

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Enhanced Oil Recovery (EOR)

Enhanced oil recovery (EOR) is a production of oil from reservoir by applying some specific techniques after primary and secondary production. Primary recovery is defined as oil production by natural reservoir energy or source. Secondary recovery is applied after the production from primary recovery is decreased and the reservoir force is not enough to produce oil. The most common secondary recovery is water flooding (Collins, 1977). After the primary and secondary recovery, the tertiary recovery can be applied to recover more oil by many techniques such as thermal method, gas injection, chemical injection and so on (Al-Otaibi *et al.*, 2012). In general, the primary recovery can recover around 30 % of OOIP (original oil in place). The secondary and tertiary recovery can recover more oil at around 25-40 % and 5-20 % of OOIP, respectively.

One of the most promising techniques for EOR is gas injection. CO₂ is mostly used in EOR because of its properties such as its ability to lower miscibility pressure and better solvent properties (Al-Otaibi *et al.*, 2012). CO₂ is considered to be one of the effective techniques for several reasons. CO₂ flooding can recover 15% to 25 % of OOIP (Ghedan, 2009). There are many advantages of CO₂ flooding such as decreasing oil viscosity, lowering interface tensions, oil swelling and improving formation permeability. Figure 2.1 shows an illustration of gas flooding by using CO₂ as a miscible gas to flush residue oil.

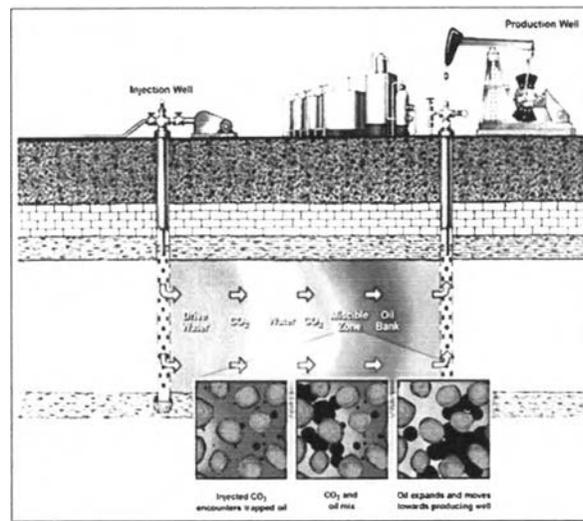


Figure 2.1 Illustration of carbon dioxide and water used to flush residual oil in reservoir (<http://energy.gov/fe/science-innovation/oil-gas-research/enhanced-oil-recovery>).

However, there are some problems for CO₂ injection in EOR, especially the high mobility of CO₂ in reservoir, the occurrence of viscous fingering and the gravity segregation (Saputra *et al.*, 2013). Generally, CO₂ is injected in reservoir as a supercritical fluid but density and viscosity are lower than water and crude oils. This can lead to the mobility issues and makes the displacement front unstable, as shown in Figures 2.2 and 2.3. CO₂ can grow from displacement front, and cause a breakthrough (Figure 2.3 (a)). Moreover, lower density of CO₂ tends to move to the upper zone, known as gravity override (see Figure 2.3 (c)). In heterogeneous reservoir, supercritical CO₂ will flow in high permeable paths. This can make CO₂ lose contact with oil in lower permeable zones (see Figure 2.2) (Talebian *et al.*, 2013).

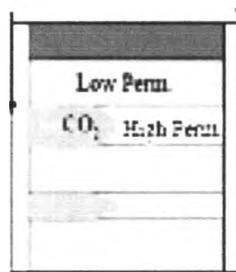


Figure 2.2 Supercritical CO₂-EOR conformance issue (Talebian *et al.*, 2013).

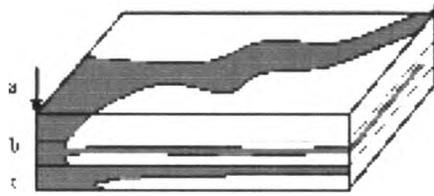


Figure 2.3 Supercritical CO₂-EOR mobility issues: (a) Poor area sweep, (b) Gas channelling, (c) Gravity override (Talebian *et al.*, 2013).

