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Foaming properties, wettability alteration and interfacial tension reduction by saponin extracted from soapnut (Sapindus Mukorossi) at room and reservoir conditions

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A R T I C L E   I N F O

Keywords:
Saponin
Foaming properties
Wettability alteration
Interfacial tension (IFT)
High temperature
High pressure

A B S T R A C T

In this study, a natural surfactant, saponin was isolated from soapnut (Sapindus Mukorossi). The extracted surfactant was characterized by Fourier-transform infrared spectroscopy (FTIR) analysis. The effectiveness of the isolated surfactant as EOR agent was evaluated from foam generation/stabilization properties, wettability alteration of the rock surfaces, as well as oil-water interfacial tension (IFT) reduction characteristics. The performance of the extracted saponin was compared with that of a commercial saponin and sodium dodecyl sulfate (SDS). The foaming properties of the saponin with carbon dioxide (CO₂) was characterized using Teclis Foamscan instrument at room condition and 60 °C. The IFT and contact angles at room conditions and reservoir conditions were measured using KRÜSS Drop Shape Analyzer (DSA 25 and DSA 100) via pendant drop and sessile drop techniques respectively. The foamaability of the saponin-stabilized foam was good at ambient condition and 60 °C. Moreover, the time taken for almost 100% liquid drainage was higher in saponin-stabilized foam than the SDS-stabilized foam. The optimum concentration for attaining maximum foam stability decreased from 0.4 wt% at room temperature to 0.1 wt% at 60 °C. Signifying that the quantity of the surfactant to be used in foam generation could reduce at high temperature. The isolated saponin exhibited relatively good interfacial activities individually and in synergistic interaction with silicon dioxide (SiO₂) nanoparticles at reservoir conditions. Precisely, at 8 MPa and 80 °C, the crude-oil water IFT was reduced from 23.24 mN/m to 1.59 mN/m (about 93.2%) by 0.2 wt% saponin concentration. The IFT was further reduced to 0.87 mN/m (about 96.3%) by a mixed system of 0.5 wt% saponin and 0.05 wt% SiO₂ nanoparticles concentration. Increasing IFT with increasing temperature were observed at very high temperature due to phase separation resulting from clouding phenomenon. However, the clouding temperature increased with 0.1 wt% saponin concentration, and in presence of SiO₂ nanoparticles (0.05 wt% and 0.1 wt%). The study suggests that the extracted saponin could be considered as supplementary alternative to conventional EOR surfactants.

1. Introduction

The crude oil price is plummeting in such an alarming rate that the world has never experienced for several decades due to the impact of corona virus (COVID-19) epidemic on global economy. One of the strategies being adopted for survival by the oil and gas industries is to extract surfactants from natural sources that will be environmentally friendly, stable at downhole conditions and are cost efficient at the present economic conditions. These surfactants could serve as alternatives to expensive conventional chemical surfactants that are presently being used for enhanced hydrocarbon recovery (EOR). Among the chemical EOR techniques, surfactants flooding is very popular due to...
their versatile applications in different kinds of reservoirs and conditions (Samanta et al., 2013). Surfactants can be applied in conventional and unconventional reservoirs, such as carbonate, sandstone and unconventional shale reservoirs, as well as heavy oil and light oil reservoirs.

Surfactants can be classified as nonionic, anionic, amphoteric, and cationic surfactants depending on their hydrophilic group and chemical structure (Mosayebi et al., 2016). A good number of synthetic nonionic, anionic and cationic surfactants have been experimentally investigated for oil-water interfacial tension reduction properties, as reservoir rock wettability modification agents, and as foam generation and stabilizers (Hussien et al., 2019; Kuang et al., 2018; Lokanathan et al., 2020; Ma et al., 2020; Mirchi et al., 2015; Sagir et al.; Yekeen et al., 2019a; Zhang et al., 2020; Zhang et al., 2019). Results showed that surfactants are ideal hydrocarbon recovery agents from the conventional and unconventional reservoirs, due to their excellent surface-active and foaming properties (Kumar and Mandal, 2019; Mosayebi et al., 2016).

Mechanically, in presence of the surface-active agents, the trapped hydrocarbon in the pore spaces of the reservoir rock due to capillary forces, can be release via decreasing interfacial tension (IFT), and alteration of the wettability of the rock from oil-wet or weakly-water wet state into strongly water-wet conditions (Samanta et al., 2013; Zhang et al., 2006). Besides surfactant flooding, surfactants have been applied as the conventional foam generation and stabilization agents for several decades (Syed et al.; Yekeen et al., 2017a; Yekeen et al., 2018). Significant reduction in oil-water interfacial tension and the enhancement in surfactant-foam stability and propagation in porous formation have been attributed to the concentration of the surfactant molecules at the liquid-liquid and gas-liquid interface (Roy et al., 1997; Yekeen et al., 2017b). The mobility of the injected gas can be enhance through surfactant-stabilized foamed injection. Surfactant-stabilized foams have also been applied as fluid diversion agents in heterogeneous porous formation, to redirect the injected fluid flow from the already swept high permeability layers to the low permeability layer containing the trapped hydrocarbon (Singh and Mohanty, 2017).

The performance of engineered surfactants as feasible EOR agents have been widely investigated and proven in most of the previous studies. However, the synthetic surfactants are chemically-based, and could be environmentally unfriendly and quite expensive because of the high cost of the raw materials (Nowrouzi et al., 2020; Samanta et al., 2013). The phase separation due to cloudy phenomenon at high temperature, as well as loss of surfactants molecules due to adsorption on porous matrix also increases the cost of surfactant applications in EOR. Consequently, recent research efforts are being focused on the designed and synthesized of eco-friendly, sustainable and affordable bio-surfactants that could achieve considerable reduction in oil-water IFT, alteration of wettability of porous system from oil-wet to water-wet systems, and with high stability at reservoir conditions. The advantages of the bio-surfactants over the chemical surfactants have been identified as cost minimization and sustainability, since the former can be synthesized from renewable raw materials. They are also less toxic, easily degradable and resistance to hard water compared to the synthetic surfactants (Samanta et al., 2013).

Some attempts have been made in previous studies to characterize natural surfactants for enhanced oil recovery applications (Samanta et al., 2011, 2013; Saxena et al., 2018). Isolation of bio-surfactants, particularly saponin, from soapnut have been reported in literature. Soapnut is a fruit of the soapnut tree, it belong to the plant family of “Sapindaceae”. They are largely located in sub-tropical and tropical climatic zones of the world and are popularly known with different names in such regions, like “ritchia” “reetha”, “soapnut”, “washnut”, and “soapberry” (Mondal et al., 2017; Samanta et al., 2013). “Sapindus trifoliatus” and “Sapindus Mukorossi” are the two major varieties of the soapnut that are generally obtainable in Asia, particularly in India, Pakistan, Nepal, and Indonesia (Samanta et al., 2013).

