentration sensitivity having the objective of evaluating the optimum chemical concentration needed to achieve the highest degree of wettability alteration and surface tension reduction. In addition to this research, the quantitative analysis of thermal stability of these novel chemical additives was implemented and studied separately through Thermogravimetric Analysis (TGA).

Thermogravimetric Analysis (TGA). The thermal stability of the chemical additives is very essential in steam applications. This parameter determines the degree of chemical decomposition at a very high-temperature environment. The result of TGA measurement for each chemical additive is described in **Figure 57**. According to the depicted result of the TGA measurement, most of the chemical additives—nanofluids, chelating agents, biodiesel, and SHTA—revealed very good thermal stability. These chemical additives are able to accommodate tremendously high-temperature environments above 250°C. Conversely, two chemical additives—DEE and isopropyl alcohol—were identified as low thermally-resistant chemicals. These types of chemicals could only resist at temperatures below 100°C. The TGA measurement for DME could not be performed due to its characteristic of gaseous phase.

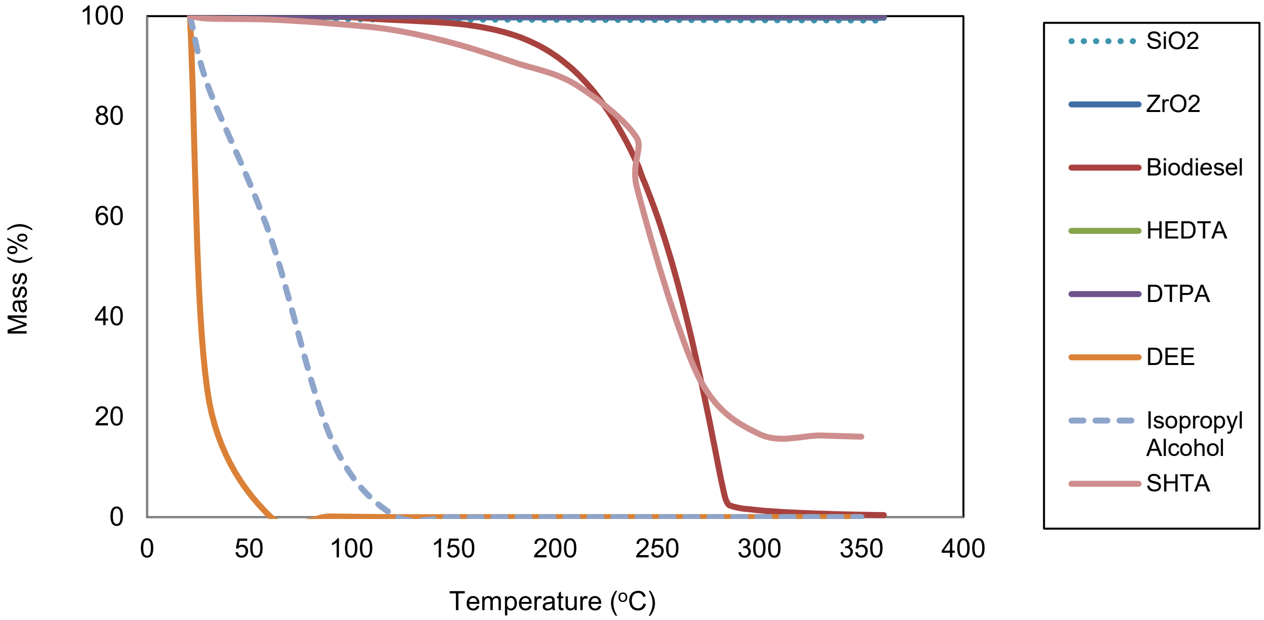


Figure 57—Thermogravimetric analysis (TGA) of each utilized chemical additive.

Base Case Comparison. Before performing the experimental study with several selected chemical additives, the base cases of contact angle and surface tension were determined. This initial study was necessary to compare the performance on wettability alteration and surface tension before and after involving the chemical additives. **Figures 58** and **59** present the base case contact angle quantitative analysis of quartz and calcite in water or steam and in the presence of the brine chemistry. It was observed that unfavorable wettability alteration occurred when the external phase was transformed from liquid phase to steam phase. Furthermore, the base case measurements of the surface tension of heavy-oil/steam and brine systems were also conducted and compared with other published research performing similar surface tension measurements for the oil/steam system. **Table 6** summarizes the surface tension results from this research and previously published research performed by Naser et al. (2015) and Huygens et al. (1995). It is perceived that the surface tension value at steam condition obtained from this research is consistent with some other published literatures.

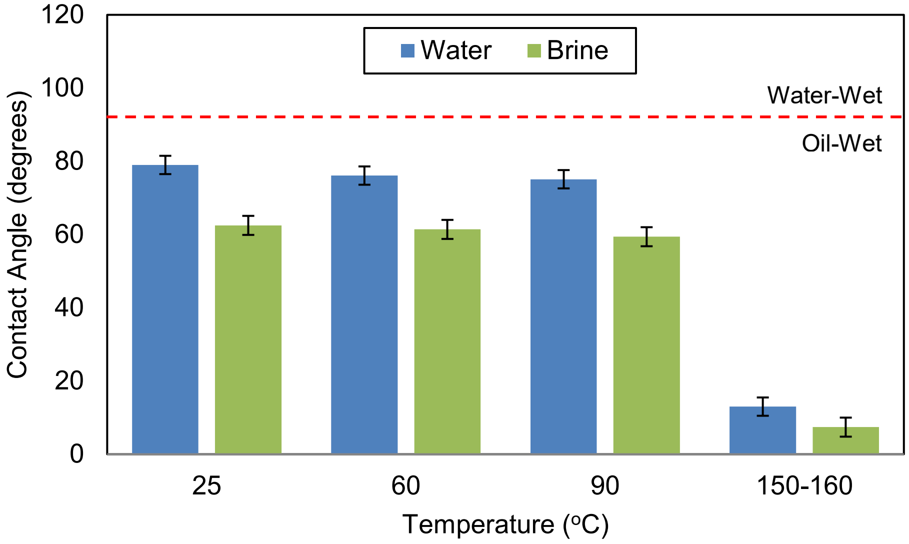


Figure 58—Base case contact angle of quartz at elevated temperature at 25-70 psi.

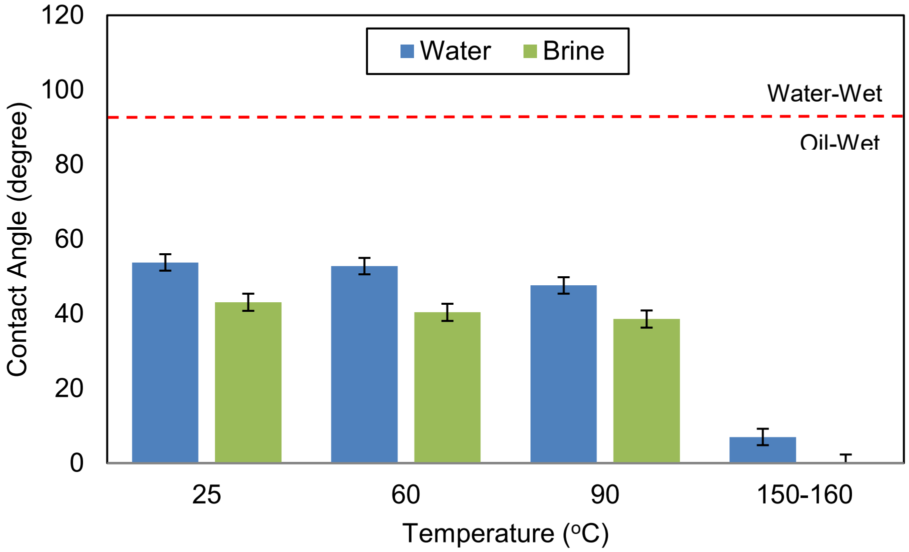


Figure 59—Base case contact angle of calcite at elevated temperature at 25-70 psi.

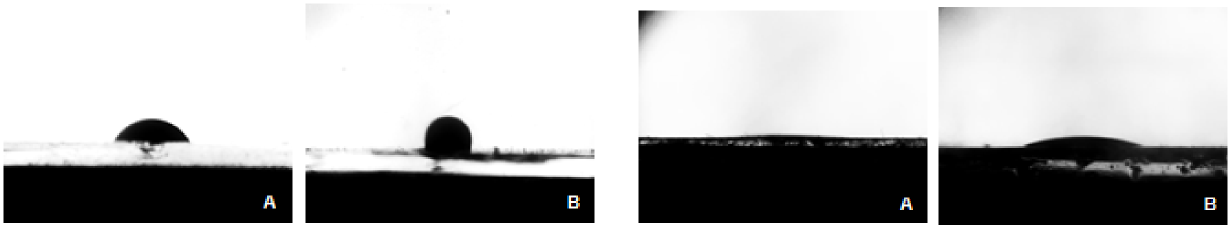
Table 6—Base case surface tension of oil/steam system comparison at steam condition.

Surface Tension (mN/m)	This Experiment (Steam by water)	This Experiment (Steam by brine)	Naser et al. (2015)	Huygens et al. (1995)
	19.6	18.8	19.0-21.0	18.0

Nanofluids. Silicone oxide (SiO_2) and zirconium oxide (ZrO_2) types of dispersed nanofluids were selected as steam additives. The SiO_2 dispersed nanofluid has a particle distribution size of 5-35 nm and the ZrO_2 dispersed nanofluid has a particle distribution size of 45-55 nm. Wettability alteration of both quartz and calcite is presented in **Figures 60-62**. The results reveal that an improvement in quartz contact angle was possible. The contact angle of the quartz substrate shifted from averagely 7.4° to 18.8° at steam pressure and temperature. Similarly, an improvement in the wettability state of calcite was also observed and the contact angle of the calcite substrate increased from 0o to averagely 14.2°. Optimum chemical additive concentration was recorded as SiO_2 type nanofluid on quartz and calcite substrates at 1 wt% in order to achieve the highest degree of wettability alteration at steam conditions. In addition, the surface tension measurement between heavy-oil and steam was also performed after adding SiO_2 nanofluid to evaluate its potential in reducing surface tension. SiO_2 nanofluid did not deliver a favorable surface tension reduction and it did not improve from the initial measurement of 18.8 mN/m.

Similar to SiO_2 nanofluid, a ZrO_2 nanofluid was also tested on quartz and calcite substrates. **Figures 63-65** exhibit the wettability alteration on quartz and calcite substrates after involving ZrO_2 as a steam additive. In general, performance of ZrO_2 nanofluid was better in both liquid phase and steam phase compared to SiO_2. On the quartz substrate, ZrO_2 improved the contact angle from averagely 7.4° to 24.2°. Similar wettability alteration was also observed on the calcite substrate and the contact angle increased to 18.0° on average. For the ZrO_2 nanofluid, the optimum chemical additive concentration was observed to be 1 wt%, of which yielded the highest degree of wettability alteration for both quartz and calcite substrates.

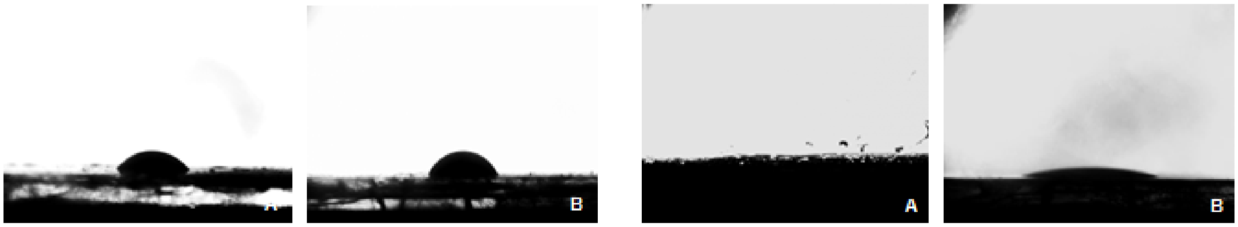
Additionally, a surface tension measurement of the heavy-oil/steam system at steam was performed. ZrO_2 nanofluid delivered a better surface tension reduction compared to SiO_2 nanofluid performance at steam condition. Surface tension between heavy-oil and steam was reduced from an initial value of 18.8 mN/m to averagely 15.9 mN/m. To summarize, ZrO_2 nanofluid presented a more favorable performance compared to SiO_2 nanofluid in term of wettability alteration and surface tension reduction. Cao et al. (2017) also confirmed through their research in nanofluids that ZrO_2 nanofluid performed more favorable than SiO_2 nanofluid in altering the wettability at elevated temperatures, but not at steam conditions.



Liquid Phase at 90ºC and 30-40 psi

Steam Phase at 150-160ºC and 60-70 psi

Figure 60—Wettability state observation on quartz (a) before and (b) after applying SiO_2.



Liquid Phase at 90ºC and 30-40 psi

Steam Phase at 150-160ºC and 60-70 psi

Figure 61—Wettability state observation on calcite (a) before and (b) after applying SiO_2.

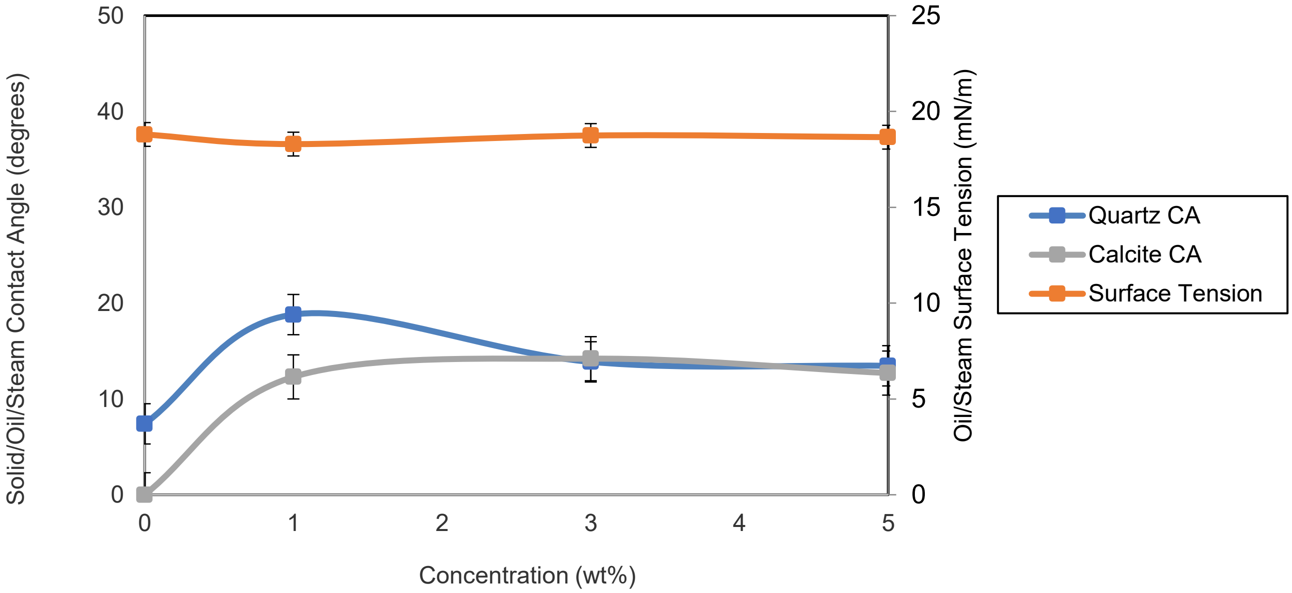
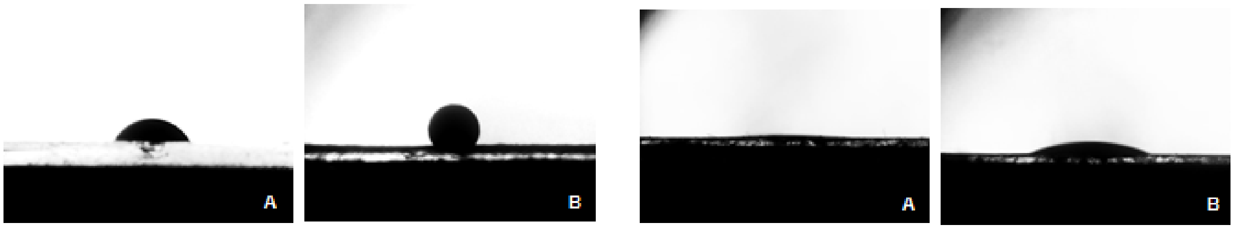


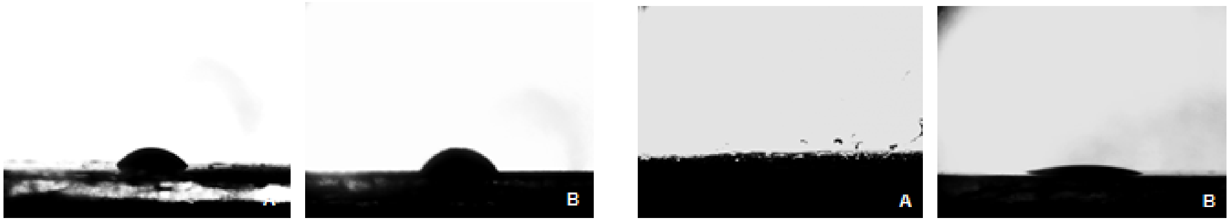
Figure 62—Wettability state and surface tension profile under steam condition with SiO_2.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 63—Wettability state observation on quartz (a) before and (b) after applying ZrO_2.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 64—Wettability state observation on calcite (a) before and (b) after applying ZrO_2.

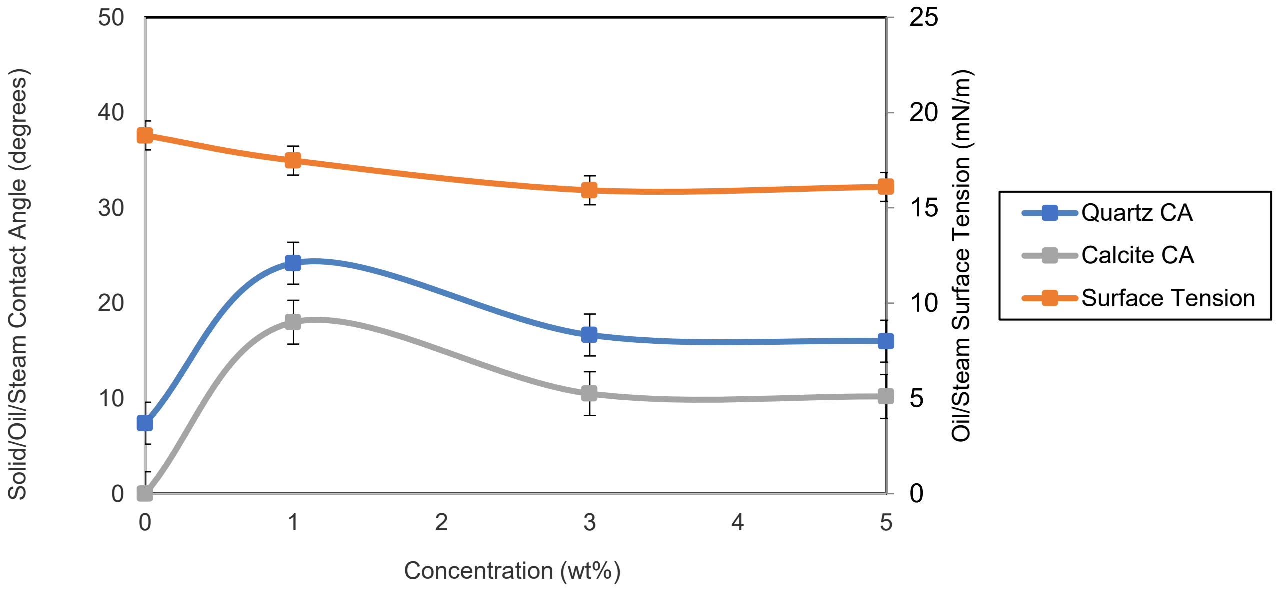


Figure 65—Wettability state and surface tension profile under steam condition with ZrO_2.

Alcohol. An alcohol type of chemical was also included as a chemical additive for steam applications. Isopropyl alcohol or 2-propanol was tested in this research to represent a material of which is soluble in both water and oil. The result of an experimental study with isopropyl alcohol is shown in **Figures 66-68**. The isopropyl alcohol did not show any substantial wettability alteration on both quartz and calcite substrates.

