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Probing the role of associative polymer on scCO₂-Foam strength and rheology enhancement in bulk and porous media for improving oil displacement efficiency



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ABSTRACT

Foam mobility control technique has been extensively applied to encounter unfavorable sweep efficiency during CO₂ injection in heterogeneous reservoirs. Harsh reservoir conditions have encouraged a need of effective mobility control agent. In this study, we present a comprehensive experimental investigation utilizing a newly developed water-soluble associative polymer as additive to foam system for stability and rheology enhancement. The performance of polymer enhanced foam on residual oil displacement was also evaluated in porous media. A significant increment in foam longevity and improved foam rheological behavior were obtained with associative polymer presence. Compared to conventional polymer's performance, the associative polymer enhanced foam could establish the higher flow resistance and better compatibility with reservoir conditions. The addition of associative polymer profoundly increased the foam apparent viscosity and gas mobility reduction factor at optimum foam quality in the absence and presence of oil. A noticeable improvement in oil recovery efficiency was also observed in the case with associative polymer by which 28% incremental oil recovery was achieved, 14% higher than that obtained from polymer-free foam injection. The utilization of associative polymer enhanced foam is considered promising for a deepers foam propagation in the formation to recover substantial amount of residual oil.

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1. Introduction

According to field implementation history in several decades, CO₂ injection is one of widely used methods for enhanced oil recovery (EOR) with well-defined technical and economic framework [1]. In addition to hydrocarbon production enhancement, CO₂ injection in depleted reservoir has been promising to be implemented as nontoxic carbon sequestration method to minimize the environmental impact of industrial emission [2]. However, unfavorable CO₂ mobility during CO₂ injection process leads to some challenges that lower overall sweep efficiency. An extensive development of mobility control technique has been established to overcome the impact of CO₂ mobility issue. Several techniques,

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such as alternating or simultaneous injection of water and gas, insitu foam generation, and simultaneous injection of miscible gas and chemical additives have been promoted to improve the effectiveness of CO_2 utilization [3,4]. To make the process efficient, the selection of mobility control agent should be suitable to the reservoir conditions, such as the salinity of formation brine, temperature, pressure, wettability, the extent of oil saturation, and reservoir heterogeneities [5-7]. Reservoir simulation studies have reported that simultaneous injection of miscible gas incorporated with polymer can provide more stable and feasible process in highly heterogeneous formations [8]. The injection of polymer solution into high permeability zones and subsequent miscible CO₂ into low permeability zones can result in a more uniform saturation profile where the polymer is able to reduce cross-flow of gas from the low permeability to high permeability zone. On the other hand, the application of foam for gas mobility control has also been recognized to provide superior sweep efficiency as long as the foam resistance factor is sufficiently high to hinder gas fingering and



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gravity override [7,9]. CO₂-foam injection, for instance, has been frequently evaluated for mobility ratio and oil displacement improvement in heterogeneous porous media under reservoir conditions [10]. CO2-foam has also been in high demand for application in unconventional reservoir as a fracturing and drilling fluid due to its favorable performance in minimizing formation damage [12,13,87]. Nevertheless, in EOR applications, foam is susceptible to large permeability contrast and the environments that lead to foam destructions. Foam strength is strongly influenced by the co-existence of gas and surfactant, surfactant concentration, critical water saturation, and critical oil saturation [7,14]. Besides, the stability of surfactant as a foaming agent needs to be maintained at high temperature, high salinity and high water hardness. A number of attempts have been made to stabilize the foam, for instance, the incorporation of CO₂-philic and oil-resistant surfactant to suspend foam decay [15,16]. The use of different types of ionic liquids to prolong the foam stability, hence improved mobility control at high pressure and high temperature conditions has also been investigated [17,18]. Furthermore, some researchers have employed nanoparticles to establish viscoelastic property on the created foam thin film, called lamellae, to overcome small deformations without rupturing the lamellae wall [19,20]. However, in any case, surpassing the limiting lamellae thickness will cause the foam to collapse. As foam contains considerably high amount of gas with less liquid fraction, the appropriate liquid mixtures that can lengthen the foam endurance will make the foam performance more effective. The capability of polymer to enhance foam rheology properties have been previously evaluated [21,22]. An increase in the viscosity of solution containing polymer is expected to prolong the strength of foam lamella and improve the apparent viscosity of foam [22]. With a significant increment in foam stability and apparent viscosity, acceptable mobility control effect can be achieved [23]. In this regard, many researchers have studied different types of polymer for foam stabilization. Hydrolyzed polyacrylamide (HPAM) polymers, for instance, have been frequently used as additive to surfactant-stabilized foam for rheology enhancement. Incorporating HPAM polymers with alpha olefin sulfonate (AOS) and sodium dodecyl sulfate (SDS) surfactants have been reported to provide a significant improvement in foam stability due to increasing foaming solution's viscosity [24,25]. The addition of HPAM in AOS surfactant solution was able to exhibit a prominent delay in liquid drainage in foam lamellae [26]. Experimental studies utilizing HPAM polymer to stabilize CO₂-foam have been conducted using a specially designed fractured micromodel to compare the performance of CO₂-foam with and without polymer presence [27,28]. It was reported that the polymer enhanced foam (PEF) could provide an additional force to push the injected surfactant/ polymer into the unswept matrix regions. The higher stability of PEF led to an oil displacement improvement, hence increased oil recovery. Different studies reported that a low polymer concentration could provide significant enhancement in foam strength, resistance factor, and tolerance to oil [29,30]. The optimization of PEF is strongly reliant on the polymer types, surfactant-polymer interaction, polymer's molecular weight and charge, and surfaceactive capability [31-33]. However, the instability of conventional polymers under harsh conditions i.e., high shear, temperature, and salinity can reduce their performance consistency during the process [26,34]. For example, HPAM polymers may undergo thermal and mechanical degradation due to high temperature and shear conditions. The viscosity of HPAM polymer is also susceptible to saline environment because of coiling up of polymer backbone driven by the charge shielding mechanisms [26,34]. Besides, the anionicity of HPAM polymers determines their physical properties and their degree of hydrolysis controls their chemical stability and viscosity.

