NANOSILICA-STABILISED SUPERCRITICAL CARBON DIOXIDE FOAM FOR ENHANCED OIL RECOVERY APPLICATION

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To the Lord God Almighty *Yahweh*,

and my parents,

for their unfailing support and love

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ABSTRACT

Various enhanced oil recovery (EOR) methods have been studied intensively and proven to mobilize, and aid in improving the flow of remaining oil in the reservoirs to producing wells, thus leading to better oil recoveries. Gases have been commonly used in EOR, such as natural gas, carbon dioxide (CO_2), and nitrogen while CO_2 is the most commonly used gas. Foam flooding has started to gain more interests in the field for its promising gas mobility reduction. However, foam generated with surfactant suffers instability under harsh reservoir condition, such as high pressure, high temperature and high salinity. Nanoparticle has then come into play for the role to stabilise foam and several studies on the subject have shown favourable results. Nevertheless, nanoparticle-stabilised foam requires more studies and understanding. This thesis involved the study of nanoparticle-stabilised supercritical CO_2 foam in the presence of surfactant. Foams with different formulations (supercritical CO_2, brine, surfactant and nanoparticles) were generated using a customised glass-bead packed column (GBPC) under 1,500 psi pressure, 25 °C, and a constant flow rate of 6 ml/min. The effect of different nanoparticle concentrations (0%, 0.1%, 0.5%, 0.6% and 1%) and brine salinities (0%, 0.5%, 2% and 10%) on foam are of the key objectives of the study and were both tested. Foam stability and foam mobility tests were carried out quantitatively and qualitatively. Pressure difference valued across the GBPC were recorded. Foam structures and formations were monitored using a camera to capture the images every three minutes throughout the duration of 60 minutes. Nanoparticle-stabilised supercritical CO_2 foam successfully shows significant improvement on foam stability over surfactant foam by 27% as well as slight improvement on foam mobility reduction. Nanoparticle-stabilised foam stability in the presence of oil was also tested. Sodium dodecyl sulfate surfactant foam stabilised with 1.0 wt% nanoparticle concentration shows superior foam stability in the presence of oil.

ABSTRAK

Pelbagai kaedah perolehan minyak tertingkat (EOR) telah dikaji secara intensif dan terbukti mampu untuk meningkatkan aliran baki minyak dari reservoir ke telaga pengeluaran bagi menambah perolehan minyak. Gas kerap digunakan dalam EOR, misalnya gas asli, gas karbon dioksida (CO_2), dan gas nitrogen dengan CO_2 ialah gas yang paling biasa digunakan. Banjiran busa menjadi popular dalam bidang ini berikutan kemampuannya untuk mengurangkan pergerakan gas. Walau bagaimanapun, busa dihasil yang menggunakan surfaktan mengalami ketidakstabilan dalam keadaan melampau misalnya yang tekanan tinggi, suhu yang tinggi dan kemasinan yang tinggi. Nanopartikel boleh memainkan peranan dalam menstabilkan busa dengan beberapa kajian tentang subjek ini telah menunjukkan hasil yang menggalakkan. Busa terstabil nanopartikel memerlukan lebih banyak kajian dan pemahaman. Tesis ini melibatkan kajian terhadap busa CO_2 supergenting terstabil nanopartikel dengan kehadiran surfaktan. Busa dengan formulasi yang berbeza (CO_2 supergenting, kemasinan air, surfaktan dan nanopartikel) telah dihasil menggunakan turus padat manik kaca (GBPC) pada tekanan 1,500 psi, suhu 25 °C, dan kadar aliran mantap 6 ml/min. Kesan kepekatan nanopartikel (0%, 0.1%, 0.5%, 0.6% dan 1%) dan kemasinan air garam (0%, 0.5%, 2% dan 10%) terhadap busa menjadi objektif utama kajian dengan kedua-duanya diuji. Ujian kestabilan dan pergerakan busa telah dilaksanakan secara kuantitatif dan kualitatif. Perbezaan tekanan merentasi GBPC telah direkod. Struktur dan pembentukan busa pula dipantau menggunakan kamera bagi merakam imej setiap tiga minit untuk tempoh kajian selama 60 minit. Busa CO_2 supergenting terstabil nanopartikel berjaya memantapkan kestabilan busa secara ketara sebanyak 27% berbanding busa surfaktan dan sedikit pembaikan dalam pengurangan pergerakan busa. Kestabilan busa terstabil nanopartikel dengan kehadiran minyak juga telah diuji. Busa surfaktan natrium dodekil sulfat yang distabilkan dengan 1.0% berat kepekatan nanopartikel menunjukkan kestabilan terbaik busa pada keadaan terbabit.

