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Separation of Water-in-Heavy Oil Emulsions Using Porous Particles in Coalescence Column

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Separation of Water-in-Heavy Oil Emulsions Using Porous Particles in Coalescence
Column

by

Yanghong Liu

A THESIS

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ABSTRACT

Separation of water from water-in-heavy-oil (W/O) emulsions has been a costly problem. Due to the high viscosity of heavy oil, increasing the temperature of the emulsion has been one of the most common methods of separating water from W/O emulsions. The other methods include adding demulsifiers and using coalescence media. For the treatment of water in oil emulsions, providing a strongly water-wet coalescing media is the key for the coalescence of water droplets when the oil is the continuous phase. Various pack materials and methods have been tested for coalescence media by many researchers with no success due to the fact that water-wet material packed in a coalescence column is not able to remain water-wet in a heavy oil environment.

In this study the principle of capillarity and the mechanism of wetting film in porous media are applied in designing the coalescence media. Water-wet porous particles are used for the first time in the coalescing column to enhance the separation of water from water-in-heavy-oil emulsions. Experimental results of this study show this type of particles can remain water-wet in an oil environment and can significantly enhance the coalescence of water droplets in water-in-heavy-oil emulsions. The coalescing column test results show that the flow of the emulsion through the 10 cm coalescing column reduced water content from 44.37% to 21.54% (51% reduction) at 80°C, without using demulsifier. This result indicates that the coalescing column is effective in helping water droplets coalesce. The results also demonstrate that the coalescing column can reduce the water content beyond what was reached in gravity separation with a high dosage of

demulsifier. At a fixed temperature of 80°C, and with a settling time of 4 hours, when the dosage of the selected demulsifier changed from 50 to 100 to 150 ppm, water content reached 10.49%, 1.32% and 0.64%, respectively, with the use of a 10 cm coalescing column. Using the coalescing column reduced water content in the heavy oil by 38%, 89%, and 93%, compared to the water contents reached in the separation with demulsifier dosages of 50, 100, and 150ppm, respectively, without using the column. These results indicate that the effect of adding a coalescing column to water separation is significant, as compared to just using a demulsifier in gravity separation. More importantly, flow through the coalescing column could reduce the water content in the heavy oil to a very low level (<1.0%) and, at the same time, reduce the consumption of demulsifier.

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DEDICATION

To my mother, Chundi Dai, and my father Jianguo Liu, who always give me all their supports.

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CHAPTER ONE: INTRODUCTION

Crude oil is seldom produced alone; it is generally commingled with water, which creates a number of problems during oil production (Abdel-Khalek et al, 1999). Produced water occurs in two ways: either as free water (i.e. the water that settles out fairly rapidly) or in the form of emulsions – dispersions of water droplets in oil.

Emulsions are difficult to treat and cause a number of operational problems, such as the surging in separation equipment in gas-oil separating plants, the production of off-spec crude oil, and the creation of high pressure drops in flow lines. Emulsions have to be treated to remove the dispersed water and associated inorganic salts, in order to meet crude specifications for transportation, storage and export, and to reduce corrosion and catalyst poisoning in downstream processing facilities (Abdel-Khalek et al, 1999).

Emulsions can be encountered in almost all phases of oil production and processing (Chen and Hsiao, 1999): inside the reservoirs, well bores and well heads, wet crude handling facilities, transportation through pipelines, crude storage and during petroleum processing. Most recent research tends to look at the characteristics, occurrence, formation, stability, handling and breaking of produced oilfield emulsions (Akbarzadeh et al, 2004). This dissertation provides a review of crude oil emulsions and demulsification. However, this research has been somewhat limited to the experimental oilfield emulsions at a laboratory, which simulates the well head at wet crude handling facilities.

1.1 Research Background

The water-in-crude-oil emulsion of heavy oil is generally a thermodynamically unstable system (Moatadid et al, 2007); however, additives can be used to provide the necessary kinetic stability (Gondelaz, 2007). The stability of water-in-crude-oil emulsions depends, in part, on the irreversible adsorption of asphaltenes at the oil-water interface. Asphaltenes can create a steric barrier around the water droplets, which prevents coalescence and hinders the separation of water from the emulsion (Yarranton et al, 2007). The natural surfactants in the crude oil, such as colloid, asphaltenes, naphthenic acid and clays, can absorb on the water-oil interface and form a steric barrier (Hey and Symonds, 2001). Particularly, heavy oil with a high content of colloid and asphaltenes can form a very stable reticular formation barrier (Tian et al, 2000).

Due to the high price of crude oil, unconventional oils, such as oil sands and extra heavy oils, which were not considered as oil reservoirs decades ago, are more in demand (Baydak 2008). However, unconventional oil production is a less efficient process and has greater environmental impacts than that of conventional oil production (Kokal and Wingrove, 2000); it is an expensive process to break the water-in-oil emulsion. Thus, it proves more and more important to search for effective techniques to reduce the environmental impacts of unconventional oil production. Therefore, it looks promising to find a new, but easy, method to treat produced water-in-oil emulsions from heavy oil or extra heavy oil fields, not just to help reduce the energy cost (McLean & Kilpatrick, 1997)

Ideally, before produced fluid from an oil field is transported to the oil refinery, the impurities (such as basic sediment, solution gas, solution salt and water) in the fluid must be removed (Moses, 1984; Ng, 1980). Generally speaking, high concentrations of water, salt and basic sediment can damage the refinery equipment, corrode the equipment and pipes, and poison the catalyst (Xia et al, 2002).

In the oil industry, the typical basic sediment and water limit of produced oil is from 0.5% to 3.0% depending on location and the typical salt limits are 10 to 25 pounds of salt per thousand barrels (100-400ppm) (Ken & Maurice, 1998). Removing the water from the water-in-heavy-oil emulsion is a high-energy-consumption process (Abdel-Khalek et al, 1999; Basu 1993; Bhardwaj and Hartland 1994), which accounts for a large percentage of the cost in the oil production process (Schramm, 1992).

Serious treatments are required to break the water-in-oil emulsion and accelerate water separation. Along with gravity separation, heating, and centrifuge and hydro cyclone separation, chemical treatment with demulsifiers (surface active agents) remains the most common process for breaking emulsions, although this technique is not always competitively effective. Above all, an optimization is much preferred, although laboratory and field research is much needed.

1.2 Research Objectives

Water-in-oil emulsions are common during heavy crude oil production, oil sands extraction processes and oil spills in aquatic environments (Basu, 1993; Strassner, 1968). There has been much research discussing how to apply a coalescer to coalesce dispersed

droplets in oil-water emulsions (Buzzacchi et al, 2006)

However, there is limited research that applies the process to a real-world problem (Kokal and Al-Juraid, 1998). Beyond that, there is a lack of new technologies that can tackle emulsions economically and environmentally (Tambe and Sharma, 1993; Tian et al, 2000; Yarranton et al, 2007). This thesis focuses on the new technology for the coalescence of the concentrated water-in-oil emulsions.

In relation to the heavy oil and heavy oil production processes at the present time, some oilfields in China and Canada are producing heavy oil or extra heavy oil. Some of the produced fluid from these oil fields is water-in-oil emulsions (Chang and Fogler, 1993). If attention is paid to the treatment process of this produced fluid, one will find that the separation cost is the largest fraction of the operating expenses. According to a small survey from existing oilfields (Kokal and Juraid, 1999), battery operators showed that demulsifier concentrations at heavy oil batteries ranged from 200 to 333 ppm (1L/5m³ to 1L/3m³); heating costs were also considerable. Some heavy oil batteries heat their pressurized treating vessels to 130°C. The water-in-oil emulsion is around 30% Wt. (Renouf, 2001). Thus, it is much more meaningful to find a new method to treat the water-in-oil emulsion.

The primary objective of this research is to test the idea of using a porous particle in the coalescence column for separating water from water-in-heavy oil emulsions. A mechanical method, which uses a coalescer column, is applied in this research. During the last two years, this author focused mainly on how to make use of a coalescer column

to break the water-in-oil emulsions. A coalescer column is a pipe filled with some sort of porous packing material, which aids in the coalescence of the dispersed droplets of an emulsion. A series of experiments have been conducted to demonstrate that the dispersed phase can coalesce at the same wetting material. The key point is to determine the long term effect of coalescence material on breaking the emulsions by employing a new coalescer column to remove water and basic sediment from produced heavy oil emulsions at a laboratory scale.

1.3 Thesis Structure

This thesis is separated into five chapters, i.e. Chapter One through Chapter Five:

Chapter 1 offers a brief introduction covering Research Background, Research Objectives and Thesis Structure.

Chapter 2 presents the basic concepts needed to understand water-in-crude oil emulsions. First, crude oil emulsion is introduced. Next, the dynamics of emulsions and their stabilization are described. Then, the factors and breaking mechanism that affect the stabilities of water-in-oil emulsions are discussed. From there, the coalescence mechanism is discussed, and a way of how to find the material which is the most effective for coalescence is briefly introduced. Finally, past research on emulsions and/or demulsification is widely reviewed.

Chapter 3 describes the experimental design, equipment, experimental steps and sample materials required to achieve the proposed objectives. This includes a description of the material selected as coalescing media, the crude oil properties tested, and of the

instruments used for testing the water contents of the samples. Experimental techniques for emulsion preparation are also introduced.

Chapter 4 concentrates on several series of experiments in this research. It, firstly, introduces the setting of the experiments, secondly, summarizes the results in tables and then depicts research results graphically and finally focuses on analyses of the long term effects of varying kinds of water-wetting materials.

Chapter 5 summarizes the experimental findings of this research, provides a qualitative review of emulsion and demulsification, and, finally, presents some beyond-the-experiment-result recommendations for future research and practices.

CHAPTER TWO: LITERATURE REVIEW

In this chapter, crude oil properties are briefly reviewed, with a strong focus on heavy oil. The factors affecting the stability of emulsions will be discussed, and mechanisms involved in demulsification will be introduced. The final two parts will provide several demulsification methods and past research on the separation of water-in-oil emulsions.

Crude oil is a mixture of hundreds of thousands of different hydrocarbons, as well as other components such as sulphur, nitrogen, oxygen, containing compounds and sometimes organometallics at low concentrations (Gruse, 1960). The composition of crude oil varies according to the origin of the crude oil, which can be classified in several ways. It can be classified its physical properties (e.g. specific gravity, viscosity), elemental composition (e.g. amount of carbon, hydrogen, sulphur, nitrogen), carbon distribution, distillation curve, the nature of the residue after distillation (e.g. paraffinic, naphthenic, aromatic, asphaltic), or solubility class (SARA fractionation into saturates, aromatics, resins and asphaltenes). For example, the classification into conventional oil, heavy oil, or bitumen is based on physical properties, as indicated with the UNITAR classification shown in the Table 2.1 (Gray, 1994).

Table 2.1 UNITAR classification of oils by their physical properties at 15.6°C (Gray.1994).

	Viscosity (mPa·s)	Density (kg/m ³)	API Gravity (API)
Conventional Oil	<10 ²	<934	>20
Heavy Oil	10 ² ~10 ⁵	934~1000	10~20
Bitumen	>10 ⁵	>1000	<10

2.1 Emulsion

An emulsion is a heterogeneous system which contains two immiscible liquids, with one dispersed as droplets in the other (Laurier, 1992). One phase is the droplet (or discontinuous) phase and the other is the external (or continuous) phase. For the water-in-oil emulsion, the water phase is the discontinuous phase and the oil phase is the continuous phase. The boundary between these phases is called the interface.

Due to high interface area between the two phases, the emulsion system is a thermodynamically unstable system, which has very high interface energy (McKelier and Wardlaw, 1982). In this system, a dispersion of one liquid in another will minimize its free energy by reducing the total interfacial area per droplet. Small droplets will connect with each other and coalesce to form larger droplets, until they form into two single phases. But, most emulsion systems have kinetic stability, which is demonstrated by a resistance to this breakdown. A third component in the emulsions provides the long term stability (Kokal, 2002). Such additives included: simple inorganic electrolytes; natural resins and other macromolecular compounds; finely divided, insoluble solid particles

located at the interface between the two phases; and, amphiphilic or surface-active materials (Tian et al, 2000; Yarranton et al, 2007).

2.1.1 Crude oil emulsion classification

A crude oil emulsion can be classified into three broad groups (Sunil, 2002):

- 1) Water-in-oil (W/O): the water-in-oil emulsions consist of water droplets in a continuous oil phase. In the petroleum industry, water-in-oil emulsions are more common (most produced oilfield emulsions are this kind of emulsion). A water-in-oil emulsion is shown in Figure 2.1
- 2) Oil-in-Water (O/W): the oil-in-water emulsions consist of oil droplets in a continuous water phase. An oil-in-water emulsion is shown in Figure 2.2.
- 3) Multiple or complex emulsions: multiple emulsions are more complex and consist of tiny droplets suspended in bigger droplets, which are suspended in a continuous phase. For example, a water-in-oil-in-water (W/O/W) emulsion consists of water droplets suspended in larger oil droplets, which in turn are suspended in a continuous water phase. A W/O/W emulsion is shown in Figure 2.3.

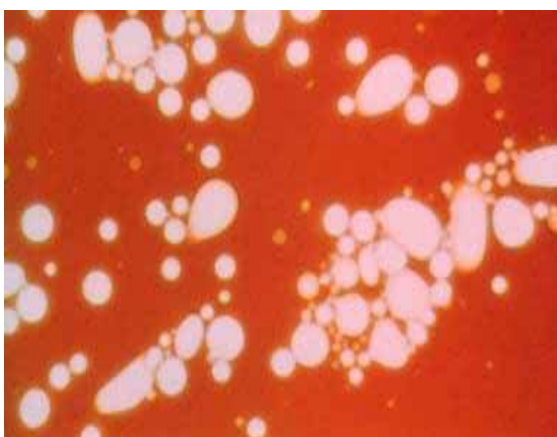


Figure 2. 1 Water-in-Oil Emulsions (Kokal, 2002)

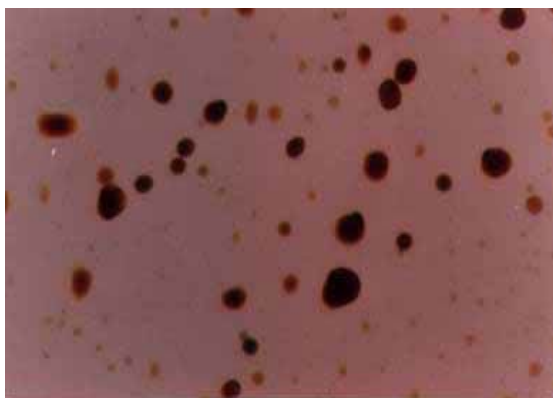


Figure 2. 2 Oil-in-Water emulsion (Kokal, 2002)

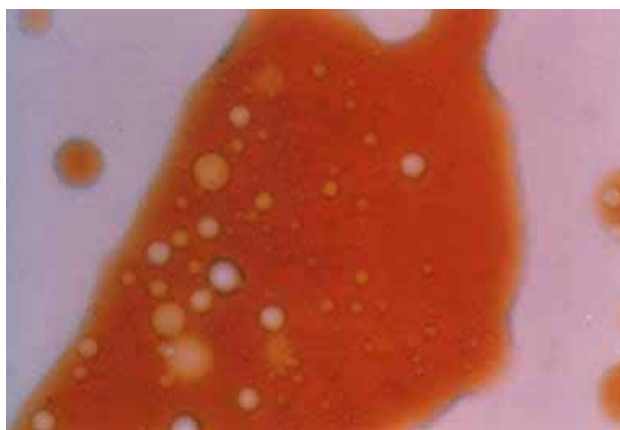


Figure 2. 3 Water-in-Oil-in-Water Emulsion (Kokal, 2002)

The formation of stable emulsions needs a surface active agent as an emulsifier, in combination with mechanical shear. The emulsifying agent, or surfactant, has two main functions (Walstra, 1993): first, to allow emulsion formation and, second, to provide stability to the emulsion. The mechanical shear is required to create dispersed droplets in the first place. For example, Figure 2.4 illuminates the four mechanisms to form the emulsions by the different additives.