The saponaceous constituents of “Sapindaceae” known as “saponin” has been generally studied for enhanced hydrocarbon recovery purposes (Bajad and Pardeshi, 2016; Roy et al., 1997). Saponins were identified as nonionic surfactants comprising of hydrophobic tail and hydrophilic head (Nowrouzi et al., 2020). The structure of saponin is presented in Fig. 1. Despite the existing studies on the potential application of saponins for EOR processes, the oil-field application of these surfactants for enhanced hydrocarbon recovery (EOR) is yet to be fully realized due to several issues. In most of the previous studies, the potential of saponin extracted from Sapindus Mukorossi for reducing oil-water interfacial tension, as well as its foaming properties have been investigated at ambient conditions. The foaming and interfacial properties of this surfactant at downhole conditions have not been extensively investigated.

The molecular structure of the synthesized saponin showed that it is a kind of nonionic surfactant. Nonionic surfactant solutions could become turbid and unstable at certain temperature. This temperature is known as the critical solution temperature or the cloud point. This clouding phenomenon usually results in phase separation and thermal instability during the enhanced oil recovery applications at high temperature (Chatterjee et al., 2002; Ribeiro et al., 2014). Meanwhile, the occurrence of clouding phenomenon in saponin solution is still unclear. Some researchers emphasized that saponins are expected to be hydrolyzed and degraded by high pressure and temperature conditions (Ribeiro et al., 2014). They further stated that a reduction in saponin extraction yield is expected at temperature beyond 70 °C because of the degradation phenomenon at high temperature (Güçlü-Üstündag and Mazza, 2007; Ribeiro et al., 2014). Others categorically stated that saponins do not cloud, and that they can even improve the thermal stability of cloudy nonionic surfactants (Chatterjee et al., 2002). Results of Chatterjee et al. (2002) studies showed that the low concentrations of saponins inhibited the clouding properties of TX-100 and polymer methylcellulose (MC) solutions.

Hence, further studies is necessary to understand the performance and effectiveness of saponin, as well as its influence on liquid-liquid and liquid-solid interfacial properties and foaming properties at high temperature and pressure. Moreover, the synergistic influence of saponin and silicon dioxide (SiO₂) nanoparticles on crude-oil water IFT are rarely reported in literature. In previous studies, the interfacial and foaming properties of saponin extracted from soapnut is usually compared with the same plant extracts sold in commercial quantity in the market. The performance of saponin extracted from soapnut is hardly compared with the popular synthetic surfactants, such as sodium dodecyl sulfate, while the oil-water IFT reduction effectiveness at extreme temperature (80°C-150°C) and pressure (8 MPa–22 MPa) is yet to be extensively studied.

Motivated by the limitations of previous studies, a bio-surfactant (saponin) was isolated from soapnut (Sapindus Mukorossi) in this study. The effectiveness of the isolated surfactants as EOR agent was characterized by foam generation/stabilization properties, modification of rock wettability, as well as oil-water interfacial tension reduction. The foam stability was investigated at high temperature while the IFT reduction capacity of the synthesized surfactant at high temperature (80°C-180°C) and elevated pressure (8 MPa–22 MPa), representative of enhanced hydrocarbon recovery applications (Samanta et al., 2011, 2013; Saxena et al., 2018).

![Fig. 1. Molecular structure of saponin, adapted from (Nowrouzi et al., 2020).](image-url)
reservoir conditions was then investigated for potential applications at harsh downhole conditions. Influence of the synergistic interaction between the saponin surfactant and silicon dioxide (SiO₂) nanoparticles, on oil-water IFT, at high temperature and pressure was also investigated. The performance of the synthesized saponin was compared with that of commercial saponin and an anionic surfactant, sodium dodecyl sulfate (SDS). The choice of SDS surfactant was based on their popular oilfield applications and the fact that this surfactant has demonstrated considerable ability to reduce IFT, alter rock wettability, as well as improve the foaming capacity and stability in previous studies.

2. Materials and methods

2.1. Materials

Soapnut pericarp fruits (Sapindus Mukorossi) were purchased from a local market in Ipoh, Perak, Malaysia. N-Hexane (99% pure) was purchased from Merck Sdn Bhd Malaysia. Ethanol (95% pure) for extraction was purchased from HmbG Reagent Chemicals (Kuala Lumpur, Malaysia). Commercial saponin was purchased from Sigma Aldrich (Sigma Aldrich (M) Sdn Bhd, Selangor, Malaysia). Sodium dodecyl sulfate (with molecular weight of 288.38 g/mol and purity of ≥99.0%) was purchased from Sigma-Aldrich. Normal heptane (C₇H₁₆) was the mineral oil used in the experiment. The model oil was purchased from a local Malaysian Supplier, Merck Sdn. Bhd. Shah Alam, Selangor, with purity of 99%.

A light crude oil from Malaysia was used for the high temperature and high pressure experiments. The viscosity and the density of the oil was measured as 5.84 cp and 0.811 g/cm³ respectively while the API gravity was determined as 41.37. The dispersant used for the experiments is deionized water. All chemicals used were of analytical grade and were used as received without further purification. Two types of rock substrates, Berea sandstone and shales were used for investigating the influence of the surfactants on the wetting properties of rocks. The black shales were obtained from the Timah Tasoh Formation, Sanai Hill. At the North East of Hutan Lipur Bukit Ayer in Kampung Guar Jentik, Beseri District, Perlis of Peninsular Malaysia, just south of Timah Tasoh Dam. The area is located at the coordinates of 6°33’18.00”N 100°12’24.00”E.

2.2. Methods

2.2.1. Extraction of saponin

A minor modifications of previous protocols employed by Sharma et al. (2012) and Roy et al. (1997) were adopted for the saponin isolation. Using an oven (Thermo/OGS-100), the soapnut pericarps were dried at a temperature of 60 °C for 24hr to remove the moisture. The pericarps were then grinded into a fine powder using conventional grinder (FRITSCH/Pulverisette 2). To ensure that the dried sample was defatted, 100 g of the dried saponin powder was then mixed with n-hexane for about 120 min s, using the Soxhlet apparatus. The defatted sample was extracted with ethanol. To do this, 40 g of the defatted saponin was mixed with 200 ml ethanol for 5min using electromagnetic stirrer. The mixture was then loaded into the ultrasound equipment for hours for the extraction process. After the ultrasound extraction, the mixed ethanol was removed from the extracted saponin filtrate, as the saponin filtrate is then dried at a temperature of 60 °C in an oven for 24 h.s. Further investigations were conducted using the extract obtained from the solvent after the evaporation. A stock solution was prepared from the dry paste by re-dissolving the paste in water. Different concentration of the surfactant solution used in this study were then prepared. For instance, The extraction of 1 g of the fruit pericarp powder in 100 ml of the distilled water was used to make 1 wt% natural surfactant solution (Roy et al., 1997).

