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Removal of dispersed oil drops by induced gas flotation

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Dedicated to my lovely parents

Abstract

Produced water is an important byproduct of oil and gas production. With increasing number of maturing reservoirs, global oil to water cut is in the ratio of 1:3. Treatment of produced water is essential due to its detrimental effects on the environment and marine life. Gas flotation is identified as effective secondary treatment method for treating produced water. Induced gas flotation is the widely used gas flotation method due to its low retention time and high separation efficiency.

Synthetic produced water was prepared using three different crude oils. Experiments were carried out for gravity and gas flotation by varying different brine solutions, pH, mixing speed and initial oil concentrations. Influence of parameters like bubble sizes and type of gas used for flotation was also conducted for gas flotation. The objective of the thesis is to identify major influential parameters affecting the separation process. Droplet sizes were measured before and after separation process using gravity or gas flotation methods. Oil removal efficiency for the samples were calculated and the influence of the parameters were discussed in detail. It was found that the oil removal efficiency of gravity separation and gas flotation ranged from, 29-65% and 54-96% respectively. The type of crude used was identified as the major influencing factor for separation.

Acknowledgement

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I will always be indebted to my mom and dad for every effort they have taken in giving me this life that I have now. They are my pillars of strength, love and wisdom.

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γ	Interfacial tension
μ_l	Viscosity of continuous phase
ρ_l	Density of continuous phase
ρ_p	Density of droplet/bubble
A	Interfacial area
d_p	Droplet/bubble diameter
G	Gibbs free energy
g	Acceleration due to gravity
L/D	Length to diameter ratio
n	No. of components
N_{Re}	Reynolds number
P	Pressure
S_o	Spreading co-efficient
T	Temperature
v	Terminal velocity

Chapter 1

Introduction

1.1 Produced Water

Oil and natural gas plays a vital role in modern industrial civilization in its current configuration. According to International energy agency's report, oil and natural gas combined accounted for 57% of world's primary energy consumption in 2015 [9]. The production process generates large volumes of water that comes along with crude oil. This waster water is termed as produced water. Produced water contains various organic and inorganic components. Treatment of produced water is crucial because of its effect on flora and fauna. The environmental regulation for treating and handling produced water is different for different countries. For example, the permitted oil and grease limits for treated produced water in Australia is 50 mg/L on an instantaneous basis and 30 mg/L on a daily basis [27]. Based on Convention for the protection of the Marine Environment of the North-East Atlantic (OSPAR Convention), the discharged oil concentration limit is set as 30 mg/L [10].

Many countries with oil fields, are generally water-stressed countries, so extra focus and efforts are taken to find efficient, cost effective treatment methods to mitigate pollutants in order to complement their fresh water resources. Recycling and reusing of produced water is increasing in the recent years. Re-injection of produced water back to the oil wells to maintain well pressure is one of the primary areas of reusing produced water. Few fields where recycled water can be used include irrigation, livestock or wildlife watering and habitats, and various industrial uses (Vehicle washing, power-plant make-up water among other things)[17].

1.1.1 Origin

Subsurface rock formations are naturally permeated and saturated by saline water. Organic matter buried deep under the surface transforms to hydrocarbons under high temperature and pressure. The formed hydrocarbons, migrate and displace some of the saline water till it gets absorbed by reservoir rocks. Therefore there are three sources for saline water [17],

- Flow from above or below the hydrocarbon source.
- Flow from within the hydrocarbon zone.
- Flow from injected fluids and additives resulting from production activities.