The contact angle of the quartz substrate did not significantly improve after adding isopropyl alcohol. At steam condition, the contact angle shifted from averagely 7.4° to only 13.7°. Similar to the chemical additive performance on quartz, favorable wettability alteration was not perceived on the calcite substrate either. The contact angle changed slightly from the initial value of 0° to averagely 10.3°. Moreover, the highest degree of wettability alteration was noticeable at 3 wt% on both quartz and calcite substrates.

Despite the unfavorable wettability alteration carried by isopropyl alcohol, however, a slight surface tension reduction was still observed during steam injection. The surface tension was reduced from initially 18.8 mN/m to be about 16.0 mN/m at an optimum chemical concentration of 3 wt%. In summary, isopropyl alcohol is not a thermally stable chemical additive to be used at extremely high-temperature as confirmed by the TGA measurement, wettability alteration, and surface tension experimental studies. This isopropyl alcohol might only have potential in a low temperature environment, such as waterflood applications.

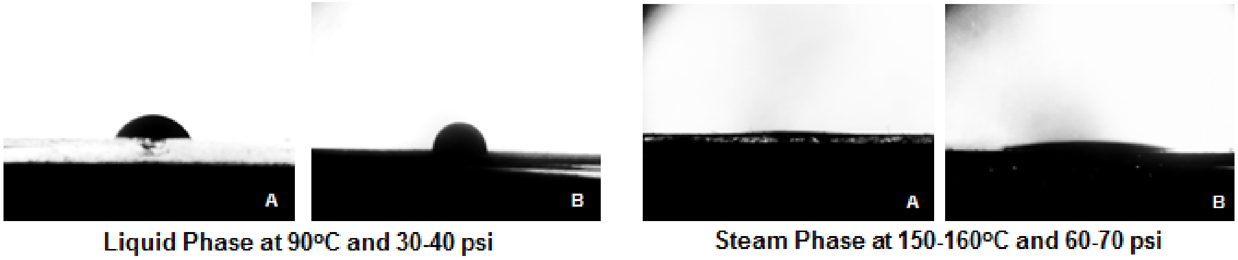
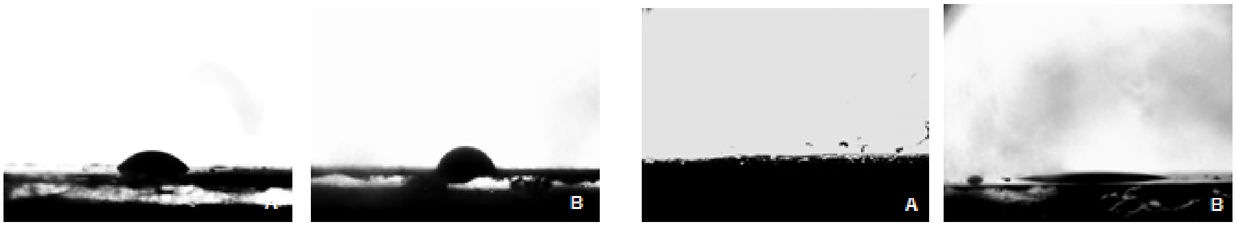


Figure 66—Wettability state observation on quartz (a) before and (b) after applying isopropyl alcohol.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 67—Wettability state observation on calcite (a) before and (b) after applying isopropyl alcohol.

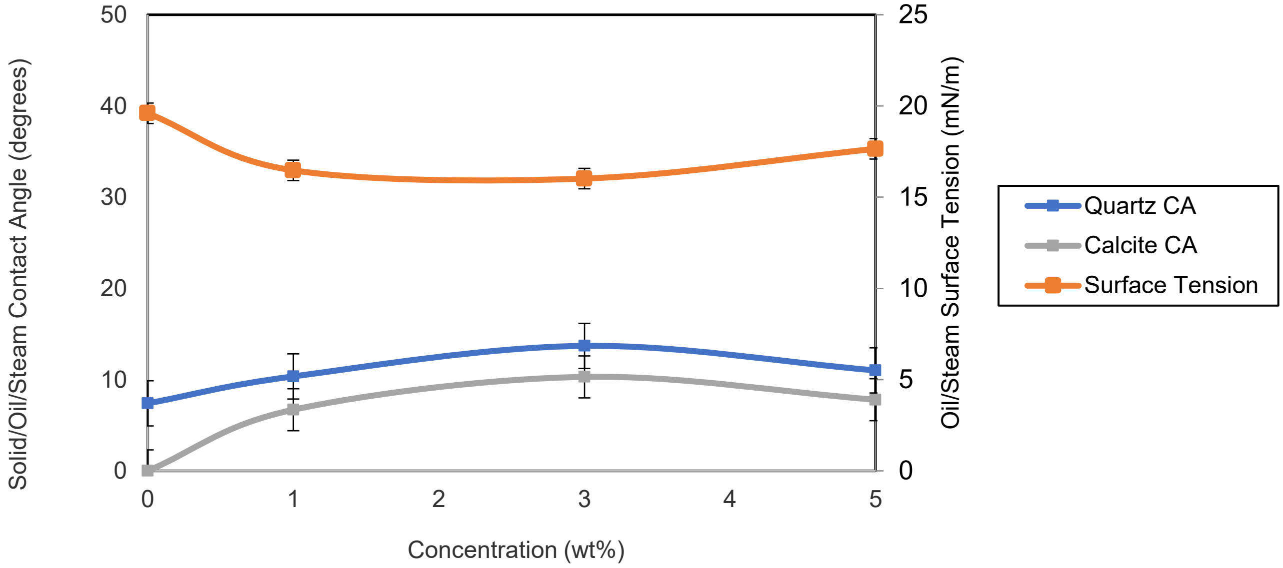
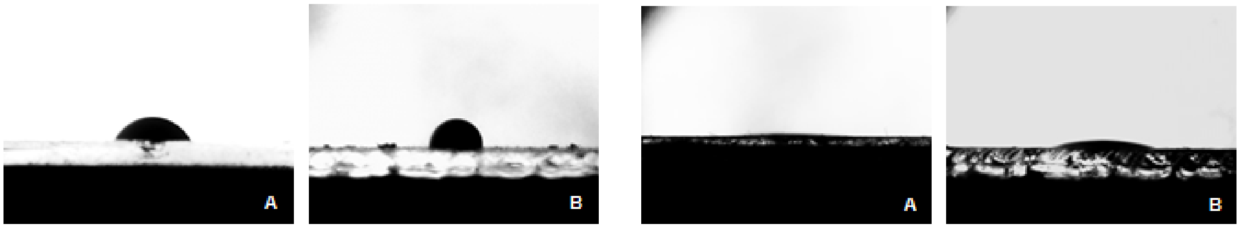


Figure 68—Wettability state and surface tension profile under steam condition with isopropyl alcohol.

Ethers. These types of solvent-based chemical additives have been previously studied for their potential in enhancing oil recovery. In this research, dimethyl ether (DME) and diethyl ether (DEE) were tested for their performance on wettability alteration and surface tension reduction. Overall, DME presented a very promising result for both liquid and steam phases on the quartz substrate, as the surface of the quartz substrate became more water or steam-wet after adding DME. On the other hand, promising wettability alteration was not observed on the calcite substrate at steam condition. The overall DME performances at steam condition on quartz and calcite substrates are presented in **Figures 69-71**. At steam temperature and pressure, DME was able to improve a contact angle on the quartz surface auspiciously. After applying DME to the rock/heavy-oil/steam system, the contact angle increased to 23.8^o on average from a previous 7.4^o. To obtain the favorable wettability alteration degree, at least 3 wt% chemical concentration was demanded.

DME did not present any promising results on calcite substrate. A change in the contact angle of calcite was only perceived to be increasing to a value of 17.7^o with observed chemical concentration of about 1 wt%. The change in wettability degree was not favorable because the contact angle was originally 0^o on the calcite surface. Very significant surface tension reduction was perceived in the heavy-oil/steam system with this DME. The magnitude of the surface tension could be reduced to the minimum value of 13.7 mN/m after adding 3 wt% chemical concentration. This evidence shows that DME is not only very promising in altering the wettability but also very favorable in reducing surface tension at steam condition.

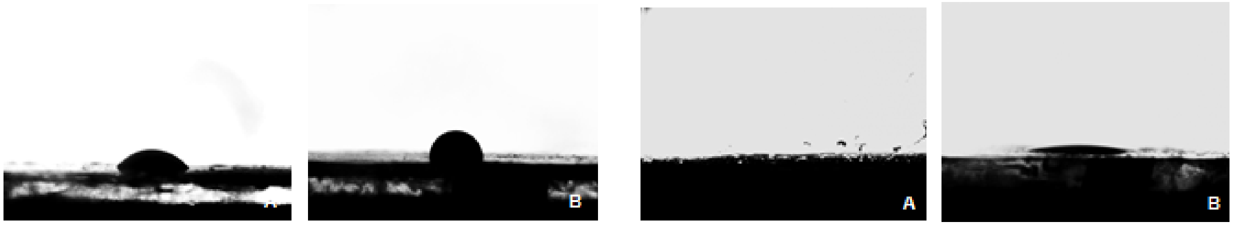
Similarly, DEE was also tested for its ability to alter the wettability on quartz and calcite and reduce the surface tension at steam environment. Generally, DEE presented less favorable wettability alteration and surface tension reduction compared to DME. **Figures 72-74** represent the wettability alteration and surface tension reduction mechanism of DEE on quartz and calcite substrates conducted at steam condition. An improvement on the wettability state of the quartz surface was obtained through a contact angle measurement. At the initial state (base case), the contact angle was perceived to be at a value of 7.4^o, but then increased to 20^o averagely. Because of these measurements and observations, the optimum DEE concentration was perceived at around 3 wt%; however, a favorable wettability improvement was not achieved when DEE was tested on calcite substrate. A contact angle of 15.6^o was recuperated on this calcite substrate from a completely oil-wet state. An optimum DEE concentration was obtained at around 3 wt% and after that point a contact angle started to decline. A slight reduction of surface tension between the heavy-oil and steam was also observed, being reduced to 16.5 mN/m on average. When the minimum surface tension was observed, the DEE concentration was at 3 wt%. According to the result of experiments on ethers types of chemical additives, DME performed better in wettability alteration and surface tension reduction during steam applications.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 69—Wettability state observation on quartz (a) before and (b) after applying DME.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 70—Wettability state observation on calcite (a) before and (b) after applying DME.

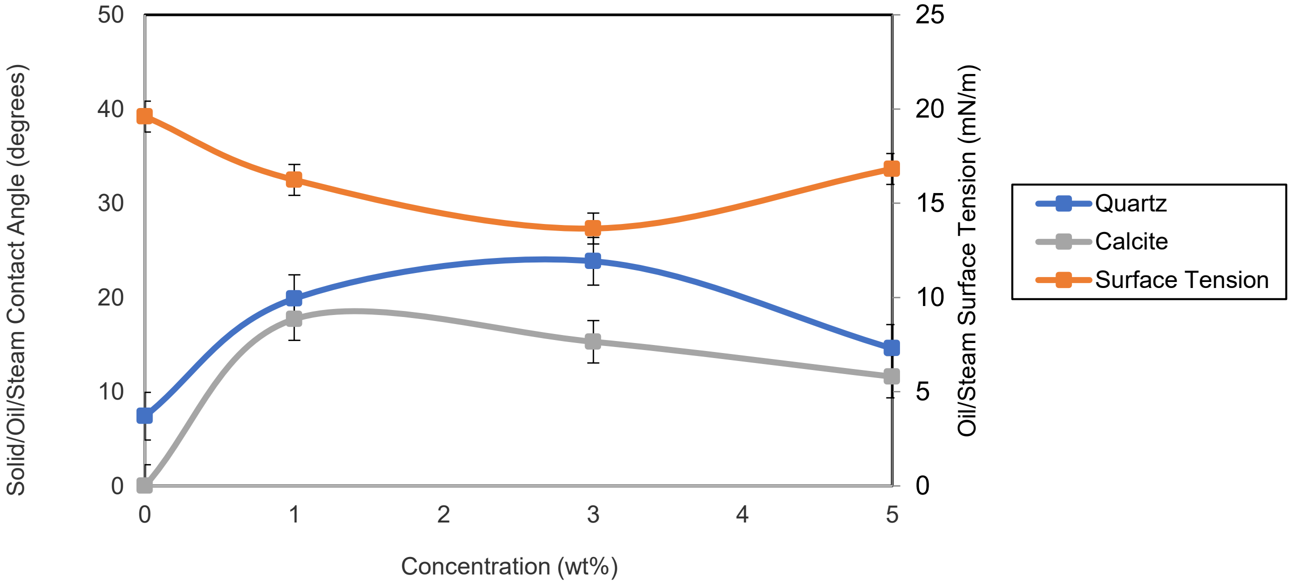
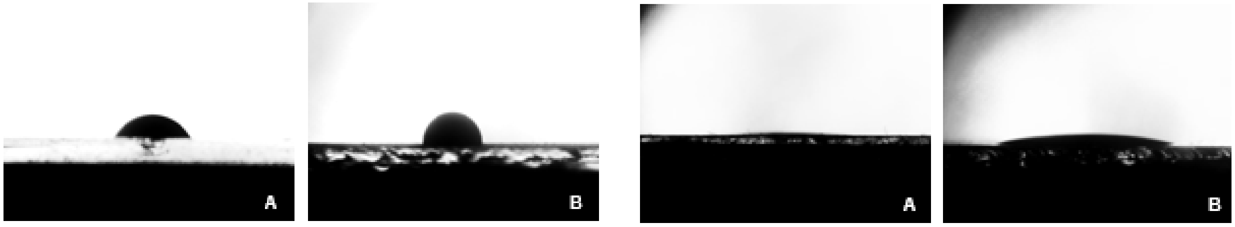


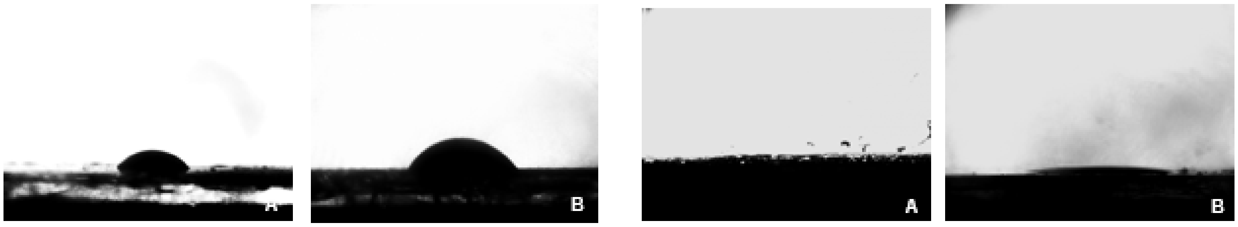
Figure 71—Wettability state and surface tension profile under steam condition with DME.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 72—Wettability state observation on quartz (a) before and (b) after applying DEE.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 73—Wettability state observation on calcite (a) before and (b) after applying DEE.

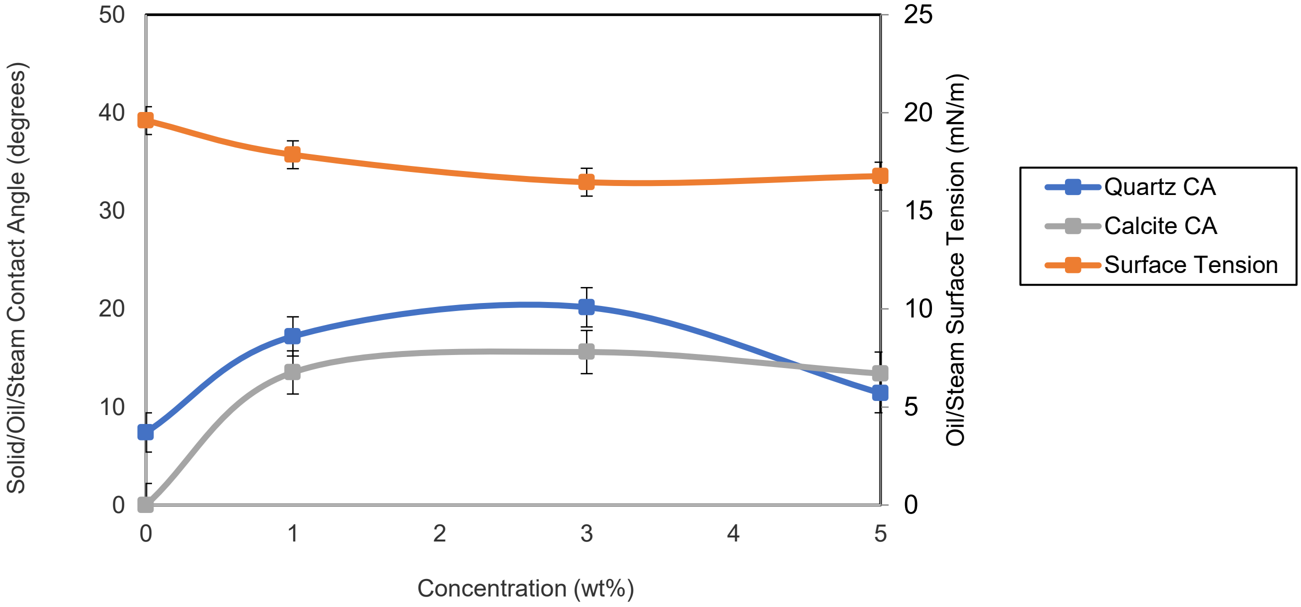
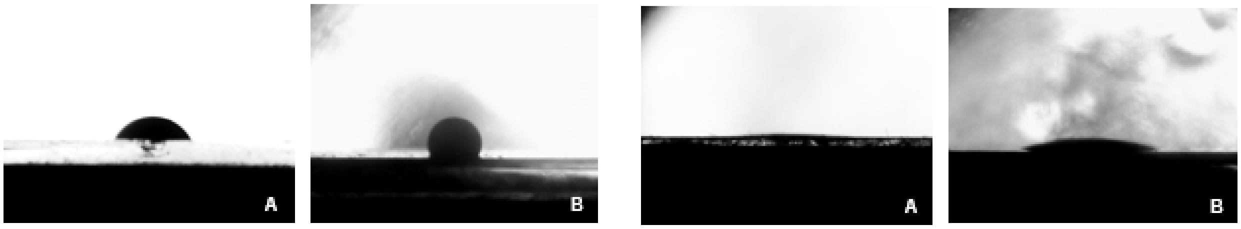


Figure 74—Wettability state and surface tension profile under steam condition with DEE.

Chelating Agents. Two types of chelating agents were selected as chemical additives: diethylenetriaminepentaacetic acid (DTPA) and hydroxyethylethylenediaminetriacetic acid (HEDTA). **Figures 75** and **76** exhibit the wettability alteration of quartz and calcite substrates after adding DTPA. It was observed that DTPA promoted very favorable wettability alteration on the quartz surface in both liquid and steam phase. On the other hand, wettability alteration seemed to be more favorable on the calcite surface, but only in liquid phase. Contact angle and surface tension profiles for both quartz and calcite substrates at steam condition are presented in **Figure 77**. Substantial improvement of the surface contact angle of quartz was obtained at 29.1° from the initial 7.4° indicating that the quartz surface turned out to be more water or steam-wet. Oppositely, on calcite substrate, the contact angle was not favorably improved; the contact angle only escalated to a value of 16.4° on average. The optimum chemical concentration of around 3 wt% was noticed on both quartz and calcite presenting the maximum degree of wettability alteration at steam condition.