2.2.2. Spectral analysis of the extracted saponin

A confirmatory test was conducted using Fourier Transform Infra-red Spectrometer (FTIR; Model: PerkinElmer, Spectrum One) to investigate if the synthesized substance is saponin or not. The functional groups and the absorption/molecular vibration peaks present in the extracted saponin was identified through the FTIR analysis and compared with that of the commercial Saponin. About 10 mg of the grounded sample was mixed with KBr salt and then compressed into a thin pellet with the aid of KBr press (Samal et al., 2017). The sample was placed with care on already cleaned ATR diamond crystal surface. The analysis was conducted and the infrared spectra were recorded within the wavelength interval (wavenumber) of 4000–500 cm⁻¹. Background scan was conducted for each sample and the FTIR spectra was recorded as KBr matrix and processed using spectrum PerkinElmer software. The results was compared with FTIR transmittance spectra of the commercial saponin.

2.2.3. Foam generation and stability experiments

The rate of bulk foam generation and foam stability by the saponin was studied using the Teclis Foamscan equipment (Teclis Scientific, France). The use of Teclis foamscan for investigating foam generation and stabilization properties have been reported in previous studies (Ahmed et al., 2017; Hanamertani et al., 2018; Jones et al., 2016; Simjoo et al., 2013). The bulk stability experiment was conducted at room temperature and at 60 °C. CO₂ gas was used for the foam generation. The foam was generated through sparging of the CO₂ gas via a porous plate (with pore size of 40 μm–100 μm) affixed at the base of the glass chamber foam column (with inner diameter ±32 mm). The glass tube foam column was filled with 60 ml of the surfactant solutions, and the foam generation was ensured by sparging of the CO₂ gas at a fixed flow rate of 100 ml/min through the solution. The foam generation commenced and stopped automatically when the foam reached a stipulated volume (100 ml). The foam generation and stability process is monitored by a connected software.

The rate of the decrease in foam volume with time after reaching the pre-set generation volume was monitored. The volume of the generated foam throughout the CO₂ gas sparging process was measured, and the decay profile of the foam with time just after the generation of the foam was recorded by the Charged-Coupled Device (CCD) camera connected to the foam column. The device determined the foam volume through the gray level of the foam in glass tube. The volume of the liquid in the foam with time was measured with the conductivity electrodes fitted into the foamscan. The high temperature experiment was conducted using the thermo-stated glass chamber at 60 °C. The foam bulk stability was estimated from the decay profile of the foam with time, as well as the liquid drainage trend obtained from the plot of liquid volume in the foam with time. Example of visual image of the foam decay profile with time observed in this study is presented in Fig. 2.

Decreasing foam height with time in the foam column.

2.2.4. Surface/interfacial tension and contact angle measurements

KRÜSS Drop Shape Analyzer, KRÜSS DSA25 (KRÜSS GmbH, Germany) was used to measure the surface/interfacial tensions as well as the wetting properties of rocks in presence of the different concentration of the saponin at ambient conditions. Similar protocols used in previous studies were adopted (Yekeen et al., 2020). The surface/interfacial tensions were measured through the Pendant drop techniques. For interfacial tension measurement, the pendant drop of the oil was formed and suspended from a metal syringe needle (with a diameter of 1.825 mm) in a surfactant solution environment.

For surface tension measurement, the pendant drop of the surfactant was created and suspended from the metal syringe needle in the air environment. To determine the critical micelle concentration (CMC) of the saponin surfactant, the surface tension values were measured at different surfactant concentrations. A plot of the surface tension versus the surfactant concentration was made and the surfactant CMC was taken as the surfactant concentration with no significant change in
surface tensions henceforth. Generally, sessile/captive drop analysis techniques are normally employed for measuring contact angles using the KRÜSS DSA25.

For contact angle measurement, the rock substrate was prepared by trimming the slides into an appropriate size (length = 2 cm X width = 2 cm X height = 0.3 cm) with the help of Vinci’s radial core slabling saw. The trimmed substrate was then gently polished with a silicon carbide abrasive paper to minimize the influence of contact angle hysteresis arising from the roughness of the rock piece (Yekeen et al., 2020). The rock piece was then cleaned with acetone and deionized water before being place on the stage for contact angle measurements. The wetting properties of rocks (contact angles) as a function of different saponin concentrations was measured through a sessile drop techniques. The sessile drop profiles (5 μl) of the different surfactant solutions was created and then drop on the rock substrate surface through a metal syringe needle (with diameter of 0.515 mm). The contact angle was taken as the angle formed between the droplet and the solid interface at the point of contact. The sessile drop profiles were measured using the Young–Laplace equation to determine theIFT (Zhang et al., 2018).

2.2.5. Oil-water interfacial tension measurements at high temperature and pressure

A Krüss drop shape analyzer (DSA 100) apparatus (KRÜSS GmbH, Germany), was used to measure the crude-oil water IFT, in absence and presence of SiO2 nanoparticles at downhole conditions. The oil-water interfacial tension was measured at elevated temperature (80 °C–180 °C) and pressures (8 MPa–22 MPa). The maximum operating pressure and temperature of the DSA 100 used in this research is 68.95 MPa and 200 °C respectively. A pendant drop method was employed for measuring the IFT at reservoir conditions. To measure the IFT, the experimental set-ups were checked for leakages by flushing the whole set-up with nitrogen. Then the temperature was pre-set at the desired temperature. Temperature equilibration was ensured by increasing the temperature step-wisely at every 10 °C before progressing with further temperature increase.

When the temperature reached the desired temperature. The pressure in the view chamber was increased to the desired level by pressurized through the saponin surfactant solutions. Immediately the pressure stabilization was achieved, the pendant drop of the oil droplet was introduced from the bottom of view chamber using a dispensing needle (0.77 mm). The oil droplets (~6 ± 1 μL) swiftly expanded, and then suspended at the tip of capillary tube surrounded by the surrounding fluid (different concentrations of the saponin) at the desired temperature and pressure. The density and the viscosity of the brine and oil at the varying temperature and pressure was used in the automatic computation of the interfacial tension (IFT) in (mN/m) by the software. At constant pressure (10 MPa), the IFT was measured at different temperature (80 °C, 100 °C, 120 °C, 140 °C, 150 °C, 160 °C or 180 °C). Similarly at constant temperature (80 °C), the IFT was computed at different pressure (8 MPa, 10 MPa, 12 MPa, 14 MPa, 16 MPa, 18 MPa, 20 MPa or 22 MPa). The IFT values were determined from an average of 10 data. The detailed diagram of the DSA 100 used in this study is provided in Fig. 3.