Due to all those challenges from gas injection, foam is considered to be one of alternation of EOR. Since foam has higher effective viscosity than gas, foam can reduce viscous fingering and gravity override (Yan *et al.*, 2006). The following section describes more about foam.

2.2 Foam

Foam is a gas phase that is dispersed and separated by a liquid phase. Foam is used in many industries such as foods, detergency, care products and so on. In petroleum industry, foam is occurred in some petroleum processes, for example, oil well drilling fluid and foam in-situ generation for enhanced oil recovery process. The dispersed phase (gas) is defined as an internal phase, whereas the continuous phase is referred to the external phase. A two-dimensional slice of a general foam system is shown in Figure 2.4. Foam structure is the gases that are separated from liquid thin films by a two dimensional interface. The lamella is defined as the region that includes the thin film, interphases and the junction between those lamellae. The conjunction of three lamellae at an angle of 120° is called the Plateau border (Schramm, 1994).

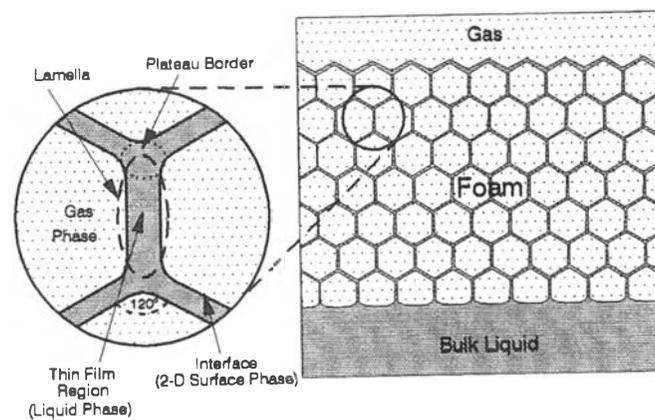


Figure 2.4 A generalized foam system (Schramm, 1994).

2.2.1 Surfactant

In order to generate foam, surfactant is needed as a foam agent. Surfactant is a material that can lower the surface tension of liquid. They contain one part that has an affinity for a nonpolar media like hydrocarbon chain and the other part that has an affinity for a polar media like water as shown in Figure 2.5. These molecules are at interfaces, which each part resides in the fluid that has greatest

affinity for each part (Schramm, 1994). Surfactants can be divided according to their polarity: nonionic surfactants, anionic surfactants, cationic surfactants and zwitterionic surfactants. Surfactant molecule will stay between gas and liquid interface in foam structure. Because many factors has an impact on foam stability.

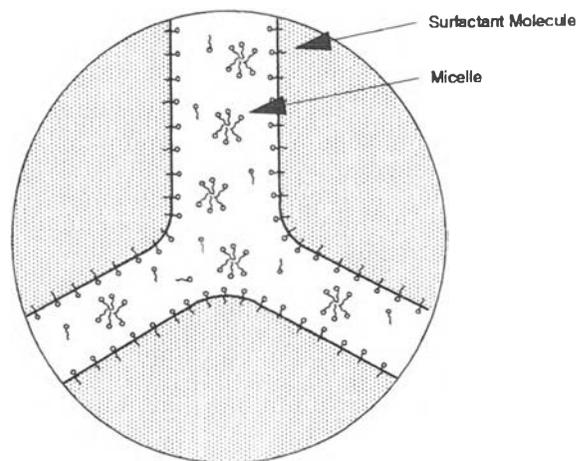


Figure 2.5 Surfactant molecules in a foam lamella. This size of the surfactant molecules compared to the lamella is not reasonable just for the purpose of illustration (Schramm, 1994).

2.2.2 Type of Surfactants

2.2.2.1 Anionic Surfactants: The most common hydrophilic groups are carboxylates, sulphates, sulphonates and phosphates. Anionic surfactants are used widely in industrial application.

2.2.2.2 Cationic Surfactants: The most common surfactants are the quaternary ammonium compound. They mostly are compatible with inorganic ion and nonionics but they are incompatible with most anionics.