A previous study has introduced the utilization of associative polymer to optimize the flow properties of polymer enhanced foam for water profile control, proven by the significant improvement of resistance factor [35]. The use of associative polymer has also been extended to mobility control and shale fracturing applications [12,36,37]. With this regard, the evaluation of rheological behavior of CO₂-foam stabilized by surfactant in combination with associative polymers containing relatively high degree of hydrophobes has been performed using foam rheometer system and their stabilization performances have been compared to that of different HPAMstabilized foams. The hydrophobes moieties in associative polymer structure was believed to contribute to an excellent performance of associative polymer in enhancing the foam viscosity at highpressure and high-temperature conditions [38,86]. Furthermore, the associative polymer has also been found to extend the temperature tolerance of conventional viscoelastic surfactantstabilized fluids, providing additional benefits on its applications for polymer/surfactant fracturing fluid [39]. Another study on the effectiveness of water-soluble associative polymer as foam stabilizing agent has been conducted by Hernando et al. [40] in porous media by evaluating the pressure drop during foam displacement and its resistance factor. Their experimental results show that the synergistic effect between surfactant and associative polymer has been noticed and developed due to the presence of amphiphilic property in the polymer structure. The generation of a stronger foam due to the presence of associative polymer was indicated by the greater resistance factor obtained in the porous media. compared to foam generated with single surfactant or surfactant/ conventional polymer mixture. The presence of anionic backbone and cationic hydrophobic part in associative polymer structure allows the placement of polymer molecules at the liquid/gas interface as well as at the surfactant micelles. The adsorption of polymer molecules at the interface depends on the available area which can be provided when the films are compressed or stretched during their propagation in porous media which can also be affected by the flow rate applied. This occurrence increases the viscoelasticity of lamella as the adsorbed polymers hinder the motion and the hydrophilic parts that enhance the bulk viscosity are dangling in the inner part of lamella. It can be ascertained that the mixture of surfactant and associative polymer could generate the foam with stronger structures due to the established surfactant/polymer interactions in addition to the viscosifying power. An increase in the viscosity of aqueous phase is not sufficient to provide a strong foam as the polymer addition can dramatically reduce the foamability and negatively affect the foam structure [41]. Different behaviors of polymers can be tuned by its hydrophobic groups and ionicity which affect their interactions with surfactant. The ability of polymer to alter surface tension that indicates the availability of surface activity also highly benefits the aqueous system to provide high foamability. It has also been reported that the use of polymer possessing amphiphilic structure can prolong the foam stability due to the formation of bridges between the interfaces of lamella [42]. Owing to their unique properties, the associative watersoluble polymer has been extensively promoted to eliminate the limitations of existing conventional polymers during oil recovery process. To date, a thorough evaluation under actual reservoir conditions remains limited. The subsequent effect of rheological properties improvement of the associative polymer-stabilized foam on residual oil mobilization is still inadequately studied. Therefore, this work is aimed to present a comprehensive investigation on the performance of foam in the bulk and porous media using conventional and associative polymers as foam stabilizing agents in the absence and presence of oil under reservoir conditions. Bulk foam properties assessments were initially conducted through foam stability and foam rheology tests. Foam rheology properties were

investigated under controlled reservoir conditions using highpressure and high-temperature foam rheometer apparatus. In this experiment, foam was generated by circulating the foaming agent together with the supercritical CO₂ under certain range of shear rate at known foam quality. The effect of polymer types on foam properties was investigated and the most effective formulation was then identified. In core flooding experiments, the selected foaming agent and supercritical CO₂ were injected simultaneously and the established foam strengths were assessed at different foam qualities. To evaluate the oil displacement efficiency, the incremental oil recovery obtained after polymer enhanced foam (PEF) flooding were evaluated in comparison with that after polymer-free foam flooding. Secondary CO₂ flooding was performed prior to foam flooding in each case and the result was used as a base case. The key findings found in the entire bulk foam experiments for polymer enhanced and polymer-free foam were correlated with the foam strength and the oil displacement performance in porous media.