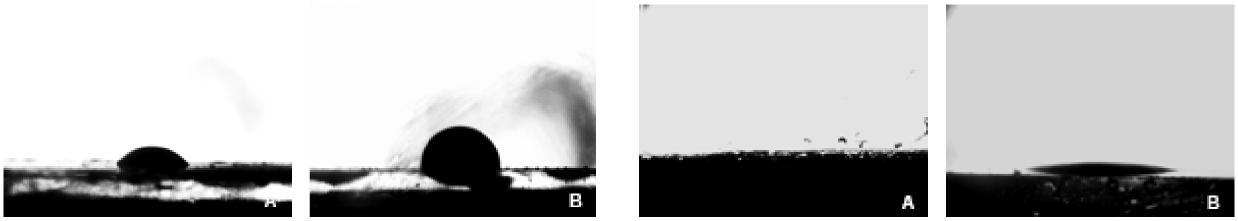
Another chemical additive test was performed with HEDTA. Overall, HEDTA did not present promising wettability alteration during steam application. Favorable wettability alteration was observed only on the calcite substrate in liquid phase. **Figures 78-80** summarize the wettability alteration degree on quartz and calcite substrates, as well as the surface tension between heavy-oil and steam after applying HEDTA. Almost no improvement in wettability state was observed on quartz and calcite surfaces. The wettability state of quartz remained constant whereas only a slight change in wettability was conspicuous on the calcite substrate. The contact angle only shifted to 12.6° averagely. In spite of the unfavorable wettability alteration, HEDTA still presented an auspicious surface tension reduction in the heavy-oil/steam system. The surface tension was evidenced to be improved from initially 18.8 mN/m to 14.4 mN/m at 3 wt% HEDTA concentration. In summary, only DTPA presented great wettability alteration and surface tension reduction at steam condition whereas HEDTA presented favorable performance only on surface tension reduction conducted at steam condition.



Liquid Phase at 90ºC and 30-40 psi

Steam Phase at 150-160ºC and 60-70 psi

Figure 75—Wettability state observation on quartz (a) before and (b) after applying DTPA.



Liquid Phase at 90ºC and 30-40 psi

Steam Phase at 150-160ºC and 60-70 psi

Figure 76—Wettability state observation on calcite (a) before and (b) after applying DTPA.

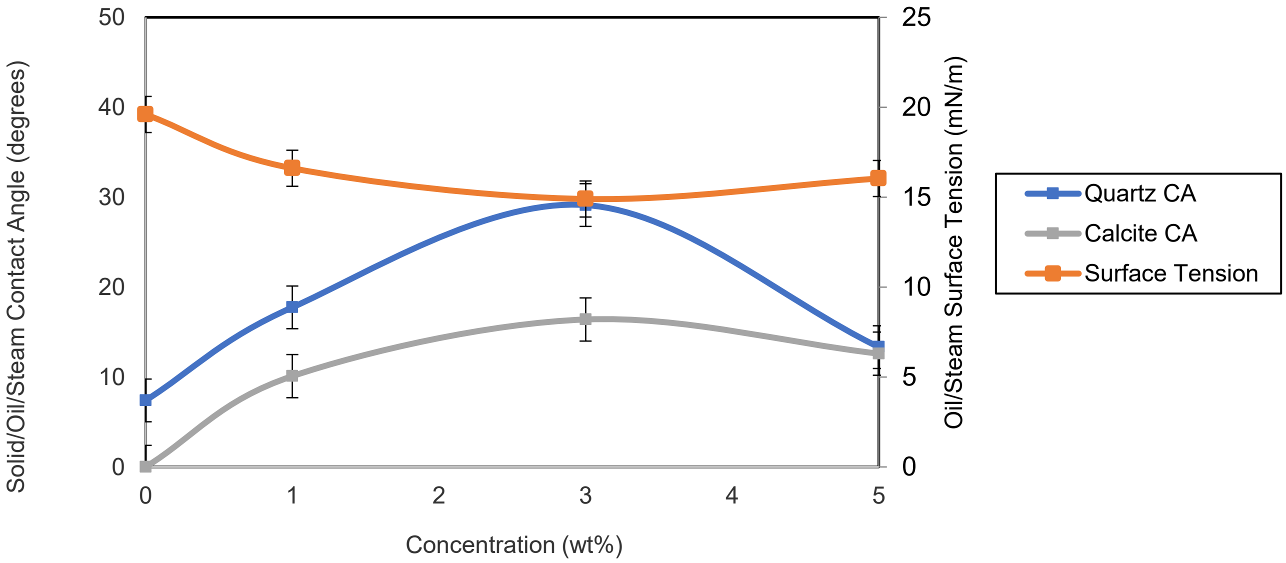
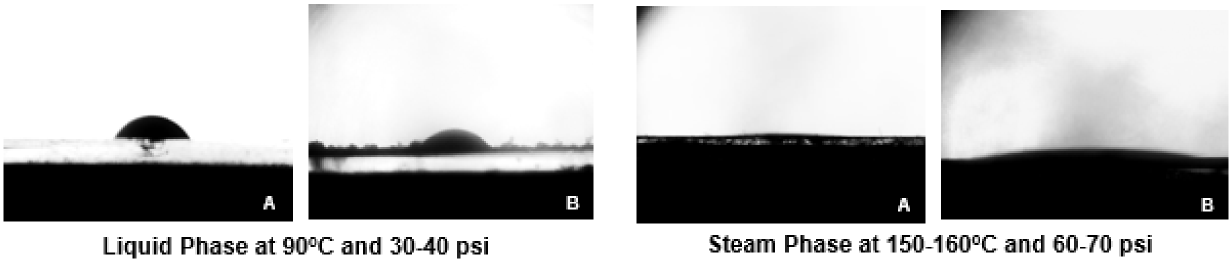


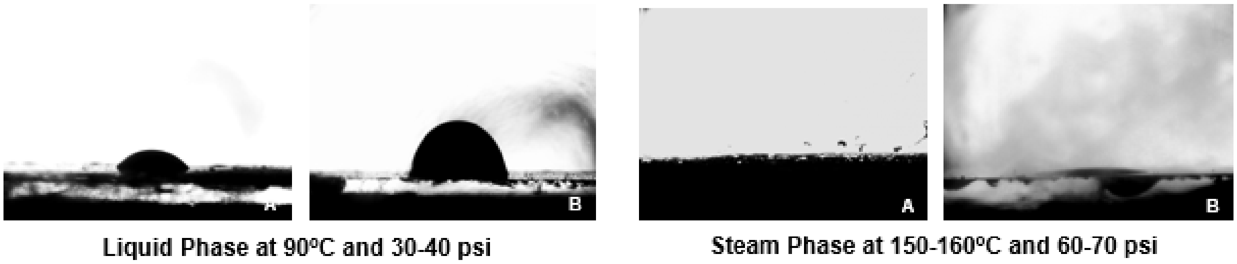
Figure 77—Wettability state and surface tension profile under steam condition with DTPA.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 78—Wettability state observation on quartz (a) before and (b) after applying HEDTA.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 79—Wettability state observation on calcite (a) before and (b) after applying HEDTA.

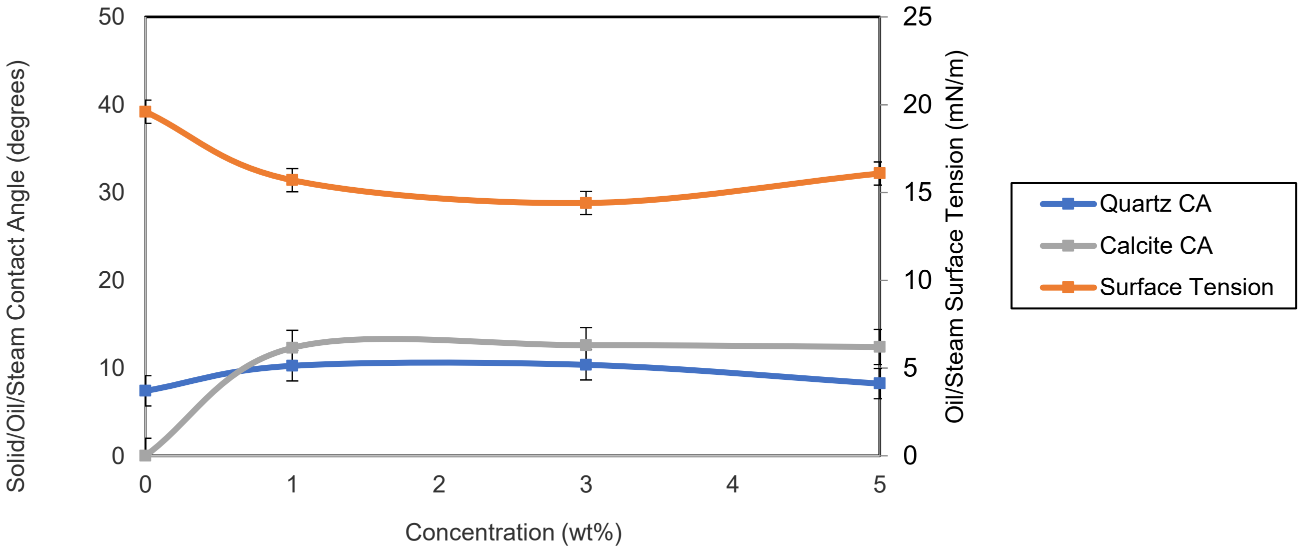


Figure 80—Wettability state and surface tension profile under steam condition with HEDTA.

Biodiesel. Another type of chemical additive tested in this research was biodiesel. Biodiesel is not soluble in water; therefore, oil-in-water emulsion type of biodiesel was prepared and injected with steam as suggested by Lee et al. (2018). A range of 0.25-1 wt% biodiesel concentration oil-in-water emulsion was applied to study its performance on wettability alteration and surface tension reduction. Favorable wettability alteration and surface tension reduction at steam conditions were observed (**Figures 81-83**). When the biodiesel concentration of 0.25 wt% was applied initially, the quartz surface showed a great wettability alteration degree. The contact angle improved from 7.4° originally to 26.6° on average indicating that the quartz surface had become more water or steam-wet. Opposite, this behavior was not acquired on the calcite surface leading. An experiment on calcite concluded that the contact angle only elevated to a magnitude of 13.3°. Beyond this concentration (0.25 wt%), the wettability state still showed an increasing trend. The wettability alteration degree did not change much on quartz substrate, but there was noticeable improvement on calcite substrate. The highest value of wettability alteration degree was observed to be 26.6° for quartz and about 24.5° for calcite on average at 1 wt% of biodiesel concentration. This observation shows that the wettability of both quartz and calcite surfaces could be restored to more water or steam-wet state. The biodiesel oil-in-water emulsion did not only deliver very favorable performance on wettability alteration, but also reduced the surface tension at steam conditions. An average surface tension of 16.3 mN/m was achieved from 18.8 mN/m at initial condition after applying biodiesel oil-in-water emulsion to the heavy-oil/steam system. This result is also in line with the previous published research by Babadagli et al. (2010), Babadagli and Ozum (2010), and Argüelles-Vivas et al. (2012). This concluded that biodiesel could lead to favorable IFT reduction and incremental heavy-oil recovery at steam environment.

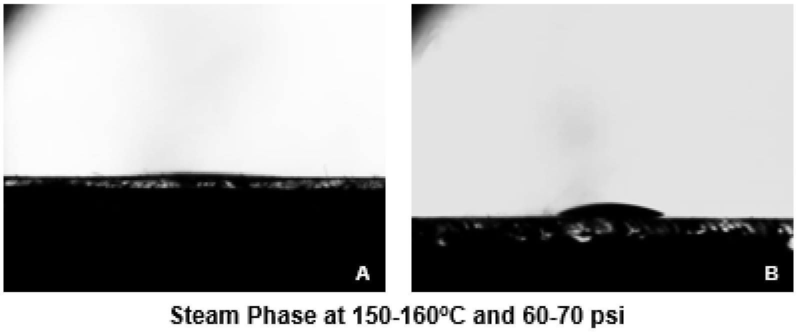


Figure 81—Wettability state observation on quartz (a) before and (b) after applying biodiesel.

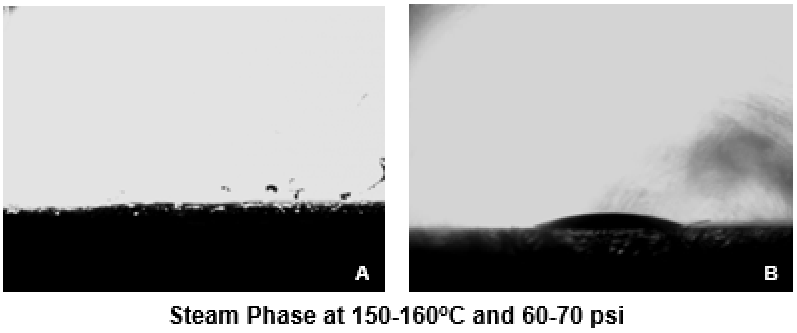


Figure 82—Wettability state observation on calcite (a) before and (b) after applying biodiesel.

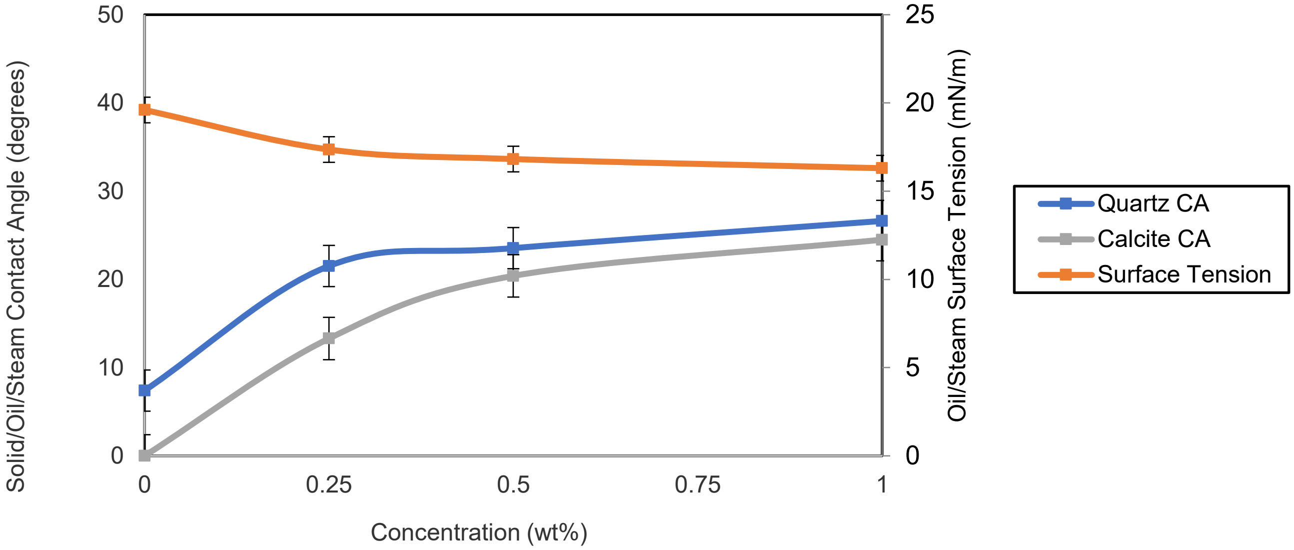


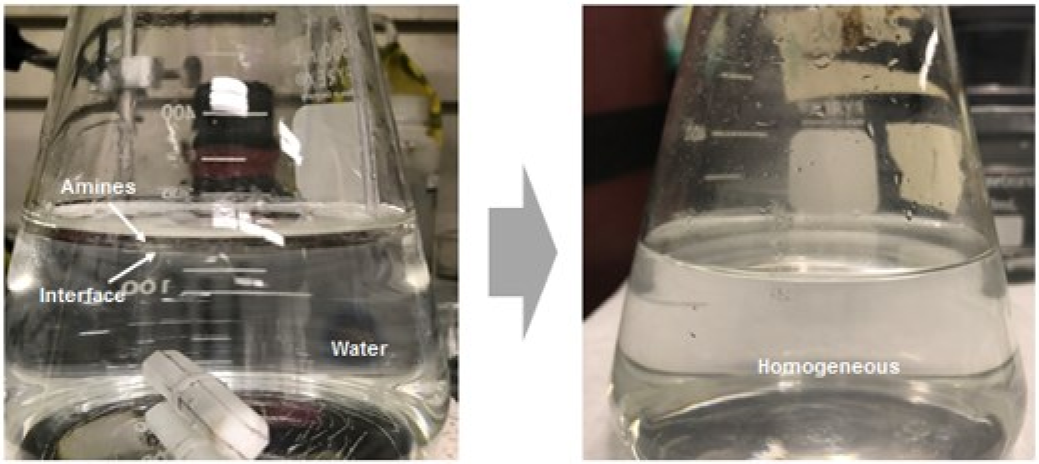
Figure 83—Wettability state and surface tension profile under steam condition with biodiesel.

Switchable-Hydrophilicity Tertiary Amines (SHTA). Initially, SHTA was synthesized using a tertiary amine (N, N-dimethylcyclohexylamine) presented in **Figure 84**. Fundamentally, there was a shift in physicochemical properties such as hydrophilicity and SHTA became hydrophilic with CO_2 addition in a reversible chemical reaction. Because of this reversible chemical reaction, SHTA can potentially be retrievable by shifting the chemical reaction satisfying the following reversible chemical reaction:

$$NR_3 + H_2O + CO_2 \leftrightharpoons NR_3H^+ + HCO_3^- \quad (2)$$

This research focused on the study of wettability alteration and interfacial properties modification affected by this synthesized SHTA to the rock/heavy-oil/steam system. **Figures 85-87** present the favorable wettability alteration on quartz and calcite substrates, and also surface tension reduction after adding SHTA at steam condition. Substantial improvement of quartz surface contact angle was noticed after introducing this synthesized SHTA during steam application. The contact angle improved from completely oil-wet averagely 7.4° to be more water or steam-wet around 30.2°. This significant change on quartz surface contact angle was perceived at 3 wt% optimum SHTA concentration.

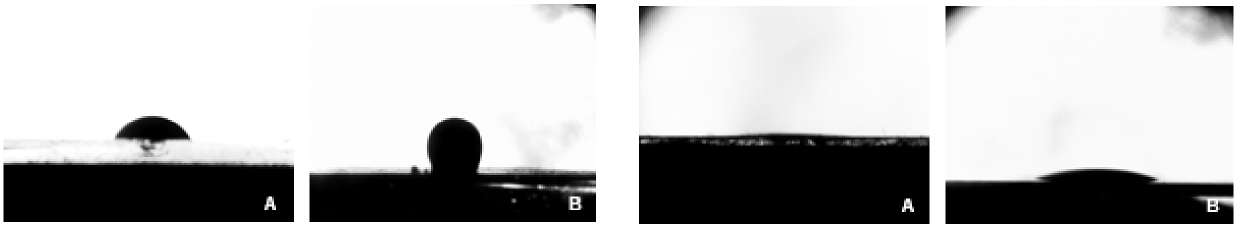
Similarly, promising wettability alteration was also perceived on the calcite substrate when SHTA was added to the system. The contact angle of the calcite surface was observed to increase to 22.9° on average, thus indicating the surface has been shifted to be more water or steam-wet. The maximum change in the contact angle of the calcite surface was observed at optimum SHTA concentration around 3 wt%. In addition to wettability alteration, the surface tension measurement between the heavy-oil and steam with SHTA was also performed. SHTA was able to reduce the surface tension to 16.5 mN/m averagely. The minimum surface tension was observed at 3 wt% SHTA concentration. The study on SHTA from this research clearly shows that this chemical additive is very promising on wettability alteration and interfacial properties modification. Previous research on bitumen recovery by using SHTA also concluded that up to 98% bitumen was extracted from the oil sands (Sui et al. 2016; Holland et al. 2012).



Hydrophobic

Hydrophilic

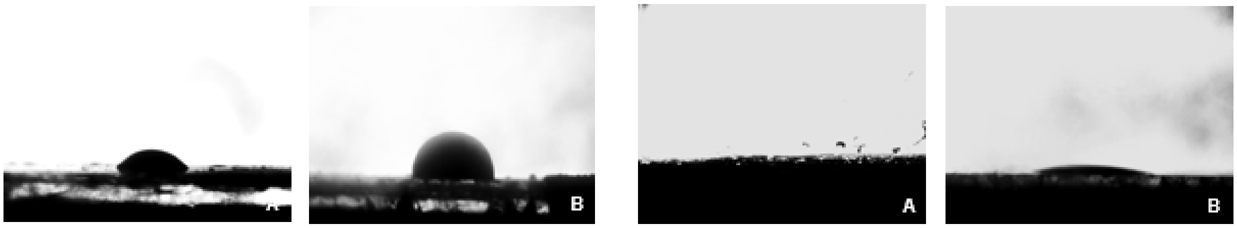
Figure 84—Process of synthesizing SHTA from initially hydrophobic to hydrophilic solution.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 85—Wettability state observation on quartz (a) before and (b) after applying SHTA.



