Full Length Article

Investigation of synergism between surface-grafted nano-cellulose and surfactants in stabilized foam injection process

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ABSTRACT

The enhanced oil recovery (EOR) efficiency of a foam injection is largely dependent on the stability of foam film especially when crude oil is present. In this study, a surface-grafted nano-cellulose (sgNC) was used to stabilize the film of a surfactant foam and then employed in foam EOR process. The synergism between sgNC and the surfactant was first investigated in bulk through direct measurements of oil/water/solid interfacial behaviors, foam morphology, foam decay, interfacial dilational rheology, *etc*. Particular emphasis was placed on the microflow behaviors of the sgNC stabilized foam in porous media with crude oil to understand the EOR mechanisms behind. The results showed that the incorporation of sgNC in the surfactant solution further reduced the oil/water IFTs, and enhanced the emulsifiability and wettability alteration of the surfactant because of its amphiphilicity. The presence of sgNC in the surfactant foam film significantly increased the film thickness and obstructed liquid drainage. The resultant foam film was fairly viscoelastic, as revealed by the rheological analysis. The oil displacement dynamics observed in the visual microflow model indicated that the viscoelasticity of the foam film rendered the gas bubbles superior stability during migrating in porous media, thus leading to a favorable mobility control and significant reduction in the residual oil saturation. Emulsification, Jamin effect and squeezing accounted for the EOR of foam injection at pore scale.

1. Introduction

Gas injection has been widely used in oilfield to further produce the waterflooding unrecovered reserves. However, due to the high mobility of gas phase, gravity override and reservoir heterogeneities, the injected gas prefers to quickly finger through the formation leaving part of the reservoir unreached [1]. Given this issue, foam injection was subsequently developed for mobility control in 1958, and patented by Boud and Holbrook [2]. Since this pioneering work, many studies at both academic and industrial levels were reports in the past decades [3], proving the significance of this technology in EOR industry. Foam is defined as a dispersive system with gas bubbles dispersing in a continuous liquid phase [4], and the thin liquid film between the bubbles is called foam film (lamella). The EOR mechanisms of the foam injection are attributed to two predominant factors, apparent viscosity and low interfacial tension (IFT). The embedded bubbles increase the apparent viscosity of the displacing agents, and then divert the subsequent fluids to reach the low permeability regions, thus improving the macroscopic sweep efficient. The presence of surfactants reduce the IFTs between water phase and oil phase, which accordingly causes the decrease of the

capillary forces that trap the residual oil [5,6]. These facts make foam injection fairly advantageous in EOR relative to other methods.

Despite the aforementioned facts, a major concern with this technology is the stability of foam during propagating in porous media especially when crude oil is present because many reports have proven the detriment of crude oil on foam life in bulk and porous media [6–9]. It is briefly accepted that oil drops destabilize the foam films through the three modes, 1. Bridging two film surface; 2. Disturbing surfactant alignment at interface; and 3. Squeezing away film liquid [10]. These destabilizing impacts closely determine the foam stability, flow behavior and EOR efficiency of a foam injection process. Thus, substantial efforts have been made in the past decades to address this issue.

The use of solid particles to stabilize foam film was intensively studied recently. Farhadi et al. reported a silica stabilized CO_2 foam system. Due to the incorporation of silica, the bubbles generated are more uniform, which thus leads to high apparent viscosity [11–13]. Binks and Horozov adopted a series of hydrophobic silica nanoparticles to enhance the foam stability [14]. Gonzenbach et al. claimed that the sequential assembly of the amphiphiles on the particle surface and air-water interface was the mechanism for the superior stability of the

generated foams [15]. In addition to silica, the possibility of other particles as aluminum, fly ash, Laponite and $CaCO_3$ in stabilizing foam was also evaluated [16–19]. Based on the previous reports, three possible mechanisms of using nanoparticles to stabilize foam film were proposed by Horozov, *i.e.* bridging particles, bilayer of close-packed particles, and network of particle aggregates [20]. The use of polymeric materials to enhance foam film was also investigated before [21]. For example, Sydansk demonstrated that the polymer enhanced foam (PEF) was more tough and viscous than the surfactant only foam [22]. Shen et al. compared the physical properties of HPAM- and xanthan gum stabilized foams and studied their flow behaviors in porous media [23]. More recently, an associative polymer was used to stabilize foam *via* synergistic effect between polymer and surfactant for water profile control [24]. Zhao et al. reported a phenolic resin cross-linked gel stabilized foam for in-depth profile control. They observed that the thickness and strength of the foam film were significantly improved after adding the gel [25]. Zhang et al. proved that starch particle could mitigate foam film drainage and accordingly improve the strength and viscosity of the generated foams [26].