3. Result and discussions

3.1. FTIR analysis of saponin

To confirm if the extracted substance is actually a saponin or not, the infrared spectra of the extracted saponin were recorded between 4000 and 500 cm⁻¹ and compare with the infrared spectra of the pure commercial saponin and the identified infrared spectra of saponin reported in literature (Bajaj and Pardeshi, 2016; Nowrouzi et al., 2020; Samal et al., 2017; Wang et al., 2014). The similarity between the FTIR transmittance spectrum of the extracted saponin and the commercial (pure) saponin is presented in Table 1 and Fig. 4. The results showed that the transmittance spectra of the extracted saponin is similar to the spectra of the commercial saponin and that of the pure saponin reported in previous studies. For instance, the infrared spectra of the extracted saponin shows the hydroxyl group (-OH stretching) peaks at 3390.62 cm⁻¹, while that of the commercial saponin, was obtained at peak of 3400.45 cm⁻¹.

This observation is also consistency with literature, Samal et al. (2017) obtained the transmittance spectra of the –OH stretching of extracted saponin from the aqueous reetha solution and that of the pure saponin at 3455 cm⁻¹ while Bajaj and Pardeshi (2016) reported that the infrared spectra of the hydroxyl group of saponin extracted from “Sapindus emarginatus” peaked at 3434 cm⁻¹. In this study, the infrared spectra of the extracted and commercial saponin shows the carbon-hydrogen (–CH2 group) stretching peaks at 2939.60 cm⁻¹ and 2931.69 cm⁻¹ respectively (Table 1 and Fig. 4). Similarly, Bajaj and Pardeshi (2016) obtained the aliphatic –CH2 stretching at 2928 cm⁻¹ while the results of Samanta et al. (2013) shows that the infrared spectra of the saponin extracted from the soapnut shows the aliphatic –CH2 stretching peaks at 2931.41 cm⁻¹. Generally, the FTIR analysis of the extracted saponin in comparison with the pure commercial saponin and the infra-red spectra of saponin reported in various literature confirmed that the substance isolated from Sapindus Mukorossi is indeed a saponin.

3.2. Critical micelle concentration (CMC) of the extracted saponin

The surface tension of different concentrations (0.01–1 wt%) of the extracted and commercial saponin was measured using DSA 25 and plotted against the surfactant concentrations to determine the critical micelle concentration (CMC). The plot of the surface tension versus the saponin concentration is shown in Fig. 5. The plotted graphs showed that the surface tension decreases with the increasing surfactant concentration. After a certain concentration, the change in surface tension was almost insignificant with the increasing surfactant concentration. This inflection point was found to be 0.1 wt % saponin for the commercial saponin and 0.2 wt % for the extracted saponin. This concentration is called the critical micelle concentration (CMC) of the
Previous studies suggested that surfactant could demonstrate the most favorable interfacial activity, as well as the best foam generation and stabilizing capacity at surfactant concentration close to the CMC. This is due to the fact that surfactant molecules are expected to be optimally and systematically arranged at the oil-water interface as well as at the gas-liquid interface of the foam at CMC (Hanamertani et al., 2018; Mannhardt and Svorstol, 2001). Generally, the functionality of the isolated saponin for wettability alteration of rock surfaces, oil-water IFT reduction, as well as foams stabilization will depend on the quantity of adsorbed surfactant molecules at the saturated interface as well as amount of monomers in the micelle (Mitra and Dungan, 1997). Hence, it is essential to determine the CMC of the extracted saponin in order to determine the impact of extra surfactant molecules on the interfacial energies (Mitra and Dungan, 1997). Moreover, the knowledge of the micelle-forming characteristics of the isolated saponin is vital for predicting the optimum surfactant concentration for maximum foam stability as well as minimal reduction in oil-water interfacial tensions.

### 3.3. Foaming properties and stability

The foam generation/stabilization properties of the extracted saponin was characterized at room temperature and 60 °C using the foamscan. The performance of the saponin-stabilized foam was compared with the performance of the sodium dodecyl sulfate, SDS-stabilized foam. This is to ascertain if the synthesized saponin can be proposed as supplementary alternative to conventional foam-stabilization surfactants. The foam generation property was inferred from the variation of foam volume with time. The foam stability was estimated from the decay profile of foam volume versus time, as well as the foam half-life. The foam half-life is the time taken for the foam to decay into half of its original volume after the termination of the gas sparging. Since the foam volume was fixed as 100 ml in this study, the half-life was the time taken for the foam to decay into 50 ml. The variation of foam volume with time, as well as the foam decay profile versus time for the saponin-stabilized foam at room condition is presented in Fig. 6 while that of the SDS-stabilized foam is presented in Fig. 7.
For all concentrations investigated in this study, Fig. 6 showed that the saponin-stabilized foam volume increases linearly with time, as demonstrated by the straight-line from time zero to the maximum foam volume. This result is an indication that the buildup of the saponin-stabilized foam during gas sparging was very stable. It can be inferred that the saponin-stabilized foamability is likely not to be affected by the three mechanisms of foam destruction, that is liquid drainage, bubble coalescence and coarsening (Simjoo et al., 2013; Yekeen et al., 2018).

The foam stability analysis showed that the volume of foam stabilized by higher saponin concentration (0.3 wt%, 0.4 wt%, 0.5 wt% and 1.0 wt%) was quite stable and eventually attains a fixed value at particular time. The 0.3 wt% and 1.0 wt% saponin-stabilized foams attained fixed volume of 20 cm³ after 2000 s while the 0.5 wt% saponin-stabilized foam attained a fixed volume value of 20 cm³ after 1000 s. The most stable foam was obtained in presence of 0.4 wt% saponin solution. The foam volume decay profile was characterized by a slower destruction in foam volume for a longer time, maintaining a kind of plateau at some specific period, before achieving a constant value of 25 cm³ after 4000 s.

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This result showed that there is an optimum concentration for the maximum stability of saponin-stabilized CO₂ foam. This concentration was identified as 0.4 wt% in this study.

The stability of the saponin-stabilized foam was compared with that of the SDS-stabilized foam, using the surfactant concentration that produced the highest stability for the saponin-stabilized foam. The decay profile for the SDS-stabilized foam shown in Fig. 7, suggests that the foaming characteristics of the SDS-stabilized foam also demonstrated stable buildup almost like that of the saponin-stabilized foam. However, the half-life of the 0.1 wt% and 0.3 wt% SDS-stabilized foam was at 500 s while that of different concentration of the saponin-stabilized CO₂ foam ranges between 500 s and 1500 s. The total collapse of the 0.1 wt% and 0.3 wt% SDS-stabilized foams occurred before 2000 s. The optimum surfactant concentration for the maximum stability of SDS-foam was obtained at 0.2 wt%. However, unlike the 0.3 wt% and 1.0 wt% saponin-stabilized foam volume that levels off to a plateau at 20 cm, the SDS-stabilized foam volume did not levels off to a plateau at 0.2 wt% SDS. The curve pointed downward suggested that the total collapse of this foam could occur faster than the collapse of the similar concentration of the saponin-stabilized foam. These results generally suggest that the extracted saponin can generate more stable foam compared to the SDS-stabilized foam. Fig. 7 further confirmed that there is an optimum surfactant concentration for maximum foam stability.