2.2.2.3 Amphoteric Surfactants: This type of surfactant contains both cationic and anionic groups. The most common are N-alkyl betaines. The characteristics of amphoteric surfactant are depending on the pH solution. If they are in acid solution, they behave like cationic surfactant. Amphoteric surfactants referred to zwitterionic sometime.

2.2.2.4 Nonionic Surfactant: The most common surfactants are based on ethylene oxide (Ethoxylated surfactants). They are compatible with other types of surfactants.

2.2.3 Micelle

If the concentration of these surfactant molecules are increased, the formation of aggregate will be formed as micelles which their hydrophobic part forms a core of the aggregate and their hydrophilic part contacts with the aqueous medium. The concentration which micelles formed is significant. It is called the critical micelle concentration (CMC) (Schramm, 1994). When the concentration of surfactant is increased, the interfacial tension will decrease until it reaches CMC, which is lowest level of interfacial tension. Beyond the CMC, the increasing of concentration does not reduce interfacial tension (Khosravi, 2010). Figure 2.6 illustrates the increase of concentration corresponding to the surface tension.

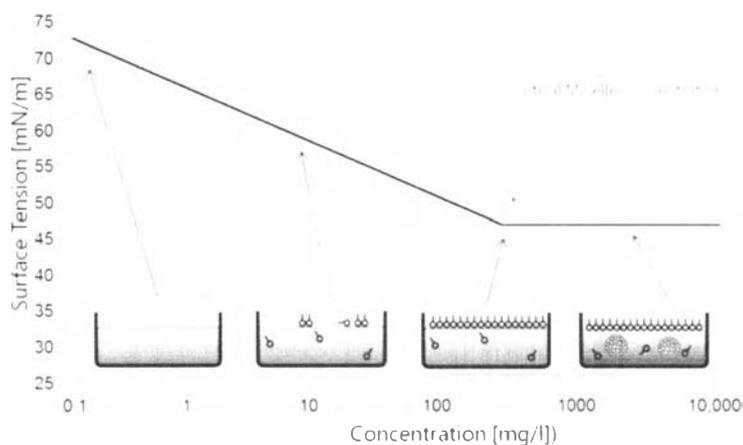


Figure 2.6 Surface tension with increase of concentration solution and micelle formation (<http://www.kruss.de/services/education-theory/glossary/cmc/>).

2.3 Foam Stability

Foam films are surrounded by gases. Foaming agents are needed to reduce the interfacial tension and increase interfacial area while minimizing energy. Foam can be considered as metastable dispersion. The definition of foam stability can be considered as film thinning and coalescence (film rupturing). In film thinning, bubbles are closed together and separated by the liquid-films but the bubbles do not touch each other. Coalescence is the bubbles that are fused together and become bigger and as a result the decreasing total surface area (Schramm, 1994). There are some factors that impact on foam stability such as gravity drainage, capillary suction, viscosity, and force attraction and chemical concentration. Even when foam applied in reservoir, the presence of crude oil and severe condition can decrease foam stability. These are the reasons why the foam stability test is required in order to find longevity of foam and find the right surfactant to use in EOR application.

There are several methods to perform the foam stability test. For example, The Bartch method (shaking) and the Ross-Miles method. For the shaking method, surfactant solution will be poured into a glass cylinder and shaken vigorously to create foam. In Ross-Mile Method, surfactant solution is poured from upper vessel through the orifice to standard vessel below with the same solution located in vessel (Rosen *et al.*, 2012). Foam is produced in the vessel. According to Lunkenheimer *et al.* (2003) the set up of foam stability test constitutes of a glass column with a frit glass at the bottom for gas distribution. The syringe is connected to the bottom of column to introduce a certain amount of gas into the solution to create foam. Figure 2.7 illustrates the schematic of this set up.