Cellulose is one of the most abundant natural biopolymers on earth and widely contained in wood, cotton, and other plant-based materials [27–30]. When cellulose is in nano-size, many distinctive chemical and physical properties are observed such as high strength, large surface area, and chemical accessibility [31,32]. The superior viscoelasticity and chemical stability observed in our previous works, promised nano-cellulose an eco-friendly material in EOR applications [33–35]. However, the results also showed that the nano-cellulose easily flocculated in electrolytes. To further improve the colloidal stability, surface-grafting with AMPS and hydrophobic chains was successfully conducted on nano-cellulose, thus making the resultant sgNC fairly tolerant to salts [34,35].

The potential of sgNC in stabilizing foam film has been preliminarily verified as reported in Ref. [36]. Herein, the primary attention was given to the synergism behind between the surfactant and sgNC based on the previous results. To accomplish this research objective, the bulk properties of the foaming solutions and generated foams, including oil/water/solid interfacial behaviors, interfacial dilational rheology, emulsification, foam decay, *etc.*, were systematically investigated in order to understand the synergism between sgNC and surfactant at the foam film. Based on the static tests, the microflow behaviors of the foams in porous media with crude oil were studied using a visual micromodel to correlate the bulk properties to the displacement dynamics.

2. Experimental section

2.1. Materials

The crude oil with a viscosity of 9.2 mPa·s at 25 °C was kindly provided by Xinjiang Oilfield. The foaming agent, nonionic surfactant alkyl polyglycoside (APG, 98%), was purchased from Chengdu Kelong Chemicals Inc., China. The surface-grafted nano-cellulose (nanofibrils), sgNC, was supplied by Tianjin Woodelf Biotechnology Co., Ltd. The chemical structure and micromorphology are shown in Fig. 1. Table 1 lists the chemical composition of the sgNC. 0.5 wt% of NaCl brine was used throughout this work. According to the foam screening criterion, the optimal dosages of APG and sgNC for foaming were determined as reported in Ref. [36]. The formulations used in this work are, surfactant-only foam, 0.2 wt% APG; sgNC stabilized foam, 0.1 wt% sgNC and 0.2 wt% APG.

2.2. Interfacial tension (IFT) and interfacial dilational rheology

Measurements of the IFTs between the foaming solution and crude oil were carried out using a Bowing TX-500C spinning drop tensiometer (Stafford, TX). The interfacial dilational rheology of the foam-air interface was measured using a Tracker H tensiometer (Teclis, France)

[37]. A small volume of the foaming solution was used to form a drop pending on the needle, and then a sinusoidal variation with a small amplitude ($\Delta A/A$, 10%) in the drop surface area was induced by a piezoelectric pump (frequency, 0.01–1 Hz). The instrument camera captured the images of the drop including shape, volume and area, and then analyzed using image software. Since this work was a mechanistic study, all the measurements were conducted at 25 °C without considering the variety of the reservoir temperatures. The interfacial dilational modulus (E) is defined as the change in interfacial tension (γ) over relative interfacial area (A) as follows:

$$E = \frac{d\gamma}{d\ln A} \tag{1}$$

This modulus has contributions from both elastic (E') and viscous (E'') components which can be expressed as

$$E = E' + iE'' \tag{2}$$

and

$$E' = E(\sin\theta)$$

$$E'' = E(\cos\theta)$$

$$\tan\theta = \frac{E''}{E'}$$

The phase angle, θ, is the phase difference between the interfacial tension and surface area oscillations.

2.3. Rheological analysis

The steady shear viscosities of the foaming solutions and foams were measured at 25 °C using an Anton Paar MCR 302 rheometer equipped with a CC27 measuring system (Measuring Bob, D = 26.6 mm, L = 40.0 mm; Cup, D = 28.9 mm). A shear rate sweep from 0.1 to 1000 s^{-1} was performed to correlate the viscosities with the experienced shear.

2.4. Contact angle measurements

The wettability of the sandstone rock surface was quantified by contact angle measurements. Polished rock slides were cleaned with alcohol and distilled water and then dried in an oven at 60 °C. The slides were then aged in the crude oil at 60 °C for 3 days to create oil-wet surfaces. The wettability variations of the slides were tested *via* soaking the slides in the foaming solutions. Then, the contact angle of an oil drop on the surface was re-measured as a function of the soaking time at 25 °C using a Kruss 25 drop shape analyzer. Before each test, the instrument chamber was filled with 0.5 wt% NaCl brine, and then an oil droplet was injected onto the rock surface using a needle tip. The instrument camera captured the image of the oil drop on the surface, and the contact angle was determined using the software.

2.5. Emulsifying tests

The crude oil was mixed with the foaming solutions in one of the commonly used oil:water volume ratio in emulsification study, *i.e.* 2:8. The mixtures were then emulsified *via* hand-shaking for 4 min at ambient temperature. The prepared emulsions were then transferred to graduated cylinders, and the phase behaviors were then recorded upon storage.

2.6. Microscopy studies of the emulsion and foam morphologies

The morphologies of the emulsions and foams were studied at ambient pressure and temperature using a Nikon 501 microscope (Japan). A small volume of the prepared emulsion and foam was loaded onto a glass slide for observation, and a series of magnified images were