The mechanisms of foam decay was elucidated from the plots of the liquid volume in the foam versus time presented in Fig. 8. Using 0.2 wt% concentration for the two surfactants, the decay profile for the saponin-stabilized and SDS-stabilized foams demonstrated uniform increase in foam volume with time during the gas sparging process. However, after the CO₂ gas sparging, the SDS-stabilized foam volume profile showed a sharp decrease in volume with time. No steadied value for liquid volume in the foam was observed in profile of SDS-foam throughout the measurement signifying that the rate of liquid drainage from the SDS-foam was very high compared to the saponin-stabilized foam. Almost 100% of the initial liquid was drained from the SDS-foam after 100 s while 100% liquid drainage from the saponin-stabilized foam structure took about 350 s. Beyond this period, it is likely that the foam decay process was governed by other decaying mechanisms such as bubble coalescence and coarsening (Simjoo et al., 2013; Tcholakova et al., 2011). Film thinning and rupture could arise from the pressure created in the liquid fraction of foam during liquid drainage. Consequently, the liquid in the film migrate to the Plateau border with low pressure (Ahmed et al., 2017).

Simjoo et al. (2013) emphasized that bubble coarsening plays a prominent role in foam decay process if the distribution of the bubble size in the foam structure is highly disperse. The morphology of the generated foam under the Leica EZH4 microscope presented in Fig. 9 provided further insight into the mechanisms of foam decaying process. When the bubble size distribution of the generated foam was quite uniform (Fig. 9a), the foam remained stable with thicker lamellae with time (1800 s) as shown in Fig. 9b. However, when the generated foam bubble size distribution was highly disperse and non-spherical as shown in Fig. 9c, the rate of bubble coalescence was faster with the time. The foam lamellae become thinner while smaller unstable and inhomogeneous bubbles quickly merged to become larger bubbles (Fig. 9d). Hence bubble coalescence and Ostwald ripening is a principal foam decay process when the bubble size distribution in the foam structure is highly disperse and irregular.

The foam generation/stabilization of surfactants depends on the surface activity of the surfactant molecules at the gas-liquid interface of the foam (Hanamertani et al., 2018). The high stability of the saponin foam compared to the SDS-stabilized foam can be attributed to the presence of hydrophilic sugar part and fat soluble (hydrophobic) saponogenin in their structure. Fig. 6 further showed that at concentration above CMC, the extracted saponin has lower surface tension than SDS, indicating that lower pressure could exist in the foam generated with saponin compared to SDS-stabilized foam. Hence, slower flow of liquid and slower rate of oswald ripening is anticipated in the saponin-stabilized foam. Moreover, Fig. 8 showed that it could take longer time from the liquid to drain from the structure of the saponin-stabilized film compared to SDS-stabilized lamellae. These results suggest that the surface viscosity and strength of the saponin-stabilized foam film is high due to the adsorption and aggreation of the molecules of the surface-active species at the foam lamellae. A dense monolayer is formed from the accumulated species at the lamellae, which delayed the diffusion of the gas through the foam film (Chen et al., 2020). Moreover, the strength of the foam lamellae was very significant in delaying bubble coalescence and oswald rippening.

3.4. Foaming properties and stability at high temperature (60 °C)

The stability of the extracted saponin foam was investigated at 60 °C to examine the performance of the saponin-stabilized foam at high temperature. The decay profile of the saponin foam versus time at high temperature is shown in Fig. 10. The plotted curves showed that the foaming procedures of the foam was quite consistent with the foam behaviours at room temperature, indicating that the saponin-stabilized foam can be successfully generated at high temperature with almost the same rate as ambient conditions. However, the foam volume decay profile showed that the foam stability was lower at high temperature. Lower foam stability at high temperature is due to lower solution viscosity. Although the foam stability was lower at high temperature, however, the optimum concentration for attaining maximum foam stability decreased from 0.4 wt% at room temperature to 0.1 wt% at 60 °C. This will possibly reduce the quantity of the surfactant to be used in foam generation at high temperature. As the temperature was increased, the surfactant molecules moved faster. The increasing molecular activity of the surfactant can aids in quick formation of the micelles, as well as the aggregation of the surface-active species at the gas-liquid interface of the foam. The thermal agitation can decrease the cohesive forces between the surfactant molecules but increases the adhesion action of the surfactant molecules at the interface at lower saponin concentration. However, this process will not be sustained for a long time due to decreasing solution viscosity at high temperature.

It can be inferred from the results, that the saponin-stabilized foam could be generated at high temperature, remaining fairly stable before total collapse. Surfactant concentrations around the critical micelle concentration is recommended for the optimum foam generation and stability.

The lower stability of generated foam at high temperature observed in this study is consistent with literature (Hanamertani et al., 2018; Kapetas et al., 2016; Yekeen et al., 2017b). This incident can be attributed to the lower viscosity of the foam film at high temperature due to thermal agitation and movement of the adsorbed surfactant molecules at gas-liquid interface of the foam at high temperature. Moreover, there is
possibility of lesser hydrogen bond formation at higher temperatures while the flow and diffusion of the gas through the foam film increases with the increasing temperature (Farajzadeh et al., 2009; Mohajeri and Noudeh, 2012). This eventually results in film thinning, film rupture and bubbles coalescence.

3.5. Rock wettability alteration by the extracted saponin

The potential applications of the isolated saponin for the wettability alterations of the conventional and the unconventional reservoir rocks, was inferred from the changes in the contact angles of two types of shales (shale 1 and shale 2) and aged Berea sandstone rock surfaces. Fig. 9. Foam structure under the microscope showing that when the bubble size distribution are disperse and irregular, bubble coalescence and Ostwald ripening are prominent mechanisms of foam decay (a) foam with uniform size distribution after generation (b) foam with size uniform distribution after 1800 s (c) foam with irregular size distribution after generation and (d) foam with irregular size distribution after 1800 s.

Fig. 10. Foam decay profile for various concentration of saponin-stabilized foam at high temperature (60 °C).

Fig. 11. Comparison of the wetting properties (contact angles on shale1) of different concentrations of the synthesized saponin with the sodium dodecyl sulfate.

Fig. 11 shows the curves of the contact angle versus concentration of the drops of the extracted saponin and sodium dodecyl sulfate on the shale 1 surface. The curves of the contact angle versus concentration of the drops of the extracted saponin and commercial saponin on the aged Berea sandstone surface is presented in Fig. 12. The sessile drop profiles of drop of deionized water in comparison with the drops of the different concentration of the extracted saponin on the shale 1 and shale 2 surfaces are displayed in Figs. 13 and 14 respectively. Considerable reduction in contact angles of the shale was generally noticed with the drops of varying concentration of the extracted saponin on the substrate surface.
For instance, the drop images in Fig. 13 showed that the contact angle of the shale in presence of deionized water (68.5°) reduced to 34.16° in presence of the lowest saponin concentration (0.01 wt%) and 20.62° in presence of the highest concentration (0.5 wt%). This is about 50% and 70% reduction in the original contact angle of the shale. The contact angle of the shale 2 surface reduced from 52.44° to 38.3° (about 27% reduction) and 8.85° (83% reduction) in presence of 0.01 wt% and 1.0 wt% saponin concentration respectively. These results suggest that the isolated saponin can effective reduce the contact angle of rock surface from strongly water-wetting to weakly-water wetting condition, as well as from oil-wet state to water-wet state. The tendency to reduce the contact angle increased with the increasing saponin concentration.