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LIST OF SYMBOL AND ABBREVIATIONS

K	-	Permeability, mD
q	-	Flow Rate, cm^3/s
L	-	Length, cm
A	-	Area, cm^2
ρ_o	-	Oil Density, Ib/ft
μ	-	Viscosity, cP
ΔP	-	Differential Pressure, psi
λ	-	Mobility, mD/cP
γ	-	Mobility Reduction Factor
wt%	-	Weight Percentage
ppm	-	Part Per Million
EOR	-	Enhanced Oil Recovery
BHP	-	Bottomhole Pressure
OOIP	-	Original Oil-In-Place
WAG	-	Water-Alternating-Gas
SAG	-	Surfactant-Alternating-Gas
ASP	-	Alkaline Surfactant Polymer
IFT	-	Interfacial Tension
AOS	-	Alpha Olefine Sulphonate
SDS	-	Sodium Dodecyl Sulfate
CMC	-	Critical Micelle Concentration (CMC), wt%
MMP	-	Minimum Miscibility Pressure, psi
GBPC	-	Glass Bead Packed Column
BPR	-	Back Pressure Regulator
SC	-	Supercritical
NP	-	Nanoparticle

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CHAPTER 1

INTRODUCTION

1.1 Background

Since the mid 1980s, EOR gas injection projects have been globally implemented and a growing trend has been evident since year 2000, especially with the increasing number of CO_2 projects. Indeed, since year 2002, EOR gas injection projects have outnumbered thermal projects for the first time in the last three decades (Manrique *et al.*, 2010). CO_2 flooding projects are in steady growth in recent years – in contrast to other EOR methods. The method is poised to become an even more popular oil recovery implementation in the foreseeable future. The distinctiveness of CO_2 flooding is its ability to sweep the oil. Most optimistically, it could recover virtually all the remaining oil where it sweeps. The wide application of CO_2 flooding for enhanced oil recovery is also due to its availability at low cost. However, there are three problems that causing the poor efficiency in CO_2 gas flooding, which are viscous fingering, gravity segregation and early gas breakthrough. Water-alternating-gas (WAG) flooding has been introduced to counter especially viscous fingering of gas flooding. In fact, WAG shows better sweep efficiency, but it could not overcome the existing problems such as gravity segregation and reservoir heterogeneity. The very low viscosity of CO_2 is the factor causing preferential channeling of the CO_2 through high-permeability layers, and low density of CO_2 has resulted in gravity segregation. Extensive studies have been then carried out to remedy the problems by reducing the CO_2 mobility.

Over the last three decades, surfactant has been used to stabilise CO_2 foams in numerous approaches. A conclusion can be drawn that adding surfactant to the water injected along with CO_2 flooding would reduce its mobility and improve sweep efficiency, both in areal and vertical by impeding viscous fingering as well as flow through the higher permeability zones. However, weaknesses of surfactant-stabilised CO_2 foams have also been identified. Surfactant has high retention rate in porous media and it is unstable under reservoir with high-temperature conditions. Surfactant foam is ultimately unstable and it is challenging to keep up a long-term stability during field application. When it is in contact with residual oil, surfactant foam appears to be unstable. Surfactants tend to degrade under high-temperature reservoir conditions before they manage to perform better sweep efficiency.

At 21st century, nano-science has been under progressive development and alternative of nanoparticle-stabilised supercritical CO_2 foam emerges as one of the new technologies. Extensive research efforts regarding nanoparticle-stabilised air/water foams are being carried out. There are many research efforts related to nanoparticle-stabilised air/water foams (e.g., Binks, 2002; Binks and Horozov, 2005). There are supercritical CO_2-in-water emulsions as well as water-in-supercritical CO_2 emulsions. Under reservoir of high pressure and relatively low temperature CO_2 will be in supercritical condition. Being able to use nanoparticle to stabilise and generate foam in supercrtitical CO_2 is therefore a crucial breakthrough. Nanoparticles have higher adhesion energy to the fluid interface than the surfactant, which gives the potential for nanoparticles to stabilise longer lasting foams, as nanoparticles would require more energy to destabilise the foam. The foams made by solid nanoparticles are stable over long periods (up to a year), in contrast with foams stabilised by surfactant molecules whose lifetime is in the order of a few hours (Alargova *et al.*, 2004).

Nanoparticle-stabilised foams have its characterization in various aspects, including foam type, stability, size of droplet, interfacial properties and bulk viscosity. Furthermore, the impacts of conditions during experiments such as concentration of nanoparticle, aqueous phase salinity, pH and wettability are determined systematically under ambient conditions. In comparison with the studies on nanoparticle-stabilised-air/water foams, the studies relating to nanoparticle-stabilised CO_2 with water foams are much less. A pressure releasing method has been demonstrated by Dickson *et al.* (2004) to study the effects of particle concentration, particle hydrophilicity, dispersed phase volume fraction and CO_2 density on foam stability. The results showed that the foam stability increased with decreased hydrophilicity and increased particle concentration, at the designed pressure and ambient temperature. Espinosa *et al.* (2010) reported on nanoparticles stabilised supercritical CO_2 foams for potential mobility control applications by using the commercial surface modified nanosilica dispersion. Their results concluded that the supercritical CO_2 foams stabilised with nanoparticle concentrations as low as 0.05 wt%, and that larger particle concentration was required to maintain foam stability at greater salinities. Experiments that have been carried out by (Jianjia Yu *et al.*, 2012) revealed that stable CO_2 foam was generated in nanosilica dispersions at static conditions, with the particle concentration in the range of 4000 to 6000 ppm in the experiments reported. Mixing surfactant and nanoparticles to stabilised foam is a new area for research. Preliminary tests have been initiated and showing positive results (Worthen *et al.*, 2013). In this study, based on the results of static experiments, a series of flow experiments of the simultaneous injection of CO_2 and nanosilica with surfactant dispersion through glass bead packed column were conducted to investigate nanosilica stabilization of CO_2 foam in different nanoparticle concentrations. Sodium dodecyl sulphate was selected as the base surfactant in this study due to its ionic formulation that is also widely used for different industrial purposes. Primary focus of this study was to enhance surfactant foam by adding foam-stabilizing nanoparticles under high pressure condition. The effects of brine salinity on apparent foam viscosity and total foam mobility were investigated. Effect of oil on nanoparticles stabilised foam was also tested.