2. Materials and methods

2.1. Materials

The primary foaming solution was formulated by mixing alpha olefin sulfonate (AOS, 36% active content), supplied by Akzonobel, and cocamidopropyl betaine (TEGO Betain C60, 32.6% active content) from Evonik Industries. Different types of hydrolyzed polyacrylamide (HPAM) polymers and associative polymers containing hydrophobic and hydrophilic moieties (Superpusher series), supplied by SNF Floerger SAS Company, were used as foam additives. General properties of each chemical are listed in Table 1.

All foaming solutions were prepared in brine composed of sodium chloride (NaCl, Merck) with 3 wt% salinity. The light crude oil (43°APl) was used in bulk foam stability tests and core flooding experiments. Purified CO₂ (99.99%) was used as gaseous phase. Berea sandstone core samples having 15.24 cm length and 3.81 cm in diameter were used for core flooding experiments. The physical properties of core samples are given in Table 2.

2.2. Experimental procedures

2.2.1. Sample preparation

The stock solutions of different polymers were initially prepared by dissolving polymer powder in deionized water with vigorous agitation. The solutions were stirred at high speed (700 rpm) until the vortex approached 75% into the solution. The required polymer powder was sprinkled uniformly on the sides of the vortex within 30 s to avoid any improper hydration of the dissolved polymer into the highly viscous polymer solution. The amount of powder added was also adjusted to hinder the formation of *fish eye* in the polymer solution. After the addition of desired amount of polymer, the overhead stirrer was kept at the low speed (300 rpm) in order to prevent the settling of polymer at the bottom and to avoid any mechanical degradation due to high shear. Polymer stirring was carried out for 2–3 h and then the solution was left overnight. Furthermore, the polymer solution was filtered through 1.2 μ m filter paper inside filtration assembly which was pressurized at 15 psi (103.421 kPa) using N₂. The solutions collected with the filtration ratio less than 1.2 were used in all experiments in order to minimize pore plugging during injection process [43–46]. Certain concentration of polymer solutions in combination with surfactant was then prepared in brine at fixed salinity and stirred at 300 rpm for 2 hours.

2.2.2. Bulk foam stability tests

Foam stability measurements were performed at 353.15 K using Foamscan (Teclis, France) with the schematic shown in Fig. 1. The system allows foam stability measurements in the presence of crude oil at high temperature conditions. Foam generation was carried out by purging the gas into surfactant solution in the absence and presence of polymer at constant flow rate. The volume of foam generated was noted and its reduction was recorded as a function of time. The stability of foam was determined based on the time taken by the generated foam to reach a half of initial volume, known as foam half-life. The surfactant in this experiment contains 0.5 wt% of AOS and 0.5 wt% of betaine. Different polymer types were employed to enhance the stability of surfactant foam and their stabilizing performances were compared.

2.2.3. Bulk foam rheology tests

The quantification of foam apparent viscosity in bulk condition were made based on foam rheology experiments performed using Pressurized Foam Rheometer (Ametak Chandler Engineering) with the schematic shown in Fig. 2. The foam rheometer system allows foam rheology measurements with known foam quality under controlled testing conditions. This system was equipped with foam generator, recirculation loop/flow loop (Hastelloy tubing), Coriolis mass flow controller, positive displacement (PD) pump, and HPHT view cell which are placed inside the oven, displayed in Fig. 3. The length and internal diameter of circulation loop tubing was 304.8 cm and 0.775 cm respectively. Two pressure transducers were attached to measure the differential pressure (dP) across the test section in the circulation loop. CCD camera was used to obtain foam texture in the view cell during the test. Similar to bulk foam stability test, foam rheology experiments were controlled by using consistent foam formulation which was a combination of AOS and betaine surfactants with the addition of different polymer types. The foaming solution and supercritical CO₂ were allowed to flow simultaneously in a circulation loop at known foam quality under increasing shear rate from 10 to 500 s⁻¹ at temperature of 353.15 K and pressure of 1500 psi (10342.14 kPa). During foam circulation, the density of mixture was monitored until the stable value was achieved. The stable density and shear stress values indicated that the uniform foam texture has been achieved. The differential pressure at each shear rate was recorded to be used for apparent viscosity calculation.

The apparent viscosity, μ_{app} (cP) was calculated based on the

Table 1

List of chemicals and their general properties.

Chemical type	Chemical Name	Molecular weight	Charge	Anionicity	Ref.				
Surfactants	Alpha olefin sulfonate (AOS)	298.4 g/mol	Anionic	_	AOS				
	Cocamidopropyl Betaine	342.5 g/mol	Zwitterionic	-	Betaine				
Hydrolyzed polyacrylamide polymers	FP3330S	8 million g/mol	Anionic	Medium to high	HPAM1				
	FP3430S	12 million g/mol	Anionic	Medium to high	HPAM2				
	FP3630S	20 million g/mol	Anionic	Medium to high	HPAM3				
Associative polymers	SP P329	15-17 million g/mol	Anionic	High	AP1				
	SP B192	8-10 million g/mol	Anionic	Low	AP2				

Table 2

Physical properties of the core samples.