Generally, the water-wetting capacities of the shale increased with the increasing saponin concentration. A general comparison between the wettability alteration potential of the extracted saponin and sodium dodecyl sulfate showed that the extracted saponin could be considered as supplementary alternative for the wettability alterations of the reservoir rocks. For instance, Fig. 13 showed that 0.2 wt% SDS reduced the contact angle of shale substrate to 26.5° while the same concentration of the extracted saponin decreased the contact angle to 28.48°. Similarly, the contact angle of shale was reduced from 52.44° to 19.66° by 0.5 wt% SDS. The same concentration of the isolated saponin reduced the contact angle to 20.62°. These results also demonstrated that the extracted saponin could be an effective wettability alteration agent for unconventional reservoir rocks such as shale.

When the rock wettability alteration capacity of the extracted saponin was compared with that of the commercial saponin, results presented in Fig. 12 clearly showed that the wetting tendency of the rock inclined towards more hydrophilic conditions in presence of the extracted saponin compared to the commercial saponin. Specifically, the contact angle of the aged Berea sandstone were obtained as 64.8° and 24.8° in presence of the 0.2 wt% and 0.5 wt% concentration of the extracted saponin. In presence of the same concentration of the purchased commercial saponin, the contact angles were obtained 73.3° and 46.0° respectively. Previous studies generally showed that the contact angles could increase when the charges on the rock surfaces and the

(a) $\theta = 68.5^\circ$

(b) $\theta = 34.16^\circ$

(c) $\theta = 30.58^\circ$

(d) $\theta = 28.77^\circ$

(e) $\theta = 20.62^\circ$

Fig. 12. Comparison of the wetting properties (contact angles on berea sandstone) of different concentrations of the extracted saponin with the commercial saponin.

Fig. 13. Trends of the contact angles of the drops of the synthesized saponin solutions on shale 1 surfaces (a) deionized water drop on shale 1 surface (b) 0.01 wt% saponin drop on the shale surface (c) 0.05 wt% saponin drop on shale surface (d) 0.1 wt% saponin drop on shale surface (e) 0.5 wt% saponin drop on shale surface.
charges on the surface-active species (surfactants) are different. This can be attributed to the formation of hydrophobic bilayer arising from surfactant adsorption on the rock surfaces (Yekeen et al., 2020).

Increasing water-wetting tendency and hydrophilic bilayer formation have been attributed to the existence of similar charges on the substrate and surfactants surface because of high disjoining pressure (Bhushan, 2012; Menezes et al., 1989; Yekeen et al., 2020; Zhang et al., 2014). Saponin, being a non-ionic surfactant does not demonstrate any strong adsorption onto charged surfaces. Hence, more surfactants molecules are present in the bulk solutions to increase the water-wetting tendency. Moreover, saponin as a non-ionic surfactant is soluble in water via hydrogen bonds formation of the hydrophilic moieties with water. Hence more surface-active components could be released into the bulk solution, resulting in formation of water-wet thin film on the aged Berea sandstone and shale surfaces.

3.6. Oil-water interfacial tension at room conditions

Interfacial tension between the oil and water has a unique role in promoting hydrocarbon recovery, because microscopic displacement efficiency increases as the oil-water interfacial tension decreases (Mosayebi et al., 2016). Influence of varying concentration of the isolated saponin on the oil-water interfacial tension was study and compared with the performance of conventional synthetic surfactant, sodium dodecyl sulfate (SDS). Fig. 15 shows the plots of heptane-water interfacial tension versus surfactant concentrations. The experiments were conducted at room conditions. The plotted curves showed that the increasing surfactant concentration generally resulted in drastic

![Fig. 14. Trends of the contact angles of the drops of the synthesized saponin solutions on shale 2 surfaces (a) Deionized water drop on shale 2 surface (b) 0.01 wt% saponin drop on the shale surface (c) 0.05 wt% saponin drop on shale surface (d) 0.1 wt% saponin drop on shale surface (e) 0.2 wt% saponin drop on shale surface (f) 0.5 wt% saponin drop on shale surface and (g) 1.0 wt% saponin drop on shale surface.](image1)

![Fig. 15. The plots of interfacial tension versus surfactant concentrations for Heptane-water interfacial tension.](image2)
reduction in heptane-water IFT until certain concentration close to the critical micelle concentration. Precisely, at the CMC of the extracted saponin and the SDS (0.2 wt%), the heptane-water IFT decreased from 48.5 mN/m to 11.81 mN/m (about 76% reduction) in presence of extracted saponin and decreased from 48.5 mN/m to 7.31 mN/m (about 85% reduction) in presence of SDS. Beyond the CMC, the change in heptane-water IFT with increasing surfactant concentration was not very significant.

At some surfactant concentration below the CMC, lower interfacial tension were even obtained in the presence of the extracted saponin compared to the sodium dodecyl sulfate. For instance, at 0.1 wt%, the extracted saponin solution reduced the heptane-water IFT from 48.5 mN/m to 12.69 mN/m while SDS solution decreased the IFT to 16.07 mN/m (about 67% reduction). These results showed that the extracted saponin could be consider as supplementary alternative to convention EOR surfactants, such as sodium dodecyl sulfate, for reducing interfacial tension and enhancing hydrocarbon recovery.

Generally, oil and water interface could be the ideal location for the systematic orientation of the saponin molecules due to their dual molecular structure and the presence of the hydrophobic and hydrophilic components (Mosayebi et al., 2016; Nowrouzi et al., 2020). The change in oil-water IFT can be attributed to arrangement of surface-active species at the oil-water interface such that the hydrophilic head is dissolved in aqueous solution while the hydrophobic tail dissolve in oil (Nowrouzi et al., 2020). The IFT of the system decreased with the increasing surfactant concentration due to the adsorption of the surfactant molecules at the oil-water interface (Wu et al., 2018). The IFT decreases as the surfactant concentration increases, signifying that a rising number of surfactant molecules migrate to the oil/water interface (Zhang et al., 2018).

However, at CMC, the bulk solutions is essentially saturated with the surfactant molecules, as the molecules attain the adsorption saturation due to significant formation of micelles (Chen et al., 2020; Kumar and Mandal, 2016). At this point, the free migration of the surfactant molecules from the bulk solution to the oil-water interface are inhibited by the denser surfactant monomers. Previous studies showed that the function of the surfactant molecules can diminished with micelles formation (Najimi et al., 2019; Nowrouzi et al., 2020). Beyond the CMC, the added surfactant molecules in solutions are only involved in the micelles formation and formation of larger aggregates in bulk solutions. They do not necessarily increase the migration rate and surface-activity of the surfactants at oil-water interface. Hence, no noticeable change was observed in the oil-water IFT with increasing surfactant concentration beyond the CMC in this study. The aggregation of surfactant molecules in bulk solution prevented their adsorption and accumulation at the oil-water interface to decrease the oil-water interfacial tension (Jiravivitpanya et al., 2017).