Liquid Phase at 90°C and 30-40 psi

Steam Phase at 150-160°C and 60-70 psi

Figure 86—Wettability state observation on quartz (a) before and (b) after applying SHTA.

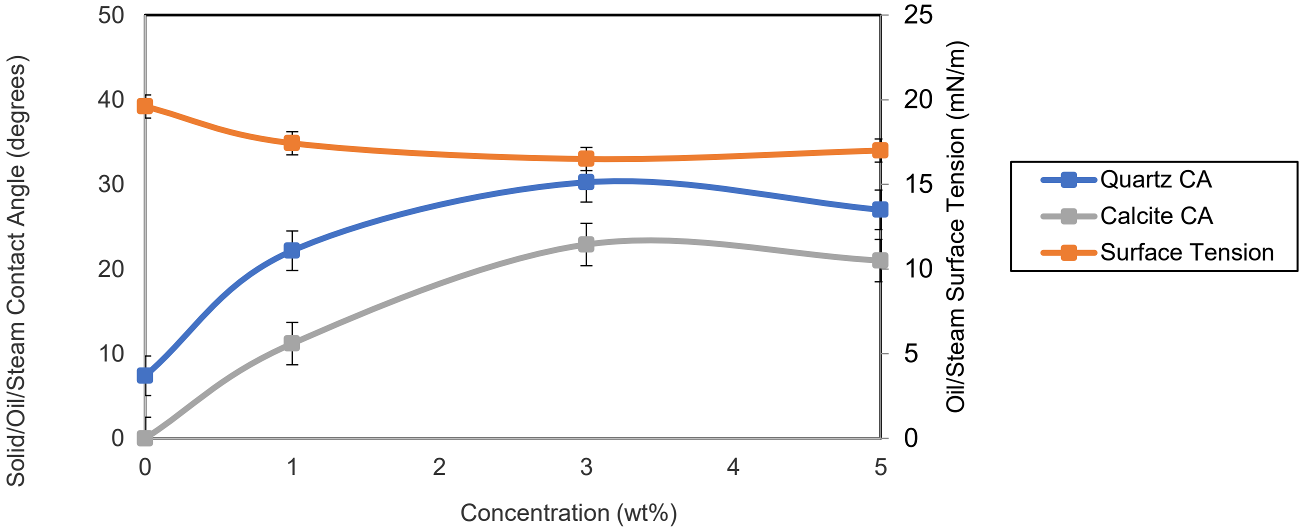


Figure 87—Wettability state and surface tension profile under steam condition with SHTA.

Chemical Additives Performance Comparison. The performance of all tested chemical additives is summarized and compared in **Figures 88-90**. In general, SHTA and biodiesel oil-in-water emulsion presented the most favorable wettability alteration degree on both quartz and calcite substrates amongst all tested chemicals. These two chemical additives also showed strong thermal stability through TGA measurement; therefore, SHTA and biodiesel oil-in-water emulsion are very promising for steam applications on sandstone and carbonate reservoirs. In terms of surface tension, DME delivered very auspicious surface tension reduction amongst all tested chemical additives. This novel chemical could also be the potential steam additive in steam applications. Additionally, **Figure 91** depicts the commercial price comparison of all tested chemical additives. Most of the tested chemical additives are still economical for field applications, particularly SHTA and biodiesel.

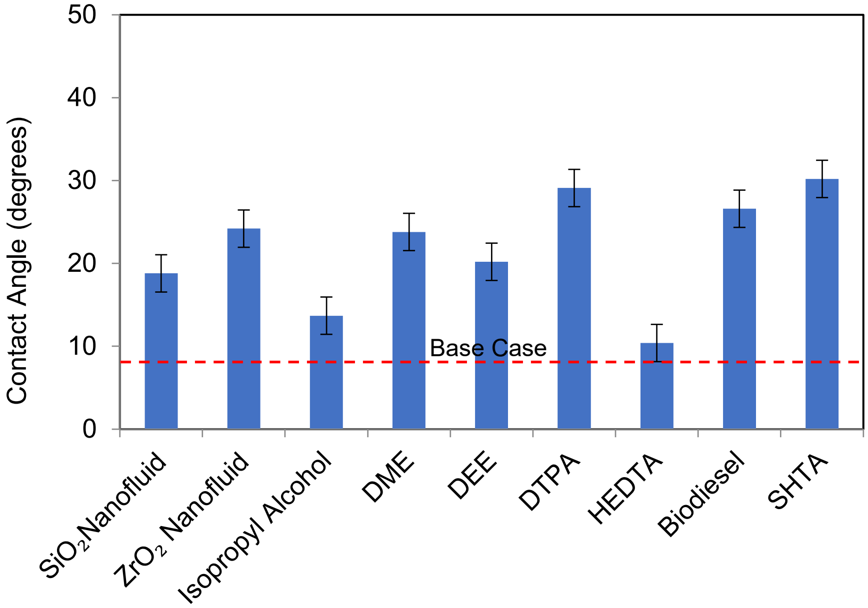


Figure 88—Comparison of change in wettability state on quartz with tested chemical additives at optimum concentration.

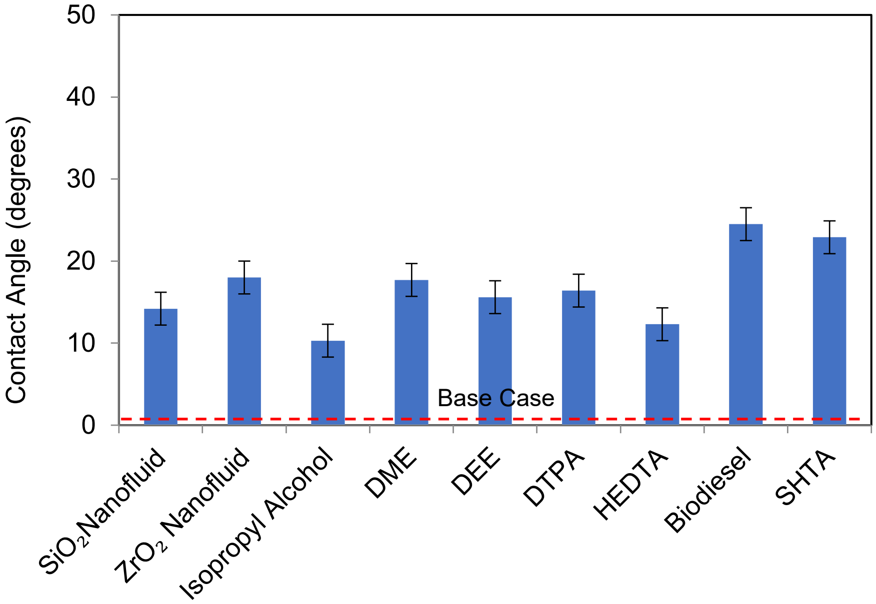


Figure 89—Comparison of change in wettability state on calcite with tested chemical additives at optimum concentration.

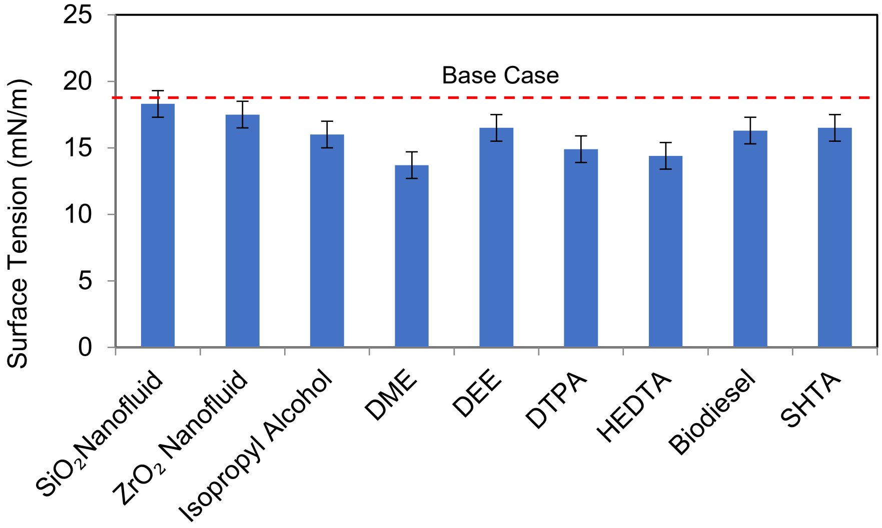


Figure 90—Comparison of change in surface tension with tested chemical additives at optimum concentration.

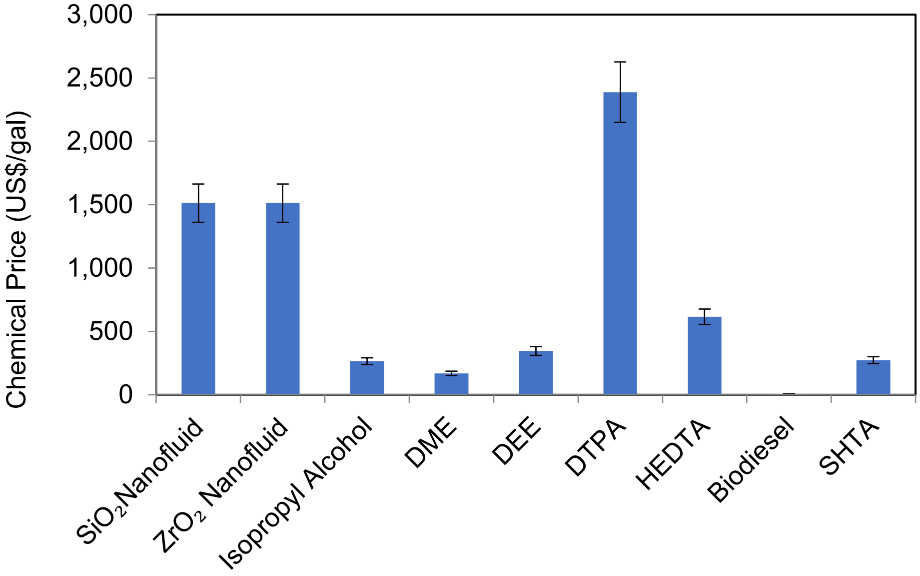


Figure 91—Commercial price comparison of tested chemical additives.

3.5 Conclusions

1. Elevated pressure on the rock/heavy-oil/brine system did not present any substantial effect to the wettability of the substrates.
2. Brine chemistry could lead to unfavorable wettability alteration. Adsorption of cations, both monovalent and divalent, to the solid surface led to the modification of total solid surface charge to acquire a more positive charge. This phenomenon was verified by the electrokinetic analysis through streaming potential measurement showing that when the salinity was increased, total solid surface charge—represented by zeta potential—moved towards the positive value. This mechanism presented attractive forces when the negatively-charged heavy-oil was introduced to the rock surface, yielding to the more oil-wet surface.
3. Transformation of the external phase from initial liquid phase to steam phase turned the wettability state of the rock surface to be completely oil-wet. This steam-induced wettability alteration behaves irreversibly. Intervention from the steam additives is necessary to restore the wettability state to more water or steam-wet state.
4. In general, most of the studied novel chemical additives are very promising in alternating the use of conventional chemical additives, specifically for steam applications. Most of the tested novel chemical additives delivered favorable thermal stability through TGA measurement. However, two tested chemical additives—isopropyl alcohol and DEE—presented unfavorable thermal stability. These two chemical additives were not suitable for steam applications.
5. Nanofluids are promising novel chemical additives for steam applications yielding to auspicious wettability alteration and surface tension reduction. However, only ZrO_2 nanofluid exhibited a favorable performance in altering wettability and reducing the surface tension.
6. DME type of solvent-based chemical additive was very promising for sandstone with steam applications. This chemical additive presented favorable wettability alteration and surface tension reduction at an extremely high-temperature.
7. Chelating agents are also considerable for applications on sandstones combined with steam injection. Nevertheless, only DTPA promoted auspicious wettability alteration and surface tension reduction in the rock/heavy-oil/steam system.

8. Biodiesel oil-in-water emulsion is a good steam additive for sandstones and carbonates presenting good thermal stability, favorable wettability alteration, and surface tension reduction. Optimal concentration should be determined (possible lower biodiesel concentrations than used in this research) to attain the maximum degree of wettability alteration and surface tension reduction, particularly at steam pressure and temperature.
9. SHTA could also be an alternative to conventional chemical additives. This novel chemical additive is very promising, for applications to sandstones and carbonates, in altering the wettability and reducing the surface tension between heavy-oil and steam. Furthermore, SHTA could also be more economical in steam applications because it is a retrievable chemical additive. However, further studies on certain aspects—potential heavy-oil recovery through core steam flooding and maximum numbers of SHTA re-utilization—are still needed to comprehend its application in in-situ thermal recovery.
10. SHTA and biodiesel presented the most favorable wettability alteration amongst all tested chemical additives. For surface tension reduction, DME is recommended as a steam additive.
11. Some of the tested novel chemical additives are considered to be economical for steam applications. These chemicals could be alternatives to conventional chemical additives for thermal enhanced oil recovery.

Chapter 4: Wettability State and Phase Distributions during Steam Injection with and without Chemical Additives: An Experimental Analysis Using Visual Micro-Models

This chapter of thesis is a modified version of a published research paper SPE 196253. The conference paper version SPE-196253-MS was presented at SPE/IATMI Asia Pacific Oil and Gas Conference and Exhibition held in Bali, Indonesia, 29-31 October 2019. The journal version of this research paper was submitted to SPE Reservoir Evaluation & Engineering.

4.1 Preface

Our previous contact angle measurements showed that phase change plays an essential role in wettability, thus impacting heavy-oil recovery. While oil is the strongly wetting phase in the steam zone, it becomes the opposite in the condensation (hot-water) zone—regardless of temperature. We also showed that the reverse wettability can be changed using new generation chemicals including thermally resistant chemicals (special surfactants, alkalis, water soluble solvents, and ionic liquids). Even though they reveal useful information, contact angle measurements are limited in accounting for the importance of the wettability alteration effect on the phase distribution/entrapment and oil recovery. Micromodel studies are then preferred to assess these characteristics.

All observations and measurements in this research were conducted at temperatures up to 200°C on glass bead micromodels. The models were initially saturated with brine solution and then displaced by two types of mineral oils (450 cP and 111,600 cP at 25°C) to maintain initial water and oil saturation. Hot-water was then constantly injected into the micromodels to evaluate the impact of phase change and wettability status on residual saturation development. Similar parameters were also evaluated in pure steam injection by elevating the temperature to match the steam temperature and maintaining pressure below saturation pressure. Next, several chemical additives screened from the previous contact angle and thermal stability measurements were introduced during both hot-water and steam applications to observe their ability in modifying phase distribution, wettability state, and oil recovery at different pressures and temperatures.

The result of the experiments in the glass bead micromodel presented that phase distribution and wettability state were sensitive to steam phase (vapor yielded oil-wet or condensate yielded water-wet case). This phenomenon also aligned with the previous hypotheses indicating that phase change has an impact on the wettability state and residual oil saturation. At any circumstances, wettability alteration with chemicals was possible with the anionic surfactant and SiO_2 nanofluid. The shape and characteristics of the trapped oil with and without chemicals were identified through micromodel images and suggestions were made as to the conditions (pressure, temperature, and time to apply during the injection application) at which these chemicals show optimal performance.

Study and analysis of phase distribution and wettability change in micromodels during hot-water and steam applications provide useful data and understanding of interfacial properties, oil trapping mechanism, and recovery performance of rock/bitumen/hot-water or steam system in the reservoirs. For practitioners, chemical additives were recommended, validated by visual images and thermal stability tests.

Key words: Steam injection, phase distribution, wettability change, micromodels, chemical additives.

4.2 Introduction

The petroleum industry has placed more attention on heavy-oil recovery to unlock its potential reserves above 500 billion barrels (Meyer 1998). Efforts in intensifying the steam injection—Steam-Assisted Gravity Drainage (SAGD) and Cyclic Steam Stimulation (CSS)—efficiency have been established to reduce the steam usage, excessive operational costs, and energy utilization. On the other hand, unresolved concerns impacting heavy-oil recovery remain challenging and need further actions.

Reservoir rock wettability is a critical parameter in thermal oil recovery. Applications of this recovery technology—particularly in heavy-oil fields—evidenced an unfavorable field production falloff after perceiving the field maturity phase (Blevins 1990; Winderasta et al. 2018; Jones et al. 1995). Thermal oil recovery could enhance the water-wetness of the reservoir rocks by promoting an extrication of polar components encompassed in heavy-oils—mostly resins and asphaltenes—from the surface of the rocks. In contrast, the mechanism of phase change plays more substantial part in undesirable wettability alteration. Our previous research proved that injecting steam to the rock/heavy-oil system triggered a wetting phase transformation—from initially liquid phase to steam phase—leading to an inauspicious irreversible steam-induced wettability alteration (Pratama and Babadagli 2018, 2019a, 2019b, 2019c). Furthermore, favorable wettability alteration was attainable with the implementation of steam additives according to the research. However, the study of reservoir rocks wettability alteration—particularly with chemical additive applications—throughout quantitative contact angle analysis is still limited to comprehend the phase distribution or oil entrapment behavior in the pores. Thus, micromodel experimental study is necessary to represent those phenomena in the pores of reservoir rocks.

Micromodels are defined as a scaled-down model replicating a porous medium that is able to qualitatively visualize the fluid distribution inside the pores. In the early 1950s, the first micromodel was developed to model the fluid behavior in porous media; Chatenever and Calhoun (1952) were the pioneers in developing glass bead micromodel packings to visualize the waterflood behavior in the porous matrices. In the experimental study, they used 0.2 mm glass beads placed and packed in between two flat glass plates observed through a 10X magnification microscope. They were able observe and visualize particular flood pattern—comprising fingering phenomenon—during water injection in the oil-saturated glass bead micromodel. Furthermore, residual oil formations were also perceived during water injection through the micromodel according to their research.

In the early 1960s, a capillary type of micromodel was developed to visualize the fluid behavior in the pore networks (Mattax and Kyte 1961). This capillary micromodel was very useful to determine the water-oil displacement mechanisms—channel flow, water flow, and oil flow. The application of micromodel is not limited to petroleum engineering. Corapcioglu et al. (1997) and Corapcioglu and Fedirchuk (1999) visualized and quantified the solute transport using glass bead and diamond-shaped network glass-etched micromodels. Their observation and evaluation of fluid behaviors through the pore networks—flow regions, solute concentrations, and injection breakthrough—were satisfactorily achieved throughout these micromodels visualization. Moreover, three-phase (water, oil, and air) flow in porous media was also successfully modelled by Soll et al. (1993); they were able to identify and evaluate the fluid saturation and capillary pressure relationship amongst three non-miscible fluids.

In the area of enhanced oil recovery, the use of micromodels keeps developing and is believed to be the effective methodology in qualitatively observing and evaluating the fluid flow behaviors in porous media and oil recovery performance. Numerous published research in this particular area—utilizing micromodels—presented favorable visualization. Yeh and Juárez (2018) conducted a waterflood behavior study by using packed glass bead micromodel in the microfluidic apparatus supported by optical fluorescence tracing the injection front. They concluded that oil displacement behaved differently and presented favorable improvement with surfactant and polymer addition. Another research in polymer flooding was also conducted by involving micromodel. Herbas et al. (2015) stated that the magnitude of viscoelastic polymer affected the oil displacement behavior in porous media—giving higher total oil recovery for higher polymer concentration. They also observed that no significant discrepancy of oil recovery performance between the micromodel and core flooding.

The study of fluid displacement behavior in porous media employing micromodel was also applied to the heavy-oil recovery. Recently, Dong et al. (2012) visualized displacement behavior of heavy-oil with alkaline and surfactant injection through the glass-etched micromodel. Observation of displaced residual oil was observed during the experiment. They concluded that the residual oil displacement was triggered by wettability alteration and emulsification. Similar behavior was also evidenced by Sedaghat et al. (2016) when the residual or trapped oil was observed in the pores. Reduction of residual oil and incremental ultimate oil recovery were achieved after applying alkaline, polymer, and surfactant (ASP). However, a high value of mobility ratio remains challenging in visualizing heavy-oil displacement behavior using a micromodel.