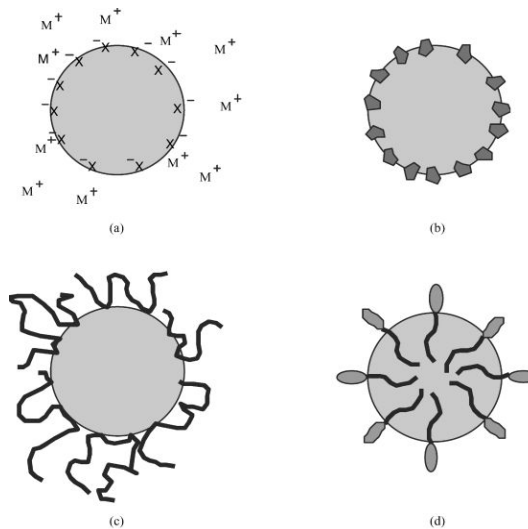


Figure 2. 4 Mechanisms for the Stabilization of Emulsions (Drew, 2006).

(a) Adsorbed ions—specific-ion adsorption; (b) Solid particles; (c) Colloidal sols—adsorption of polymer chains; (d) Surfactants—amphiphile adsorption.

2.2 Stability of Emulsions

From a purely thermodynamics point of view, an emulsion is an unstable system. This is because there is a natural tendency for a liquid-liquid system to separate and reduce its interfacial area and, hence, its interfacial energy.

There are several factors which affect the stability of water-in-oil emulsions: the emulsifying agent, viscosity, specific gravity, water percentage, emulsion age and agitation. (Richard, 1992)

- 1) Emulsifying agent: When people consider how stable the emulsion is, the emulsifying agent is the primary factor. Only with an emulsifying agent can the stable emulsion be formed. In other words, a stable emulsion cannot exist without an emulsifying agent. Several materials can cause the formation of stable oilfield emulsions, such as asphaltenes, clays, and various types of salt and finely divided solid particles.
- 2) Viscosity: the viscosity of a liquid is its resistance to flow. When people treat high viscosity oil, more time is required for the water droplets to coalesce and settle out than in the case of an oil of low viscosity.
- 3) Specific Gravity: if the dispersed liquid and the continuous liquid have a significant gravity difference, it is easier for the droplets to come out of the emulsion than if the specific gravities of the two phases are similar. For instance, in a water-in-oil emulsion, heavy oil (one with high specific gravity) tends to keep water droplets in suspension longer in than oil with low specific gravity.
- 4) Water percentage: in general, water-in-oil emulsions with high water percentages tend to form less stable emulsions. In some industries, people put water into the emulsions to make the emulsion unstable, or to change water-in-oil emulsions to oil-in-water emulsions.

- 5) Age of Emulsions: If an emulsion is produced into a tank and not treated, a certain amount of water will settle out by gravity and coalescence. Unless some form of treatment is used to accomplish a complete breakdown, there will be a small percentage of water left in the oil, even after extended settling.
- 6) Droplet size: Because of the random nature of the various types of energy causing emulsions in oil well systems, the droplet size of the dispersed phase varies considerably. Droplet radii from 1 micron to several hundred microns have been measured in a single emulsion, with a wide range of intermediate droplet sizes present. The importance of droplet size is apparent when it is realized that, to promote emulsion breaking, the smaller droplets must collide with other small droplets to form larger droplets, which then settle more rapidly. The collision incidence rate must be very high. In an emulsion with 20% of the water existing with a 50 micron radius, droplets must collide with each other or other larger/smaller droplets to form big droplets. The complete separation of very small droplets from an emulsion cannot be reasonably expected.
- 7) Temperature: Temperature can affect emulsion stability significantly. Temperature affects the physical properties of oil, water, interfacial films, and surfactant solubility in the oil and water phases. These, in turn, affect the stability of the emulsion. Perhaps the most important effect of temperature is on the viscosity of emulsions; it decreases with increasing temperatures. This decrease is mainly due to a decrease in the oil viscosity. When waxes are present (crude below its cloud point) and are the source of emulsion problems, application of heat can eliminate the emulsion problem

completely by dissolving the waxes into the crude oil. Temperature increases the thermal energy of the droplets and, hence, increases the frequency of drop collisions. It also reduces the interfacial viscosity and results in a faster film drainage rate and enhanced drop coalescence. The effect of temperature on interfacial films was studied in some detail (Jones et al, 1978). It was shown that an increase in temperature led to a gradual destabilization of the crude oil/water interfacial films (Jones et al, 1978). However, even at higher temperatures, a kinetic barrier to drop coalescence still exists. Temperature influences the rate of build-up of interfacial films by changes in the adsorption rate and characteristics of the interface. It also influences the film compressibility by changes in the solubility of the crude oil surfactants in the bulk phase. Slow degassing (removal of light ends from the crude oil) and aging leads to significant changes in the interfacial film behavior at high temperatures. The films generated by this process remain incompressible and non-relaxing (solid films) at high temperatures and emulsion resolution is not affected by heating.

2. 3 Demulsification

Much research has been done in terms of demulsification (e.g., Tambe and Sharma, 1993; Tian et al, 2000; Yarranton et al, 2007; Gonzalez, 2009). In the oil industry, crude oil emulsions must be separated almost completely before the oil can be transported and processed further (Xia 2003; Jiang et al 2008). Emulsion separation into oil and water involves the destabilization of emulsifying films around water droplets. This process is accomplished by any one or combination of the following methods (Schramm, 1992;

Tambe and Sharma, 1993):

- 1) Reducing the flow velocity that allows gravitational separation of oil, water (and gas). This is generally accomplished in large volume separators and desalters.
- 2) Adding chemical demulsifiers.
- 3) Increasing the temperature of the emulsion.
- 4) Applying electrical fields that promote coalescence.
- 5) Changing the physical characteristics of the emulsion.

Due to the wide variety of crude oils, brines (and hence emulsions), separation equipment, chemical demulsifiers and product specifications, demulsification methods are very application specific (Kokal and Sayegh, 1995; Kokal, 2003). Furthermore, emulsions and conditions change over time and add to the complexity of the treatment process (Kokal and Sayegh, 1995; Kokal and Wingrove, 2000; Kokal, 2003). The most common methods of emulsion treatment have been the application of heat and an appropriate chemical demulsifier, to promote destabilization, followed by a settling time to allow gravitational separation to occur (Kokal and Wingrove, 2000; Kokal, 2003).

2.3.1 Thermal Methods

Heating the emulsion enhances its breaking or separation (Kokal and Sayegh, 1995; Kokal, 2002). It reduces the viscosity of the oil and increases the water settling rates. Increased temperatures also result in the destabilization of the rigid films, due to reduced interfacial viscosity. Furthermore, the coalescence frequency between water droplets is

increased due to the higher thermal energy of the droplets. In other words, heat accelerates the emulsion breaking process. However, very rarely does it resolve the emulsion problem alone. Increasing the temperature has some negative effects. First, it costs money to heat the emulsion stream. Second, it can result in the loss of light ends from the crude oil reducing its API gravity and the treated oil volume. Finally, increasing the temperature leads to an increased tendency towards scale deposition and an increased potential for corrosion in treating vessels.

Application of heat for emulsion breaking should be based on an overall economic analysis of the treatment facility. The cost effectiveness of adding heat should be balanced against longer treatment time (larger separator), loss of light ends and a resultant oil-product price, chemical costs and the costs of installation of electrostatic grids or retrofitting (Kokal, 2003).

2.3.2 Mechanical Methods

There is a wide variety of mechanical equipment available for the breaking of oil-field produced emulsions (Kokal and Sayegh, 1995; Kokal, 2003). These include free water knock out drums, two and three phase separators (low and high pressure traps), desalters and settling tanks. These vessels separate the free water and break emulsions.

2.3.3 Electrical Methods

High voltage electricity (electric grids) is often an effective means of breaking emulsions (Carale et al, 1994). It is generally theorized that water droplets have a charge associated and, when an electric field is applied, the droplets move about rapidly and collide with

each other and coalesce. The electric field also disturbs the interfacial rigid film by rearranging the polar molecules, thereby weakening the tight film and enhancing coalescence. The electrical system consists of a transformer and electrodes that provide high voltage alternating-current. The electrodes are placed in such a way so as to provide an electric field that is perpendicular to the direction of flow. The distance between the electrodes, in some designs, is adjustable so that the voltage can be varied to meet the requirement of the emulsion being treated.

Electrostatic dehydration is rarely used alone as a method of breaking emulsions; it is generally used in conjunction with chemical and heat addition (Carale et al, 1994). Invariably, the use of electrostatic dehydration will result in a reduction of heat addition. Lower temperatures result in fuel economy, reduced problems with scale and corrosion formation and reduced light-ends loss. Electrostatic grids can also lead to a reduction in the use of emulsion breaking chemicals.

2.3.4 Chemical Methods

By far, the most common method of emulsion treatment is adding chemicals called demulsifiers (Chen, 2008). These chemicals are designed to neutralize the effect of emulsifying agents that stabilize emulsions. Demulsifiers are surface active compounds and, when added to the emulsion, they migrate to the oil-water interface and rupture or weaken the rigid film and enhance coalescence of water droplets (Bhardwaj and Hartland 1994).

Optimum emulsion breaking with a demulsifier requires:

- 1) A properly selected chemical for the given emulsion.
- 2) Adequate quantity of this chemical.
- 3) Adequate mixing of the chemical in the emulsion.
- 4) Sufficient retention time in emulsion treaters to settle water droplets.
- 5) The addition of heat, electric grids, coalescers, etc to facilitate or completely resolve the emulsions.

Selection of Chemical: Selection of the right demulsifier is very crucial in the emulsion breaking process (Jones et al, 1978). The selection process for chemicals is still viewed as an art rather than a science. However, with an ever increasing understanding of the emulsion breaking process, the availability of new and improved chemicals, new technology and R&D efforts, selection of the right chemical is becoming easier and more organized, and many of the failures have been eliminated (Chen, 2008; Jiang et al 2008).

Demulsifiers are chemicals that contain solvents (benzene, toluene, xylene, short-chain alcohols, heavy aromatic naphtha), surfactants, flocculants and wetting agents. The demulsifiers act by total or partial displacement of the indigenous stabilizing interfacial film components (polar materials) around the emulsion droplets (Kokal and Wingrove, 2000). This displacement also brings about a change in properties, such as the interfacial viscosity or elasticity, of the protecting film, thus, enhancing destabilization. In some cases the chemicals (demulsifiers) act as a wetting agent and alter the wettability of the stabilizing particles, which leads to a breakup of the emulsion film (Xia 2003; Chen, 2008; Jiang et al 2008).

Testing procedures are available to select appropriate chemicals (Jones et al, 1978; Kokal and Wingrove, 2000). These tests include bottle tests, dynamic simulators and actual plant tests. All test procedures have limitations. There are hundreds of Commercial Demulsifier products available that may be tested. Add to this the changing conditions at the separation facilities; this results in a very slow selection process, especially at larger facilities. It is, therefore, important at such facilities to maintain a record of operational data and testing procedures as an on-going activity (Xia 2003; Xia and Cao 2002; Chen, 2008).

Dosage: The amount of chemical added is also important (Kokal and Wingrove, 2000). Too little demulsifier will leave the emulsion unresolved. On the other hand, a high dosage of demulsifier (an over treat condition) may be detrimental to the treatment process. Since demulsifiers are also surface active agents, like the emulsifiers, an excess quantity of demulsifier may also produce very stable emulsions. In this case, the demulsifier simply replaces the natural emulsifiers at the interface (Xia 2003; Jiang et al 2008).

Due to the wide variety of chemicals available as demulsifiers, the different types of crude being handled, the choice of separation equipment and the variations in product qualities, it is difficult to prescribe "standard" or typical dosage rates for treating emulsions (Jones et al, 1978; Kimbler et al, 1966). Furthermore, some of the chemicals come in different concentrations (active ingredient in a carrier solvent). The amount or dosage of demulsifier required is very site specific and depends on a number of factors. Based on an evaluation of the literature, the demulsifier rates quoted vary from less than

10 ppm to more than 100 ppm (based on total production rates). These numbers are provided for primary or secondary oil recovery emulsions. During tertiary oil recovery (especially during surfactant or micellar flooding), demulsifier rates can be typically in the thousands of ppm and higher in extreme cases (Chen, 2008).

2.3.5 Coalescence

Coalescence is the second step in the demulsification process and follows flocculation (Figure 2.5). During coalescence water droplets fuse, or coalesce, together to form a larger drop. This is an irreversible process that leads to a decrease in the number of water droplets and, eventually, to complete demulsification (Bobra, 1990; Schramm, 1992). Coalescence is enhanced (Bobra, 1990; Schramm, 1992; Tambe and Sharma, 1993) by a high rate of flocculation, the absence of mechanically strong films, high interfacial tensions, low oil and interfacial viscosities, high water cuts and high temperatures.

2.4 Past Research on Coalescence as Demulsification Method

Coalescence implies that two or more single droplets or small particles merge and make a single new larger drop (Basu, 1993). During coalescence, two droplets approach each other, as depicted in Figure 2.5, due to convection of creaming. As they approach each other, their surface may deform and create planar surfaces between the two droplets (Figure 2.5a). At the same time, the liquid between the two droplets starts to drain, allowing the droplets to approach even closer (Figure 2.5b). During drainage, the surface material spreads and gaps with less interfacial material being formed on the surface. Bridges between droplets can form from the gaps (Figure 2.5c) and then the fusion of the

two droplets can occur (Figure 2.5d).