Core sample	Experiment	Length (cm)	Diameter (cm)	Pore Volume (ml)	Porosity (%)	Brine Permeability (mD)
A	Foam quality scan (polymer-free)	15.47	3.75	32.99	19.31	321
В	Foam quality scan (PEF)	15.45	3.75	31.74	18.60	314
С	EOR by polymer-free foam	15.45	3.65	29.83	18.45	302
D	EOR by PEF	15.43	3.70	32.83	19.79	326



Fig. 1. Schematic diagram of Foamscan instrument [17,47].



Fig. 2. Schematic diagram of HPHT foam rheometer.

ratio of shear stress, τ (dyne/cm²), to shear rate, $\dot{\gamma}$ (s⁻¹) which are given by Eq. (1) and Eq. (2) [48–50],

$$au = \frac{D\Delta P}{4L}$$
 Eq. 1

$$\dot{\gamma} = \frac{8\vartheta}{D}$$
 Eq. 2

where ϑ is velocity (cm/s), D is the inner diameter of the tubing (cm), ΔP is the differential pressure between the test sections (psi), and L is the tubing length (cm). Hence, the apparent viscosity can be expressed in Eq. (3).

q. 2
$$\mu_{app} = \frac{D^2 \Delta P}{32L\vartheta}$$
 Eq. 3

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Fig. 3. Circulation loop of foam rheometer.

2.2.4. Core flooding experiments

2.2.4.1. Experimental set up. Core flooding system with schematic diagram shown in Fig. 4 was used to evaluate the performance of polymer-free and polymer enhanced foam to recover the residual oil in porous media under HPHT conditions. The system was equipped with liquid piston pumps (Stigma 300, Sanchez technologies, France) for fluids injection (crude oil, formation brine, and foaming solution), setting the confining pressure, and controlling back pressure. The core holder, fluids' accumulators, and back pressure regulator were placed inside the oven. All core flooding experiments were conducted at constant temperature of 353.15 K and back pressure of 1500 psi (10342.14 kPa). Under these conditions, the supercritical CO₂ was injected using syringe pump (Isco, Teledyne, USA). Two pressure taps were connected to the inlet and outlet parts of core holder and pressure sensors with high sensitivity were embedded to record the differential pressure across the core sample. In addition, four temperature gauges were attached along the core holder. The inlet of core holder was equipped with two injection ports connected to two different injection lines that were allocated for gas and liquid/aqueous phases.

2.2.4.2. Experimental procedures. The porosity of core samples was

initially determined prior to core flooding experiment. After loading the core samples and mounting the core holder, temperature was set to 353.15 K and confining pressure was built up. Back pressure was set gradually and pressure test was performed. Core sample was flooded with 10 PV brine at 0.2 cc/min injection rate to remove the air and followed by brine injection at different flow rates (0.2-2 cc/min) until reaching steady-state condition. The differential pressure obtained at each flow rate was recorded to determine the absolute permeability. Core flooding tests were accomplished in two sets of experiment. The first set was foam injection at varying fractional gas flow rate ($f_q = 30-90\%$) in the absence of oil to determine the strength of foam generated at different foam qualities. This foam quality screening was carried out by co-injecting supercritical CO₂ and foaming solution at fixed total flow rate (1.5 cc/min). The fractional flow rates of gas (q_g) and liquid (q_1) were determined based on the desired foam quality (f_a) , following Eq. (4). The optimum foam quality with the maximum apparent viscosity was selected and further used for the second set of experiment which was conducted in the presence of crude oil.

$$f_q = \frac{q_g}{q_g + q_l}$$
 Eq. 4

In the second set of experiment, core was initially saturated with brine and drained with crude oil at 0.2 cc/min flow rate. The injection rate of crude oil was then increased to 0.5, 1, 1.5, and 2 cc/ min to establish irreducible water saturation (Swi) and original oil in place (OOIP). The core sample was then flooded with at least 10 PV of crude oil. The oil displacement was initially performed by supercritical CO₂ injection at flow rate of 1.5 cc/min until no more oil was produced. The effluent was collected and its increase in volume was measured as a function of injected pore volume (PV) to eventually determine the cumulative oil recovery. Foam was then generated *in-situ* by injecting CO₂ and foaming solution simultaneously at the optimum foam quality. An increment in oil recovery was recorded over time. Besides oil recovery, pressure drop across the core during gas injection and foam injection in the presence of oil was compared with oil-free case to investigate the effect of oil on



Fig. 4. Schematic diagram of core flooding set up.