The use of micromodels in thermal recovery research—particularly steam applications—to replicate phase distribution in porous media is still limited. Only few published research are available—focusing on visualizing heavy-oil thermal recovery. Roosta et al. (2009) published a research presenting residual oil behavior with steam application in porous media. They utilized quartz-type glass bead micromodel to replicate pore networks in the reservoirs. It was observed that favorable wettability alteration was impossible to accomplish after steam injection, unless the original wettability state was affected by the polar components interaction, according to their research. Recently, another pore-scale thermal heavy-oil recovery research using glass bead micromodel was conducted by Argüelles-Vivas and Babadagli (2016). The research focused on observing trapped oil during the SAGD process. According to their experimental study, residual or trapped oil was caused by wettability state, heterogeneity, and steam expansion.

In summary, phase change is the major contributor in inauspicious wettability alteration during steam injection. This phenomenon was verified by our previous research focusing on steam-induced wettability alteration. Although involvement of chemical additives could lead to a favorable wettability alteration through quantitative contact angle observation, this evidence still has limitations in explaining the phase distribution or oil entrapment behavior in porous media. Thus, the objective of this research paper is to qualitatively observe and investigate unfavorable wettability alteration caused by phase change and chemical induced favorable wettability alteration in a rock/oil/steam system through glass bead micromodel visualization. Study and analyses resulted from this research will be valuable to comprehend the phase distribution and residual oil behavior in porous media.

4.3 Materials and Experimental Setup

Oil Samples. Two types of mineral oils were used in this research (**Table 7**). **Figure 92** illustrates the viscosity profile of each utilized mineral oil with temperature. When performing the experiments, oil-based dye was added to the mineral oil to make it discernible from any other fluid.

Table 7—Properties of utilized mineral oils at specific temperature.

Oil Type	Viscosity, cP	Temperature, °C
Heavy oil	450	25
Extra-heavy oil	111,600	25

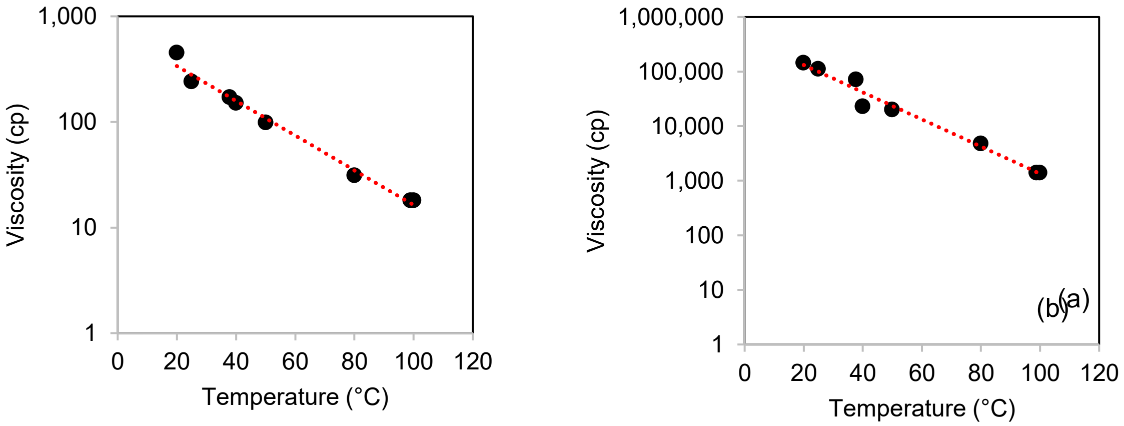


Figure 92—Oil viscosity profile with temperature: (a) heavy oil and (b) extra-heavy oil.

Chemical Additives. In these glass-bead micromodel experiments, four chemical additives were selected based on the wettability alteration and interfacial properties results from our previous research conducted by Pratama and Babadagli (2018, 2019a, 2019b, 2019c). The list of utilized chemical additives—with the optimum concentration resulted from our previous research—is given in **Table 8**. Each chemical solution was synthesized using deionized (DI) water. The use of chemical additives in this part of the research is to observe and compare the wettability alteration and interfacial property behavior in the pores before and after adding the chemicals. Additionally, brine solution was used in this research to initially saturate the micromodel. The concentrations of the brine solution were designated to represent reservoir water salinity in Alberta, Canada.

Table 8—List of chemical additives used in glass bead micromodel.

Chemical Classification	Chemical Name	Concentration
Brine Solution	NaCl, $CaCl_2$, $MgCl_2$	30,000 ppm, 1,000 ppm, 100 ppm
Nanofluid	SiO_2	1 wt%
Anionic surfactant	Linear-alkyl toluene sulfonate (LTS)	3 wt%
Nonionic surfactant	Sorbitan monooleat	1 wt%
Ether	Dimethyl ether (DME)	3 wt%
SHTA	N, N-dimethylcyclohexylamine	3 wt%

4.3.1 Micromodel

Instrument Setup. The micromodel was built with 3-mm glass beads made of silica. The glass beads were arranged and packed in between two plexiglass plates with the thickness of 9 mm. The micromodel was then placed and pressurized inside the 5 cm x 5 cm steel frame and put in the sealed transparent box made of acrylic to minimize the heat loss while working on steam condition. Initially, the glass bead micromodel was saturated with the brine solution. Said micromodel was then displaced by the mineral oils. This process is essential to represent a saturation history in the reservoir rocks. Hot-water was then constantly injected at 0.5 mL/min into this glass bead micromodel for the maximum time of 40 minutes or 3 pore volume injected (PVI) to observe phase distribution and wettability change. Furthermore, similar parameters were also observed and evaluated in pure steam injection along with chemical additives—generated from the high-temperature oven—by elevating the temperature to the steam temperature up to 200°C and maintaining pressure below saturation pressure. Phase distribution and oil entrapment behavior in the porous media resulted after the injection was captured by high-speed high-resolution camera equipped with 65-mm optical macro lens. The complete experimental setup is depicted in **Figures 93** and **94**.

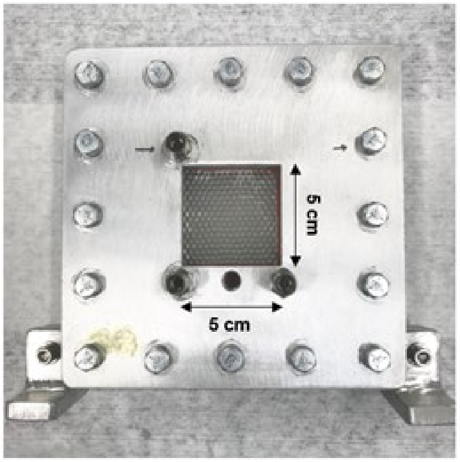


Figure 93—Glass bead micromodel in pressurized steel frame.

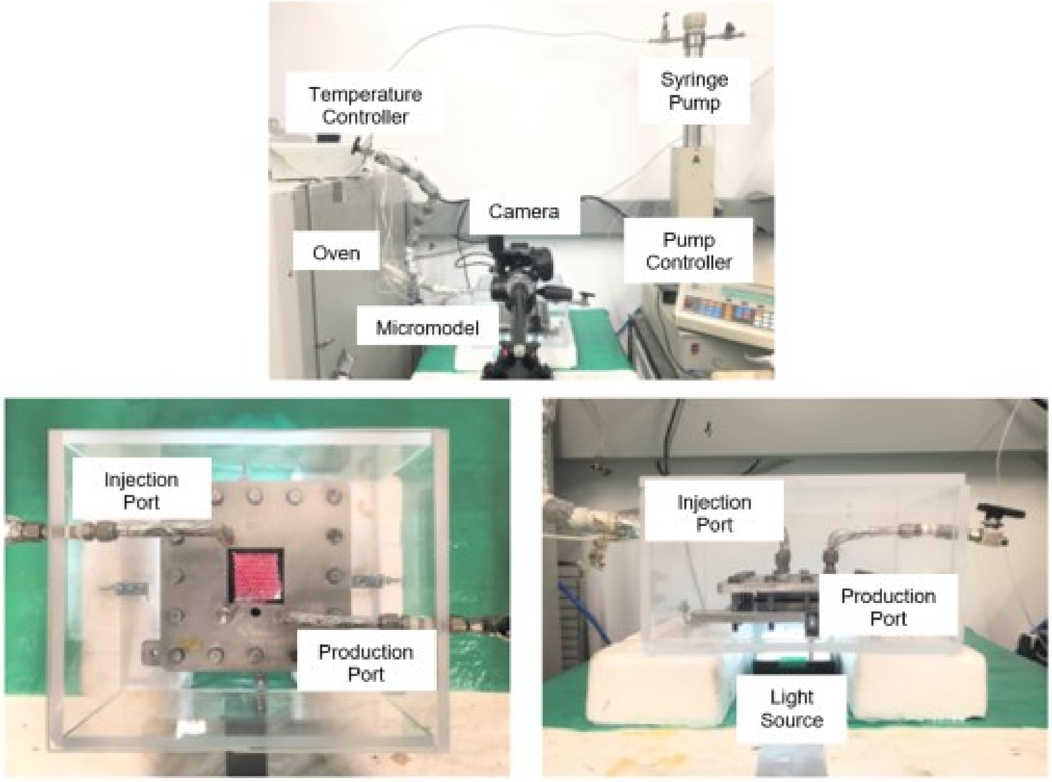


Figure 94—Glass bead micromodel complete experimental setup.

Porosity and Permeability Estimation. The glass beads were arranged and packed in a rhombohedral structure—the most compact arrangement. This structure was adopted to replicate the pores and pore throats found in the most reservoirs—particularly sandstones. **Figure 95** presents the packing of the utilized glass bead micromodel. Porosity for this rhombohedral packing was estimated around 26% (Amyx et al. 1960). For permeability calculation, the Kozeny-Carman model was utilized to estimate the value by also incorporating the estimated rhombohedral structure porosity. The permeability of this glass bead micromodel satisfies the following equation (Carman 1937):

$$k = \frac{{d_m}^2}{180} \frac{n^3}{(1-n)^2} \tag{2}$$

where d_m is the particle or glass bead size and n is an estimated porosity value yielding to $k = 1.61 \times 10^{-3}$ mm^2.

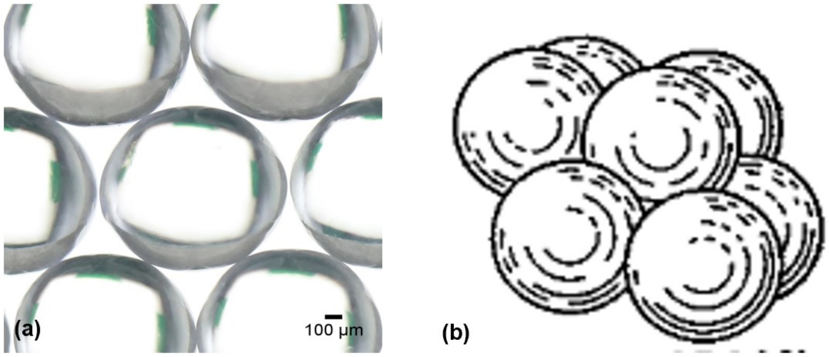


Figure 95—Glass beads with rhombohedral structure obtained from (a) this research and (b) after Amyx et al. (1960).

Wettability Status. To further comprehend the wettability alteration analysis of glass bead micromodel, qualitative analysis of wettability was conducted. An oil drop was placed on the plexiglass and glass bead surfaces and captured by using 65-mm macro lens. This experiment was performed under the effect of brine chemistry. **Figures 96** and **97** present the wettability state of the plexiglass and glass bead. It was perceived that the silica glass bead surface showed a more water-wet state. On the other hand, the plexiglass surface presented a less water-wet state in solid/oil/brine system.

Figure 96—Wettability state observation on plexiglass surface for (a) 450 cP and (b) 111,600 cP mineral oils at 25°C.

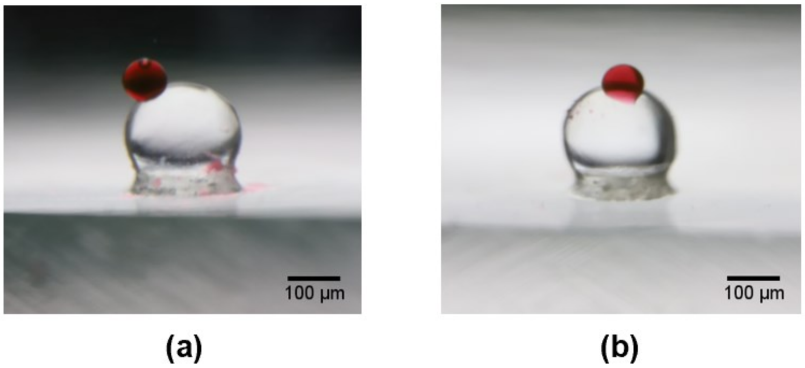


Figure 97—Wettability state observation on glass bead surface for (a) 450 cP and (b) 111,600 cP mineral oils at 25°C.

4.4 Results and Discussion

4.4.1 Phase Change Observation

As concluded in our previous research performed by Pratama and Babadagli (2018, 2019a, 2019b, 2019c), unfavorable irreversible wettability alteration occurred when a liquid phase was transformed to a steam phase in rock/oil/water system. In the present study, a visualization of this phase change was performed in a micromodel to further observe and investigate phase distribution/oil entrapment behavior and wettability alteration at the pore-scale. **Figures 98** and

101 display the pore-scale phase change phenomenon affecting the wettability state and residual oil shape for both 450 cP and 111,600 cP heavy mineral oils.

Initially, the model was saturated with heavy-oil and brine to represent the reservoir saturation history—initial oil and water saturation (**Figure 98a**). When hot-water was injected to the micromodel, some of the heavy-oil was produced and residual oil was observed post hot-water injection. At this circumstance, the oil was bound by the water acting as a wetting phase—having a direct contact with the solid surface (**Figure 98b**). However, pendular-ring distribution was perceived after hot-water injection. The water—as a wetting phase—did not continuously cover the glass bead surface, letting a part of the oil—as a non-wetting phase—interact with some of the glass bead surface. It seemed that the elevated temperature affected the water-wetness of the glass bead surface. This evidence was also proved by our previous research. The wettability state of the quartz surface tended to be less water-wet when the temperature was elevated (Pratama and Babadagli 2018, 2019a, 2019b, 2019c).

Phase change occurred when the steam was introduced to the model. A combination of both water phase and steam phase were observed during this steam injection (**Figure 98c**). This process causes the surrounding water to evaporate, yielding a direct interaction between glass bead surface and the oil. This mechanism leads to an unfavorable wettability alteration from an originally water-wet state to an oil-wet state and behaves irrevocably—leaving some oil film on the glass bead surface (**Figure 98d**).

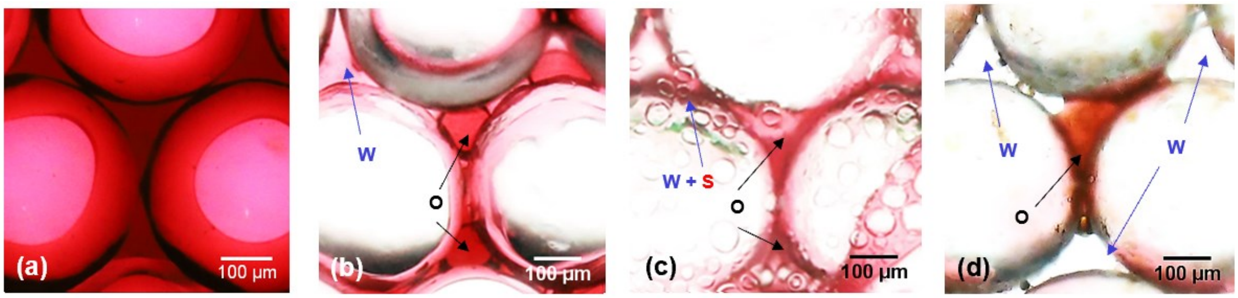


Figure 98—Phase change in glass bead micromodel with 450 cP mineral oil: (a) initial saturation, (b) post hot-water injection, (c) during steam injection, and (d) post steam injection; (W = water, O = oil, and S = steam).

A similar phenomenon was also perceived on the glass bead micromodel saturated with 111,600 cP heavy mineral oil (**Figure 99a**). It was noticed that there was some trapped oil in the pores after the hot-water injection process (**Figure 99b**). The shape of the observed residual oil was similar to that of the residual oil in the glass bead micromodel saturated with 450 cP heavy mineral oil, but more residual oil was observed in the micromodel saturated with 111,600 cP heavy mineral oil. Capillary pressure might influence the residual oil distribution (Roof 1970). At this particular condition, the water phase still surrounded the trapped oil phase in the pores and was in a direct interaction with the glass bead surface indicating the glass bead surface was still at a water-wet state. Moreover, a pendular-ring distribution was also perceived during hot-water injection indicating a reduction in glass bead surface wettability, meaning a less water-wet state. Correspondingly, phase change was observed when the injected fluid was switched to steam (**Figure 99c**). The presence of the steam caused the micromodel to become slightly cloudy. Nevertheless, our high-speed high-resolution camera could still capture the phase change phenomenon. **Figure 99d** presents the unfavorable wettability alteration after steam injection. It was noticeable that the water was no longer the continuous phase on the glass bead surface. This evidence indicates that the wettability of the glass bead surface had been altered to a fully oil-wet state.

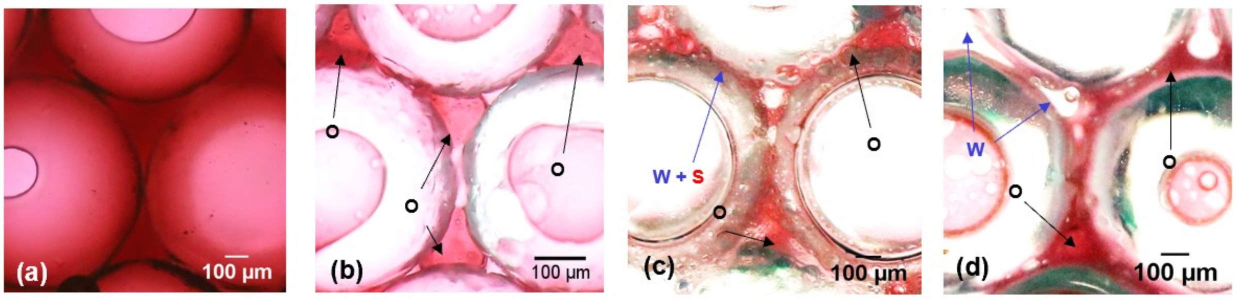


Figure 99—Phase change in glass bead micromodel with 111,600 cP mineral oil: (a) initial saturation, (b) post hot-water injection, (c) during steam injection, and (d) post steam injection; (W = water, O = oil, and S = steam).

4.4.2 Effect of Chemical Additives

Anionic and nonionic surfactants, SiO_2 nanofluid, dimethyl ether (DME), and switchable-hydrophilicity tertiary amines (SHTA) were used in this micromodel experimental study. These chemicals were selected to be involved in this research because of their favorable thermal stability, wettability alteration, and interfacial/surface tension reduction at steam condition (Pratama and Babadagli 2018, 2019a, 2019b, 2019c). Since said chemical additives could potentially improve the wettability alteration and interfacial/surface tension, this could also potentially lead to the phase distribution or entrapment improvement by reducing the capillary pressure (P_c) which satisfies the following equation:

$$P_c = \frac{2\, \sigma\, Cos\, \theta}{r} \tag{3}$$

where σ is the interfacial/surface tension, θ is the contact angle, and r is the pore radius.

Each experiment was performed at two steps, i.e. base case (without chemical additive) and with chemical additive. For the latter, each chemical additive was applied along with the hot-water and steam injections. Each case was run for 40 minutes or equivalent to 3 PVI. The optimum concentration of each chemical additive has also been determined from our previous research correspondingly.

Thermogravimetric Analysis. To further evaluate the thermal stability, thermogravimetric analysis (TGA) was performed for each chemical additive. The results of the TGA performance are depicted in **Figure 100**. According to the result, it was perceived that nonionic surfactant, SiO_2 nanofluid, and SHTA presented excellent thermal stability. The disintegration of said chemicals emerged at the temperature beyond 250ºC. Alternatively, medium thermal stability was observed on anionic surfactant. The decomposition of this type of chemical additive started at the temperature over 120ºC. In addition, TGA measurement for dimethyl ether (DME) was not able to be implemented because of the gaseous characteristic of the chemical.