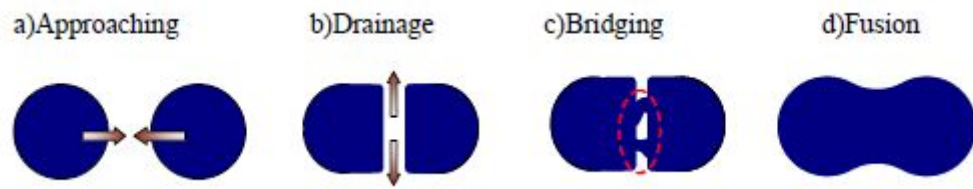


Figure 2. 5 Steps in Coalescence (Kokal, 2002)

An important fact in coalescence is that the total surface area can be reduced, or compressed, when a large particle is formed from the fusion of smaller particles (Hiemenz & Rajagopalan, 1996). In order to achieve the coalescence of emulsified water droplets in water-in-crude oil emulsions, the stabilizing material on the interface, such as asphaltenes, solids, resins, waxes and natural surfactants, should be replaced or removed to make weaker films in order for coalescence to occur. It is believed that (Gonzalez, 2009) (a) surfactants form reversible films and destabilize emulsions and (b) surfactants maintain the irreversible adsorption at the interface and could enhance emulsion stability.

The first stage of the development of porous coalescers involved mainly experimental testing and was concerned with specific applications. Most of the contributions were documented in the patent literature. A review of some of the earlier patents has been presented by Sherony et al. (1978). A survey of patents is also available (Langdon and Wasan, 1979). Many materials have been suggested for use as porous coalescers: glass fibres, glass spheres, Teflon, polyethylene, etc.

In the second stage, systematic experiments were performed to investigate the effects of various factors on the performance of porous coalescers. The investigations were mainly qualitative in nature. Voyutskii et al. (1953, 1958) investigated, among other things, the effect of wettability on coalescence; they claimed that intermediate wettability was the most effective in separating a water-in-oil emulsion. Gudesen (1964) used cotton and glass wool to break oil-in-water emulsions. He found that complete separation was achieved when the flow rate was below a certain critical value. Vinson and Churchill (1970) used fine mesh screens to study the coalescence of organic-in-water emulsions.

They varied the interfacial tension, and found that the separation efficiency dropped sharply at low interfacial tension values. Moreover, they reported that the performance was insensitive to the viscosity of the dispersed phase. In the work by Sarcen et al. (1966), among other things, bed depth was varied. It was concluded that a long bed enhanced the degree of coalescence. However, no suggestions were made as to what should be the optimal bed depth. A long bed requires a higher pumping cost.

Bitten (1970), in his visualization study of the coalescence of water droplets on single fibres, observed the presence of chain-like structures, consisting of individual water droplets piling one on top of another. Bitten and Fochtman (1971) were the first to measure the distribution of the dispersed phase in a porous coalescer. Results indicated that the highest retention occurred at the inlet face of the coalescer, followed by a sharp decrease. This was later confirmed by Spielman and Su (1977), who used X-ray absorption techniques to measure the dispersed phase saturation. Hazlett (1969a, b) examined a number of parameters in the breakdown of water-in-aviation fuel emulsions. Included were surfactant concentration, fibre size and material, bed depth, packing density, water content and the flow velocity of the continuous phase. Hazlett (1969a, b) found that efficiency was not raised by increasing the bed depth beyond a certain length. In beds composed of two different-sized fibres, the small fibres should precede the large ones for good separation. It was concluded that the downstream fibre size has a marked control on separation efficiency. Additionally, the surfactants were found to interfere with drop release from the outlet face of the coalescer by limiting droplet growth prior to detachment from the bed.

Jeater et al. (1979) and Davies (1980) reported that phase inversion might occur at the coalescer outlet, forming a liquid membrane structure which would break down to produce a swarm of very small droplets of the dispersed phase. This, of course, has an adverse effect on the subsequent separation by gravity.

Mose and NG (1984) conducted research where a two-dimensional photo etched glass flow cell was used to observe the process by which an emulsion was broken down by a granular porous coalescer. The effects of wettability, emulsion and collector zeta potentials and emulsion droplet size on the coalescence phenomenon were studied. The possible use of a graded medium or a coalescer with mixed wettability to enhance the coalescence process was also examined. It was found (Mose and NG, 1984) that:

- 1) A less negative, or even positive, collector zeta potential is preferred in order to obtain a higher rate of adhesion.
- 2) A higher surface-to-volume ratio would also enhance the rate of adhesion. This is in agreement with other investigations (Voyutskii et al., 1953, 1958).
- 3) The observation that blob size did not grow much beyond the size of a pore chamber lends support to the conclusion (Hazlett, 1969a, b) that increased bed length might not lead to better separation. Hence, the coalescer should be just long enough to form blobs; any extra length simply incurs a higher pumping cost and does not result in any improvement in separation efficiency.
- 4) In case a graded medium is used, small pore chambers should precede the larger ones (Hazlett, 1969a, b).

- 5) The wettability at the outlet of the coalescer should be no wetting to the dispersed phase (Jeater et al., 1979).

For over three decades, the Saskatchewan Research Council (SRC) and the University of Regina have applied this technique to break water-in-oil emulsions (Renouf et al., 2007) in studies where the coalescer column was applied to the treatment of wellhead emulsions. Renouf et al (2007) claims that a literature survey on the subject of coalescer and resolving crude oil emulsions is deceptive because a number of researchers use the word coalescer, but apply it to plate separators or pipes with no packing. The Saskatchewan Research Council restricted their use of the term of coalesce to a pipe filled with some sort of porous packing material that aids in the coalescence of dispersed droplets of an emulsion.

In a review of the literature on coalescing media, Stocker et al. (1988) listed the many types of packing materials that have been tested. These fall into the categories of fixed media, granular packing and fibre packing. The materials range from high-tech oleophilic plastic fibres to such exotic packing materials as granulated black walnut shells. Some of the more common packing materials tested include glass, fibreglass, peat, coal, sand and polyethylene fibres (Stocker et al., 1988a; Viraraghavan and Mathavan, 1989; Stocker et al., 1988b; Chambers, 1979; Chambers and Walker, 1980; Hughes, 1987; Jeffreys, 1978).

As indicated by Renouf et al.(2007), of the hundreds of papers published in the area of using porous media to coalesce dispersed droplets of oil-water emulsions, very few apply

to real-world problems. A huge portion dealt with oil-in-water emulsions and, typically, with dilute oil concentrations. Many studies on water-in-oil emulsions employed synthetic emulsions, and often use simple, oils such as kerosene, diesel or mineral oils, rather than crude oils. The few studies that have examined resolving oilfield-derived emulsions include very early studies on light crude oil emulsions (Burtis and Kirkbride, 1946; Hayes et al., 1949; Stocker et al. 1988a,1988b). Stocker et al. (1988b) tried to separate similar feedstocks to water-in-oil emulsions of heavy crude oils (12°API). Their tests on five kinds of coalescer packings (mesh and fibre-based) were unsuccessful.

The nature of the wettability of the packing materials is a matter of some disagreement in the literature. Madia et al. (1976) concluded that oleophilic packing best coalesces oil droplets. Other studies have shown that neutral wettability packings yield the highest success (Mose and NG, 1985). Still others claim that packings composed of “mixed media”—oleophilic and hydrophilic materials in the same bed—have a symbiotically enhanced success (Stocker et al., 1988b; Davies et al., 1972; Sokolovic, 1992). Their studies over the course of a decade showed that the packing should have the same wettability as the dispersed phase. Of the materials they tested—red rock from three different locations, fibreglass, polypropylene, coal, sand, lava rock, carbon granules, zorball (a commercial oil-absorbing mineral) and crusher dust—the most effective was a certain red rock which can maintain its water-wet character (Renouf et al., 2007). For instance, regarding the SRC’s research on coalesce column, Renouf et al. (2007) claimed in their study (over 100 tests were performed and 24 pairs of tests compared the treating effects with and without the column) that the coalescer column was very successful at

improving water removal from heavy oil battery emulsions (Figure 2.6). According to Renouf et al., every one of their 24 tests showed an improvement in water content when the coalescer column was incorporated into the flow loop. The use of the column improved BS&W measurements after 4 hours of settling time by an average of 38%

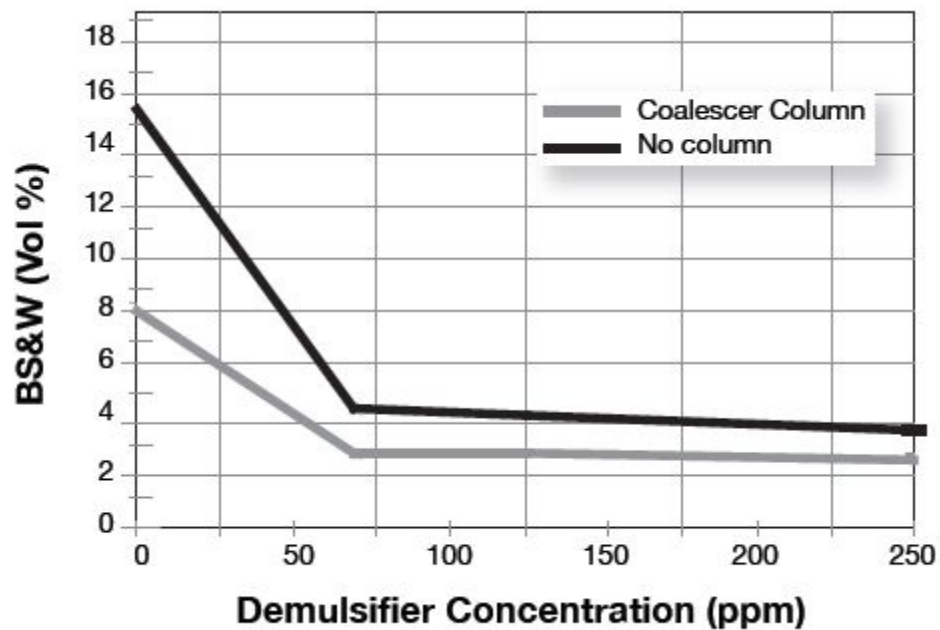


Figure 2. 6 Effect of Demulsifier Concentration on Water Removal (Sunil, 2002)

Incorporating the coalescer column suggests that operators may be able to reduce both temperatures and demulsifier concentrations (Viraraghavan et al, 1988; Scoular et al., 1996; Renouf et al., 1998; Kurucz et al, 2002, Renouf et al, 2007) . In their laboratory replication of the field operating conditions, oil containing equal or less water was obtained with the coalescer column. It was found by Renouf et al. (2007) that equivalent

treating could be obtained when a coalescer column is added and faster treating also occurred with the coalescer column in their study. They concluded that (a) a coalescer column could significantly reduce demulsifier concentrations and possibly reduce temperature as well, and (b) water droplet size measurements suggested that adding the column would speed treating greatly.

It has also been suggested that the effects of column length, column packing size, temperature, flow rate, demulsifier concentration and water addition were investigated in this study (Renouf et al., 2007):

- 1) Longer columns improved treating, but also increases the pressure drop across the column.
- 2) Higher flow loop temperatures are most effective when no demulsifier is used. When demulsifiers are added, many tests showed that lower temperatures treated more effectively. No tests were made on whether the settling temperature could be reduced.
- 3) The effect of flow rate is not conclusive. On average, the moderate flow rate dewatered most effectively, but this varied inconsistently with demulsifier concentration and column temperature.
- 4) Incorporating the column allows a much lower concentration of demulsifier to be used.
- 5) Adding produced water into the pipe loop along with the emulsion does not improve the effectiveness of the coalescer.

In short, in the line of investigation of a coalesce column, SRC's impressive laboratory tests in the past two decades, along with other researchers' work in the past seven decades, indicated that demulsifier concentration impacts the optimum column temperature and flow rate, and so the column will need to be individually tailored to the treating facility. It is strongly recommended that, with these excellent preliminary but convincing results, further tests on coalescer column should consider among other things: (a) to field test a coalescer column for treating heavy oil emulsions, (b) the column could be placed between a free water knockout and treating vessel, (c) the column will need to be individually tailored to the treating facility, and (d) more investigations on the long-term running of the column and how this affects the wettability of the packing are needed.

If the equilibrium contact angle of the dispersed drop in the presence of a continuous phase is less than $\sim 30^\circ$, wetting of the entire disk favors the formation of a thin dispersed phase film around it. Subsequently, dispersed droplets coalesce on this thin film to form a liquid pool at the downstream end of the disk (Basu, 1993).

If the equilibrium contact angle of the dispersed drop in the presence of the continuous phase is between 50° and 90° and the dynamic contact angle is also not too large, the disk is partially covered by adhered dispersed phase drops. These drops move while clinging to the periphery of the disk and coalesce amongst themselves at the back stagnation point, forming a liquid pool at the downstream end of the disk (Basu 1993).

Basu (1993) suggests that if the equilibrium contact angle of the dispersed drop in the presence of a continuous phase is greater than 140° , there is neither thin film formation

nor drop attachment on the disk surface and no coalescence or accumulation of the dispersed phase is observed at the downstream end of the disk. Basu (1993) also suggests if dispersed droplets can coalesce on the porous coalescer, dispersed droplets should be wetting the porous coalescer. Otherwise, the dispersed phase can form a thin film around the porous coalescer; the dispersed droplet cannot coalesce on the porous coalescer surface. Basu (1993) further suggests that if the equilibrium contact angle of the dispersed drop in the presence of a continuous phase is less than $\sim 30^\circ$, wetting of the entire disk favors the formation of a thin dispersed phase film around it. Subsequently, dispersed droplets coalesce on this thin film to form a liquid pool at the downstream end of the disk (Basu 1993).

A change of wettability results in redispersion of the coalesced dispersed phase into larger droplets (Basu 1993; Aske & Sjoblom, 2002). An appropriate fiber material can be chosen for a particular dispersion system to get high coalescence efficiency, provided that the collision between the collector and the dispersion takes place (Basu 1993).

Anklam (1997) did some experiments on emulsion flow through fibrous mats. The experiments were fairly inconclusive, but did show that (1) fibrous mats can induce coalescence for concentrated emulsions and (2) both preferential wettability and surfactant type play key roles in the effectiveness of a fibrous mat coalescer. Difficulties were encountered in obtaining materials that would allow systematic studies, and a lack of any real understanding of the mechanistic factors that underlie emulsion stability was realized. It is also reported (Madia, 1976) that oil-wet packing materials provide better

coalescing media than water-wet materials for the treatment of oil-in-water emulsions.