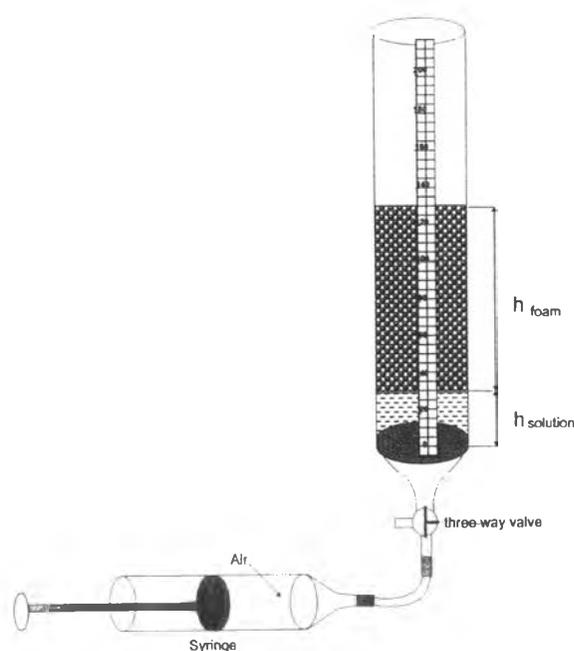


Figure 2.7 The schematic of foam stability apparatus.

There are a number of techniques to evaluate foam stability such as observing the change of foam height as a function of time or measuring time at foam ruptured to half of the initial foam height ($t_{1/2}$). Lunkenheimer *et al.* (2003) had introduced a parameter to determine the foam stability called R5. This parameter indicates the ratio of foam height at 5 minutes to the initial height. The Equation (2.1) is shown below.

$$R5 = \frac{h_5}{h_0} 100 \quad (2.1)$$

h_5 = foam height at 5 minutes

h_0 = the initial foam height

Belhaj *et al.* (2014) had also performed a foam stability test to screen foamability and foam stability of many surfactants by using the R5 method. The different concentration for each surfactant and the presence of oil were studied in their research.

Lunkenheimer *et al.* (2010) introduced two novel parameters to characterize different stages of the foam decay, namely the time of deviation (t_{dev}) and time of transition (t_{tr}). Gas is introduced into the test solution in a column to create foam. The height of the foam/air (h_f) and the height of solution/foam (h_s) boundaries were measured as a function of time. The apparatus and variables required for determining the foam stability are shown in Figures 2.8 and 2.9.

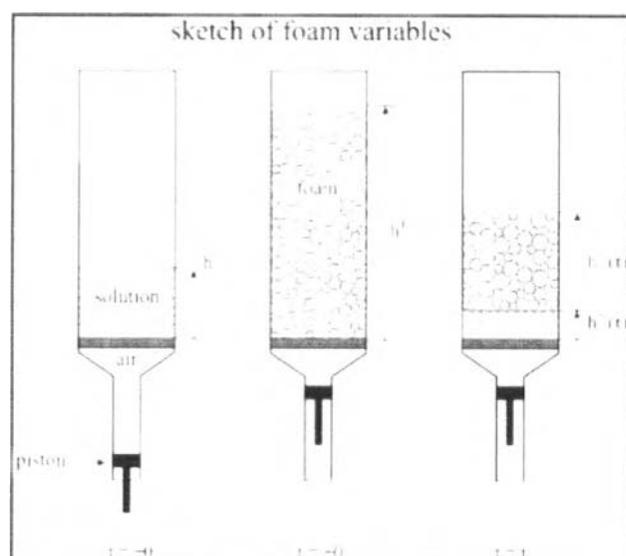


Figure 2.8 Vertical sectional view of the foam test apparatus used in the measurement (Lunkenheimer *et al.*, 2010).

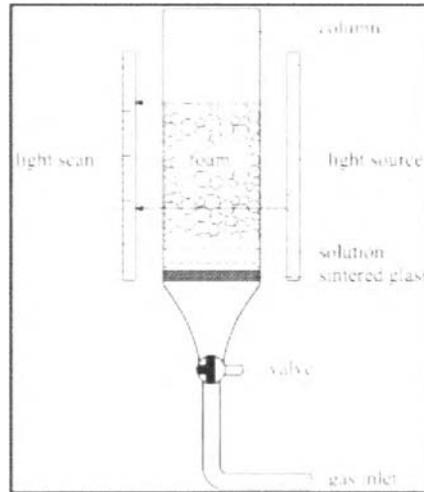


Figure 2.9 Illustration of height measurement at several times to determine the novel foam stability parameters. At $t = -0$ denotes as a condition before introducing gas. $t = +0$ denotes as heights of foam and solution after introducing air. And $t = t$ is foam height during foam decay (Lunkenheimer *et al.*, 2010).