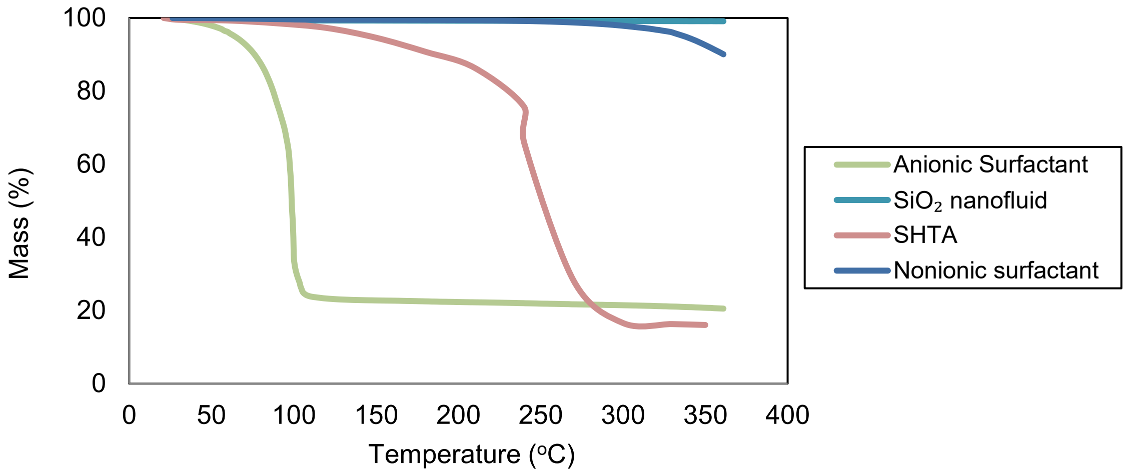


Figure 100—TGA profile for utilized chemical additives (after Pratama and Babadagli. 2018, 2019a, 2019b, 2019c).

Chemical Additives Performance. Previously, contact angle and surface tension measurements were conducted for each chemical additive to further investigate the degree of wettability alteration and surface tension reduction at steam condition. **Figure 101** shows the wettability alteration degree in the quartz/heavy-oil/steam system influenced by five chemical additives utilized in this experimental study through contact angle measurement. All of the tested chemical additives presented promising performance in altering the wettability to a more water or steam-wet state.

Additionally, favorable surface tension reduction was also presented by all experimented chemical additives. Amongst all chemical additives, DME delivered the most favorable surface tension reduction (**Figure 102**). The performance of these chemical additives is very useful for further chemical additive potential use through pore-scale investigation.

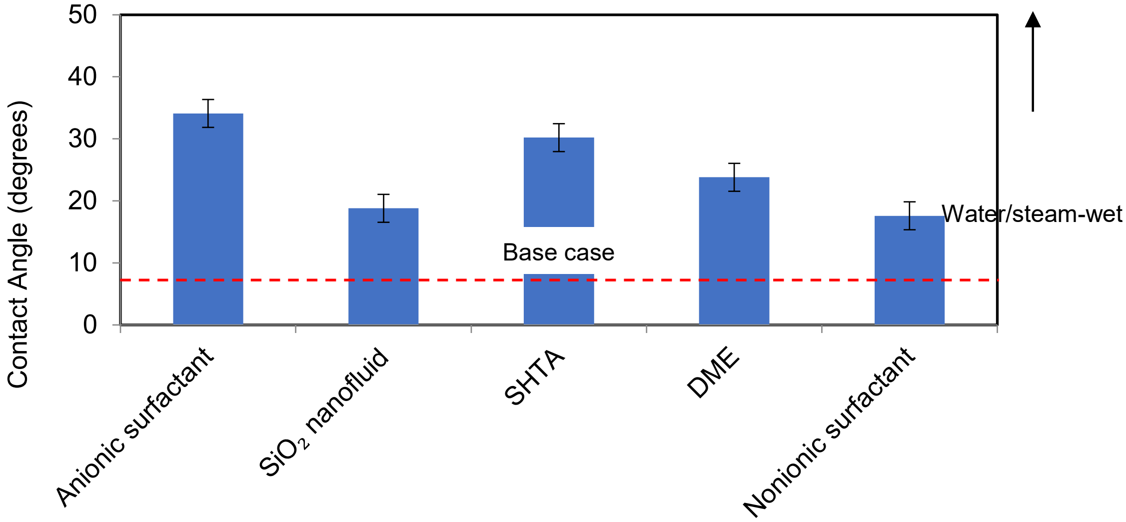


Figure 101—Comparison of change in wettability state on quartz at steam condition with tested chemical additives at optimum concentration (after Pratama and Babadagli. 2018, 2019a, 2019b, 2019c).

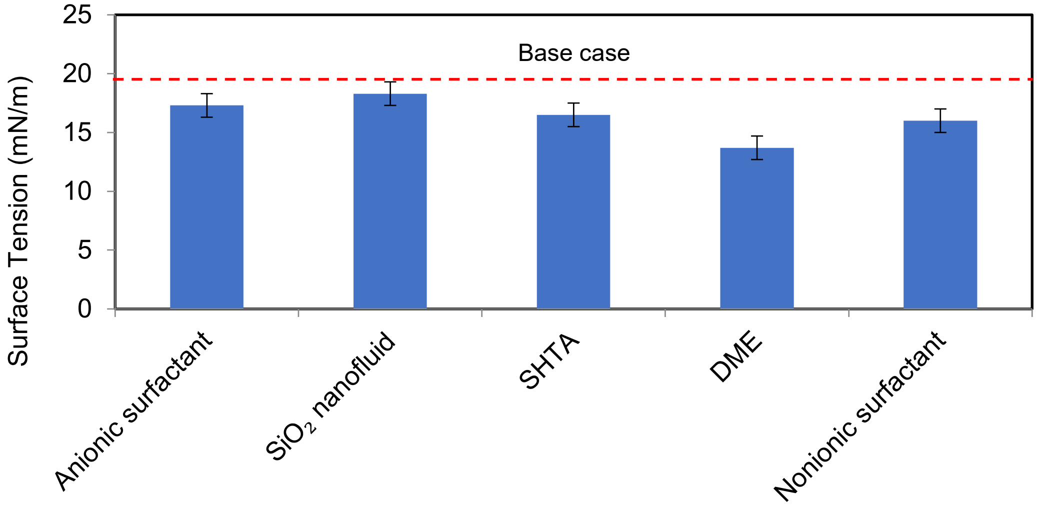


Figure 102—Comparison of change in surface tension at steam condition with tested chemical additives at optimum concentration (after Pratama and Babadagli. 2018, 2019a, 2019b, 2019c).

Base Case. Prior to the experimental study with preferred chemicals, base case experiments were conducted in this glass bead micromodel research. Base case experimental study is essential to compare the wettability and phase distribution behaviors before and after implementing chemical additives. Additionally, base case experiments were run for both types of heavy mineral oils.

Figures 103 and **104** depict the base cases for 450 cP heavy mineral oil at hot-water and steam condition. As previously explained, during the hot-water injection, the glass bead surface still had its water-wetness indicated from the shape of the trapped oil in the pores. It was also noticed that at t = 20 minutes, the non-wetting oil blob was observed in the pore throat. This trapped oil blob appeared after some oil was produced, leaving this oil blob accountable for residual oil (Ng et al. 1978). Furthermore, as the hot-water injection was continued until t = 40 minutes, the oil blob was turned into oil snap-off. Capillary pressure played an essential role on this oil snap-off as previously observed by Roof (1970).

On the other hand, phase distribution behaved differently at steam condition. Phase change phenomenon was perceived after steam was injected to the glass bead micromodel (**Figure 104**). At t = 20 minutes, two phases of fluids were observed—liquid phase and steam phase. As steam injection was continued to 3 PVI, only steam was perceived. At this circumstance, most of the water was transformed into steam phase leading to the unfavorable irreversible wettability alteration. The wettability state could not be restored even after the steam injection was stopped and the external phase re-transformed into liquid phase. Some oil films were also observed during this period indicating that the glass bead surface was turned into a completely oil-wet surface.

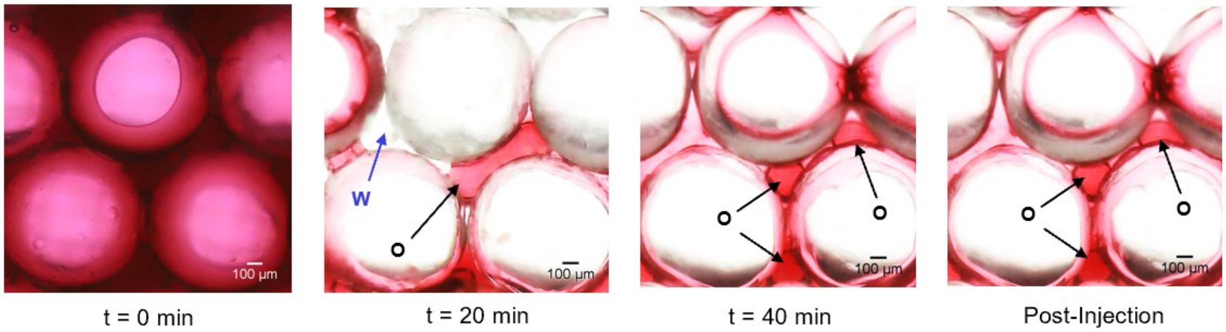
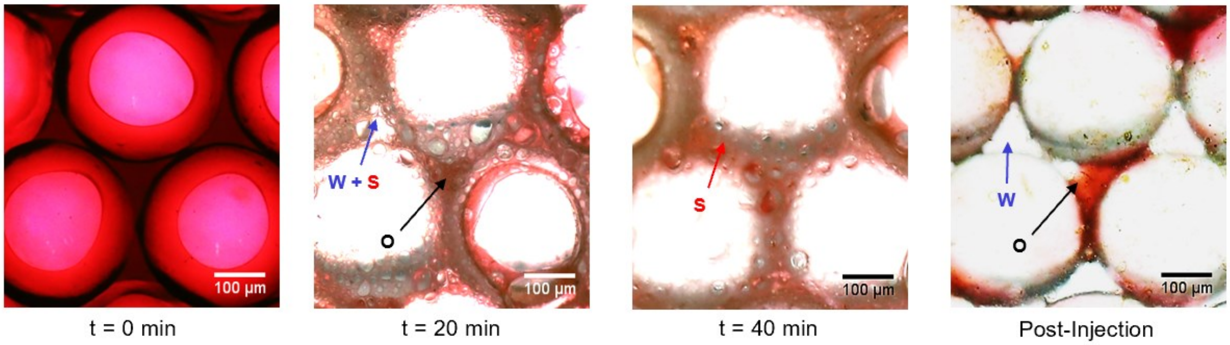


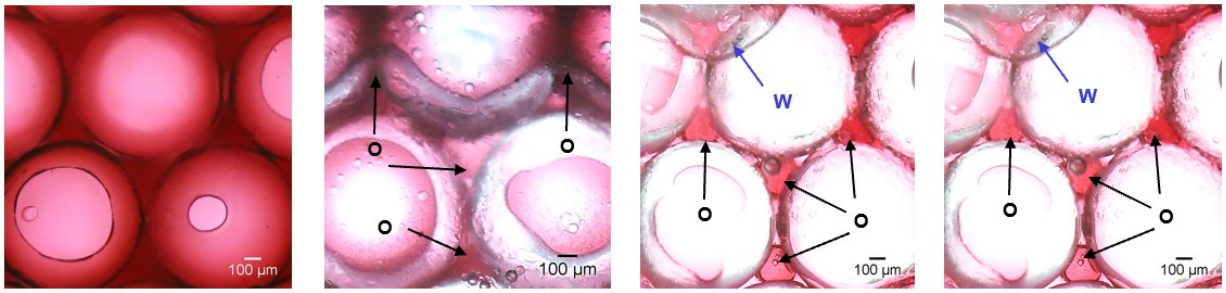
Figure 103—Base case hot-water injection in micromodel saturated with 450 cP heavy-oil; (W = water and O = oil).



t = 0 min t = 20 min t = 40 min Post-Injection

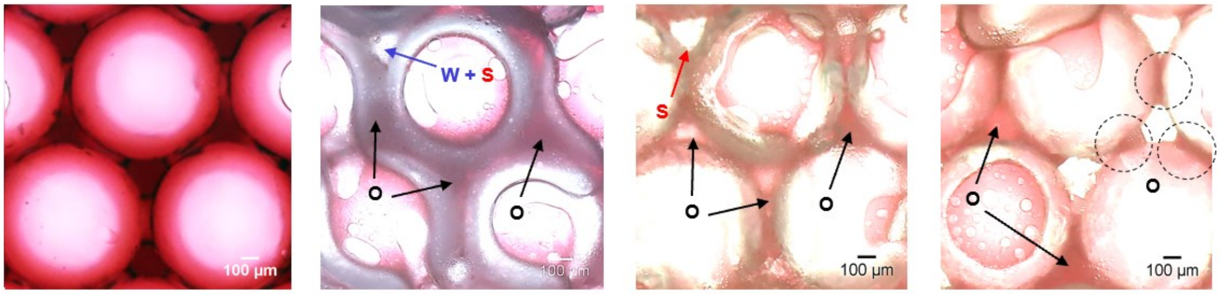
Figure 104—Base case steam injection in micromodel saturated with 450 cP heavy-oil; (W = water, O = oil, and S = steam).

In addition to the base case experimental study, 111,600 cP heavy mineral oil was also tested in the glass bead micromodel to further comprehend the wettability and phase distribution behavior in extremely heavy oil. **Figures 105** and **106** exhibit the oil entrapment and wettability behavior at hot-water and steam conditions. In the hot-water injection case, thick oil was still present filling every pore space in the glass bead micromodel even when the hot-water had been injected for 20 minutes. This phenomenon was most-likely caused by capillary pressure and mobility contrast between non-wetting phase and wetting phase since extremely heavy oil was used. As the heavy-oil began to produce, some residual oil was observed at t = 40 minutes or equivalent to 3 PVI. The shape of the residual oil was found to be similar to the residual oil observed in the glass bead micromodel saturated with 450 cP heavy mineral oil indicating the water-wetness of the glass bead surface. For this particular experiment, the glass bead micromodel was observed to have more residual oil than another glass bead micromodel with 450 cP heavy-oil. This evidence was also confirmed by Nejad et al. (2011) that there is a relationship between residual oil saturation and oil viscosity. Porous media having higher oil viscosity tend to have higher residual oil saturation. Similarly, this phenomenon was also observed in steam injection case, particularly at the pore throats. More trapped oil was evidenced at the end of the steam injection.



t = 0 min t = 20 min t = 40 min Post-Injection

Figure 105—Base case hot-water injection in micromodel saturated with 111,600 cP heavy-oil; (W = water and O = oil).



t = 0 min t = 20 min t = 40 min Post-Injection

Figure 106—Base case steam injection in micromodel saturated with 111,600 cP heavy-oil; (W = water, O = oil, and S = steam).

Anionic Surfactant. Linear-alkyl toluene sulfonate (LTS) was the type of anionic surfactant utilized in this research. This anionic surfactant presented promising wettability alteration and improvement on residual oil saturation. Experiments with this chemical additive were conducted for both types of mineral oils. **Figures 107** and **108** present the phase distribution behavior entrapment behavior at hot-water and steam injection for 450 cP heavy-oil after adding anionic surfactant to the glass bead micromodel. It was perceived that this chemical additive presented a very favorable performance on both hot-water and steam injection cases. No trapped oil and oil films were present on both cases. This evidence confirms that favorable wettability alteration occurred after involving this chemical additive as also concluded in our previous research conducted by Pratama and Babadagli (2018, 2019a, 2019b, 2019c). There was also a possibility of oil-in-water emulsion formation shown by the reddish color at t = 20 min. However, this evidence still needs further verification by conducting quantitative analysis in produced sample under the microscope.

Oppositely, favorable result was not observed in the glass bead micromodel saturated with 111,600 cP heavy mineral oil. Residual oil was still observed and the wettability state could not be restored even after involving anionic surfactant (**Figures 109** and **110**). Another chemically-induced alteration was also perceived in the glass bead micromodel saturated with 111,600 cP heavy-oil. This phenomenon is also in line with the interfacial/surface tension measurement that this anionic surfactant could potentially trigger the formation of an emulsion due to interfacial/surface tension reduction.

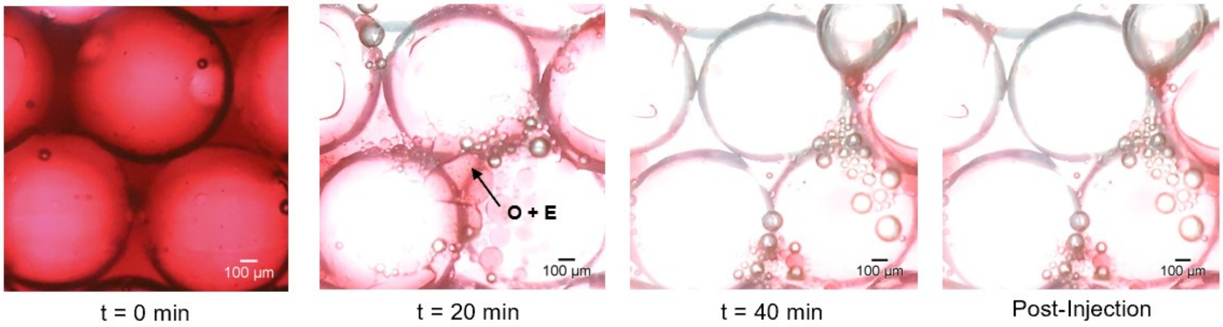


Figure 107—Hot-water injection and anionic surfactant in micromodel saturated with 450 cP heavy-oil; (O = oil and E = emulsion).

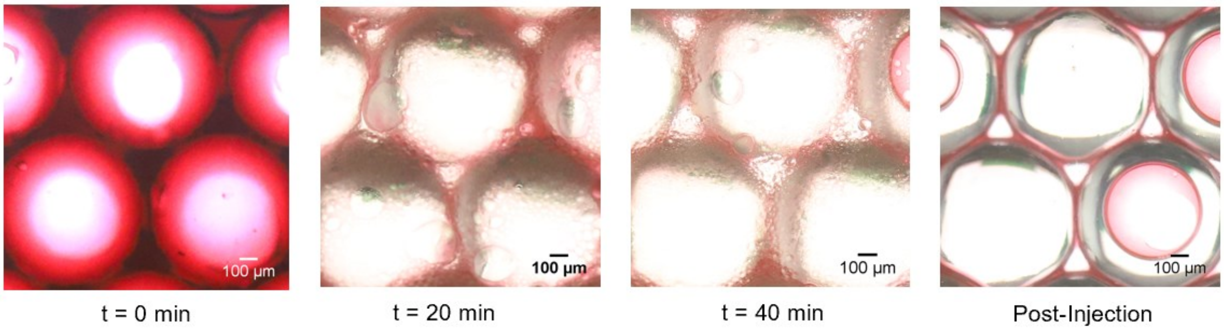
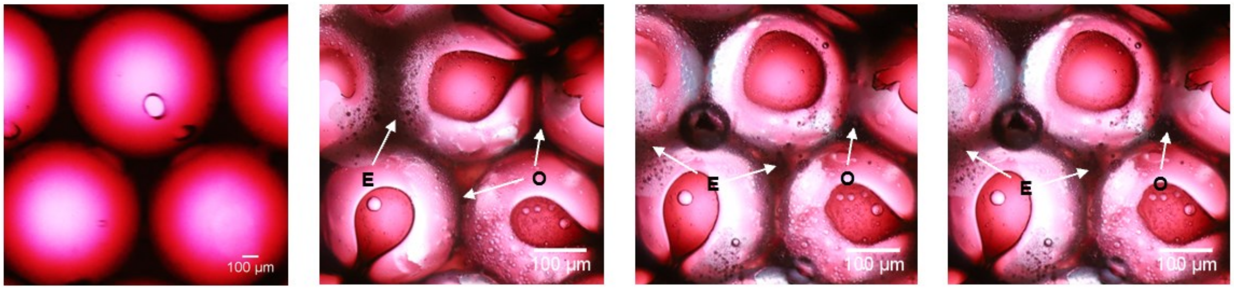
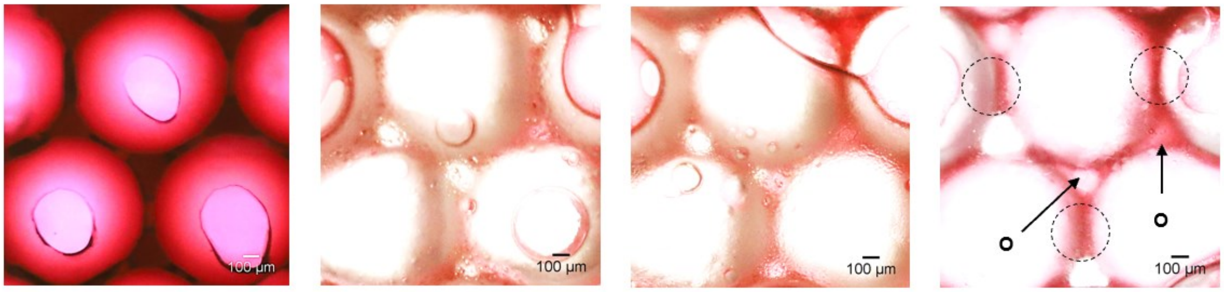


Figure 108—Steam injection and anionic surfactant in micromodel saturated with 450 cP heavy-oil.



t = 0 min t = 20 min t = 40 min Post-Injection

Figure 109—Hot water injection and anionic surfactant in micromodel saturated with 111,600 cP heavy-oil; (O = oil and E = emulsion).



t = 0 min t = 20 min t = 40 min Post-Injection

Figure 110—Steam injection and anionic surfactant in micromodel saturated with 111,600 cP heavy-oil; (O = oil, W = water, and S = steam).