A higher surface-to-volume ratio would also enhance the rate of adhesion (Moses and Ng, 1984). According to Moss & NG (1985), a number of techniques are available to break unwanted stable emulsions including: settling centrifugal, electrical and magnetically separations, and the use of chemicals and porous coalescers. There are some distinct advantages of porous coalescers over other existing methods; they have relatively low capital cost and allow for continuous operation. In a complete coalescence process, the emulsion is first passed through a coarse filter to capture any solid particles in the stream, otherwise the porous coalescer may get clogged (Kimbler et al., 1966; Kokal and Al-Juraid, 1998; Kokal and Juraid, 1999). The particle-free liquids are then pumped through the coalescer, in which the micrometer-sized, suspended emulsion droplets are coalesced to form bigger drops (Bobra, 1990; Brooks et al., 1998). The size of the exit drops becomes sufficiently large that they are susceptible to gravity separation. Reported applications of porous coalescers include the separation of water from aviation fuel (Bitten, 1970; Bitten and Fochtman, 1971), desalination of crude oil (Burtis and Kirkbride, 1946, Hayes et al., 1949), bilge water treatment (Douglas and Elliot, 1962), and the separation of emulsified oil (Sareen et al., 1966) and freon (Johnson, 1980) from water.

Despite its attractive features, the process is not completely understood, as has been repeatedly stressed by many researchers in this area (Spielman and Su, 1977; Sherony et al., 1978; Spielman and Goren, 1970). Considerable disagreement still exists concerning the mechanisms by which suspended emulsion droplets are coalesced and the movement

of the resulting larger drops through the coalescer.

Some development of porous coalescers, involving mainly experimental testing, was documented in the literature. For instance, a review of some of the earlier patents has been presented by Sherony et al. (1978; a survey of recent patents is also available (Langdon and Wasan, 1979)); Many materials have been suggested (e.g. Sherony et al., 1978) to be used as porous coalescers: glass fibers, glass spheres, Teflon, polyethylene, etc.

Some qualitative systematic experiments (e.g. Voyutskii et al. 1953, 1958; Gudesen, 1964; Vinson and Churchill, 1970) were performed to investigate the effects of various factors on the performance of porous coalescers.

Voyutskii et al. (1953, 1958) investigated, among other things, the effect of wettability on coalescence; they claimed that intermediate wettability was the most effective in separating a water-in-oil emulsion. Gudesen (1964) used cotton and glass wool to break oil-in-water emulsions. He found that complete separation was achieved when the flow rate was below a certain critical value. Vinson and Churchill (1970) used fine mesh screens to study the coalescence of organic in-water emulsions. They varied the interfacial tension, and found that the separation efficiency dropped sharply at low interfacial tension values. Moreover, they reported that the performance was insensitive to the viscosity of the dispersed phase.

CHAPTER THREE: EXPERIMENTAL

The aim of the experiments in this dissertation is to provide a basic understanding of the entire coalescence phenomenon. As will be seen below, the experimental conditions include design, equipment, steps and sample selection.

3.1 The Experimental Design

Factors which may influence the efficiency of coalesce and which will be tested in the experiments include the following:

- Temperature. In this thesis temperatures are fixed for experiments range from 60 °C, 70

°C, and 80 °C.

- Bed thicknesses. Coalescer bed thickness ranges from 10 cm to 20 cm.
- Dosages of demulsifier: Concentrations of demulsifier range from 0, 50, 100, 200 and 300 ppm.

3.2 The Oil Sample

In this research, Daqing Heavy Oil (Daqing, China) was used in all separation tests. As the Daqing oilfield enters its late production period for conventional oil, heavy oil exploitation in Daqing has been attracting more and more attention. According to the exploration prediction, the Daqing heavy oil resource is approximately 8×10^8 tons.

3.2.1 Properties of Daqing Heavy Oil

From Table 3.1 one can see that the density of crude oil at 20°C is 920.8kg/m³ and at 50 °C it is 900.6kg/m³. As for the density, the greater the density of the crude oil, the smaller

density differences between the oil and water, which will cause difficulties for the settlement of heavy oil dehydration. When the temperature is at 50 °C, the viscosity of the

crude oil is 235.6 mPa·s. Because the viscosity is larger than for ordinary crude oil, the gathering and transportation resistance will be increased. The crude oil can be characterized by the high density and high viscosity, which make it difficult to separate the water from the water-in-oil emulsion produced in the Daging Oil Field.

Table 3. 1 Properties of Daqing Heavy Oil Sample

Density @ 20°C, kg/m ³	920.8
Density @ 50°C, kg/m ³	900.6

Viscosity @ 50°C, mPa.s	235.6
Wax content, %	29.7
Colloid, %	28.70
Asphaltene content, %	0.24

Rheological measurements (using RS150 Rheology instrument) were also carried out for the purified Daqing heavy oil sample. The results are summarized in Table 3.2 and shown in Figure 3.1. The results show that over a lower temperature range, from 20 °C to 30 °C, the oil viscosity decreases with both temperature and shear rate; when the temperature reaches 30 °C, the oil viscosity continuously decreases with the increase of temperature but there is no apparent change in shear rate.

Table 3. 2 Results of Rheological Tests on Daqing Heavy Oil Sample

T(°C)	Shear rate 1/s (unit: mPa•s)					
	8	13	25	40	80	100
20	2759.0	2708.0	2592.0	2487.0	2279.0	1760.0
25	1683.0	1646.0	1584.0	1533.0	1433.0	1398.0

30	956.9	951.9	931.3	916.5	886.8	876.5
35	598.3	597.7	593.6	585.8	572.3	567.4
40	461.7	441.4	425.5	418.1	403.3	399.0
45	282.6	287.8	295.1	297.5	295.8	295.3
50	217.3	225.8	229.3	232.5	234.7	233.6
55	219.8	200.4	186.7	181.3	177.1	176.0
60	129.1	131.8	133.0	133.8	134.4	134.1
70	83.2	84.7	86.1	87.4	87.1	87.2
80	39.4	49.2	53.2	55.7	57.4	57.9

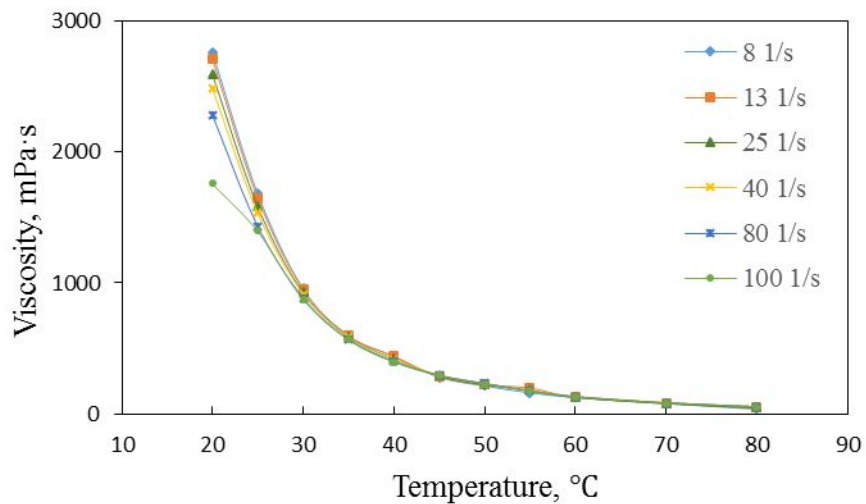


Figure 3. 1 Viscosity of Daqing heavy oil vs. temperature and shear rate

3.3 Verification of Coalescer Packing Material

After considering numerous materials (hard, soft, and porous, etc.), three materials are considered as candidates for coalescer packing materials: namely material A, B, and C (please refer to Figures 3.2, 3.3, and 3.4).

The purpose of the verification experiments is to find which out of the three candidates considered (i.e. A, B, and C) can better satisfy the porosity and the wettability requirements for the coalescer packing material. To achieve this purpose, several phenomena are to be clearly observed:

- 1) When the particles made from these materials are put into water, there are some small gas bubbles yielded from them; this should last a long time.
- 2) When the water saturated particles are first immersed in the heavy oil for 24 hours, and then contacted with water, the surface of them is clear; that is, after extended contact with heavy oil, the surface will not be contaminated.

3.3.1 *Experiment Procedure:*

- 1) Crush the three materials to obtain the 4 to 10 mesh packing particles.
- 2) Rinse the particles, using water, to remove fine particles on the surface to the particles.
- 3) Put the materials into the oven at 100°C, for 24 hours, to dry them.

4) Divide each of them into two groups (the experimental group and blank group) and place them in the beakers. Pour water into the beakers to immerse the particles completely (the water surface was 5 cm above the top layer of the particles). Observe the bubbling behavior of each packing material to determine if they are highly porous and water wet.

5) Keep the samples in water for 24 hours to make sure the particles are saturated with water. Then, pour the water out of the experimental sample breaker.

6) Add crude oil into the breakers and stir the oil and particles for at least for 10 minutes to make sure the surfaces of samples are contacted by the crude oil. Keep the oil and the particles at 60 °C for 24 hours.

Add water into the beakers and stir to make the water contact the particles. Observe and record the water-wet phenomenon of the particles.



Figure 3.2 Material A



Figure 3.3 Material B



Figure 3.4 Material C

3.4 Coalescence Flow Tests

The experimental set-up for separating water-in-heavy oil emulsions is shown in Figure 3.5. The set-up consists mainly of an oilfield emulsion tank, a coalescence column, a pump, a settling tank, and a water bath. Figure 3.6 shows the process of a water-in-oil emulsion through the coalescing and settling units. The emulsion is injected into the coalescence column from its bottom, where a fluid distributor is installed to make sure there is a uniform flow of the emulsion in the porous particle bed. The water droplets of the emulsion coalesce to form larger drops when the emulsion flows through the bed. After the mixture of the oil and water is transferred to the settling unit, oil and water separate by gravity.

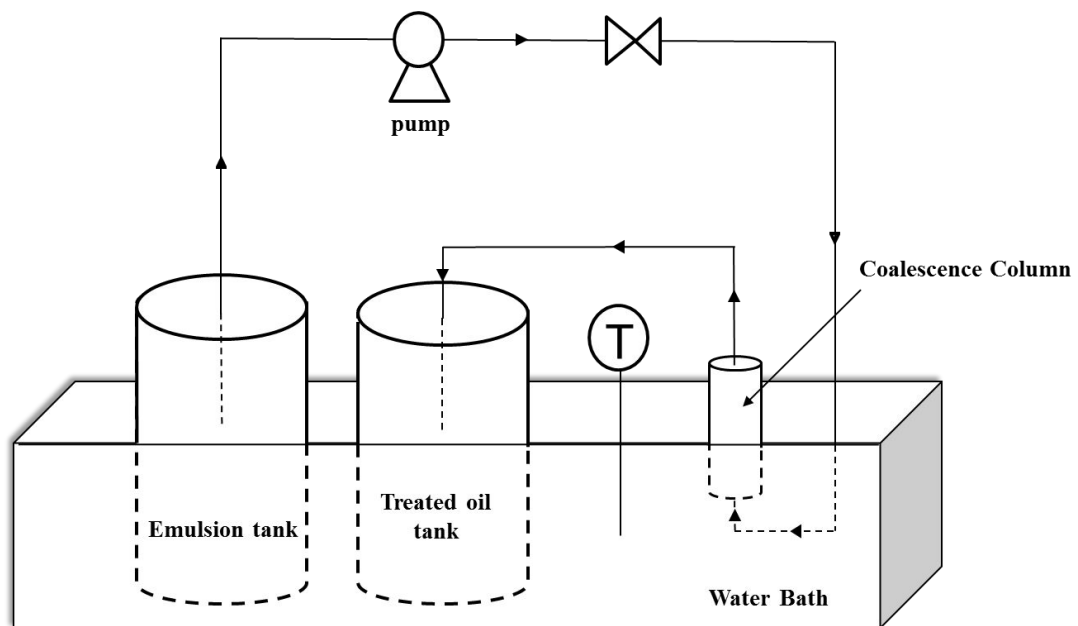


Figure 3.5 Schematic of experimental set-up

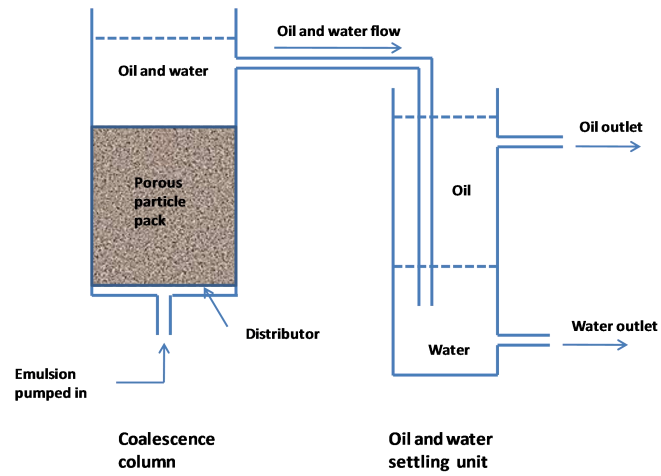


Figure 3. 6 Schematic of coalesce column and oil and water settling unit.

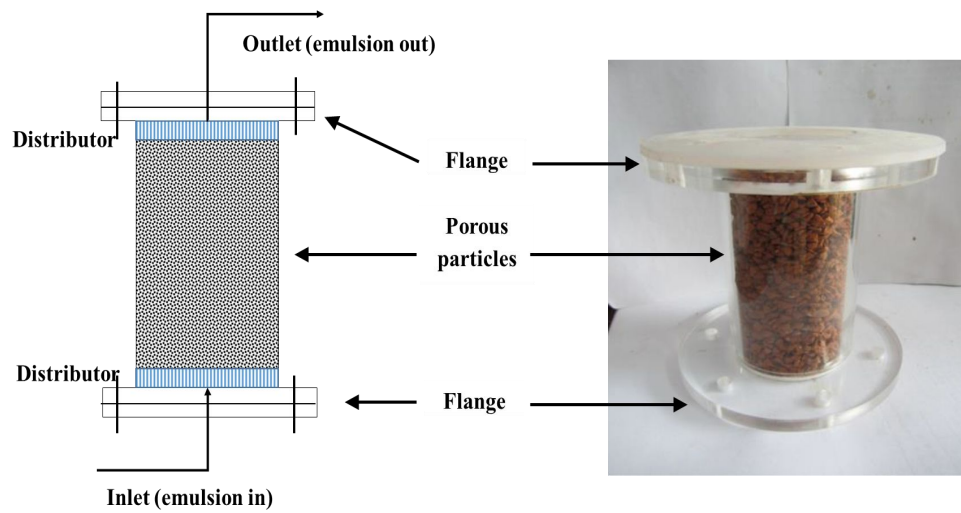


Figure 3.7 The coalesce column model

The details of the coalescence column are presented in Figure 3.7. The porous particles are tightly packed in the holder to form the coalescing column. Two distributors are used at inlet and outlet end of column to ensure a uniform flow of the emulsion through the pack.

3.4.1 Experimental Procedure

The procedure of the coalescence flow test includes the following steps:

1. Pack the coalescence column by adding water saturated porous particles into the bed holder, which is filled with water.
2. Connect the pump, emulsion tank, coalescence column, and settling unit.
3. Set the temperature of the water bath to warm up the emulsion, coalescence column and settling unit to a desired test temperature.
4. Pump 500 ml of the emulsion, at $1.0 \text{ cm}^3/\text{min}$, to flow through the coalescence column.
5. Keep the collected oil and water in the settling unit, at the same temperature, for 4 hours to allow water drop to settle by gravity.
6. Take an oil sample from the oil layer in the settling unit for determining water content of the oil.