gas mobility reduction factor. The performances of surfactant foam and polymer enhanced foam in reducing gas mobility and improving oil recovery were examined whereby the result for pure gas injection was used as a base line. Apparent viscosity and mobility reduction factor were used as the parameters to assess the foam strength generated with each foaming solution tested. The apparent viscosity was calculated according to Darcy's law, where the foam is considered as a single phase and apparent viscosity is dependent on foam quality, given by the Eq. (5) [51–53].

$$\mu_{app} = \frac{kA\Delta P}{14700(q_g + q_l)L}$$
 Eq. 5

where μ_{app} is the foam apparent viscosity (cP), k is the absolute permeability to gas (mD), A is cross sectional area of rock sample (cm²), ΔP is pressure drop across core sample (psig), q_g is gas the flow rate (cc/sec), q_l is the liquid flow rate and L is the length of core sample (cm).

The mobility reduction factor (MRF) value is given by Eq. (6),

$$MRF = \frac{(k/\mu)_{CO_2}}{(k/\mu)_{foam}} = \frac{\Delta P_{foam}}{\Delta P_{CO_2}}$$
Eq. 6

where ΔP_{foam} is the differential pressure (psig) across the porous media during foam flow that results from simultaneous injection of CO₂ and surfactant solution and ΔP_{CO_2} is the differential pressure during the CO₂ flow, without foam generation [54–57]. These two parameters were used for determining the foam flow behavior as well as the optimum foam quality in the experiments without oil presence. Meanwhile, the performance of foam in the presence of oil was evaluated based on the increment of recovery factor (RF) which is calculated using equation Eq. (7),

$$RF = \frac{V_{op}}{OOIP} \cdot 100\%$$
 Eq. 7

where OOIP is original oil in place and V_{op} is the volume of oil produced. The oil recovery during gas injection and foam injection was monitored to determine the extent of its increment due to the presence of foam in porous media.

3. Results and discussions

3.1. Bulk foam studies: foam stability and rheology

The use of different types of classical and associative polymers was aimed to compare their performance in generating stable and strong foam as well as to identify the most suitable polymer that could provide better performance under HTHP and saline conditions. In these tests, the concentration of polymer in aqueous solution was fixed at 2000 ppm, while AOS and betaine surfactant combination was kept at 1:1 concentration ratio. Fig. 5 presents the longevity and drainage profile of foam generated with formulated surfactant combined with conventional polymers and associative polymers as additives. Results show that the decay rate of foam in the presence of associative polymers, AP1 and AP2, are noticeably slower than the case of other polymers. The foam half-life was recorded after the foam volume reached 100 ml (half of initial foam volume). It was also noticed that the addition of conventional polymers with different molecular weights were able to increase the stability of surfactant foam. Among Floppam polymers, HPAM2 was able to increase surfactant foam stability by 75%. Meanwhile, the foam stability in the presence of associative polymers was found 2 times higher than polymer-free case. After foam is

generated, liquid drainage dominantly affects foam destabilization as the liquid residing in the lamellae will continuously flow decreasing the lamellae thickness. This drainage takes place within short time as it can also be observed from Fig. 5. Nonetheless, the presence of polymer can delay the drainage which leads to the lamellae thinning depending on the polymer types. It was found that associative polymers slowed down the drainage process about 600 s compared to polymer-free case until it reached a stage where the foam stability was highly dependent on the lamellae strength. After liquid fraction became less, coupled with slow liquid drainage, the bubble coarsening occurs induced by gas diffusion through the lamellae from one bubble to another bubble and some interfacial interactions [58]. Specific polymer additives are able to alter the interfacial properties through some interactions and bulk rheological properties that can suppress the rate of bubble coarsening. Besides increasing the viscosity of bulk solution which contributed to the suspension of liquid in the lamellae, the interactions between surfactant and polymer could also increase surface viscoelasticity that maintains the lamellae strength and resists bubble deformation for longer time period, hence higher foam stability [59].

The interaction of surfactant and polymer are determined by electrostatic and/or hydrophobic forces which in their turn can be affected by some factors including additive concentration and chemical structures. These factors are responsible for the formation of surfactant/polymer complex providing strong steric repulsion that is beneficial for foam stability [59]. In comparison with conventional polymers, the used associative polymers have a higher number of hydrophobic groups attached to their molecular structures that tend to upsurge the steric forces at the lamellae interface upon their combination with surfactant hydrophobic groups, leading to increased foam longevity, see Fig. 6. The case with added AP2 was found to have the highest foam stability, more than twofold increase compared to foam stability of polymer-free foam.