3.7. Influence of changing pressure on crude oil-water interfacial tension

To investigate the effectiveness of the isolated saponin at reservoir conditions and identify the temperature range for the possible occurrence of clouding phenomenon, the crude oil-water interfacial tension was determined at elevated temperature and pressure. Firstly, the temperature was kept constant at 80 °C, and the crude oil-water IFT was determined at different pressure (8–22 MPa). The pressure was then kept constant at 10 MPa and the oil-water IFT at varying temperature (80°C–180 °C) was measured. Fig. 16 shows the plots of variation in crude-oil-oil water IFT with pressure for different surfactant concentrations in absence and presence of SiO₂ nanoparticles at constant temperature of 80 °C. The pendant drop profiles of crude oil in the surfactant environment at constant temperature (80 °C) and varying pressure for 0.5 wt % extracted saponin concentration is presented in Fig. 17. Figs. 16 and 17 clearly showed that the crude oil-water interfacial tension increases with the increasing pressure.

This observation is very consistent with literature. Since pressure exert minor influence on oil-water interfacial free energy and rheological properties of liquid compare to temperature, the impact of pressure on oil-water interfacial tension is not very significant like that of temperature (Mosayebi et al., 2016). Unlike the temperature that weakened the liquid-liquid intermolecular forces, the intermolecular forces between the oil and water remained almost unchanged when the pressure is increased (Mosayebi et al., 2016). However, the packing density of surfactant molecules at the interface is decreased at high pressures because the distance between the molecules are increased by the increasing pressure. Consequently, the oil-water IFT increased with the increasing pressure.

Although the crude-oil water IFT increased with increasing pressure, significant reduction in IFT values were observed in presence of saponin and nano-saponin dispersions. Lower IFT were generally obtained in presence of nanoparticles-saponin mixtures compared to the saponin solutions only. In presence of varying concentration of the saponin solutions, the lowest reduction in oil-water IFT was obtained in presence of 0.2 wt% saponin, signifying that surfactant molecules are likely to be optimally arranged at the oil-water interface at the critical micelle concentration of the saponin. Specifically, at 0.2 wt% concentration, the extracted saponin was able to considerably reduce the crude oil-water interfacial tension from 23.24 mN/m to 1.589 mN/m (about 93.2% reduction) and 3.08 mN/m (about 87% reduction) at pressure of 8 MPa and 22 MPa respectively.

A comparison of oil-water IFT values in presence and absence of SiO₂ nanoparticles showed that much lower IFT were generally obtained in presence of nanoparticles compared to the surfactant solutions only. The surface-active complex formed from the synergistic interaction of the surfactant and nanoparticles were found to be generally effective in reducing the crude-oil water IFT compared to the surfactant solution alone.

The lowest IFT values were obtained from a mixed system of 0.5 wt% saponin concentration and 0.05 wt% SiO₂ nanoparticles concentration. The mixed system reduced the crude-oil water IFT from 23.24 mN/m to 0.87 mN/m (about 96.3% reduction) and 2.71 mN/m (about 88.3% reduction) at pressure of 8 MPa and 22 MPa respectively. Increasing nanoparticles concentration to 0.1 wt% did not necessarily resulted in much lower interfacial tension values. The IFT values were generally higher in the presence of the synergistic mixture of 0.1 wt% SiO₂ nanoparticles and 0.5 wt% saponin concentration compared to 05 wt% SiO₂ +0.5 wt% saponin concentration. This observation supports the notion that there is an existence of maximum nanoparticles and surfactant concentration for achieving the lowest reduction in oil-water interfacial tension. Beyond this concentration, there is no significant decrease in IFT with increasing concentration. When the concentration...
of the saponin and nanoparticles in the solution exceeds a certain critical value, they will start aggregating into individual micelles, hence, their contribution to mixed micellization will either reduce or remain constant (Naqvi and Khatoon, 2011).

3.8. Influence of changing temperature on crude oil-water interfacial tension

Temperature has significant effect on oil/surfactant solutions interfaces more than pressure, since they accelerate the molecules mobility, as well as the rate of surfactant adsorption and diffusion velocity of the saponin molecules at the fluid interface. Influence of pressure on crude-oil water interfacial tension was much more complex than the influence of pressure possibly due to the occurrence of clouding phenomenon at high temperature. In the first scenario, temperature were generally observed to decreased with the increasing temperature. However, this case was only observed for the influence of 1 wt% saponin concentration on crude-oil water interfacial tension values. Fig. 18 shows the plots of crude-oil water IFT changes with changing temperature for 1 wt% saponin concentrations at constant pressure (10 MPa).

The plotted graphs showed that the interfacial tension generally decreased with the increasing temperature for 1.0 wt% saponin concentration. The decreasing trend of oil-water interfacial tension with increasing temperature observed in this study is expected and can be attributed to the ability of the temperature to weaken the intermolecular forces at the oil/water interfaces, as well as the influence of temperature on the solubility of oil/surfactant solution (Karnanda et al., 2013).

The decreasing oil-water interfacial tension with increasing temperature is consistent with literature. Increasing temperature decreases the free energy of the surface by increasing the total system entropy (Moeini et al., 2014). The increasing kinetic energy at high temperature also results in successful break-up of the solvent (oil and water) molecules, hereby decreasing the force of attraction, as well as the surface free energy between the molecules at the interface (Wu et al., 2018). The increasing system entropy at high temperature, resulted in decreasing Gibbs free energy, as well as decreasing crude oil-water interfacial tension (Hamouda and Bagalkot, 2018).

However, when much lower concentration of saponin (0.2 and 0.5 wt %) were used for the experiments. The crude-oil water interfacial tension did not decreased with temperature, instead the oil-water interfacial tension increased with increasing temperature due to phase separation from clouding phenomenon (Fig. 19). The pendant drop profiles of crude oil in the surfactant solution environment at different temperature and constant pressure (10 MPa) for 0.5 wt% saponin concentration presented in Fig. 20 further confirmed the increasing crude-oil water interfacial tension with increasing pressure due to phase separation resulting from the clouding phenomenon.

The increasing crude-oil water interfacial tension with increasing pressure can be attributed to phase separation resulting from the clouding phenomenon. As a result of this phase separation, we were unable to proceed with IFT measurement for lower saponin concentration (0.2 wt% and 0.5 wt %) up to 180 °C. The measurement was stopped at 150 °C as the IFT value keep rising with increasing temperature. The temperature at the clouding points is the threshold temperature for surfactant solubility. Beyond this temperature, the surfactant undergo phase separation into two phases (Naqvi and Khatoon, 2011). The two distinct phases during phase separation consists of the bulk aqueous solution and the phase comprising of virtually the entire surfactant with little amount of water. The latter phase will go down while the former phase will remain on top due to the density difference. The saponin dispersion becomes ineffective and thermally unstable, hence when the IFT supposed to decrease with the increasing temperature. Contrary results were obtained as the IFT increased with the increasing.