3.5 Water Content Analysis

The water content in the oil after separation was analyzed using Dean-Stark method as shown in Figure 3.8.

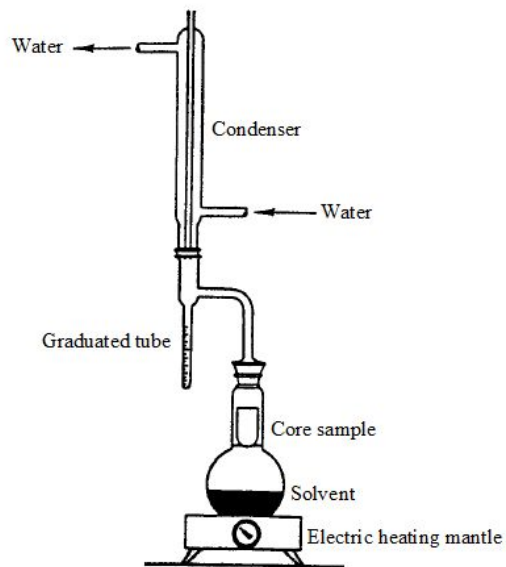


Figure 3. 8 Dean-Stark aparatus. (Dean, 1920)

The Dean-Stark apparatus is shown in Figure 3.8 (Dean, 1920). In the Dean-Stark analysis for water content in oil, the oil sample was mixed with the solvents (toluene) in the flask. The mixture was heated to vaporize the solvent and water. The vaporized solvent and water condensed in the condenser and was collected in the burette. From the water volume collected in the graduated tube (at the bottom) and the initial oil sample volume and the densities, the water content in the oil was determined.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Coalescing Material Selection

Heavy oil and oil sands are a key part of world's energy resources. However, these viscous crude liquids are tough to recover and difficult to treat. They are seldom produced alone; more often they are produced with water as water-in-oil (W/O) emulsions. Separation of the water from these emulsions has been a costly problem. Because of the high viscosity of heavy oil, increasing the temperature of the emulsion has been one of the most common methods of separating water from W/O emulsions. Other methods of separation include using demulsifiers and using coalescence media. Providing a large water-wet specific interface is the key for separating water in W/O emulsions through coalescence media. However, various packing materials and methods have been tested for coalescence media, by many researchers, with no success, largely due to the fact that water-wet material packed in the coalescence column is not able to remain water-wet in a heavy oil environment (Renoul, 2007). This is because the adsorption of the polar molecules in heavy oil into solid surfaces changes a water-wet surface to oil-wet one.

In this research, the principle of capillarity and wetting film phenomenon in porous media were applied to the coalescing material for W/O emulsion treatment. The idea is as follows: when the packing material (particles) is both water-wet and porous (containing many fine pores in them), and saturated by water prior to contacting heavy oil, these particles will remain water-wet in oil because the capillary forces keep the water phase

being networked between the water in fine pores inside the particles and the water films on particles' surfaces, as shown in Figure 4.1.

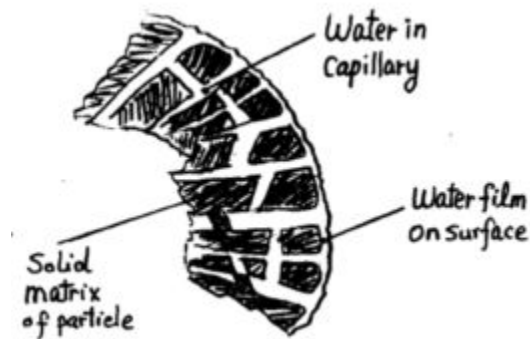


Figure 4. 1 Networked water covering particle surface

Several commercial water-wet porous powders, purchased from a manufacturer in Jiangsu, China, were tested. It was found that the pores of the particles of these commercial products were sealed at the outside surface of particles. Preliminary wetting tests with these products showed that the surfaces of the particles of these products were easily contaminated by oil, becoming oil-wet. Because there are no commercial products that meet the requirements of this research, three building materials (material A, B, and C shown in Figures 3.2, 3.3, and 3.4) were collected and smashed into small particles for wettability tests.

The purpose of the verification experiments was to find out which of the three candidates considered (A, B, or C) could better satisfy the porosity and the wettability requirements for coalescence packing material. The following are the results observed in the wetting tests:

1) Porosity and wettability in a water-air system When the dried particles of the three types of materials were immersed in water, Material A did not yield gas bubbles, material B had bubbles for a short time, and material C yielded fine bubbles and bubbling lasted for a long time. Figure 4.2a shows the bubbling phenomenon of material C. Figure 4.2b shows the dry particle of material C. The particles of material C were obtained by smashing the rubble of tiles made of clay. These particles were highly porous, with fine pores connected and open to the surface of the particles, as depicted in Figure 4.1. It was also shown that the surfaces of the pores of material C were strongly water-wet. When the particles were immersed in water, water could spontaneously imbibe into the pores and push air out. Therefore, material C was further tested for the ability of remaining strongly water-wet after being in contact with heavy oil. Materials A and B were the rubble of tiles made of cement. There were not connected pores inside of them.

2) Wettability in an oil-water system. When the water saturated particles of material C were first immersed in the heavy oil for 24 hours, then put in contact with water again, the surface of them was clear, as shown in Figure 4.3a; that is, after extended contact with heavy oil, the particles' surfaces remained water-wet and were not contaminated by the heavy oil. Figure 4.3b shows the same type of particles after first being in contact with oil, then being in contact with water. There were oil stains on the surface of some particles; this is because the oil contaminated some spots of the surface when the dry particles were touched by the oil. This also confirmed the idea that the water in the fine pores of the

particles can keep the water film on the particle surface. Figure 4.4 shows the photos of the same particles shown in Figure 4.3, after one week.

Through the above two groups of experiments, it was proven, for research purposes, that experimental material C, after a water wet process guarantees that it is water-wet, and after stirring with the crude oil, it could still keep water-wet. But, without a water wet process, after mixing the dry materials C and crude oil together, it does not have perfect water-wet characteristics, since it was partially contaminated by the oil. Therefore, the water-wet material C was convincingly selected as the right coalescing material needed for water separation from water-in-heavy oil emulsions.



(a)

(b)

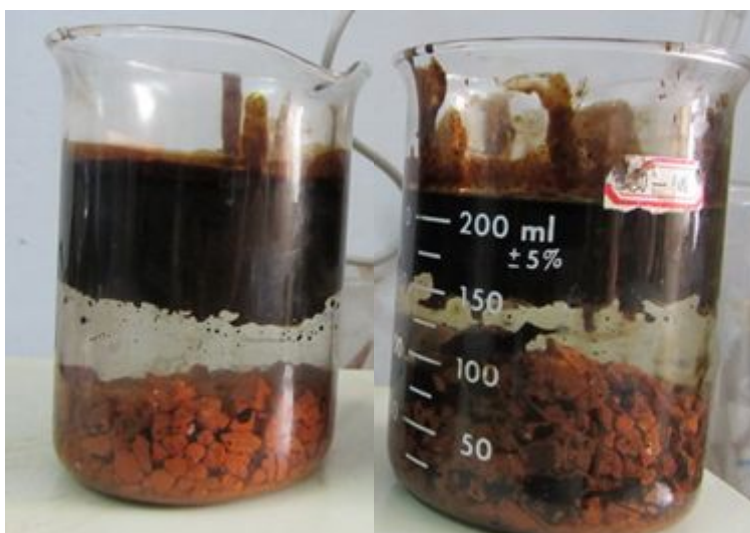
Figure 4.2 Un-wetted Material Vs. Wetted Material



(a)

(b)

Figure 4.3 Two Breakers with Crude Oil



(a)

(b)

Figure 4.4 Glasses with Water and Crude Oil

In order to demonstrate that the porosity of the water-wet material is extremely important to for keep it water wet in an oil-water system, a comparison test was conducted and shown in Figure 4.5. When the water saturated material C (left) and smashed glass (right) were first in contact with water (4.5a) and then with the heavy oil (4.5b), the material C particles were clean (see some particles near the wall of the bottle) and the glass pieces were completely wrapped by the oil. After both were immersed in the heavy oil for 24 hours, then put in contact with water again, the surface of the material C particles was clear, and the smashed glass was still in the oil as shown in Figure 4.5c. This test demonstrated that strongly water wet materials like glass can be easily contaminated by a crude oil and become oil wet in an oil-water system. The material C is less water wet compared to glass. However, it can remain water wet in oil-water system mainly because the water film on the surface of the particle that is connected and maintained by the water in the fine pores inside the particles.



(a) Material C and smashed glass pieces in water



(b) Material C and smashed glass pieces in heavy oil



(c) Material C and smashed glass pieces in oil-water system

Figure 4.5 Wettability behaviors of Material C and smashed glass.

4.2 Temperature effects on gravity separation of water-in-heavy oil emulsions

Most oil treating equipment used in the field relies on gravity to separate water droplets from the oil (continuous) phase, because water droplets are heavier than the oil. However, gravity is resisted by a drag force, caused by the viscosity of the continuous oil phase. Therefore, adding heat to the emulsion to reduce the oil viscosity is an effective method. For heavy oils, the thermal method is always applied for separating water in oils.

It has been repeatedly reported (e.g. Jones et al., 1978; Kokal and Juraid, 1999; BenGhoulam et al, 2004) that temperature has a strong effect on emulsion stability, and that emulsion tightness increases with decreasing temperatures. Temperature affects the physical properties of oil, water, interfacial films, and surfactant solubility in the oil and water phases. These, in turn, affect the stability of the emulsion. Increasing the temperature increases the thermal energy of the droplets and, hence, increases the frequency of drop collisions. For the separation of water in water-in-heavy-oil emulsions, adding heat to the emulsion is the traditional method, because increasing the temperature can reduce the oil viscosity so that water droplets can settle rapidly. It can also reduce the interfacial viscosity, resulting in a faster film drainage rate and enhanced drop coalescence.

Several tests were designed, without a demulsifier and a coalescing column, in order to determine the effect of the temperature on the separation of water from the water-in-heavy-oil emulsions. Separation tests by gravity, under three temperatures (that is, 60°C, 70°C and 80°C) were carried out to see how much water could be removed without using

other measures. The experimental results are summarized in Table 4.1 and plotted in Figure 4.6.

Table 4. 1Experimental results of heating without coalescer column

Tests	Temperature	Oil sample (g)	Distilled water (g)	Water content
Oil Sample 1	original	20.26	9.80	48.37%
Oil sample 2	60°C , 4 hours	30.26	14.55	48.08%
Oil Sample 3	70°C , 4 hours	25.45	12.46	46.95%
Oil Sample 4	80°C , 4 hours	27.12	13.03	44.37%

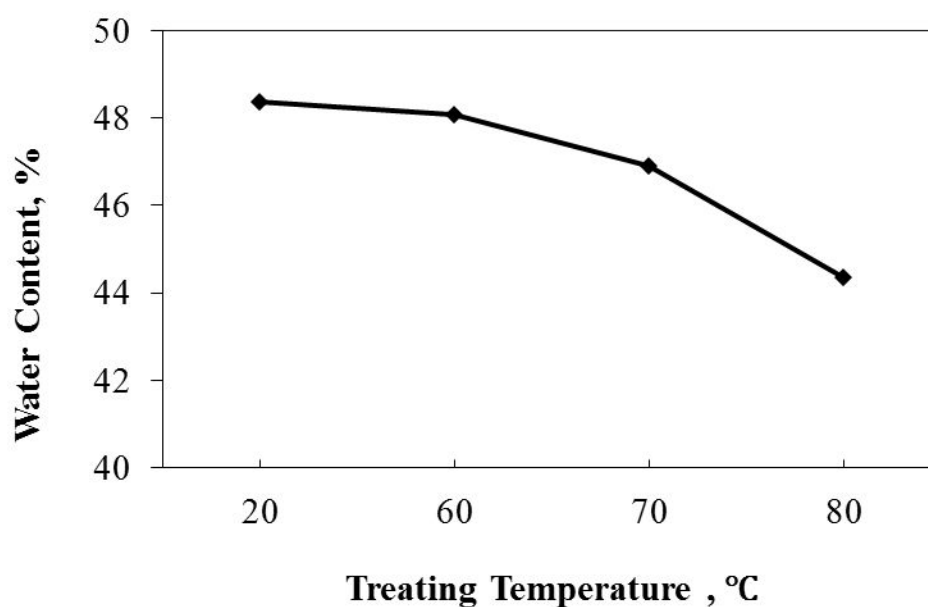


Figure 4.6 Water content vs temperature without demulsifier and coalescer

The above results reveal that, under the same conditions, as the temperature increases, the water content of the water-in-oil emulsions decreases. The research results echo the

proposition (e.g. Kokal and Sayegh, 1995; Kokal, 2003) that heating the emulsion enhances its breaking or separation.

The results showed that the water content of the oil sample dropped from the original value of 48.37% to 48.08% at 60°C, to 46.95% at 70°C, and to 44.37% when temperature was increased to 80°C. As can be seen in Figure 4.6, the relationship between water content and temperature tends to be a downward curve, though not necessarily linear. This means that if the temperature is increased higher than 80°C, more water can be removed by gravity separation. However, this may not be a practical way to reach a very low water content, such as ~1%, simply adding heat to the emulsion in order to meet the requirement of sale to a refinery.

In practice, very rarely does temperature alone resolve the emulsion problem. Increasing the temperature has some negative effects. First, it is expensive to heat the emulsion stream. Second, it can result in the loss of light ends from the crude oil, reducing its API gravity and the treated oil volume. Finally, increasing the temperature leads to an increased tendency towards scale deposition and an increased potential for corrosion in treating vessels.

Therefore, rational practical applications of heat for emulsion breaking should be based on an overall economic, technical and operational analysis of the treatment facility. The cost effectiveness of adding heat should always be balanced against longer treatment time (e.g. a larger separator), loss of light ends and a resultant oil-product price, chemical costs, and the costs of installation of electrostatic grids or retrofitting, etc.

4.3 Combination of heating and demulsifier in separation of water from W/O emulsions

The results in the previous section showed that the water content in the water-in-heavy-oil emulsion was still very high after gravity separation, at 80°C, for 4 hours. Given that when temperature increases the water content of the oil emulsions decreases (as reflected in Figure 4.6), a kinetic barrier to drop coalescence still exists even at higher temperatures. For example, it has been realized by other researchers (e.g. Kokal and Al-Juraid 1999) that complete resolution cannot be achieved, even at high temperature, and it is reported elsewhere (e.g. Renouf et al., 2007) that a combination of heat and demulsifier provides a better, if not the best, demulsification.