The heights of foam were measured to determine the corresponding variations of foam's and of solution's volume with time. The Equations (2.2) and (2.3) are shown below:

$$\Delta h^F(t) = h^F(+0) - h^F(t) \quad (2.2)$$

$$\Delta h^S(t) = h^S(t) - h^S(+0) \quad (2.3)$$

The Equations (2.4) to (2.6) shows three different as follows:

(1) initial stage:

$$\Delta h^F / \Delta h^S = 1 \quad \text{and/or} \quad \Delta h^F - \Delta h^S = 0 \quad (2.4)$$

(2) transitional stage:

$$\Delta h^F / \Delta h^S > 1 \quad \text{and/or} \quad \Delta h^F - \Delta h^S > 0 \quad (2.5)$$

(3) final stage

$$\Delta h^F / \Delta h^S \gg 1 \quad \text{and/or} \quad \Delta h^F - \Delta h^S \gg 0 \quad (2.6)$$

t_{dev} indicates the end of the initial stage while t_{tr} means the transition from the initial stage to the final stage, which is characterized by the maximum rate of rupture. To distinguish the stability of foam: $t_{tr} < 10$ s is the unstable foam, $t_{tr} > 10$ s is the stable foam and if $t_{tr} > 100$ s, foam is very stable.

There are some factors that impact on foam stability such as gravity drainage, capillary suction, viscosity, and force attraction and chemical concentration. These are a number of reasons why the foam stability test is required in order to find longevity of foam when apply in a reservoir. Several reserches have studied the foam stability.

Andrianov *et al.* (2012) studied the effect of oil on longevity of foam and conducted foam stability test by measuring the foam height in a glass column. Surfactants used in this experiment were alpha olefin sulfonate (AOS), sodium dodecyl sulfate (SDS), fluorochemical (FC) and perfluoroalkyl betaine (FS), listed in Table 2.1.

Table 2.1 Properties of the surfactants used in the work (Andrianov *et al.*, 2012)

Surfactant	Supplier	Active Content (%)	Charge	Note
AOS-1	Stepan	40	Anionic	AOS-1 and AOS-2 have different molecular weight
AOS-2	Shell chemicals	40		
SDS	Fischer	90	Anionic	-
FC-1	3M	25	Nonionic	FC-1 and FC-2 have different molecular weight
FC-2		25		
FS-1	Dupont	27	Zwitterionic	FS-1 and FS-2 have different molecular weight
FS-2		40		

In the absence of oil, SDS showed the highest stability. In the presence of alkane, oils with a higher carbon number affect the foam stability less than those with lower carbon number. In this case, n-pentane led to the destruction of foam. The combination between AOS and FC gave the most stable foam in the presence of oils. In the presence of crude oils, oils with highest viscosity caused less damage to foam stability. For core flood experiment, CO₂ was injected after water flooding and then surfactant solution (AOS+FC) was injected into the core. Next, surfactant solution and N₂ were co-injected to create foam. The results showed that gas breakthrough was observed after gas injection. Total recovery was 61 % of OOIP by water flooding and CO₂ injection. The recovery by surfactant and N₂ plus surfactant co-injection were 2 % and 15.3 % of OOIP respectively. Total recovery up to 78.3 % of OOIP compare to only gas injection. This experiment also performed N₂ foam by injecting N₂ and surfactant (AOS+FC) after water flooding and surfactant injection. Most oil production was recovered within the first PV (pore volume) of foam

injection. They also suggested that bulk foam experiment should be performed at first to screen the surfactants.

Simjoo *et al.* (2013) studied the foam stability of different types of surfactant: C₁₄₋₁₆ alpha olefin sulfonate (AOS) from Stepan, cocoamido propyl hydroxysultaine (Petrostep SB, Stepan), alkyldiphenyloxide disulfonate (Dowfax 8390, DOW) and C₁₂₋₁₅ alcohol-7EO-sulfonate (Enordet, Shell). They studied the effect of different type of alkane on surfactant and the effect of surfactant concentration. Foam column set-up was used for screening study as show in Figure 2.10. Foamscan instrument was used to characterize the foaming properties of selected surfactant obtained from the screening study. The schematic of the foamscan set-up is shown in Figure 2.11.