Nonionic Surfactant. A sorbitan monooleat type of nonionic surfactant was also tested as a chemical additive. **Figures 111** and **112** present the phase distribution in a micromodel saturated with 450 cP heavy-oil. When hot water and nonionic surfactant were injected to the glass bead micromodel, residual or trapped oil was still perceived in the pores even after the injection was continued to t = 40 minutes (**Figure 111**). At this state, trapped oil shape showed the pendular-ring characteristic which evidenced that the glass bead surface was in a less water-wet state at a higher temperature. This evidence proved that an addition of a nonionic surfactant to the system could improve some oil production but still left some residual oil in the pores. The performance of this nonionic surfactant seems to be less effective than previously tested anionic surfactant in liquid phase. In addition, no chemically-induced emulsion was observed after adding this nonionic surfactant. On the other hand, steam injected along with nonionic surfactant seemed to deliver promising performance on the glass bead micromodel (**Figure 112**). At t = 20 minutes, phase change started to occur. It was noticeable that there was a mixture of water and steam in the micromodel. Furthermore, emulsion was perceived during the steam and nonionic surfactant injections. This was most-likely thermally and chemically-induced emulsion formations inside the pores. As the phase was changed from steam phase to liquid phase by stopping the injection, some residual oil was still observed—particularly in the pore throats.

Similarly, **Figures 113** and **114** exhibit the phase distribution/entrapment in the glass bead micromodel with 111,600 cP heavy-oil. It was observed that hot water mixed with nonionic surfactant injection did not give any improvement on phase distribution in the pores even after injecting until t = 40 minutes. Much residual oil still left in both pores and pore throats (**Figure 113**). Further improvement was not achieved after injecting the steam and nonionic surfactant to this glass bead micromodel. Phase change started to occur at t = 20 minutes. At this circumstance, water and steam were observed in the micromodel. Formation of emulsion was also perceived during the steam injection. However, extensive trapped oil was still evidenced after adding this nonionic surfactant at steam condition (**Figure 114**).

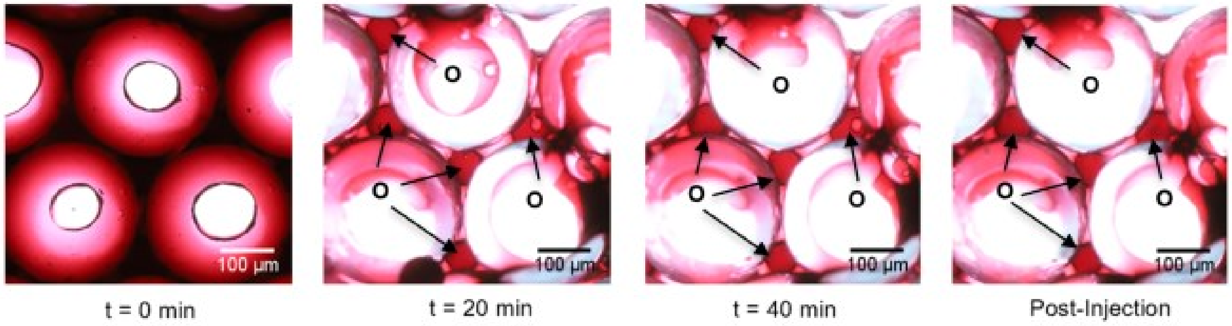
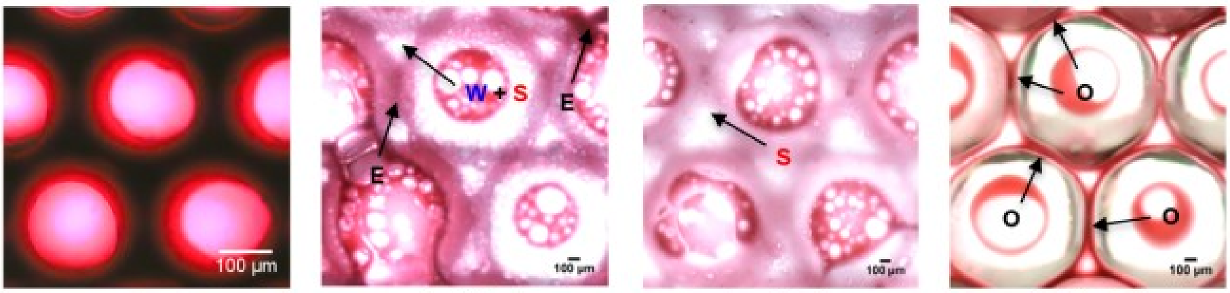
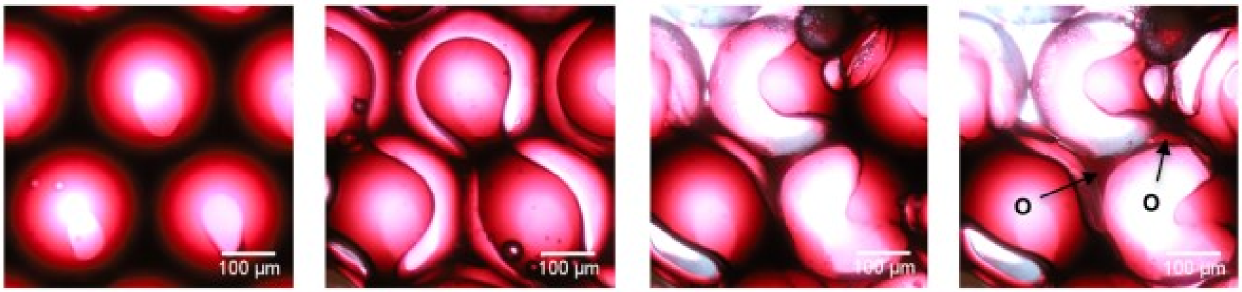


Figure 111—Hot water injection and nonionic surfactant in micromodel saturated with 450 cP heavy-oil; (O = oil).



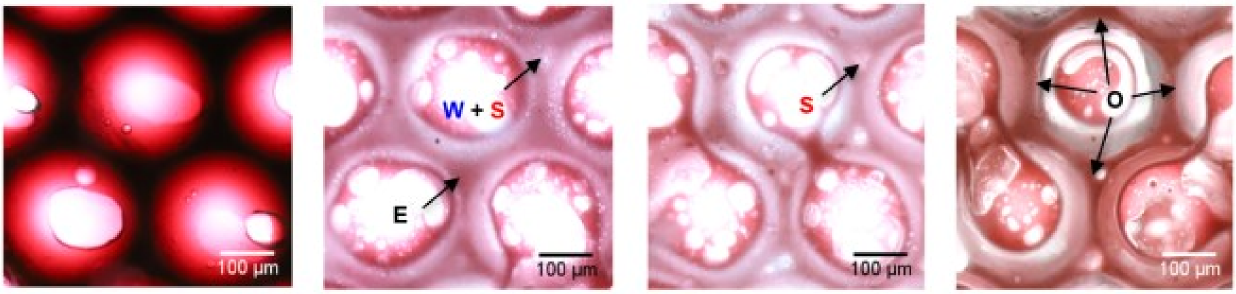
t = 0 min t = 20 min t = 40 min Post-Injection

Figure 112—Steam injection and nonionic surfactant in micromodel saturated with 450 cP heavy-oil; (O = oil, W = water, S = steam, and E = emulsion).



t = 0 min t = 20 min t = 40 min Post-Injection

Figure 113—Hot water injection and nonionic surfactant in micromodel saturated with 111,600 cP heavy-oil; (O = oil).

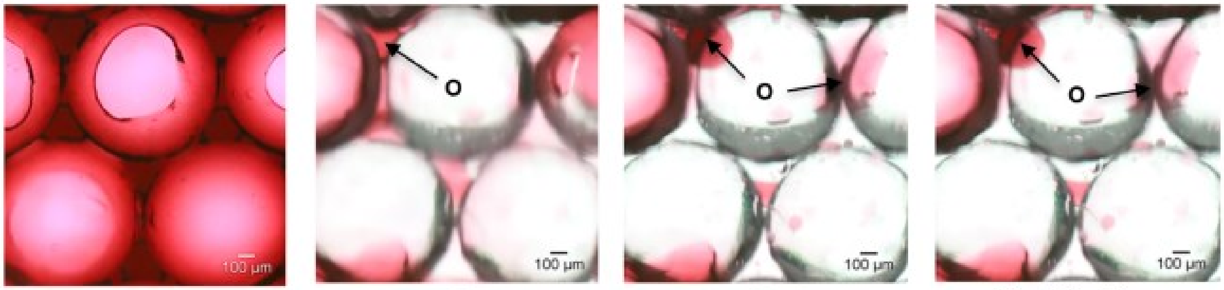


t = 0 min t = 20 min t = 40 min Post-Injection

Figure 114—Steam injection and nonionic surfactant in micromodel saturated with 111,600 cP heavy-oil; (O = oil, W = water, S = steam, and E = emulsion).

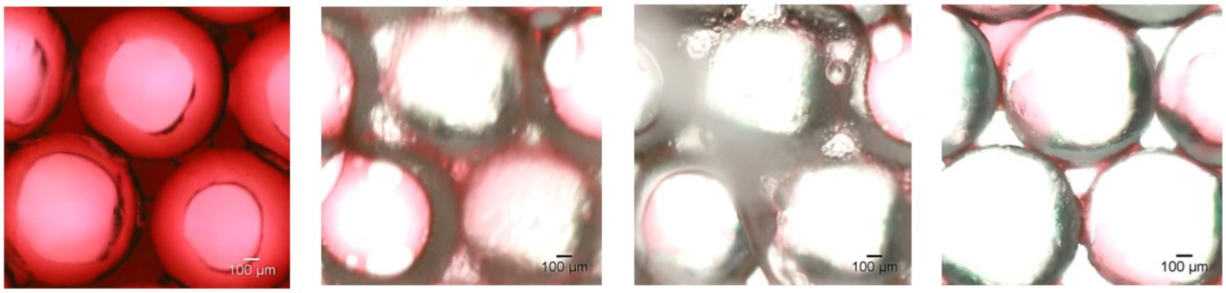
Nanofluid. Silicone oxide (SiO_2) dispersed nanoparticles was selected to be used with hot-water and steam injections. The particle distribution size of this type of dispersed nanoparticles was recorded to have a range of 5-35 nm. The phase distribution behavior of glass bead micromodel saturated with 450 cP heavy mineral oil is presented in **Figures 115** and **116**. In general, this chemical additive performed auspicious results on hot-water and steam injections. It was noticed that almost no trapped oil was evidenced. However, small amounts of oil films and residual oil were perceived, particularly at the pore throats.

Similar behaviors were also perceived in the glass bead micromodel saturated with 111,600 cP heavy mineral oil. **Figures 117** and **118** show the behavior of the phase distribution for hot-water and steam injections. Improvement of phase distribution was observed after adding SiO_2 dispersed nanoparticles. However, residual oil was still present at the pore throats of the glass bead micromodel.



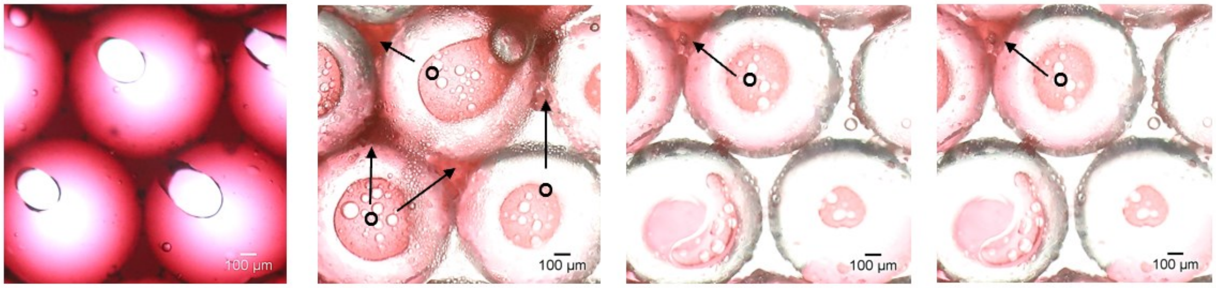
t = 0 min t = 20 min t = 40 min Post-Injection

Figure 115—Hot-water injection and SiO_2 dispersed nanoparticle in micromodel saturated with 450 cP heavy-oil.



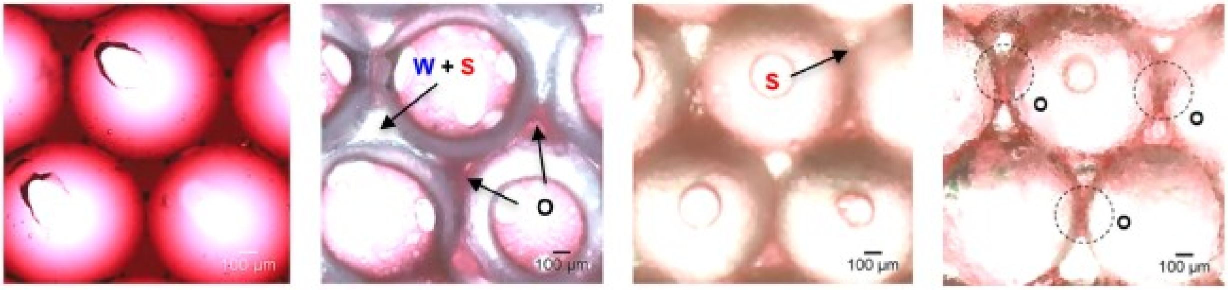
t = 0 min t = 20 min t = 40 min Post-Injection

Figure 116—Steam injection and SiO_2 dispersed nanoparticle in micromodel saturated with 450 cP heavy-oil.



t = 0 min t = 20 min t = 40 min Post-Injection

Figure 117—Hot-water injection and SiO_2 dispersed nanoparticle in micromodel saturated with 111,600 cP heavy-oil; (O = oil).

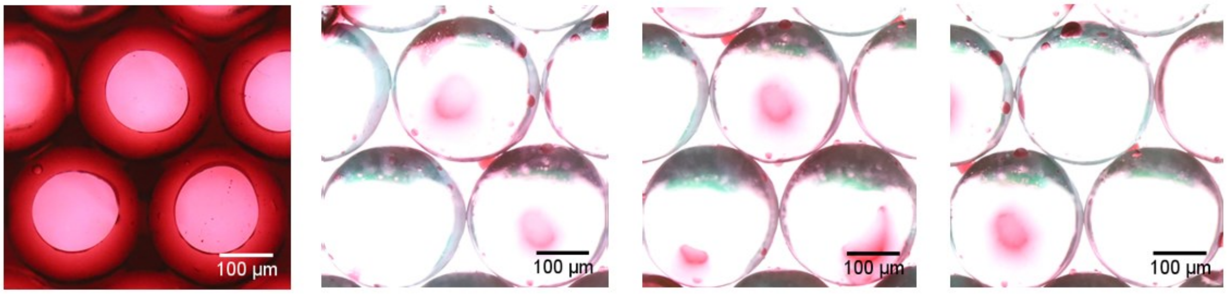


t = 0 min t = 20 min t = 40 min Post-Injection

Figure 118—Steam injection and SiO_2 dispersed nanoparticle in micromodel saturated with 111,600 cP heavy-oil; (O = oil, W = water, and S = steam).

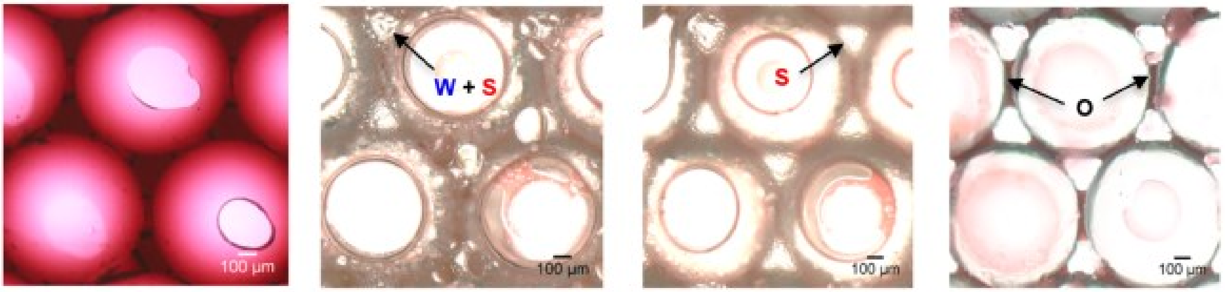
Ether. An ether type of solvent-based chemical additive was also involved in this micromodel research. Dimethly ether (DME) was used for each experimental case. Overall, DME delivered very favorable result for glass bead micromodel saturated with 450 cP heavy-oil (**Figure 119** and **120**). No residual oil was observed during hot water injection as depicted in **Figure 119**. Similar phenomenon was also perceived at steam condition. **Figure 120** presents very auspicious result of DME during steam injection. At t = 20, water and steam were present in the glass bead micromodel due to phase change. Water was completely transformed to steam as the injection was continued until t = 40 minutes or 3 PVI. Similar to the hot water injection, almost no trapped oil was evidenced after adding DME at steam condition. Only a small amount of residual oil was observed in the pore throats after steam injection.

On the other hand, hot water and steam injections combined with DME were not favorable in improving the phase distribution in the glass bead micromodel filled with 111,600 cP heavy-oil. **Figure 121** shows the hot water injection combined with DME in the micromodel. It was noticed that this DME did not give a good result during hot water injection. Most of the pores were still filled with residual oil. Similar behavior was also observed during steam injection combined with DME. As phase change occurred in the micromodel during the injection, some of emulsions seemed to appear in the pores. This phenomenon is also verified with the performance of DME through interfacial/surface tension measurement. DME could give a very favorable interfacial/surface tension reduction on oil/steam system. Nevertheless, further phase distribution improvement was not observed after DME application in the glass bead micromodel saturated with 111,600 cP heavy-oil (**Figure 122**). This evidence shows that DME might work better with oil having lower viscosity rather than oil with much higher viscosity.



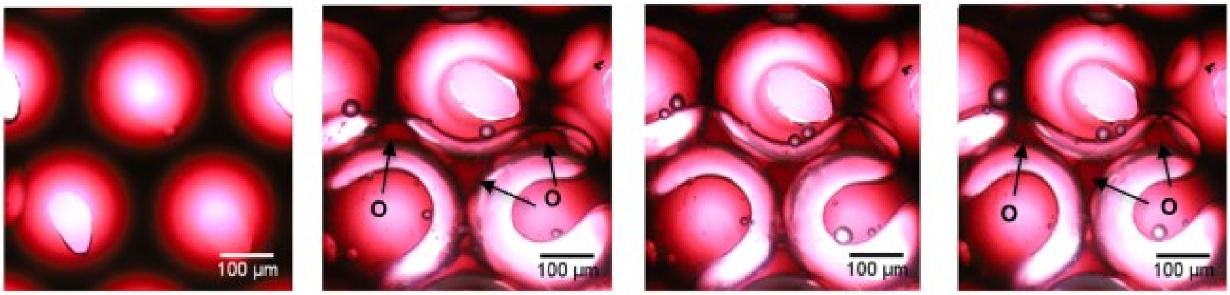
t = 0 min t = 20 min t = 40 min Post-Injection

Figure 119—Hot-water injection and dimethyl ether in micromodel saturated with 450 cP heavy-oil.