This research, therefore, was not intended to test gravity separation at temperatures above 80°C, because at that temperature the oil viscosity had been reduced to the range of 40-50 cp, that allowed water droplet settling. The problem was how to enhance coalescence of the oil droplets in the emulsion so that they could settle rapidly during gravity separation? It was realized that separation of water in a crude oil emulsion, which is stabilized by the naturally occurring emulsifiers, must use demulsifiers to eliminate them from the oil-water interface.

Demulsification using chemicals is a very complex phenomenon. When the chemicals are used as emulsifying agents, they tend to establish an emulsion opposite in type to that which is stabilized by natural surfactants. A demulsifier displaces the natural stabilizers

(emulsifiers) present in the interfacial film around the water droplets. This displacement, occurring at the oil-water interface, influences the coalescence of water droplets through enhanced film drainage. Due to the large variety of components present in the crude oil, demulsifiers are generally specific for a given emulsion (or oil-water system) and may be completely ineffective for another emulsion (Kokal and Wingrove, 2000). Therefore, the demulsifier used in this research was a commercial product used in the Daqing Oilfield. The concentration of the demulsifier (DQ-Demul) used in this field was 300 ppm. Field results showed that the adding 300 ppm of this commercial demulsifier into the oil, water content could be reduced to ~1.5% after gravity separation, at 80°C, for 48 to 120 hours.

It is widely noted (e.g. Dimitrov et al., 2012) that the amount of demulsifiers added to crude is critically important; too little demulsifier might leave the emulsion unresolved and too high of a dosage of demulsifier might be detrimental to the treatment process. In this research, several dosages of demulsifier (i.e. 50 ppm, 100 ppm, 200 ppm, and 300 ppm), without the use of coalescence column, at 80°C, were employed to determine the effect of demulsifiers on water separation. To achieve this, and to verify the hypothesis that a rational dosage of demulsifiers would lead to better water separation, the following ideas were tested:

- Whether the usage of demulsifiers leads to effective emulsion resolutions
- Whether there is a ceiling effect upon the dosage of demulsifiers.

Experimental procedures adopted in this set of tests were similar to the last set of tests, except that demulsifier was added. The demulsifier was mixed with the emulsion in the settling unit.

The experimental results are summarized in Table 4.2 and plotted in Figure 4.7. For comparison, the results of the test without demulsifier are also shown in Table 4.2 and Figure 4.7.

Table 4.2 Experimental results of combination of heating and demulsifier

Tests	Temperature	Demulsifier concentration	Oil sample (g)	Distilled water (g)	Water contents
Sample 4	80°C	0 ppm 4 hours	27.12	13.03	44.37%
Sample 5	80°C	50 ppm 4 hours	31.43	5.33	16.96%

Sample 6	80°C	100 ppm 4 hours	35.23	4.38	12.43%
Sample 7	80°C	200 ppm 4 hours	25.42	1.93	7.59%
Sample 8	80°C	300 ppm 4 hours	19.35	0.88	4.54%

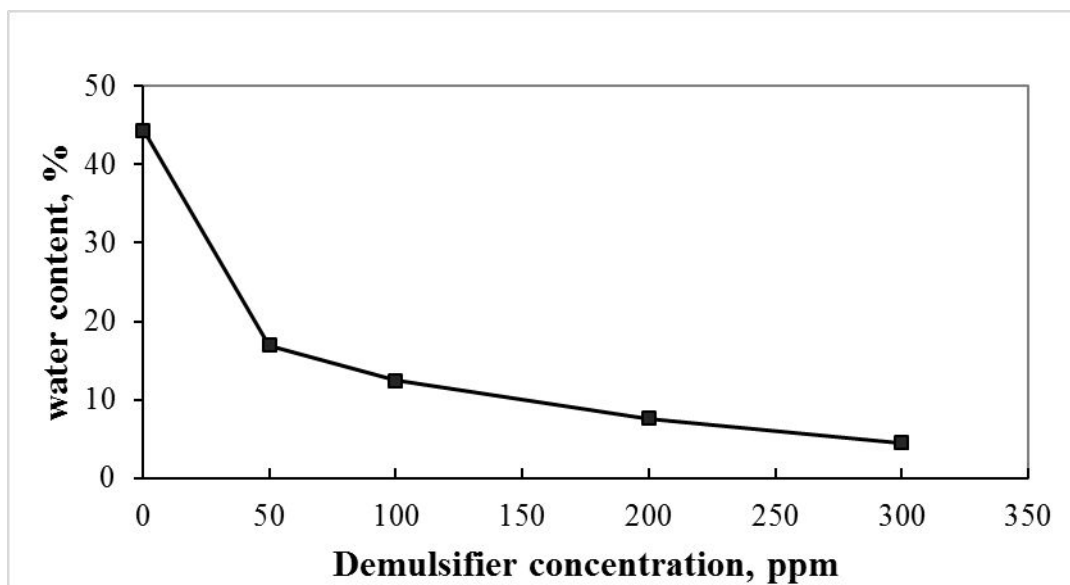


Figure 4.7 Water Content Vs. demulsifier concentration at 80 °C

As can be seen in Figure 4.7, the water content of the oil samples dropped significantly from 44.3% to 16.98% when 50 ppm emulsifier was used at 80°C. The water content decreased from 16.98% to 4.54% as the emulsifier concentration was increased from 50 ppm to 300 ppm.

The results indicate that the usage of demulsifiers leads to effective emulsion resolutions. Figure 4.7 reveals that, at the same temperature, when the demulsifier concentration increases, the water content of the oil emulsion decreases. This is because temperature affects the physical properties of water, oil, interfacial films, and surfactant solubilities in the both two phases. As the temperature increases, the viscosity of the emulsion decreases significantly. Small water droplets can coalesce easily at a lower viscosity.

The selection of the dosage of a demulsifier, along with the selection of the right demulsifier(s), remains an art rather than a science. The aforementioned experiments verified that the dosage of demulsifiers plays an important role in producing coalescence. Seemingly when demulsifiers were added to the emulsions the oil droplet size increased.

The results in Figure 4.7 also show that although the water content decreases with increasing demulsifier concentration, the efficiency of demulsifier decreases with concentration. The trend of the curve in Figure 4.7 also indicates that at 80°C it is will be difficult to reduce the water content to about 1.0% by simply adding more demulsifier. Adding too much demulsifier is not economic but may also create some problems to the refinery process due to the introduction of surfactant to the crude oil.

4.4 Coalescing enhancement of water separation from W/O emulsions

The results of the previous section showed that the addition of demulsifiers to the emulsion can significantly improve the coalescence of oil droplets. The results also showed that there was still 4.54% water in the oil when 300 ppm emulsifier was used at 80°C.

In this study, in addition to heating and the use of demulsifier, a coalescing column packed with water-wet porous particles was used to promote coalescence of the water droplets in the water-in-heavy-oil emulsions.

In total, 9 coalescing column tests were carried out to investigate the enhancement of water separation from a water-in-heavy-oil emulsion by using the water-wet porous particles as the coalescing media. In these tests, three demulsifier concentrations were applied (50, 100, 150 ppm) and three temperatures (60, 70, and 80°C) were used. The coalescing column had a diameter of 4.0 cm and a height of 10.0 cm (see Figure 4.8). The emulsion was pumped through the coalescing column at a flow rate of 1 cm³/min. The demulsifier was mixed with the emulsion in the emulsion tank before entering the coalescing column.

The experimental results of the above 9 tests are summarized in Table 4.3 and plotted in Figure 4.9.



Figure 4.8 Coalescing column packed with water-wet porous particles

Table 4. 3 the water content at the coalesce column and demulsifier condition

Tests	Temperature	Demulsifier concentration	Oil sample (g)	Distilled water (g)	Water contents
Sample 9	60°C	50 ppm 4 hours	26.00	5.62	21.62%
Sample 10	60°C	100 ppm 4 hours	27.73	3.66	13.20%
Sample 11	60°C	150 ppm 4 hours	29.17	2.91	9.98%
Sample 12	70°C	50 ppm 4 hours	29.17	4.95	16.97%
Sample 13	70°C	100ppm 4hours	21.77	1.77	8.13%
Sample 14	70°C	150 ppm 4 hours	20.12	0.89	4.42%
Sample 15	80°C	50 ppm 4 hours	20.01	2.10	10.49%
Sample 16	80°C	100 ppm 4 hours	17.38	0.23	1.32%
Sample 17	80°C	150 ppm 4 hours	21.77	0.14	0.64%

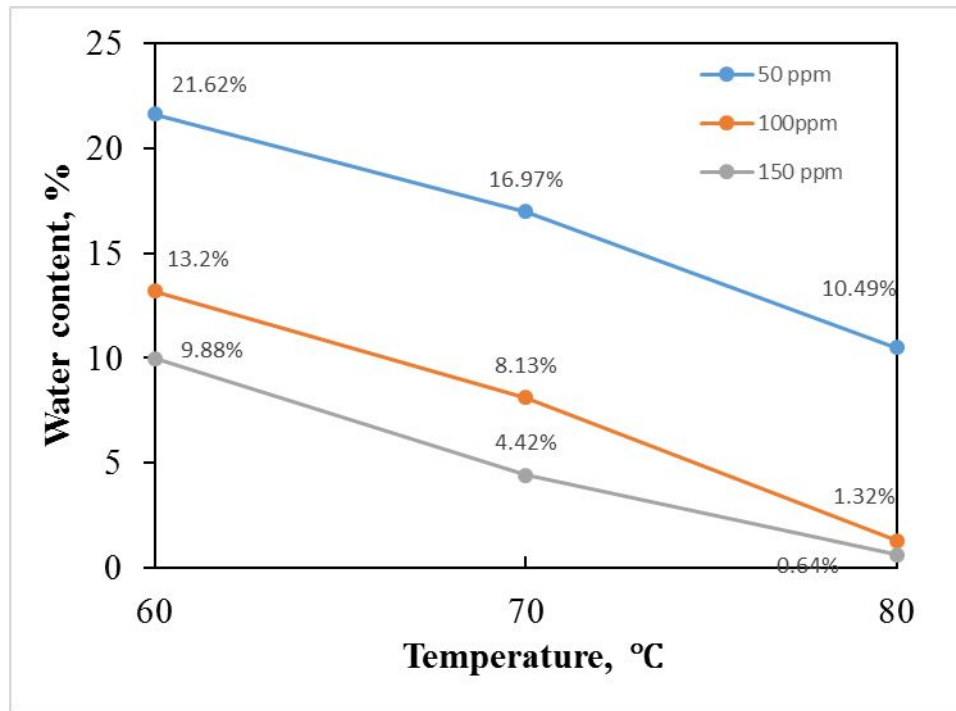


Figure 4.9 Water content Vs the Temperature, demulsifier concentration in coalescing column.

As can be seen from the curve of 50 ppm in Figure 4.8, the water content in the oil samples, after flowing through the coalescing column, was reduced to 21.62, 16.97 to 10.49% at separation temperatures 60, 70 and 80 °C, respectively. Recall that the water content in the test of 50 ppm and 80 °C was 16.96% without coalescence column. For the test of 50 ppm at 80 °C, flowing emulsions through the coalescence column dropped the water content down to about 60% of the value in the test without coalescence column. Comparing the results of the tests with and without using the coalescing column shows that the coalescing media invented in this study does enhance the separation efficiency.

Similarly, as can be seen from the curve of 100 ppm in Figure 4.8, the water content in the oil samples, after flowing through the coalescing column, was reduced to 13.20, 8.13, and 1.32% at separation temperatures 60, 70 and 80 °C, respectively. Recall that the water content in the test of 100 ppm and 80 °C was 12.42% without coalescence column, compared with 1.32% of the test with coalescing column. Therefore, for the test of 100 ppm at 80 °C, flowing emulsions through the coalescence column dropped the water content down to nearly 10% of the value in the test without coalescence column. It shows that increasing the dosage of emulsifier can also enlarge the enhancement of the coalescing media for the separation of water from the water-in-heavy-oil emulsions.

As can be seen from the curve of 150 ppm in Figure 4.8, the water content in the oil samples, after flowing through the coalescing column, was reduced to 9.98, 4.42 and 0.64% at separation temperatures 60, 70 and 80 °C, respectively. The water content in the coalescing column test of 150 ppm and 80 °C reached 0.64%. As mentioned in the beginning of this section, to reduce the water content in the emulsion to ~1.5% by using heating (80°C) and a demulsifier (300 ppm) in the Daqing Oilfield, settling time was very long (48 -120 hours). The results of the coalescing column show that the effect of adding the coalescer column is dramatic. The flow of the emulsion through the coalescing column dramatically reduced the water content of the oil, as compared to the separation by gravity only.

The experimental results in Figure 4.9 reveal that, at the same emulsifier concentration, the water content of the oil emulsions rapidly decreased when the temperature increased. This is because temperature affects the physical properties of water, oil, interfacial films,

and surfactant solubilities in the both two phases. With the temperature increase, the viscosity of the oil decreased significantly and small water droplets coalesced easily inside the low viscosity oil. The experimental results in Figure 4.9 also show that, at the same temperature, the water content of the oil emulsions rapidly decreased with an increase in the demulsifier concentration. All of the above results indicate that flowing an emulsion through the coalescing column significantly enhanced the temperature and demulsifier effects. This implies that incorporating the coalescing column in fields should be able to reduce temperatures and demulsifier consumption and shorten the settling time.

4.5 Effect of coalescing column thickness on water separation from water-in-heavy oil emulsion

The results in the previous section have demonstrated that flowing an emulsion through the coalescing column packed with water wet porous particles can significantly enhance the coalescence of water droplets in the heavy oil and improve the separation efficiency. The thickness of the coalescing column was 10 cm. In this study, the effect of the coalescing column on water separation from water-in-heavy-oil emulsion was also investigated. Three additional tests were conducted using a 20 cm coalescing column at three different temperatures (60, 70, and 80°C). In all three tests, 100 ppm demulsifier was used. The flow rate and settling time were the same as in the previous tests. The experimental results of the three 20 cm column tests, along with the results from the 10 cm column, for comparison, are summarized in Table 4.4 and compared in Figure 4.10.