Further evaluation was performed in term of foam apparent viscosity which was aimed to ascertain an improvement in the strength of polymer added foam while the shear was applied at fixed foam guality i.e., 80%. In this experiment, the mixture of similar surfactant composition and polymers were used to generate foam that was then circulated in the recirculation loop at 353.15 K and 1500 psi (10342.14 kPa) within applied shear rate. Results presented in Fig. 7 show that all the generated foams exhibit shear thinning behavior in which the viscosity decreases as the shear rate is increased. This behavior is typically observed for foam containing polymers due to their non-linear viscoelastic properties [60,61]. Bubble's deformation, stretch, and collapse contribute to the reduction of viscosity as the shear rate increases. Fig. 7 also indicates that the addition of AP1 and AP2 could improve the foam viscosity more than other conventional polymers. The increment in foam viscosity in the use of conventional polymers was not considerable at all the tested shear rates as it was found to be quite similar with the viscosity of polymer-free foam. HPAM polymers are known to have linear chains which are sensitive to temperature and salinity. Additionally, due to charge shielding phenomena, the polymer may coil up and degrade. Driven by these reasons, the presence of conventional polymer is considered not favorable for enhancing the foam apparent viscosity performance. This was revealed when the effluent from the recirculation loop was visually inspected.

In the use of conventional polymer, the effluent was found unclear and containing black residues, indicating its degradation due to exposure to the experimental conditions. Such polymers might not be recommended to be used for EOR processes as these may cause plugging in the porous channels. Furthermore, polymer degradation is also not favorable during foam flooding because the change in polymer's structure and molecular weight due to



Fig. 5. CO2-foam volume (left) and liquid drainage in foam (right) generated with formulated surfactant in combination of different types of polymer recorded as a function of time.



Fig. 6. Effect of different polymer types on surfactant-stabilized $\rm CO_2$ -foam half-life at high temperature.



Fig. 7. CO_2 -foam apparent viscosity with increasing shear rate in the absence and presence of different polymer additives at 80% foam quality.

degradation will weaken its ability to strengthen the foam lamella [62]. Nevertheless, the used conventional polymers still provided stabilizing effect on foam. In contrast, the effluent containing AP2 was found clear without any contaminant. In comparison with

conventional polymers, associative polymers have a greater capability of maintaining its properties at high pressure and high temperature due to their strong hydrophobic associations that provide cross-linked networks of multiple polymer chains. This behavior imparts the viscosity characteristic with tolerable sensitivity to shear and temperature, compared to HPAM [63,64]. As a result, associative polymers offer a better foam stabilization as well as noticeable improvement in apparent foam viscosity.

3.2. Foam performance evaluation in porous media

3.2.1. Quality scan for polymer-free and polymer enhanced foam

The capability of associative polymer (AP2) selected from bulk foam experiments to improve the strength of surfactant foam in controlling gas mobility was evaluated in porous media under reservoir conditions. The evaluation was conducted based on the pressure drop profiles at different foam qualities that were translated to mobility reduction factor, calculated using Eq. (6). Initially, different injection schemes were performed in order to investigate the ability of polymer-free foam and polymer enhanced foam to generate the effective flow resistance at steady-state condition which was obtained after sufficient total pore volume injected while controlling the gas/liquid fractional flow (foam quality). Fig. 8 shows pressure drop profiles at the entire range of foam qualities for polymer-free and polymer enhanced foams. The injection was started from the higher to lower foam quality. This method was aimed to generate relatively dry foam that has less saturation of foaming solution then gradually followed by wetter foam with a higher foaming solution saturation. These experiments were conducted at fixed total flow rate of 1.5 cc/min which corresponds to superficial velocity of 4.3 ft/day, sufficient to minimize the capillary end effect. In both cases, the coarse foams were initially generated at all the foam qualities which provide low pressure drop and then the foam generation was gradually adjusted based on the gas and liquid fractional flow applied. The condition where the minimum pressure gradient has been reached favors the generation of stable foam [65,66]. The competition between foam generations and coalescences during injection results in pressure drop fluctuation within certain extent until reaching steady-state in which the pressure drop gets stabilized.

During foam injection, it is crucial to control the injection rates of gas and foaming solution. A higher gas fractional flow is able to increase the foam flow resistance [67], however, it is up to certain extent. At high gas fractional flow, above certain value, the foam will get drier, hence increasing the capillary pressure and exceeding



Fig. 8. Pressure drops profiles for both polymer-free and polymer enhanced foam at different foam qualities.

the critical lamella thickness which lead to decreased foam resistance factor [68–70]. The high-quality regime is not only controlled by the *in-situ* foam stability and coalescence but also by the fluctuation in foam generation [71,72]. It is required to determine the optimum foam quality for each case where the foam strength reaches the maximum value, therefore, the transitions from a lowquality to high-quality foam can be identified [72,73].