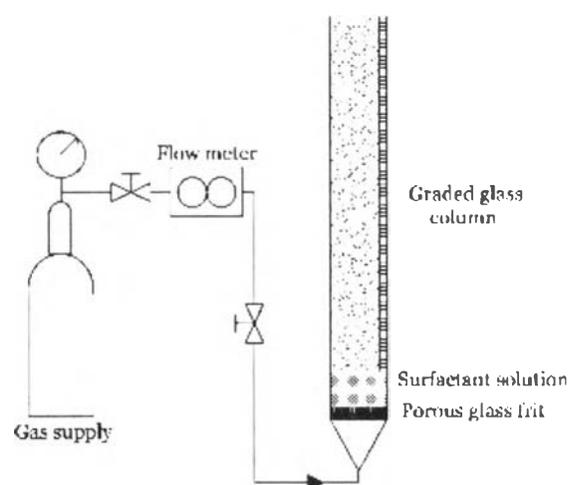


Figure 2.10 Schematic of foam column set-up used to screen surfactant. Gas is purged through the surfactant solution to create foam in a glass column (Simjoo *et al.*, 2013).

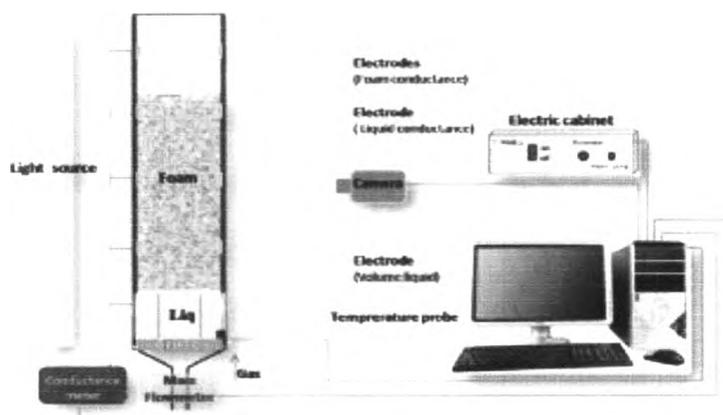


Figure 2.11 Schematic of Foamscan set-up. Camera is set to determine the foam volume and conductivity data will give liquid volume in the foam structure (Simjoo *et al.*, 2013).

The results showed that petrostep SB gave the highest foam stability in the absence of oil but AOS was the most stable foam in the presence of oil. AOS was used in the next experiment in the presence of alkane, $n\text{-C}_6$, $n\text{-C}_{10}$ and $n\text{-C}_{16}$. In the presence of $n\text{-C}_6$, AOS gave the least stable foam which concluded that the shorter hydrocarbon chain give a higher tendency of alkane to destroy the foam. Surfactant concentration also affected the foam stability. Increasing the surfactant concentration from 0.1 to 1.0 wt% resulted in an increase of foam stability.

Foam stability test was performed in Lee *et al.* (2014) by shaking glass cylinder filled with SDS surfactant solutions 20 times. The foam height was measured as a function of time. The surfactant solutions containing swollen micelle (micelle with solubilized oil) were compared with the foam without oil. The result showed that the foam with swollen micelle gave the decrease rate in foam height more than without swollen micelle.

Vikingstad *et al.* (2005) performed static foam tests and studied the effect of concentration, the presence of oil, alcohol, salt concentration and the variation of oil polarity. They observed the height of foam column as a function of time after

mixing. AOS surfactant was used in all experiment. They found that foam could be generated even below CMC. Increase in surfactant concentration also resulted in increase in foam height. Molecular weight of hydrocarbon related to foam stability. Shorter alkanes would solubilize in micelles and destabilize foam while the larger alkanes stabilized foam. In 2006, Vikingstad *et al.* (2006) continued a study and compared fluorinated surfactant (FS-500) with alpha olefin sulfonate (AOS) by performing a static foam experiment. They found that surfactant concentration had an effect on foam generation. In the presence of oil, FS-500 surfactant gave very stable foam. For AOS surfactant, short chain alkanes tended to destroy the foam stability but long chain alkanes gave stable foam. For FS-500 surfactant, there was more foam with pentane than other alkanes.