Table 4. 4 Experimental results of water separation in 10 and 20 cm coalescing columns

Tests	Column thickness	Temperature	Demulsifier concentration	Oil sample(g)	Distilled water(g)	Water contents
Oil Sample 10	10cm	60°C	100 ppm 4 hours	27.73	3.66	13.20%
Oil Sample 18	20cm	60°C	100 ppm 4 hours	19.69	2.55	12.95%
Oil Sample 13	10cm	70°C	100 ppm 4 hours	21.77	1.77	8.13%
Oil Sample 19	20cm	70°C	100 ppm 4 hours	31.47	2.03	6.45%
Oil Sample 16	10cm	80°C	100 ppm 4 hours	17.38	0.23	1.32%
Oil Sample 20	20cm	80°C	100 ppm 4 hours	27.69	0.36	1.30%

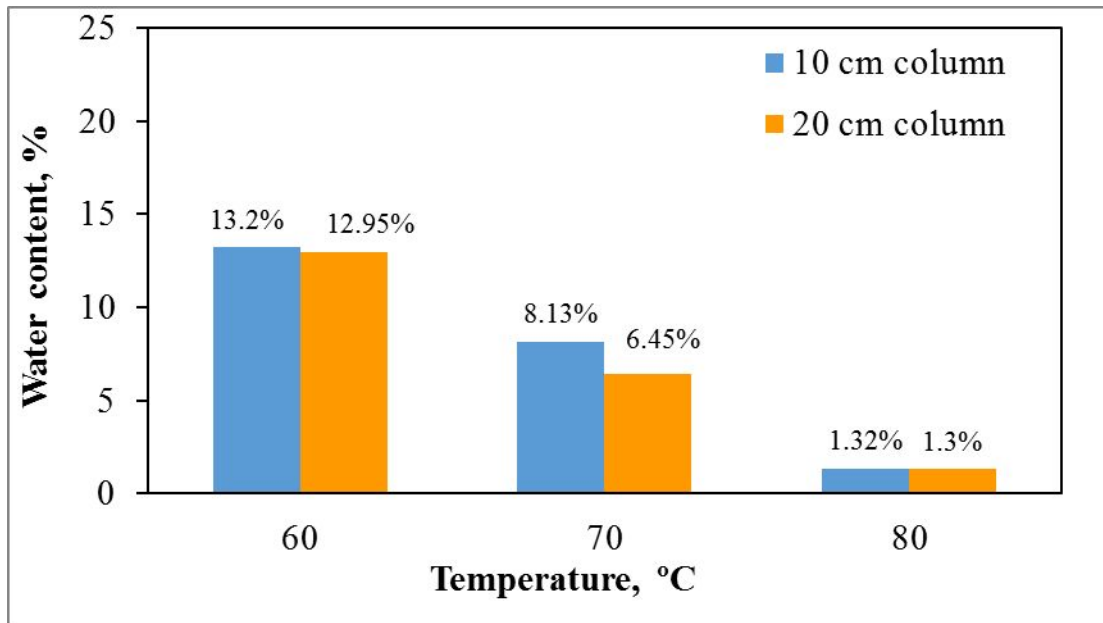


Figure 4. 10 Water content Vs different Column Thickness

The results reveal that, under the same test conditions (temperature, demulsifier concentration, flow rate and settling time), when the coalescing column thickness was increased from 10 cm to 20 cm, the water content of the oil emulsions decreased very slightly, as shown in Figure 4.10. That means that the thickness of 10 cm was sufficient for the coalescing column, under the test conditions used in this study. However, this does not mean that 10 cm is the optimal thickness of the coalescing column. In field applications, more work is needed to find the optimal thickness for the coalescing column.

4.6 Summary of coalescing column tests and analysis

In this section, the experimental results of the coalescing column tests are summarized and analyzed. In order to reveal the enhancement of the separation of water-in-heavy oil by using the coalescing column invented in this study, two sets of data were re-tabled and re-plotted for comparison and analysis.

The first set data includes gravity separation and coalescing column enhanced gravity separation at three temperatures (60, 70, and 80 °C). Demulsifier concentration in all the tests was 100 ppm. The results are summarized in Table 4.5 and compared graphically in Figure 4.11. In addition to the data shown before, two new tests were reported: gravity separation at 60 and 70 °C (without using demulsifier and coalescence column).

Table 4. 5 Experimental results for comparison of gravity separation and coalescing column enhanced gravity separation

Tests	Column thickness	Temperature	Demulsifier concentration	Oil sample (g)	Distilled water (g)	Water contents
Oil Sample 10	10 cm	60°C	100 ppm 4 hours	27.73	3.66	13.20%
Oil sample 21	No column	60°C	100 ppm 4 hours	23.17	4.97	21.45%
Oil Sample 13	10cm	70°C	100 ppm 4 hours	21.77	1.77	8.13%
Oil Sample 22	No column	70°C	100 ppm 4 hours	29.22	3.67	12.56%
Oil Sample 16	10 cm	80°C	100 ppm 4 hours	17.38	0.23	1.32%
Oil Sample 23	No column	80°C	100 ppm 4 hours	35.23	4.38	12.43%

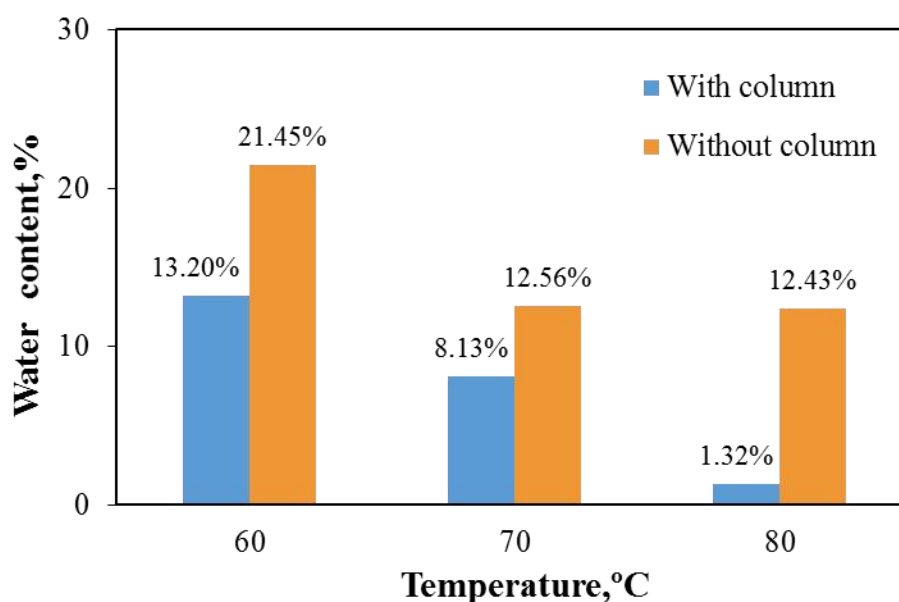


Figure 4. 11 Comparison of gravity separation and coalescing column enhanced gravity separation

The results in Table 4.5 and Figure 4.11 show that the flow of the emulsion through the 10 cm coalescing column reduced water content from 21.45% to 13.20% at 60°C, from 12.56% to 8.13% at 70°C, and from 9.35% to 1.32% at 80°C. The effect of adding a coalescing column to water separation is significant, as compared to just using a demulsifier in gravity separation.

The second set of data includes gravity separation and coalescing column enhanced gravity separation at 80°C. In the simple gravity separation tests, demulsifier concentration was changed from 0 to 300 ppm as shown in Table 4.2 and Figure 4.7; in the coalescing column enhanced gravity separation tests, demulsifier concentration was changed from 1 to 150 ppm, at which the water content had been reduced to below that 1.0%. In all the tests, settling time was 4 hours. The results are summarized in Table 4.6

and compared graphically in Figure 4.12. In addition to the data shown before, two new tests were reported: gravity separation with 150ppm demulsifier and coalescing column tests without added demulsifier.

Table 4.6 Experimental results for comparison of gravity separation and coalescing column enhanced gravity separation at 80°C with different demulsifier concentrations

Tests	Temperature	Demulsifier concentration	Oil sample (g)	Distilled water (g)	Water contents
Sample 4	80°C no column	0 ppm, 4 hours	27.12	13.03	44.37%
Sample 5	80°C no column	50 ppm 4 hours	31.43	5.33	16.96%
Sample 6	80°C no column	100 ppm 4 hours	35.23	4.38	12.43%
Sample 24	80°C no column	150 ppm 4 hours	23.28	2.23	9.58%

Sample 7	80°C no column	200 ppm 4hours	25.42	1.93	7.59%
Sample 8	80°C no column	300 ppm 4hours	19.35	0.88	4.54%
Sample 25	80°C column	0ppm 4hours	20.57	4.43	21.54%
Sample 15	80°C column	50 ppm 4hours	20.01	2.10	10.49%
Sample 16	80°C column	100 ppm 4hours	17.38	0.23	1.32%

Sample 17	80°C column	150ppm 4hours	21.77	0.14	0.64%
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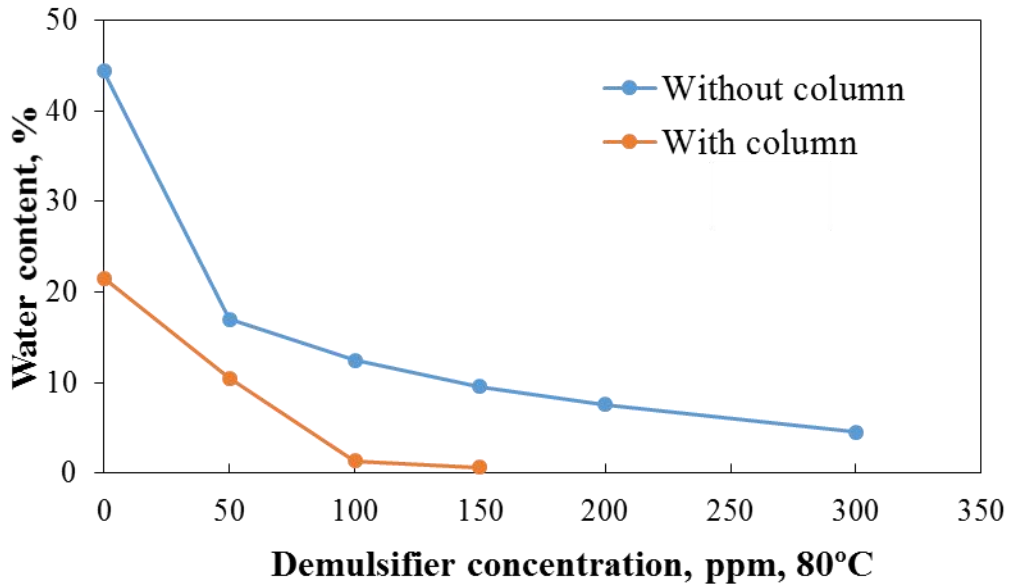


Figure 4.12 Comparison of water separation results by gravity separation and coalescing column enhanced gravity separation at 80°C with different demulsifier concentrations

Results shown here are several tests at a fixed temperature (80°C), with varying dosages of demulsifier and coalescing conditions (i.e. with or without a coalescing column) in order to analyze the relationship between the separation of water with different concentrations of demulsifier and the use of coalescing media. To achieve this one needs to look at following phenomena cautiously:

- Whether the coalescing column is effective in breaking water-in-heavy oil emulsions.

- Whether the coalescing column can reduce the water content further than the level reached in gravity separation with a high dosage of demulsifier.
- When a coalescing column is applied, what is the dosage of demulsifiers needed for approaching a water content that satisfies the refinery requirement (i.e., <1.0%)?

The results in Table 4.6 and Figure 4.12 show that flow of the emulsion through the 10 cm coalescing column reduced water content from 44.37% to 21.54% (51% reduction) at 80°C, without using demulsifier. This result indicates that the coalescing column is effective in helping water droplets coalesce. The results also demonstrate that the coalescing column can reduce the water content beyond what was reached in gravity separation with a high dosage of demulsifier. At a fixed temperature of 80°C, and with a settling time of 4 hours, when the dosage of the selected demulsifier changed from 50 to 100 to 150 ppm, water content reached 16.96%, 12.43% and 9.59%, respectively, in the gravity separation (without using a coalescing column). At the same separation temperature and the same three demulsifier dosages, water content reached 10.49%, 1.32% and 0.64%, respectively, in the gravity separation with the use of a 10 cm coalescing column. Using the coalescing column reduced water content in the heavy oil by 38%, 89%, and 93%, compared to the water contents reached in the separation with demulsifier dosages of 50, 100, and 150ppm, respectively, without using the column. These results again indicate that the effect of adding a coalescing column to water separation is significant, as compared to just using a demulsifier in gravity separation. More importantly, flow through the coalescing column could reduce the water content in

the heavy oil to a very low level ($<1.0\%$) and, at the same time, reduce the consumption of demulsifier.

4.7 Mechanism of coalescence using water-wet porous particles

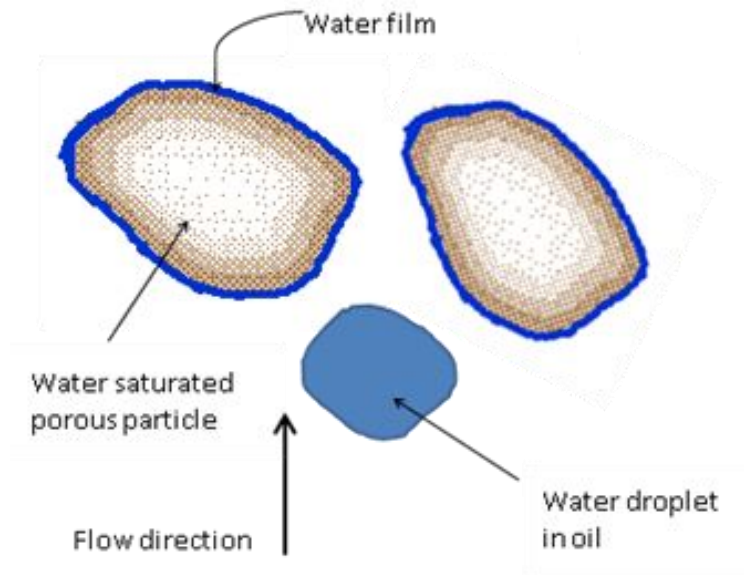
In the treatment of water-in-oil emulsions, the purpose of using coalescing media is to promote coalescence of the water droplets in the water-in-heavy-oil emulsions. It is expected to provide a large surface area upon which water droplets can collect. It has been known that the collection of water droplets on the surface of the coalescing media depends on the equilibrium contact angle (in some cases, the dynamic contact angle) of the dispersed water droplets on the media surface (e.g., Basu, 1993). If the equilibrium contact angle of the dispersed phase droplets in the presence of a continuous phase is less than $\sim 30^\circ$, the wetting of the media surface favors the formation of a thin film of the dispersed phase on the media surface. Subsequently, the dispersed phase droplets coalesce on this thin film to form a liquid pool. If the equilibrium contact angle of the dispersed phase in the presence of a continuous phase is greater than 140° , there is neither film formation nor drop attachment on the media surface and no coalescence or accumulation of the dispersed phase on the surface of the coalescing media. Therefore, an appropriate coalescing material should be chosen for a particular dispersion system in order to get high coalescence efficiency, and the coalescing media also need to provide a large surface area upon which the dispersed droplets collide and accumulate.

In a packed coalescer, the wetting behavior of the water phase in the packing material is considered to be important in determining the performance of the coalescer. The water saturated porous particles must remain water wet after being in contact with the heavy crude oil for a long time. This is because 1) the material of the porous particles is water wet, and 2) the capillary forces of the water/oil interface keep the water filling the fine pores up to the surface of the particles. In this case, the porous particles are covered by a thin layer of water or water film. The contact angle of water on this type of surface is definitely zero, or completely perfect wetting. If water droplets come in contact with the water film, the droplets should coalesce into the water film.