In this study, based on the calculated mobility reduction factors for each foam quality, low-quality and high-quality regimes were indicated and the optimum foam quality was found at 80% for the case with and without polymer, see Fig. 9. The ability of generated foam to control gas mobility gradually increased with increasing gas fractional flow in low quality regime until reaching the highest value at 80% quality, then it dramatically dropped as the quality increased to 90%. The low foam quality regime from 30% to 60% is predominated by bubble trapping and release leading to insignificant increase in foam strength [74,75]. Increasing foam quality is able to produce a greater number of lamella, hence high density foam system. This results in increased foam strength until it reaches

critical condition with limiting capillary pressure [71] above which the disjoining pressure is not sufficient to stabilize the foam lamella. Further increase of foam guality above this critical point, the governed lamella becomes less dense and the formed foams have coarser textures due to limited supply of foaming solution. Therefore, the established mobility control relies on the continuous re-generation of dry and coarse foams with minimum lamella thickness. As the foam generation is challenging at foam quality higher than 80%, the mobility control effect becomes much lesser. The optimum quality which has the highest flow resistance is also presented in Fig. 10. The apparent viscosity for each tested foam quality was calculated using Eq. (5). An improvement of foam strength was pronouncedly observed in the presence of associative polymer. The mobility reduction factor at optimum foam quality was found to be approximately 2.5 times higher than polymer-free case. The apparent viscosity of polymer enhanced foam was also found two-fold higher than that of foam without polymer addition. In addition, it was previously observed in Fig. 8 that the established pressure drop was very low at the highest foam quality which is



Fig. 9. Mobility reduction factor established by polymer-free and polymer enhanced foam at different foam qualities.



Fig. 10. Apparent viscosity of polymer-free and polymer enhanced foam at different foam qualities.

controlled under fixed total flow rate. High gas fractional flow allows the gas to breakthrough rapidly and additional drainage occurs slowly as the pressure drop across the continuous gas channels is much smaller than the pressure drop built across the liquid channels [76,77]. During the flow of polymer enhanced foam, the gas channels couldn't be constantly discontinued by lamella at the highest foam quality as foam generation might require higher triggering velocity. In this case, the required velocity to generate foam might be insufficient as foam quality increases and can be decreased with increasing the fractional flow of foaming agent [78]. It indicates wetter foam with polymer presence could promote effective foam generation and transport in porous media. Additionally, foam strength enhancement in porous media due to polymer presence corresponds to the bulk foam stability and viscosity behavior of polymer enhanced foam discussed in previous section. The presence of associative polymer could improve crosslinked and bridge micellar structure that can attribute to the alteration of rheological properties of foaming solution [79]. Additionally, the formation of entangled networks and association group can establish stronger interactions between polymer molecules and surfactant clusters through their hydrophobic groups. The established steric forces at the interface due to aforementioned interactions yield more elastic and stronger foam thin films that lead to finer foam texture with larger apparent viscosity.

3.2.2. Foam strength with and without polymer addition in the presence of oil

The ability of associative polymer to stabilize surfactant foam was further evaluated at the optimum foam quality in the presence of residual oil. Fig. 11 presents the pressure drop profiles established during the injection of polymer-free and polymer enhanced foam and calculated apparent viscosities with and without residual oil presence after secondary gas flooding. In both cases, the pressure drops were significantly reduced by oil presence indicating the instability of foam front that eventually allowed the gas to breakthrough. Foam destabilization due to remaining oil saturation was more prominent in polymer-free case as the pressure drops barely increased during the injection even after two PV injected. Meanwhile, a gradual increase in pressure drops was observed in the case of polymer enhanced foam. At initial stage, polymer enhanced foam was also encountering residual oil that results in slow pressure build up, however, after certain amount of oil has been swept through some displacement mechanisms, the foams started gaining the strength as the injection was continued. Polymer-free foam

was found less tolerant to crude oil suggesting that the formed foam lamellae inside the pores did not possess sufficient strength. On the other hand, foam stabilized by polymer exhibited a higher tolerance to oil, hence, offering greater flow resistance indicated by higher pressure drops across the core sample. It has been extensively reported in the previous studies that the presence of crude oil is not favorable for foam to maintain its bulk stability and endurance during porous media flow [47,56,80]. The occurrence of oil spreading in foam lamellae induces the formation of pseudoemulsion film that weaken the initial stability of foam lamellae unless the stabilizing agent consistently maintains the strength of lamellae or foam films by producing a large interfacial tension gradient to hinder pseudo-emulsion film thinning [81,82]. Lamella stabilization exhibited by the foaming agent has direct impact on apparent viscosity of foam flowing in porous media. The effect of oil was found more severe for polymer-free foam indicated by a significant decrease in the steady-state pressure drop from 80 psi (551.581 kPa) to 15 psi (103.421 kPa), while 135 psi (930.79 kPa) to 45 psi (310.26 kPa) for polymer enhanced foam. The presence of polymer was able to build up the steady-state pressure drop more than two times higher than that of polymer-free foam in the presence of oil which corresponds to foam apparent viscosity enhancement during the transport of polymer enhanced foam.