Saputra *et al.* (2013) studied the effect of surfactant concentration on the foam stability of CO₂ foam, the swelling effect of CO₂ in the crude oil and also with interfacial tension of the crude oil. In the experiment, C14-16 alpha olefin sulfonate (AOS) and TMN-6 which is polyglycol were used. The results showed that foam stability was better when surfactant concentration was higher for both surfactants. But TMN-6 gave better stable foam in higher temperature. At the same concentration and temperature, TMN-6 gave lower IFT than AOS. At high temperature, TMN-6 gave more stable foam.

Farzaneh *et al.* (2015) studied foam behavior and divided their work into three parts. The first part was to study the effect of concentration and the ability of different surfactants to create foam. The second part was to study two different gases (N₂ and CO₂) to generate foam in the presence of oil and the last was to investigate the effect of different alkalis on foam stability. They concluded that anionic surfactant gave the better foam stability and there was an optimum concentration to generate the most stable foam. N₂-foam also had better foam stability compared to CO₂-foam. Adding an appropriate alkaline could increase foam stability. Adding NaOH in the presence of oil resulted in the decrease in foam stability whereas Na₃CO₃ in the presence of oil increased foam stability. However, adding borate gave the highest increase in foam stability.

Beside foam stability test, there are some research studied surfactants used in EOR. Chen *et al.* (2012) introduced surfactants that can be soluble in CO₂ and stabilize CO₂/water foams at 120 °C in the presence of concentrated brine. Ethoxylated amines were introduced which are switchable from being nonionic in CO₂ to cationic in the presence of an acidic aqueous phase. In low pH aqueous phase, the positively charged protonated amine makes surfactant more hydrophilic and leads to a raise in cloud point. Cationic head group also reduces adsorption on limestone. They concluded that the variation of the degree of ethoxylation was flexible to meet significant criteria for CO₂-EOR at high temperature. An appropriate number of EO groups gave a maximum aqueous solubility. In this research also characterized foam strength and foam stability by the apparent viscosity in sand pack column. Ethoxylated with 2EO groups was shown to stabilize C/W (CO₂/water) foam in high brine. Barnes *et al.* (2008) investigated two families of surfactants, internal olefin sulfonates (IOS) and branched C16, 17 alcohol based alkoxy sulfonates. They conducted phase behavior tests. The results showed that IOS could be used and covered a wide range of salinity at higher temperature. For surfactant based on a branched C16, 17 alcohol, they concluded that this family of surfactant had a promise for higher salinity and containing hard water in reservoir. The following table (Table 2.2) shows the summary of various surfactant structure from several researches.