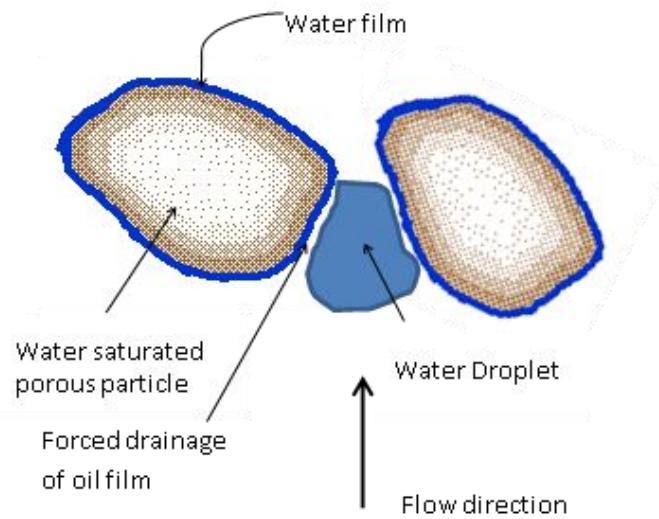
How does a water droplet in the water-in-heavy oil emulsion coalesce upon to the water film which covers the porous particle in a coalescing column? The cartoon in Figure 4.13 depicts the process as follows.

The particles' surfaces are covered by the water film and would be in contact with the continuous oil phase at the beginning of the coalescence process. The water droplets are entrained in the oil phase and flow through the narrow space between the particles, as shown in Figure 4.13a, where a droplet moves toward the particle and the water films. Eventually, the water droplet comes in contact with the particle surface, as shown in Figure 4.13b. At this moment, the water droplet is not in direct contact with the water film because there is an oil film between them. Due to the drag force offered by the continuous oil phase, the water droplet is forced to flow through the narrow gap between the two particles, and the oil between the water film and the water droplet is forced to

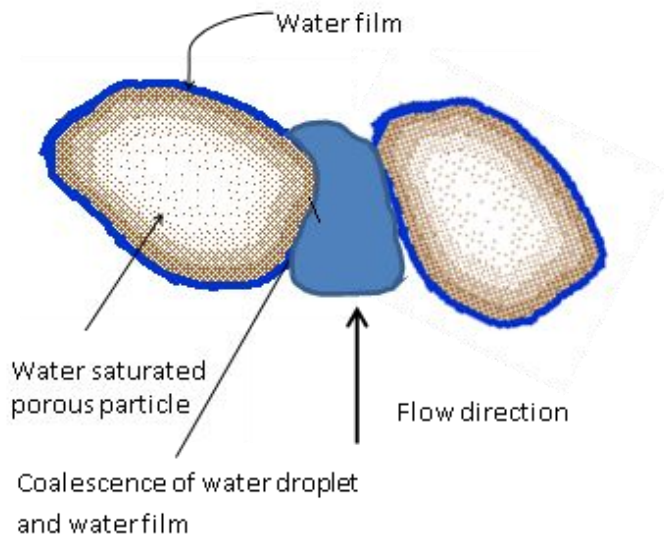
drain out, resulting in the spreading or coalescence of the water droplet on the particle surface, as shown in Figure 4.13c. As the emulsion flows through the coalescing column, more water droplets that approach the particles coalesce with the water film already formed. The coalesced dispersed water accumulates at the downstream end of the channel between the particles to form a lump of water (Figure 4.13d) and subsequently detaches and flows away as a larger drop (Figure 4.13e). The size of the blob detached from the rear of the particle should be controlled by the space between the particles, the flow rate, and the oil-water interfacial tension.



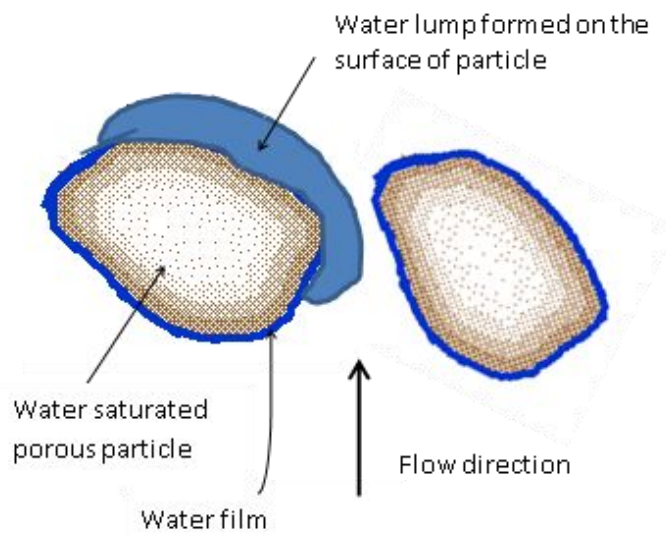
(a) Water droplet approaching the water-wet porous particles



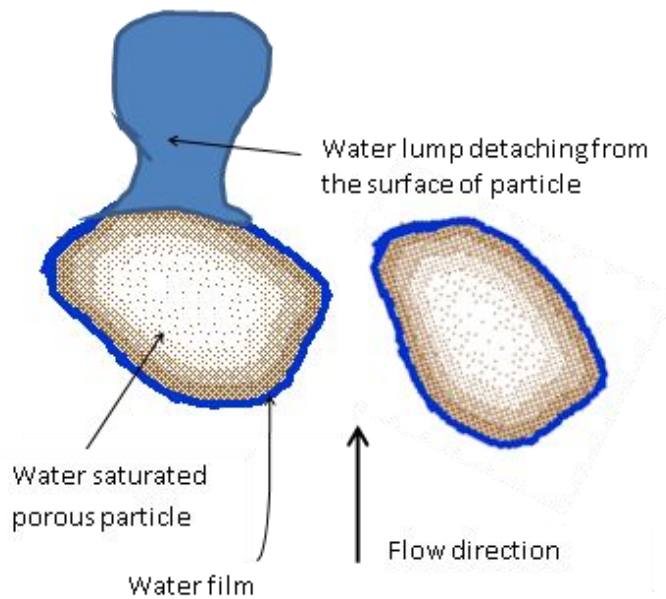
(b) Forced drainage of oil between the water droplet and the particles



(c) Coalescence of water droplet and water film



(d) Water lump formed on the surface of particle



(e) Water lump detaching and flow away

Figure 4.13 Mechanism of water separation in water-in-heavy oil emulsion in a coalescing column.

As can be seen in Figure 4.13, the reason why coalescence works effectively in the breakup of emulsions lies in the tendency that, during coalescence, water droplets fuse, unite or coalesce together to form a large, and later on even larger drop. This process of coalescence remains, most likely, irreversible and inevitably leads to a decrease in the number of water droplets and, eventually, to complete demulsification. This decrease of the number of water droplets illustrates the differences that occurred in scenarios with and without coalescence columns.

The enhancement of separation of water from the water-in-heavy oil emulsions using the coalescence column can also be further explained based on the settling equation (stock's law):

$$V_t = \frac{gd^2(\rho_w - \rho_o)}{18\mu_o}$$

Where V_t is the velocity of settling of a water droplet (cm/s), g is the gravity acceleration (981 cm/s²), d is the diameter of water droplet (cm), ρ_w is water density (g/cm³), ρ_o is oil density (g/cm³), and μ_o is oil viscosity (poise). The above equation shows the relationship of the settling velocity with the density difference between the dispersed phase (water) and the continuous phase (oil), viscosity of the continuous phase, and the size of drops of the dispersed phase (water). It can be seen from this equation that the settling velocity is proportional to the square of the diameter of the water droplet. After the emulsion goes through the coalescence column, the water in the treated emulsion will

present in larger drops and will settle much faster than the original droplets. For example, if the d increases 5 times, the V_t will increase 100 times. If some water droplets in the original emulsion are very small, they will not be able to settle down from the settling tank within a certain period of time. After going through the coalescence column, some of those small water droplets become larger ones and can be removed from the oil in the settling tank. This means that the coalescence column can not only improve the settling velocity but also reduce the water content in the oil after a certain period of settling time.

4.8 Summary

It is believed that most chemical demulsifiers are not safe, from an environmental vantage point, even if the toxicity or mutagenic effects of demulsification chemistries might not have been clearly demonstrated from a scientific and developmental view. Therefore, the increase of environmental constraints makes necessary the development of safer formulations or more green mechanisms of de-emulsification, such as coalescing column, ultrasonic or electronic methods, to replace toxic chemicals, such as aromatics or nonylphenols.

The effects of temperature, column length, column packing size, flow rate, demulsifier concentration and water addition may all jointly apply, along with temperature, in practice. Longer columns might improve treating, but also increase the pressure drop across the column. Column packing of finer media might yield better results than coarse column packing. Higher flow loop temperatures could be more effective when no demulsifier is used. While demulsifiers are employed, lower temperatures might treat more effectively. The settling temperature or time might be varied for better results.

With these excellent preliminary results, further tests on the water-wet porous coalescing media technology developed in this study can be planned to field test a coalescer column with oilfield-specific demulsifiers for treating heavy oil emulsions in oilfields. The column could be placed between a free water knockout and treating vessel. Because the demulsifier concentration might impact the optimum column temperature and flow rate, the column will need to be individually tailored to the treating facility. Also,

investigations on the long-term running of the column and how this affects the packing would be desirable.

With these excellent preliminary results, further tests on the porous media technology developed by this researcher can be planned to field test a coalescer column with a wider range of oilfield-specific demulsifiers of varying concentrations (e.g. from 5, 10, 20, 30, 40, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650 to 700 ppm) for treating heavy oil emulsions in China's nation-wide oilfields. Special effort could be focused on probing into the realistic, if not normal, distribution of the dosage of certain oilfield-specific demulsifiers, for more does not indicate greater effectiveness, nor does less mean ineffective.

This implies that both a coalescer column and demulsifier concentrations can be applied in the real world to reduce relying on the usage of temperatures. The alleged synergy of temperature and demulsifier can imply that a higher temperature assists water removal, however, this may not be always true. Sometimes, better water recovery can occur at lower temperatures when demulsifiers are used. All of this highlights the importance of optimizing the temperature of the coalescer column in the field, at the appropriate demulsifier dosages.

As explained earlier, the effects of column length, column packing size, temperature, flow rate, demulsifier concentration and water addition, inter alia, may all directly, or jointly, play as important a role in water separation as temperature changes. With these excellent preliminary results, further tests on the porous media technology developed by

this researcher can be aimed at testing a coalescer column with a wide range of oilfield-specific demulsifiers of varying concentrations (e.g. from 5, 50 up to 1000 ppm) for treating heavy oil emulsions in real oilfields.

Furthermore, looking forward, chemical enhanced oil recovery (EOR) methods are soon expected to play a major role in future global crude oil production. Thus, breaking dilute oil-in-water (O/W) emulsions produced during surfactant/polymer (SP) and alkaline/surfactant/polymer (ASP) processes for EOR is becoming more and more important.

It might also be very fruitful to look beyond demulsifier and temperatures, in that there are so many factors affecting emulsions, and some effort directed at factors that promote coalescence (e.g. applying electrical fields) and change physical characteristics of emulsions (e.g. droplets, water cut, shear, solids, and aspects relating to reservoir, drilling, acidization, EOR/IOR operation and production) might also pay off, both in the short and long term.

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

- 1) In this thesis, the principle of capillarity and wetting film phenomenon in porous media were applied to the coalescing material for W/O emulsion treatment. The invented coalescing material has proved successful in enhancing water separation from water-in-heavy-oil emulsions. This material (particles) for packing the coalescing column is both water-wet and porous (containing many fine pores in them), and saturated by water prior to contacting heavy oil, these particles will remain water-wet in oil because the capillary forces keep the water phase being networked between the water in fine pores inside the particles and the water films on particles' surfaces.
 - 2) Coalescing column tests were carried out to investigate the enhancement of water separation from a water-in-heavy-oil emulsion by using the water-wet porous particles as the coalescing media. In these tests, three demulsifier concentrations were applied (50, 100, 150 ppm) and three temperatures (60, 70, and 80°C) were used. The coalescing column had a diameter of 4.0 cm and a height of 10.0 cm.
- The results show that flow of the emulsion through the 10 cm coalescing column reduced water content from 44.37% to 21.54% (51% reduction) at 80°C, without using demulsifier. This result indicates that the coalescing column is effective in helping water droplets coalesce.

- The flow of the emulsion through the 10 cm coalescing column with 100 ppm demulsifier reduced water content from 21.45% to 13.20% at 60°C, from 12.56% to 8.13% at 70°C, and from 9.35% to 1.32% at 80°C. The effect of adding a coalescing column to water separation is significant, as compared to just using a demulsifier in gravity separation.

 - At a fixed temperature of 80°C, and with a settling time of 4 hours, when the dosage of the selected demulsifier changed from 50 to 100 to 150 ppm, water content reached 16.96%, 12.43% and 9.59%, respectively, in the gravity separation (without using a coalescing column). At the same separation temperature and the same three demulsifier dosages, water content reached 10.49%, 1.32% and 0.64%, respectively, in the gravity separation with the use of a 10 cm coalescing column. Using the coalescing column reduced water content in the heavy oil by 38%, 89%, and 93%, compared to the water contents reached in the separation with demulsifier dosages of 50, 100, and 150ppm, respectively, without using the column. These results indicate that the effect of adding a coalescing column to water separation is significant, as compared to just using a demulsifier in gravity separation. More importantly, flow through the coalescing column could reduce the water content in the heavy oil to a very low level (<1.0%) and, at the same time, reduce the consumption of demulsifier.
- 3) In this study, the effect of the thickness of the coalescing column on water separation from water-in-heavy-oil emulsion was also investigated. The results showed that the thickness of 10 cm was sufficient for the coalescing column,

under the test conditions used in this study. However, in field applications, more work is needed to find the optimal thickness for the coalescing column.

5.2 Recommendations

The effects of temperature, column length, column packing size, flow rate, demulsifier concentration and water addition may all jointly apply, along with temperature, in practice. Longer columns might improve treatment, but also increase the pressure drop across the column. Column packing of finer media might yield better results than coarse column packing. Higher flow loop temperatures could be more effective when no demulsifier is used. While demulsifiers are employed, lower temperatures might treat more effectively. The settling temperature or time might be varied for better results. With these excellent preliminary results, further tests on the water-wet porous coalescing media technology developed in this study can be planned to field test a coalescer column with oilfield-specific demulsifiers for treating heavy oil emulsions in oilfields. The column could be placed between a free water knockout and treating vessel. Because the demulsifier concentration might impact the optimum column temperature and flow rate, the column will need to be individually tailored to the treating facility. Also, investigations on the long-term running of the column and how this affects the packing would be desirable.

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