3.2.3. Incremental oil recovery by polymer enhanced foam

The selected foaming formulations were brought to the oil recovery experiments for their final evaluation under reservoir conditions. Core flood experiments were performed at foam quality of 80% which offered the highest mobility reduction factor and foam apparent viscosity in the absence of oil. In general, the injection scenario includes core saturation with brine, crude oil injection, and CO₂ injection as secondary flooding which was then followed by the co-injection of CO₂ and foaming solution. Based on the responses obtained, the recovery factor and the pressure drop profiles across the cores are shown in Fig. 12. CO₂ flooding was able to exhibit differential pressures at the beginning of injection expressing the formation of displacement front and produce about 55% original oil in place. However, gas breakthrough occurred before 0.5 PV injected hence no more oil produced. The injection of surfactant stabilized foam (without polymer presence) provided mobility control by overcoming gas breakthrough and led to oil displacement from the portion of core sample which was previously unswept. It resulted in 16.5% incremental oil recovery within 2-3 PV foam injection. A higher incremental oil recovery was



Fig. 11. Effect of residual oil on pressure drop profile and apparent viscosity obtained during polymer-free and polymer enhanced foam flooding at optimum foam quality.



Fig. 12. Oil recovery factor (RF) and pressure drop profile as a function of injected PV during CO_2 flooding followed by a foam injection.

obtained in the use of associative polymer as the additional stabilizing agent. This indicates a better mobility control effect by which associative polymer enhanced foam was able to stably penetrate swept zones and divert the flow to the unswept low permeability regions. As previously mentioned, the established foam strength of polymer enhanced foam in the porous media corresponds to the viscosity improvement governed in the bulk phase and also at the gas/liquid interfaces. The enhancement of surface viscosity is yielded from the formation of three-dimensional network structures of associative polymer in which the interactions among polymer's hydrophobic moieties and/or between polymer and surfactant molecules are governed to minimize their exposure to water system, while the charged hydrophilic backbone imparts the solubility nature [83,84]. Additionally, the associative polymer also has a good tolerance to brine salinity and temperature compared to conventional polymers, therefore, the foaming performance with higher flow resistance can be further maintained while encountering the external disturbances in porous media.

The continuous increase in oil recovery was observed after 1 PV injection of polymer enhanced foam. In contrast, the amount of produced oil remains slightly changed after 1 PV polymer-free foam injection. Polymer enhanced foam was able to produce 28% incremental oil recovery specifying that polymer presence has effectively improved the performance of foam to achieve higher final recovery factor that was about 14% higher than that resulted from polymer-free foam injection. This strongly indicates that the use of associative polymer for surfactant foam stabilization is viable and promising for enhanced oil recovery purpose.

According to the screening, optimization and evaluation results in this study, the application of associative polymer as stabilizing agent has been proven to prominently improve the foam stability in bulk and strength in porous media leading to a better mobility control and oil recovery. It is conceivable that high foam strength with a greater apparent viscosity will also provide better mobility control in the field. The developed polymer enhanced foam has exhibited prolonged stability and viscosity enhancement. These properties improvement is expected for the foam to propagate relatively deeper into the formation to recover more oil during its application in the field. Further tuning of chemical formulation could be taken into account depending on the field scenarios and challenges.

4. Conclusions

This paper present the screening and evaluation of CO₂-foam performance in the presence and absence of different types of polymer. A systematic bulk foam studies have been adapted as an essential screening stage for CO₂-foam before further evaluations in the porous media. The strong agreements of foam stability and rheology results in bulk with foam mobility control performances in the core flooding experiments have been demonstrated. The main findings from this study can be summarized as follows:

- a) The addition of associative polymer has provided a significant improvement in both foam stability and apparent viscosity. In bulk, the associative polymer was able to maintain the stability of foam after liquid drainage resulting in prolonged half-life than that of foam stabilized by conventional polymers.
- b) The associative polymer improved not only the rheological property of bulk solution, but also the entire foam system due to the improved surface viscosity.
- c) In porous media, the low- and high-quality foam regimes were identified and the optimum foam quality was found at 80% for foam generated with and without associative polymer. Foam strength enhancement was achieved when the associative polymer was employed as the stabilizing agent. The MRF and apparent viscosity at optimum foam quality was found to be 2.5 and 2 times higher, respectively, compared to the case without polymer.
- d) In the presence of residual oil, surfactant-stabilized foam strength was tremendously weakened, hence destabilizing the foam under reservoir conditions. However, the higher oil tolerance was exhibited by associative polymer (AP2) enhanced foam, therefore, it offered greater flow resistance in porous media.
- e) The polymer stabilized surfactant foam was found to be more effective in yielding a higher incremental oil recovery after gas injection. The cumulative oil recovery in the use of polymer-free and polymer cases was 74% and 88% of OOIP, respectively. Polymer enhanced foam produced 28% incremental oil recovery ascertaining that the polymer presence has effectively improved the foam performance in achieving greater final oil recovery factor. It strongly indicates a better mobility control effect with an effective fluid flow diversion.
- f) The development of a new polymer stabilized foam formulation, presented in this study, could be further helpful for controlling CO₂ mobility in more severe heterogeneous reservoirs or fractured reservoirs under harsh conditions.

Credit author statement

Alvinda Sri Hanamertani, Investigation, Writing – original draft, Writing-review, and editing, Analysis. Shehzad Ahmed, Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing-review, and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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