1.1.2 Global Statistics

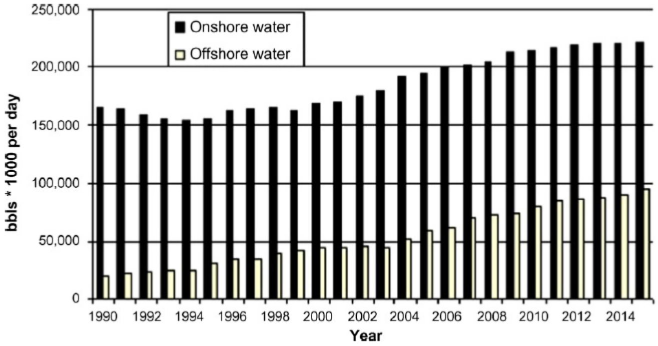


Figure 1.1: Global onshore and offshore produced water [4]

Global produced water volumes has been increasing steadily from onshore and offshore production since 1990 as shown in Figure 1.1. It was estimated that 201.4 billion barrels of produced water was generated from oil and gas wells across the globe in 2014 [48]. With the produced water generated, 136.9 Bn barrels were discharged and 65 Bn barrels were re-injected into the oil fields to maintain the well pressure [48].

1.1.3 Factors Affecting Produced Water Quantity

The factors affecting the amount of produced water generated were evaluated by Reynolds and Kiker [33] and are listed below [33],

- Well drilling method.
- Location of well within homogeneous and heterogeneous.
- Different types of completion.
- Single zone or commingled.
- Type of water separation technologies.
- Water injection or water flooding in enhanced oil recovery.
- Poor mechanical integrity.
- Underground Communications.

1.1.4 Constituents of Produced Water

Produced water contains various organic and inorganic components. The properties and characteristics of produced water are influenced by location of field, lifetime of reservoir and type of hydrocarbon product being produced [45]. The composition of produced water is different for different sources but they can be qualitatively grouped under the following components [18][21],

- Dissolved and dispersed oil.
- Dissolved formation minerals.
- Dissolved gases.
- Production Chemicals.
- Production Solids.

Dissolved and Dispersed Oil

Crude oil is a complex mixture of hydrocarbons, which includes various straight-chained and branched hydrocarbons along with benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, phenantherene, dibenzothiophene (NPD), poly-aromatic hydrocarbons (PAHs) and phenols. Most hydrocarbons are immiscible in water, so they get dispersed as small droplets in water [14]. The size and amount of dispersed oil droplets in water depends on amount of oil, interfacial tension, density of oil and shear history of the droplet [14, 32].

Many low and medium carbon range organic components with polar constituents are water soluble to an extent. Commonly found components in the dissolved oil are formic acid and propionic acid. Temperature and pH increases solubility of organics in produced water. Pressure affects the concentration of dissolved oil slightly, whereas salinity has no effect on the dissolved organic components [8]. The amount of oil soluble in water depend on the type of oil, production age and volume of water production [32].

Dissolved Formation Minerals

Dissolved inorganic components or minerals in produced water consists of anions, cations, heavy metals and radio-active materials. Cations ($Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Fe^{2+}$) and anions ($Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-$) affect salinity of the brine and scale potential which influences the chemistry of produced water [21]. Concentration of salt in produced water can be up to to 300,000 mg/L [27].

Trace quantities of heavy metals are found in produced water. This depends on the age of the well and geological formation. Cadmium, chromium, copper, mercury, lead, zinc, nickel and silver are some of the commonly found heavy metals in produced water [21, 44].

Radium is one of the naturally occurring radioactive materials (NORM), that co-precipitates in produced water along with other scales. Isotopes of Radium, $R^2 26$ and $R^2 28$ are NORMs that are found in produced water. Radium often co-precipitates with Barium Sulphate [32, 44].

Dissolved Gases

Produced water contains gases like $CO_2, O_2 and H_2S$ [21].

Production Chemicals

Chemicals used to treat or prevent various operational problems in the production process. Corrosion and scale inhibitors, de-emulsifiers, anti-foam, biocides and water treatment are some of the treatment chemicals or processes that are used [32]. The concentration of production chemicals observed in produced water is as low as 0.1 ppm [45].

Production Solids

Solids involved in the production process include a wide range of materials from bacteria, formation solids, waxes and asphaltenes, and scale and corrosion products[27]. Few micro-organisms survive the toxic chemicals in produced water [17]. Analysis of the same indicates that majority of the organisms are aerobic gram-positive bacteria with a population of 50-100 cells per mL [47]. Suspended solids contain inorganic crystalline substances like $SiO_2, Fe_2O_3, Fe_3O_4, and BaSO_4$.