Table 2.2 Summary of various surfactant structures

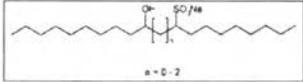
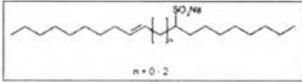
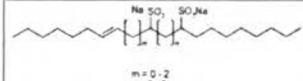
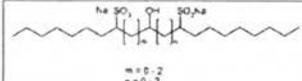
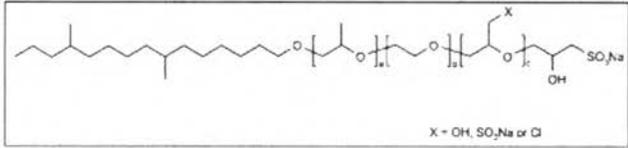
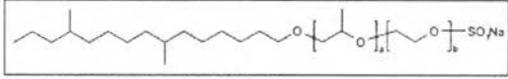
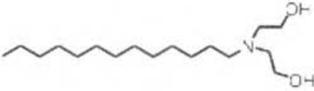
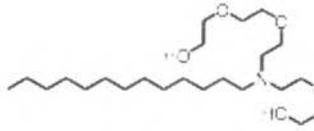
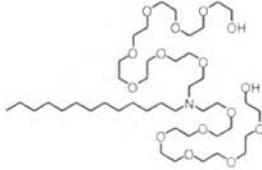
Surfactant Structure	Reference
<p>• IOS</p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;">  <p>Hydroxy alkane sulfonate $n = 0-2$</p> </div> <div style="text-align: center;">  <p>Alkene sulfonate $n = 0-2$</p> </div> </div> <div style="display: flex; justify-content: space-around; margin-top: 10px;"> <div style="text-align: center;">  <p>Olefin disulfonate $m = 0-2$ $n = 0-2$</p> </div> <div style="text-align: center;">  <p>Hydroxy disulfonate $m = 0-2$ $n = 0-2$</p> </div> </div>	Barnes <i>et al.</i> (2008)
<p>• Alcohol based alkoxy sulfonate</p> <div style="text-align: center; margin-bottom: 10px;">  <p>Branched C16, 17 alcohol-PO-EO-glycidyl sulfonate $X = \text{OH}, \text{SO}_3\text{Na or Cl}$</p> </div> <div style="text-align: center;">  <p>Branched C16, 17 alcohol-PO-EO-sulfate</p> </div>	Barnes <i>et al.</i> (2008)
<p>• Ethoxylated amine</p> <div style="display: flex; justify-content: space-between; align-items: center; margin-bottom: 10px;"> <div style="text-align: center;">  </div> <div style="text-align: center;">$\text{C}_{12-14}\text{N}(\text{EO})_2$</div> </div> <div style="display: flex; justify-content: space-between; align-items: center; margin-bottom: 10px;"> <div style="text-align: center;">  </div> <div style="text-align: center;">$\text{C}_{12-14}\text{N}(\text{EO})_5$</div> </div> <div style="display: flex; justify-content: space-between; align-items: center;"> <div style="text-align: center;">  </div> <div style="text-align: center;">$\text{C}_{12-14}\text{N}(\text{EO})_{15}$</div> </div>	Chen <i>et al.</i> (2014)

Table 2.3 Summary of surfactants that give the most stable foam in the presence of oil in each work

Surfactant	Oil	Type	Reference
FS-500	Oil	Zwitterionic	Vikingstad <i>et al.</i> (2006)
AOS+FC (1:1)	Alkane	Anionic, zwitterionic	Andrianov <i>et al.</i> (2012)
AOS	Alkane	Anionic	Simjoo <i>et al.</i> (2013)

Table 2.3 tabulates different surfactants that give stable foam in the presence of oils. However, it depends on the type of oils to choose suitable surfactant to generate stable foam. The combination between two types of surfactant can be considered to use as foam agent.

As mentioned above, foam has been applied in EOR to overcome many disadvantages from gas flooding and increase oil recovery production. Because the property of foam such as high viscosity and density can increase sweep efficiency and prevent gas channeling or gravity override. However, the stability of foam is still a major concern when it is applied in the reservoir. To find the appropriate surfactant as a foam agent, foam stability test is needed as a preliminary screen. Surfactants with different types and structures may give different foam stability. Furthermore, the introduction of co-solvent and co-surfactant may help to improve the foam stability when foam is in the presence of oil or brine.

The objectives of this thesis were: (1) to study the foam stability generated from different surfactant system structures; (2) to investigate the effect of concentration, different carbon chain lengths of alkane and high concentration of brine; (3) to improve foam stability in the presence of alkane and brine by introducing co-surfactant (nonionic surfactant) and co-solvent (long chain alcohol).

The scope of this thesis was as follows:

Scope of Objective 1: Six surfactants were studied. Foam stability tests were performed by shaking glass cylinder contained surfactant solution to generate foam.

Scope of Objective 2: Two surfactants that gave stable foam were selected to study. Critical micelle concentration (CMC) of both surfactants was measured as a reference concentration. Foam stability test was performed by purging gas through the glass column to generate foam. For the effect of concentration, five concentrations of each surfactant were varied. Three different carbon chain lengths of alkanes were used and the concentration of brine was 5 and 10 wt %.

Scope of Objective 3: Two nonionic surfactants and long chain hydrocarbon were added to surfactant system before performing foam stability test.