![Fig. 17. The pendant drop profiles of crude oil in the saponin solutions environment at constant temperature (80 °C) for 0.5 wt% saponin concentration at (a) 8 MPa (b) 10 MPa (c)16 MPa (d) 20 MPa (e) 22 MPa and (f) visual image of crude oil-water interfacial tension reading.](image)

![Fig. 18. Trends of crude-oil water IFT change with temperature for 1.0 wt% saponin at constant pressure (10 MPa).](image)

![Fig. 19. Trends of change in crude-oil water IFT with temperature at constant pressure (10 MPa) for 0.2 wt% and 0.5 wt% saponin concentration showing increasing surface tension values with increasing temperature due to occurrence of phase separation from clouding phenomenon.](image)
temperature due to occurrence of phase separation. The result for the 1 wt% saponin concentration was different possibly because of less amount of water in the dispersions. The higher the rate of dilution, the greater the tendency for liquid-liquid phase separation.

However, in presence of SiO$_2$ nanoparticles there was an improvement in the performance of saponin, lower IFT were reported and thermal stability of the saponin improved even at low saponin concentration (Fig. 21). While the presence of 0.05 wt% nanoparticles concentration in 0.5 wt% saponin solution seems to delay the clouding temperature, the crude oil-water IFT in presence of mixed system of 0.5 wt% saponin and 0.1 wt% SiO$_2$ nanoparticles demonstrated decreasing IFT with increasing temperature up to 120 ºC. This study suggests that the clouding temperature of saponin solutions could be delayed at high saponin concentration or in presence of moderate concentration of SiO$_2$ nanoparticles. Further studies will be necessary to ascertain this result.

The saponin/SiO$_2$ mixtures had significantly influence on clouding temperature and the reduction of the crude oil-water interfacial tension than the saponin solution alone, due to the formation of surface-active complex resulting from the synergistic interaction between the nanoparticle charged surfaces and the surfactants molecules. Since the saponin is a nonionic surfactant, the micelles formed by the saponin will be neutral. However, addition of negatively charged SiO$_2$ nanoparticles into the surfactant solution will give negative charge to the micelles through formation of mixed micelles with the nonionic saponin. The added surface charge will increase the repulsion within the micelles, consequently, increasing the clouding point and preventing phase separation until 120 ºC (Naqvi and Khatoon, 2011).

Spatial attraction could decrease when the saponin molecules approach the negatively charged surfaces of the SiO$_2$ nanoparticles, resulting in slow formation of the micelle in bulk solution and higher packing density of the surface-active species at the oil-water interface. The electrostatic interaction between the nanofluids and surfactants molecules could prevent phase separation, contribute to a high molecules packing density of the surface-active species at the oil-water interface. This incident eventually results in significantly lower interfacial tension data at high temperature in presence of saponin/SiO$_2$ mixtures compared to the saponin solution only. The increasing temperature reduces the IFT by promoting the dissolving and mutual

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Fig. 20. The pendant drop profiles of crude oil in the surfactant solution environment at constant pressure (10 MPa) for 0.5 wt% saponin concentration at (a) 80 ºC (b) 110 ºC (c) 130 ºC (d) 140 ºC and (e) 150 ºC.

Fig. 21. Trends of crude-oil water IFT change with temperature at constant pressure (10 MPa) for 0.5 wt% Saponin concentration in presence of 0.05 and 0.1 wt% SiO$_2$ concentration.
solubility of the hydrophilic part of the saponin in water and that of the hydrophobic part in oil (Wu et al., 2018).

4. Conclusion and recommendations

An isolated saponin from a natural source, soapnut (Sapindus Mukorossi), was investigated as an enhanced oil recovery (EOR) agent and as a prospective supplementary alternative to conventional EOR surfactants, such as sodium dodecyl sulfate (SDS), in this study.

The following conclusions and recommendations can be established from the results of this study.

- The extracted saponin is recommended as a supplementary alternative to conventional EOR chemical surfactants, with versatile oil-field application, such as sodium dodecyl sulfate (SDS), due to their comparable influence on oil-water interfacial tension (IFT), wettability alterations of the conventional and unconventional rock wetting properties, as well as high foam generation/stabilization properties.

- Based on the foaming properties of the isolated saponin determined at 60 °C using Tecdis Foamscan equipment and the results of crude-oil water IFT measurement with KRÜSS Drop Shape Analyzer 100 at high temperature and pressure. The isolated surfactant can be considered for application for unfavorable downhole conditions of high temperature and pressure.

- The buildup of the saponin-stabilized foam was very stable at ambient condition and high temperature (60 °C), suggesting that the foamability of the saponin-foam is unaffected by liquid drainage, bubble coalescence and coarsening.

- Although the foam stability was lower at high temperature, however, the IFT values achieved at critical micelle concentration (0.2 wt% saponin) in comparison to the original IFT values of Heptane (48.50 mN/m) and crude oil (23.24 mN/m) showed a considerable reduction of almost 76% at room temperature and about 93.2% at high temperature. Much lower IFT reduction could be achieve in presence of nanoparticles and with the use of much sensitive equipment for interfacial tension measurement.

- The saponin extracted from soapnut (Sapindus Mukorossi) can be considered as fair EOR agent for wettability alteration of unconventional shale reservoir with up to 50% reduction and 83% reduction in the original contact angle of the shale substrate in presence of 0.01 wt% and 1.0 wt% saponin concentration respectively.

- Since the synergistic interaction of the saponin and SiO2 nanoparticles showed almost 97% reduction in crude-oil water interfacial tension, Modification of the mixed micellar aggregates, formed from the synergistic combination of the saponin and nanofluids, is recommended to achieve ultra-low IFT values at reservoir conditions and inhibited the clouding properties of saponin.

- The clouding properties seemed suppressed by nanoparticles addition to the surfactant solution, hence optimization of mixed system of the SiO2 nanoparticles and saponin could be exploited for improving the thermal stability at high temperature and prevents quick attainment of the critical solution temperature by the saponin solution.

Declaration of competing interest

The authors would like to state that this manuscript titled “Oil-water interfacial tension reduction, wettability modification and foaming properties of saponin extracted from soapnut (Sapindus Mukorossi)” has not been published and is not under consideration for publication elsewhere. Also, there is no conflicts of interest to disclose concerning this manuscript.

Acknowledgment

The authors would like to thank Universiti Teknologi PETRONAS for supporting this research through YUTP grant (with Cost Centre: 015LC0-058) awarded to Azlinda Abdul Malik.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.petrol.2020.107591.

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