1.2 Need for Produced Water Treatment

Industries often discharge produced water into the sea. The components present in produced water have diverse effect on the environment, with some increasing toxicity in water. The effect of various components present in produced water are as follows,

Table 1.1: Impacts of produced water components

Component	Effect
Dispersed and Dissolved Oil	•Increases biochemical oxygen demand (BOD)[21] •Droplets rise to the surface of the water, where the volatile components evaporate[17] •Non-polar organics are highly toxic[16]
Salinity	•Major contributor to water toxicity[27]
Heavy Metals	•Less toxic than non-polar organics[32] •Has adverse effects on marine life[32]
Radio-active Materials	•Presence depends upon source and geological formation[32] •Risk associated with NORM on marine environment and animals are very small[32]
Production Chemicals	•Chemicals can accumulate on marine sediments[19] •Oil-soluble chemicals are more toxic than water soluble chemicals at the same concentration[22]

The knowledge of the impact of untreated produced water components before discharging, pushes on the need for produced water treatment.

1.3 Produced Water Management

Produced water is oil and gas industry's highest waste stream on a volume basis [3]. Veil *et al.* [46] suggested a three tiered prevention hierarchy for managing produced water, as follows [46, 17],

- Employing technologies to minimize production of produced water.
- Recycling and reusing produced water.
- Discharge of produced water, if above methods are not applicable.

Arthur *et al.*[3] suggested some options for managing produced water. They are[3, 17],

1. *Re-Injection*: Produced water is re-injected into the same or different formation. Treatment to remove bacteria and scale forming salts is necessary.

2. *Re-use in operation*: Produced water is treated to meet the required quality, to be used for various plant operations.

3. *Consume in beneficial use*: Significant treatment of produced water is required to meet the conditions for it to be used for irrigation, cattle and livestock consumption, and as drinking water [42].

4. *Discharge*: Treating produced water to meet discharge regulations.

In most cases, treating produced water is the most effective and economical option. By treating produced water, waste is converted to a valuable by-product which can be used in other process. Arthur *et al.*[3] offer a general list of components to be targeted while planning produced water treatment which are shown as follows [3, 17],

- De-oiling, dispersed oil droplets.
- Soluble organics removal.
- Disinfection.
- Suspended solids removal.
- Dissolved gas removal.
- Desalination.
- Water softening.
- Miscellaneous: NORM removal.

1.4 Produced Water Treatment Technologies

Produced water is treated by separate or combination of physical, chemical or biological processes [17]. Some of the widely used processes currently are,

- Gravity Settling
- Hydrocyclone
- Gas Flotation
- Membrane Separation
- Chemical Treatment
- Biological Treatment

The above listed processes are explained in detail in the following subsections and their merits and demerits are elucidated in Tables 1.2 to 1.8.

1.4.1 Gravity Settling

Gravity based separation techniques are used in various plants for treating oily waste water. Oil droplets dispersed in continuous water phase, slowly tend to rise to the surface due to the density difference between the two. On industrial scale, two technologies have been established for separation based on gravity settling, they are[17]

- Skim vessels and API tanks
- Parallel and corrugated plate separators

Skim vessels and API tanks

In these technologies, separation is primarily based on the difference in specific gravities of the immiscible liquids. These tanks are suitable for removing oil of droplet sizes >150 μm[2] with effluent concentration in the range of 50-100 mg/L [24]. The pros and cons of these are given in the following table

Table 1.2: Pros and cons of gravity settling by skim vessels[35]

Pros	Cons
Suitable for removal of large oil droplets and suspended particles.	Small droplets and stable emulsions require long settling time.
Simple equipment with minimum operating and maintenance costs.	Dissolved oil cannot be removed.
Effective when used as first treatment step for oil-water separation.	Large footprint.

Parallel and corrugated plate separators

Like gravity settling by API tanks and skim tanks, plate separators also work based on specific gravity of immiscible fluid. Plates aid to coalesce and separate the oil. Plate separators are suitable for removal of oil droplets which are $>50\mu$ m[29], with average effluent concentrations ranging from 25-100 mg/L [6, 35].