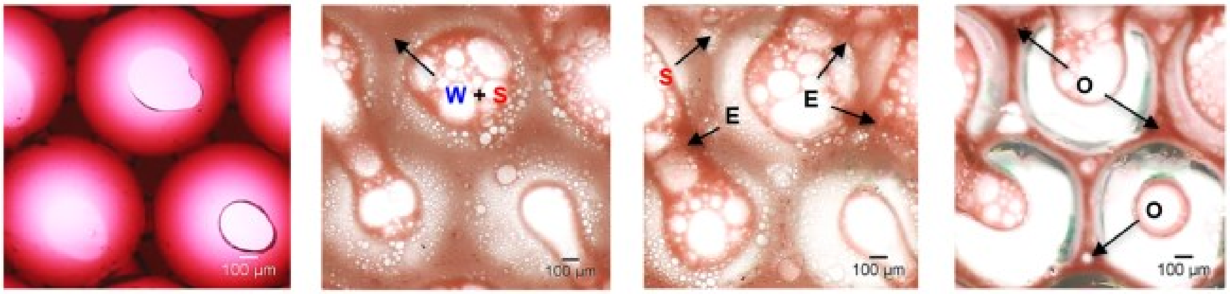
t = 0 min t = 20 min t = 40 min Post-Injection

Figure 120—Steam injection and dimethyl ether in micromodel saturated with 450 cP heavy-oil; (O = oil, W = water, and S = steam).



t = 0 min t = 20 min t = 40 min Post-Injection

Figure 121—Hot-water injection and dimethyl ether in micromodel saturated with 111,600 cP heavy-oil; (O = oil).



t = 0 min t = 20 min t = 40 min Post-Injection

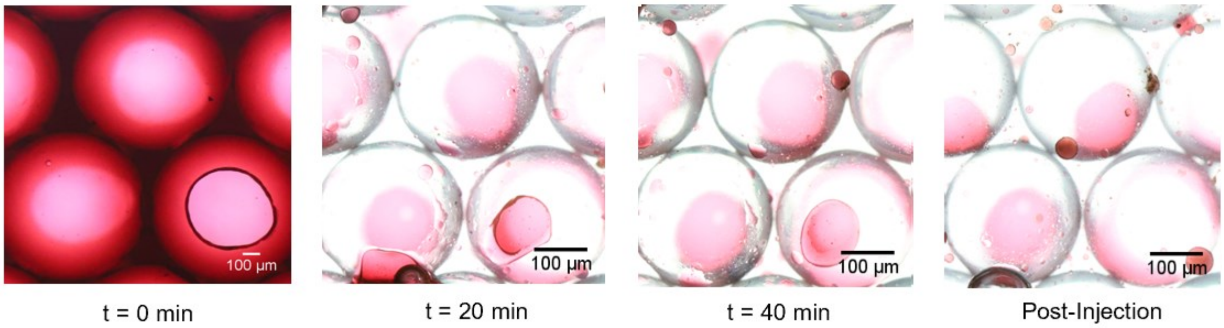
Figure 122—Steam injection and dimethyl ether in micromodel saturated with 111,600 cP heavy-oil; (O = oil, W = water, and S = steam).

Switchable-Hydrophilicity Tertiary Amines (SHTA). This chemical additive was synthesized by reacting N, N-dimethylcyclohexylamine type of amines with carbon dioxide (CO_2) by satisfying the reversible chemical reaction as follows:

$$NR_3 + H_2O + CO_2 \rightleftharpoons NR_3H^+ + HCO_3^- \qquad (4)$$

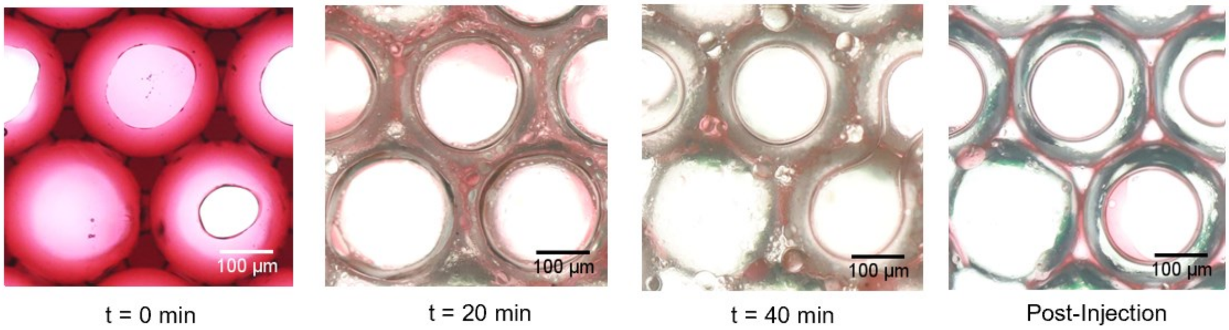
Naturally, this N, N-dimethylcyclohexylamine was a hydrophobic substance. After reacting these types of amines with CO_2, the solution became homogeneous indicating that hydrophilic state was achieved, making the amines mix with water.

Favorable improvement in residual oil saturation was delivered by this SHTA application at both hot water and steam conditions. **Figures 123** and **124** depict the phase distribution of glass bead micromodel filled with 450 cP heavy-oil. According to the result, no trapped oil was perceived in the pores of micromodel after hot water and steam injections combined with this SHTA. Nonetheless, favorable result of SHTA application was not achieved in hot water injection (**Figure 125).** Although an addition of SHTA could still move some of the heavy-oil, some residual oil remained immobile in the pores. Corresponding to the micromodel saturated with 450 cP heavy-oil, a very auspicious performance was delivered by SHTA chemical additive at steam condition in the glass bead micromodel saturated with 111,600 cP heavy-oil (**Figure 126**). There was no residual oil observed in the pores of glass bead micromodel after steam injection.



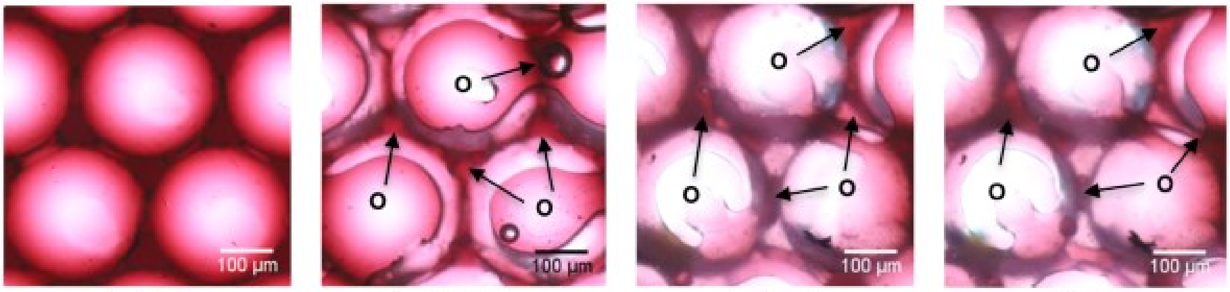
t = 0 min t = 20 min t = 40 min Post-Injection

Figure 123—Hot-water injection and SHTA in micromodel saturated with 450 cP heavy-oil.



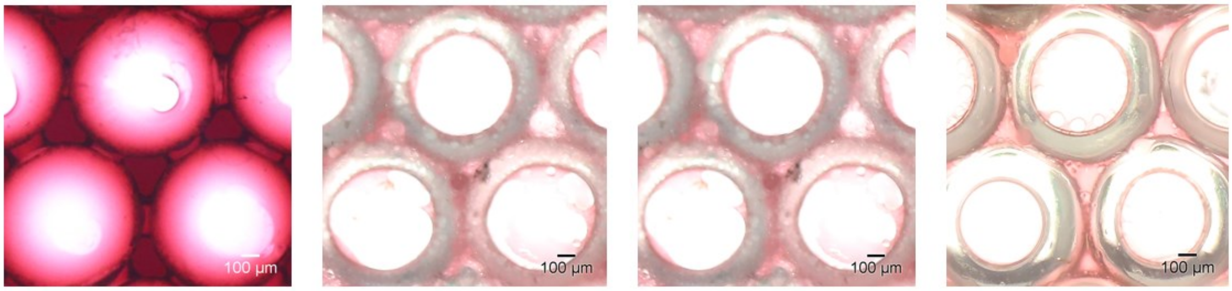
t = 0 min t = 20 min t = 40 min Post-Injection

Figure 124—Steam injection and SHTA in micromodel saturated with 450 cP heavy-oil.



t = 0 min t = 20 min t = 40 min Post-Injection

Figure 125—Hot-water injection and SHTA in micromodel saturated with 111,600 cP heavy-oil; (O = oil).



t = 0 min t = 20 min t = 40 min Post-Injection

Figure 126—Steam injection and SHTA in micromodel saturated with 111,600 cP heavy-oil.

4.5 Conclusions

1. This research is able to verify the irreversible steam-induced wettability alteration in porous media visually as a furtherance of our previous study regarding the effect of phase change on the wettability state. Transforming the fluid phase in the porous media—in the case of the glass bead micromodel—from originally liquid phase to steam phase could alter the original water-wetness of the glass bead surface to a completely oil-wet state. This phenomenon could be identified from the residual oil shape and oil film traces in the pores.
2. Phase distribution in the porous media behaves differently in each type of injection fluid phase. In hot-water injection, trapped oil was not a continuous phase having direct contact with the glass bead surface. This phenomenon indicates that the glass bead surface was still at a water-wet state. On the other hand, at steam condition, the trapped oil turned out to be the continuous phase having an interaction with the glass bead

surface—indicating the wettability of the solid surface has been altered to a completely oil-wet state.

3. Pendular-ring distribution was most-likely present at elevated temperature. No funicular distribution was observed in this research. This evidence is in line with our previous research concluding that the degree of water-wetness tended to be declining at high temperature—particularly steam condition.
4. Oil blob and snap-off most-likely occurred in the case of porous media having lower oil viscosity, according to this research.
5. Higher oil viscosity had a tendency to present more residual oil saturation, particularly at the pore throats.
6. In general, hot-water injection was not favorable for extremely high viscosity oil most likely due to the mobility contrast.
7. Regardless the medium thermal stability of anionic surfactant, this chemical could still deliver very favorable phase distribution improvement in the pores—particularly in steam applications. Anionic surfactant was not only very promising in improving wettability, but also reducing interfacial/surface tension represented by the emulsion formation in the pores.
8. Nonionic surfactant did not present promising performance in reducing trapped oil, even though this chemical additive has shown great thermal stability at extremely high temperatures. Residual oil was still perceived in both heavy-oil types even after involving this nonionic surfactant. Therefore, this chemical additive is not recommended for thermal applications in sandstone reservoirs.
9. Silicone oxide (SiO_2) nanofluid might be a good alternative in improving phase distribution in porous media. According to this research, a favorable improvement was observed after involving this chemical in both hot water and steam injections. Almost no residual oil was perceived after the injection. However, the oil viscosity parameter should also be considered since some trapped oil was still observed in the micromodel saturated with extremely high viscosity heavy-oil.
10. Dimethyl ether (DME) presented a favorable result in reducing trapped oil in the pores for hot water and steam applications. Nevertheless, this chemical additive did not deliver an auspicious result on the micromodel having the tremendously high viscosity of heavy-

oil. Therefore, DME is recommended to be applied in reservoirs having lower oil viscosity.

11. Switchable-hydrophilicity tertiary amines (SHTA) presented very favorable improvement on phase distribution. However, some residual oil was still observed during hot water injection in the micromodel saturated with oil having very high viscosity—according to this research.
12. The use of chemical additive could be very helpful in restoring the wettability state. However, this is still limited to the oil viscosity. According to this research, most chemical additives presented more favorable results on lower oil viscosity.
13. The glass bead micromodel could be a favorable instrument to represent wettability alteration and phase distribution in porous media. However, the curvature effect from the glass bead was inevitable and sometimes a small amount of the fluid could still pass through the contact area between the glass bead surface and the plexiglass.

Chapter 5: Conclusions, Contributions, and Future Work

5.1 General Conclusions and Contributions

Enhanced oil recovery (EOR) in maximizing oil production could be a challenging process—particularly in heavy-oil thermal recovery. It becomes even more complex when it arises to the petrophysics behavior. Hot-water or steam injection presents different wettability characteristics which ultimately influences the oil recovery. When the liquid phase is transformed into the steam phase during steam injection, this process could lead to unfavorable wettability alteration. Introducing chemical additives is believed to be an alternative in restoring the wettability state. Nevertheless, this phenomenon is still not clear yet. Study and research in this particular area are still limited. Therefore, this research focuses on investigating this phenomenon by conducting quantitative analyses on wettability degree and interfacial properties, and qualitative pore-scale visualization through micromodel with heavy-oil at steam condition.

Conventional and novel types of chemical additives were investigated during this experimental study including high pH solution, ionic liquid, surfactants, dispersed nanoparticles, alcohol, ethers, chelating agents, biodiesel oil-in-water emulsion, and switchable-hydrophilicity tertiary amines (SHTA). Thermal stability characteristic for each chemical additive was performed through thermogravimetric analysis (TGA). Quantitative analyses of wettability degree and interfacial properties were implemented and compared by using contact angle and surface tension measurements for each case. Since contact angle measurements are still limited in justifying the significance of the wettability alteration effect on phase distribution and oil recovery, visualization through a micromodel is essential. This investigation will contribute to the comprehensive understanding and scientific reasons behind the wettability alteration impact on the residual oil saturation—particularly at steam applications—in aiming the potential incremental oil recovery. According to this research, some conclusions can be generated as follows:

1. Wettability state does not have any correlation with pressure as long as the phase has not been transformed. Therefore, in certain cases, the pressure parameter can be neglected.
2. Phase change holds a critical role impacting the wettability characteristics in steam applications. The wettability state of the rock surface turned to be completely oil-wet and behaved irreversibly when the external phase was changed from liquid phase to steam

phase. This phenomenon has been verified through the quantitative contact angle measurement and qualitative pore-scale visualization. Involvement of chemical additives is recommended to restore the wettability state.

3. Polar components interaction on the rock surface could reduce the water-wetness of the rock surface. Therefore, in natural condition, the reservoirs are most-likely in an intermediate-wet or even oil-wet state. In field applications, this behavior should be taken into consideration in analyzing field performance.
4. Brine chemistry is also an impacting factor in wettability alteration. The presence of these cations—specifically divalent cations—could lead to a rock surface charge modification clarified by the intermolecular interaction through streaming potential measurement. According to this finding, low-salinity steam injection is recommended in steam applications. The water sources used for generating the steam should be treated first. Furthermore, in chemical enhanced oil recovery, chemical additives should be resistant enough to this brine chemistry.
5. Linear-alkyl toluene sulfonate (LTS) type of anionic surfactant presented very favorable wettability alteration and is recommended for steam application. This finding was also confirmed by the micromodel visualization. Wettability could be restored and residual oil saturation could be reduced. Some emulsion was also observed through the micromodel visualization. Following the medium-thermal stability of this surfactant through the TGA measurement, it is assumed that the mass decomposition of the chemical was because of dehydration. Therefore, in field application, it is recommended to apply this surfactant as a tertiary recovery after the field reaches its mature stage—reduction of steam injection—to reduce further thermal exposure.
6. Nonionic surfactant showed promising wettability alteration in calcite plates during steam injection. Hence, application of this type of surfactant in carbonate reservoirs is recommended in improving heavy-oil recovery. However, since this type of surfactant (Span 80) has low hydrophilic-lipophilic balance (HLB) number leading to be a more water-in-oil emulsion theoretically, further study on this emulsification is necessary.
7. The application of dispersed nanoparticles for chemical enhanced oil recovery at steam condition presented an auspicious result in improving the wettability state and residual oil saturation. However, the economic limit of applying this technology should be taken into

consideration in oil field operation since the commercial price of this chemical additive is very high. In addition, further study of nanoparticle bridging—potentially leading to the pore clogging—is also needed to avert further formation damage.

8. DME type of solvent-based chemical additives is also a promising and suitable alternative to the conventional chemical application for chemical enhanced oil recovery applications in sandstone and carbonate reservoirs. Additionally, the commercial price of this chemical additive is also considered inexpensive.
9. SHTA and biodiesel oil-in-water emulsion could also be an alternative to the conventional chemical additives. These novel chemicals presented very promising results on sandstones and carbonates. The commercial price of these chemicals is also very economical. Furthermore, due to the reversible chemical reaction of SHTA, this chemical could potentially be reused for repeat chemical enhanced oil recovery applications.
10. In general, the degree of rock surface water-wetness tends to decrease as the temperature is elevated. In oil field reservoir management—particularly with thermal recovery—this phenomenon should be taken into account specifically when it arises to the petrophysical evaluation.
11. Optimum chemical concentration is a crucial parameter in achieving the maximum wettability alteration degree. Lower chemical additive concentration is sufficient to restore the wettability at steam condition. For field application, it is recommended to conduct the preliminary chemical concentration test as it most-likely behaves differently in every oil field.

5.2 Future Works

Every single research has limitations as its own natural behaviors. These limitations appear to be the integration of resources and time. However, these limitations can be managed and overcome by performing even further investigations and analyses. According to the general conclusions, suppositions, and several uncertainties, potential future works are generated with the intent to attain a more comprehensive study as follows:

Solid Surface Charge. Wettability is not just about the contact angle magnitude presenting the water-wetness or oil-wetness. There is a correlation between the total solid surface charge and wettability due to the intermolecular interaction as also verified in this research for brine chemistry impact to wettability. Further study regarding the solid surface charge modification brought by chemical additives is essential—particularly at elevated temperatures—since each chemical additive presented its pH value. Fundamentally, pH value could lead to a solid surface charge modification as verified by numerous earlier publications related to these intermolecular forces. This potential solid surface charge research will be beneficial to further comprehend the chemical additive interaction with the reservoir rock surface.

Emulsification. This research only covers the wettability alteration degree, interfacial properties improvement, and qualitative pore-scale visualization. The effect of chemical additives to the mentioned parameters were also verified through this experimental study, including the surface/interfacial tension reduction. Since particular emulsion type could lead to a disadvantage of oil production, further investigation of this emulsification mechanism is necessary. This study is needed to identify the emulsification type—water-in-oil or oil-in-water emulsions—at steam condition by performing quantitative analysis of the produced emulsions under the microscope.

Improvement in Pore-Scale Visualization. Pore-scale visualization is important in investigating wettability state, phase change, and phase distribution/oil entrapment in porous media. The curvature effect from the glass bead micromodel remains challenging and inevitable. This limitation could cause a small amount of fluid to pass through the contact area between the glass bead surface and plexiglass. Modification of this contact area is necessary in minimizing the curvature effect. Glass-etched micromodel study is also a preferable alternative in visualizing the porous media. In addition, more chemical additives need to be tested using this micromodel in generating more robust conclusions.

Reformulation of Solvent-Based Chemical. Since SHTA has presented very favorable results in wettability alteration, surface tension reduction, and thermal stability at steam condition, reformulation of this chemical is also a potential in improving performance at steam condition. This chemical was initially synthesized using one type of amine—N, N-dimethylcyclohexylamine—with the measured pH value of 9-10. Recently, a preliminary study of hybrid SHTA was performed in our research laboratory. This hybrid SHTA was synthesized by combining both N, N-dimethylcyclohexylamine and triethylamine with certain ratio. Fundamentally, N, N-dimethylcyclohexylamine has a closed hexagonal structure which is more thermally stable. On the other hand, triethylamine has a more open chemical structure which is less thermally stable, but has a way higher pK_a number. Combining these two amines was foreseen to establish a more closed hexagonal chemical structure, theoretically, which will be even more thermally stable and able to produce a more basic solution—leading to a solid surface charge modification. Our recent preliminary study found that this hybrid SHTA solution was recorded to have a pH value of 11-12. Furthermore, favorable reduction in surface/interfacial tension was also perceived. However, further study for this hybrid SHTA—including maximum SHTA re-utilization number—is necessary to develop suitable, reusable, and economical chemical additive for steam applications.

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