1.2 Problem Statement

The application of foam generated by surfactant in EOR has been an excellent solution to the problems yielded by water-alternating-gas, such as viscous fingering, gravity segregation and reservoir heterogeneity. Foam generally has better mobility control which is important for miscible flooding. However, surfactant-stabilised has poor stability especially under harsh reservoir condition of high pressure as well as high temperature. Several initiatives aim at identifying and exploiting the capabilities to use nanoparticles to stabilise foam for EOR have been identified. Numerous researchers have been focusing on the identification of nanotech potentialities applied to Enhanced Oil Recovery (EOR) issues. Although there have been promising preliminary laboratory scale studies, this technology still suffers from requirement of high shear rate for generating foam and high amount of retention of nanoparticles in the porous media. In order to achieve polymer nanocomposite foams which is with high-dimensional stability, high surface quality, good mechanical properties, and excellent thermal still requires a lot of future work (Livi and Duchet-Rumeau, 2013).

Previous research show that agglomeration would take place in particle-stabilised foams (Kaptay and Babcsán, 2012). The concentration of nanoparticle is a significant factor that would affect the rate of agglomeration. In this study, different concentrations of nanoparticle (ppm) are used to stabilise CO_2 foams. Effect of brine salinity on foam stability has arguable results from previously done research. Therefore, the effect of different brine salinity was tested in this study. There were studies done on CO_2 foam but the CO_2 used was not in supercritical condition. For high pressure and relatively low temperature condition of the reservoirs, CO_2 will be in supercritical condition. Thus, it is significant to conduct the study in supercritical CO_2 condition due its significance.

There are also limited studies suggesting that surfactant working in synergy with nanoparticles in stabilising supercritical CO_2 foam. In this study, surfactant was included in order to study the performance of nanoparticles to stabilise surfactant foam. Sodium dodecyl sulfate (SDS) was selected as the surfactant due to its wide application in the industry. The stability of foam in porous media relies essentially on the stability of the foam films (lamellae). The oil may influence the foam performance by affecting lamellae stability being a de-foaming agent. The foam performance in the presence of oil is needed to be identified. nanoparticle-stabilised CO_2 foam specifically, when it contacts with oil were yet to be identified. Using these foams for EOR means the foam stability needs to remain in the presence of oil. Experiments that test the effects of oil contact when the three phases are present are therefore essential. The foam stability of nanoparticle-stabilised supercritical CO_2 needs to be tested in the presence of oil to study its potential to be applied in EOR. Experiments were run to observe as well as identify the effect of oil - normal hexadecane (n-C16) on nanoparticles and surfactant stabilised foam. Hexadecane was selected due to its properties that is of intermediate oil that could well represent oil.

1.3 Objectives

Three main objectives of this research are identified:

1. To study the stability and mobility of nanoparticle-stabilised supercritical CO_2 foam at various nanoparticle concentration.
2. To determine the nanoparticle-stabilised supercritical CO_2 foam stability under high pressure at various brine salinity.
3. To study the stability of nanoparticle-stabilised foam in the presence of oil.

1.4 Scope

The foam stability of nanoparticle-stabilised CO_2 foam in different nanoparticle concentration was tested. A packed glass-bead column was used as a medium to generate nanoparticle-stabilised CO_2 foam, the foam was flowed into a view cell to be observed. Temperature, pressure, type of nanoparticle, type of surfactant, injection rate, water/CO_2 volume ratio and nanoparticle surface wettability remains constant. Brine salinity and nanoparticle concentration were the key parameters to be studied during the experiments. Method to identify foam stability was foam height versus time. The foam was therefore being observed for an hour with camera to capture its image in an interval of 3 minutes.

The main objective of ensuring the constants and manipulated variables was to achieve optimum recovery of nanoparticle-stabilised CO_2 foam injection. SDS was selected and used due to its wide range of implementation in CO_2 foam applications.

The reaction of foam in the presence of oil was analyzed with the help of Dynamic Foam Analyzer DFA 100. Nanoparticle-stablized SDS foam was generated using atmospheric air using Dynamic Foam Analyzer DFA 100. The foam stability and bubble counts were recorded.

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