Table 1.3: Pros and cons of gravity settling by parallel and corrugated plate separators[35]

Pros	Cons
Smaller footprint compared to skim vessels.	Stable emulsions and dissolved oil cannot be treated Not suitable for heavy oil separation Possibility of plate clogging.

1.4.2 Hydrocyclone

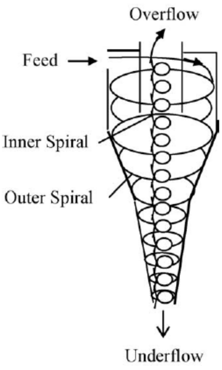


Figure 1.2: Fluid flow in a hydrocyclone [5]

Hydrocyclones consists of a cyclonic chamber in to which effluent enters at a tangential angle. Centrifugal and centripetal forces generated inside the chamber separates oil from water phase by accelerating the influent molecules based on their densities. Oil migrates to the core of the vortex due to its lower density and travel in the opposite direction to the denser liquid (water) as shown in Figure 1.2 [35, 5]. This method is suitable for treating oil droplets up to 1 - 15 μm[29] with average effluent concentration of 20 - 30 mg/L [50, 5, 35].

Table 1.4: Pros and cons of Hydrocyclone separators[35]

Pros	Cons
Compact with no moving parts	Possibility of fouling and clogging
High throughout with low retention time	Not suitable to treat stable emulsions and heavy oils
Capable of handling high initial oil concentration (up to 2000 mg/L)[29]	High maintenance and requires pressurised inlets

1.4.3 Gas Flotation

Gas flotation enhances the separation process by effectively reducing the density difference between dispersed oil and solids present in produced water. The bubbles aggregate with solids and droplets present and rise rapidly to the surface, where they are skimmed off [35]. The method is suited for removing droplets >20 μm with average effluent concentration of 10 - 40 mg/L[50].

Table 1.5: Pros and cons of gas flotaion[35]

Pros	Cons
Smaller and lighter particles can be removed	Dissolved oil cannot be removed
Compact with less footprint than gravity settlers	Producing large volumes of micro-bubbles is an energy intensive process
Good float suspension and better solid handling	Unlike hydro-cyclones, not very effective in handling oil concentrations >1000 mg/l

1.4.4 Membrane Separation

Membranes are thin films of inorganic or organic materials, which selectively separates a component from the fluid [17]. Membrane separation process are classified into many types, but the most common type of classification is based on the pore size distribution of the membrane used. They are Micro-filtration (MF), Ultra-filtration (UF), Nano-filtration(NF). Micro-filtration is used to remove suspended particles and Ultra and nano filtration can be used to remove colloidal dispersions [35]. In Reverse Osmosis separation, the membranes are designed to reject all species other than water [17]. Membrane processes are pressure driven [35].

Table 1.6: Pros and cons of membrane separation [35]

Pros	Cons
Feed water quality will have minimal effect on permeate quality	Affected by fouling from oil and biological content in influent
Easier to operate due to its modular design	Polymeric membrane material degradation at high temperatures (>50°C)
Compact and small foot print area	

1.4.5 Chemical Treatment

In chemical treatment, coagulants and flocculants are added to de-emulsify the colloidal system. The oil droplets coalesce and aggregate to form larger droplets or flocs which can be easily separated by various processes [35]. This method is one of the commonly used industrial chemical treatment process categorized as *chemical precipitation*. Other industrial chemical treatment processes are [17],

- Chemical oxidation
- Electrochemical processs
- Photochemical treatment
- Fenton process
- Treatment with ozone
- Room temperature ionic liquids
- Demulsifier

Table 1.7: Pros and cons of chemical treatment[35]

Pros	Cons
Enhance oil coalescence and aggregation.	Large volume of sludge is produced.
Contributes to removal of solids and organic carbon.	Inorganic coagulants can react with metal present in effluent.
	High operating cost (Chemical addition and pumping cost)

1.4.6 Biological Treatment

Treating produced water by aerobic and anaerobic micro-organisms are termed as biological treatment of produced water. Common biological treatment methods include activated sludge process, sequencing batch reactors, trickling filters [17]. Recent studies found that combination of activated sludge followed by membrane separation can effectively decompose and remove oil in waste water [35].

Table 1.8: Pros and cons of biological treatment[35]

Pros	Cons
High effluent quality with low sludge production	Hyper saline oil contaminated water for produced water treatment
Compact system with high loading rate and low energy cost	Sensitive to influent loading, abrupt changes could affect biological balance in reactor

Analyzing the pros and cons of various available industrial produced water treatment process, gas flotation process is of particular interest as it could remove very small oil droplets(>20 μm) to an effluent oil concentration of 10 - 40 mg/L.

1.5 Gas Flotation

Gas flotation is one of the common industrial produced water treatment methods. The primary principle behind the flotation process, is to increase the density difference between dispersed and continuous phases by introduction of bubbles. The process can be used to achieve very high separation efficiency with low retention time even with high loading rates. Flotation process is used as a secondary treatment process because of its inability to handle high initial oil concentrations. The absence of moving and mechanical parts in the system is highly advantageous as it reduces the wear and tear in machinery. The bubbles introduced into the system attach with immisicible oil droplets present in produced water. The resulting agglomerates rise to the surface at a faster rate. The effectiveness of the separation process is influenced by the interfacial interactions between the oil-water and water-gas interfaces [37]. The major steps in the flotation process were summarized by Wang *et al.*[38], as follows

- Generation of bubbles.
- Contact between bubbles and oil-droplets.
- Attachment of gas bubbles.
- Rise of aggregates and skimming the sludge.

Flotation process is classified into two types based on the method by which gas bubbles are introduced into the system as induced and dissolved gas flotation. Both methods are effective in floating small suspended particles and organic matter. Drewes *et al.*[11] reported that droplets as small as 3μm can be treated with aid of coagulants.

1.5.1 Induced Gas Flotation

Flotation process in which gas is introduced into the system as fine bubbles with the help of porous or perforated spargers is called induced gas flotation. To create large volumes of micro-bubbles, high shear impellers or dynamic spargers like jet nozzles and ejectors are used in an industrial scale. Figure 1.3 shows a typical induced gas flotation process. Gas bubbles of sizes 100-1000 μm can be generated by this process, and has the lowest retention time (4 min)[26, 35].

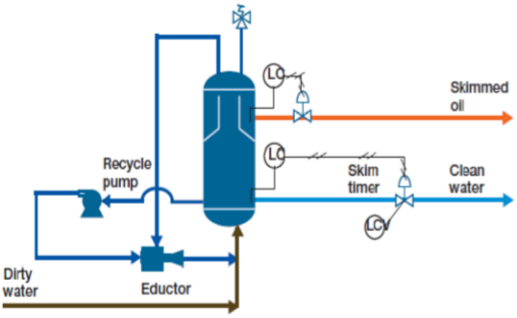


Figure 1.3: Induced gas flotation cell[43]

1.5.2 Dissolved Gas Flotation

In dissolved gas flotation, produced water to be treated is saturated with gas used for flotation under pressure and is passed to the flotation cell where the saturated water to be treated is depressurized to atmospheric pressure. The dissolved gas is released as small bubbles in the range of 10-100 μm in the process of depressurization [35]. Figure 1.4 shows the conventional dissolved gas flotation process. Due to very small bubbles generated, the retention time is slightly higher compared to IGF (15-30 min). In recent years, many developments have been incorporated in this method to improve separation efficiency, such as multistage-loop column [20], introducing a hydrocyclone in the inlet to remove large oil droplets[26] and solids and incorporating a jet pump at the inlet [49].

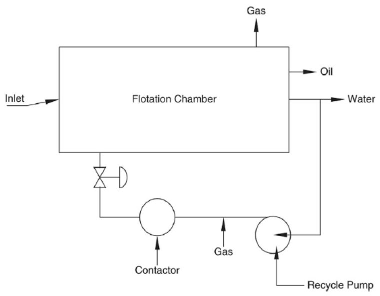


Figure 1.4: Dissolved gas flotation system [39]

1.5.3 Comparison of IGF and DGF

Induced and dissolved gas flotation processes have their own advantages and drawbacks. Table 1.9 helps in comparing they key differences between the processes.

Table 1.9: Comparison between IGF and DGF [35]

Parameters	IGF	DGF
Bubble Size	100-1000 μm	10-100 μm
Generation method	Velocity based, entrainment and dispersion	Pressure based, saturation and depressurisation
Operating Conditions	Turbulent and less quiescent; multi-cell configuration	Quiescent; single cell configuration
Retention time	<5 min [38]	5-15 min [1]
Footprints	Compact (due to low residence time)	Large (due to high residence time)
Capital cost	Low	High (Large tank and saturator system)

A comparative study for oil removal efficiency by induced and dissolved flotation methods was conducted by M. Eftekhardadkhah *et al.* [13]., the results obtained are shown in Figure 1.5. Higher separation efficiency was observed for induced gas flotation process, which emphasizes on the role of bubble generation mechanism on flotation efficiency. The observed results could be due to different attachment mechanism influencing separation between the methods.

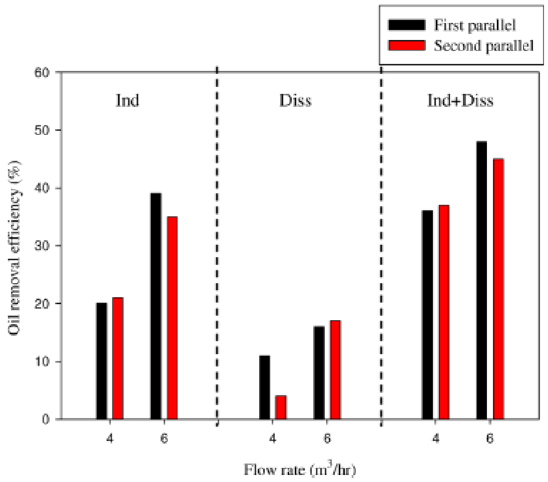


Figure 1.5: A plot of oil efficiency against flow rate for induced and dissolved gas flotation[13]

Having introduced the reader to produced water, its constituents and the environmental implications associated with the same. It becomes apparent that treating produced water is essential. Knowledge of existing technologies and their shortcomings, helps in choosing the a promising treatment method, Gas flotation. Gas flotation can be used as a secondary treatment method, downstream gravity settlers for produced water treatment. Combining this process with chemical additives (like demulsifiers and coagulants) could considerably improve the efficacy of the process. Among the available flotation methods, induced gas floating was chosen for produced water treatment in this project. The aim of this project was to find some of the major influential parameters on the separation process of flotation systems. This thesis focuses on studying various parameters and its influence on the oil removal efficiency for induced gas flotation process and gravity separation.

Chapter 2

Literature Review

2.1 Mechanism

Flotation process's efficacy for oil-water separation depends on numerous parameters, like bubble and droplet size, adherence of bubble to droplets, forming lighter agglomerates, oil concentration, surface active components present, etc,. Understanding the basic mechanisms involved in the process of separation is very important, because of the complex number of parameters or variables which influence the process [37].

Hank *et al.*[31] suggests four mechanisms for the bubble-drop attachment as listed below[31],

- Direct impingement.
- Hydrodynamic capture of oil droplets.
- Gas bubble clusters - Buoyant mat.
- Gas bubble nucleation.

2.1.1 Direct Impingement

Direct impingement is the basic flotation mechanism for bubble-drop attachment. The mechanism is as illustrated in Figure 2.1. Density difference of oil and gas with water, drives the dispersed phase and gas bubbles to rise to the surface of water, with gas rising with higher velocity than oil. When the rising trajectories of bubble and oil are mutual and reach a close proximity, an interfacial deformation is formed due to hydrodynamic forces pushing the bubble and droplet towards each other [26, 40]. A thin film of water is observed between the bubble and droplet. Thinning and rupture of the thin film is required for a successful contact between the bubble and droplet. The film gradually minimizes and reaches a certain value at which the film forms a dimple due to the interfacial tension gradients [26]. The dimple continues to thin till it reaches a critical thickness at which the film ruptures and the droplet attaches to the bubble surface. If conditions are favourable, oil droplet spreads on the surface of the bubble. The combined species of oil spread over a bubble surface is known as a full encapsulation. This formation provides the strongest bond between oil and gas bubble, resisting the removal of oil by shear forces [31]. Oil rises at a higher velocity in a full encapsulation than its initial creaming velocity [31, 26]. The flotation process efficiency is increased by a fully encapsulated oil on bubble by attracting free oil droplets in the rising path.

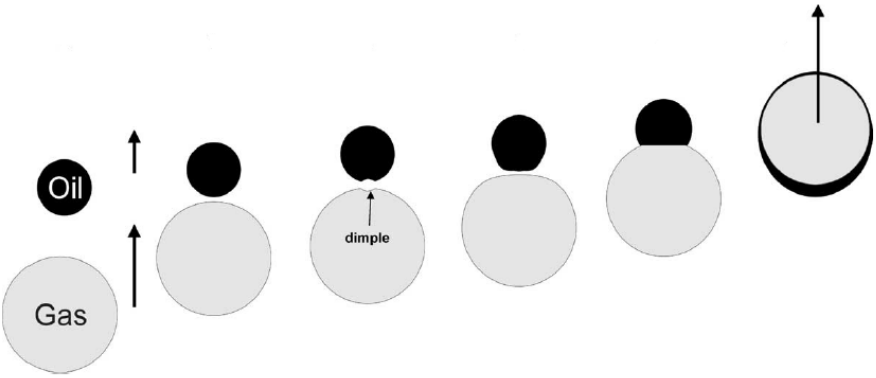


Figure 2.1: Mechanism of Attachment Process [26]

Full or complete encapsulation is not possible for all oil-bubble attachment. The criteria for a complete encapsulation to occur is that the droplet diameter should be at least 0.7 times the diameter of the bubble.[31] If the condition for complete encapsulation is not met, then the droplet-bubble attachment follows partial encapsulation, as shown in Figure 2.2 [31]. For smaller droplet sizes, oil droplet forms a lens in the aft part of the bubble, minimizing its contact with the aqueous phase [31, 37]. Point attachment is observed when the oil has a negative spreading co-efficient over the bubble surface [31]. Partial encapsulation is not favoured in flotation process because the shear forces acting on the bubble-drop conglomerate while rising, can separate the bond between bubble and oil [37, 31, 26].

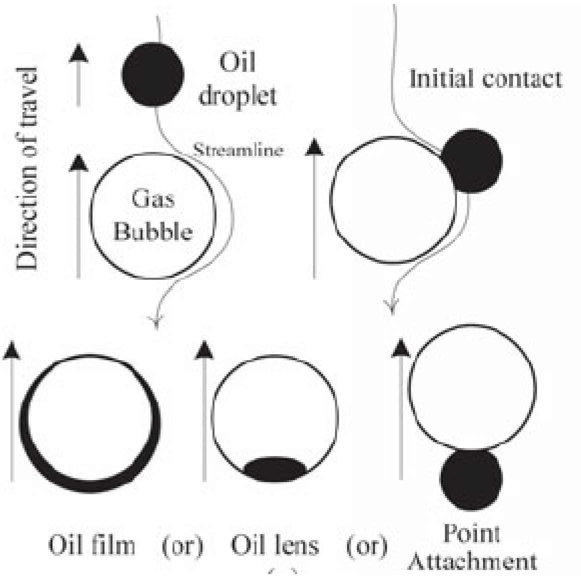


Figure 2.2: Direct Impingement with full and partial encapsulation [31]

2.1.2 Hydrodynamic Capture of Oil Droplets

When large bubbles (200-700 μm) comes in contact with very small oil droplets (1-15 μm), the hydrodynamic streamline flow of water captures oil droplets in the wake of the rising bubble [41, 37]. The mechanism is best depicted in the Fig 2.3. The trapped droplet follows the bubble in its upward trajectory, but does not form any bond with it. The size of the droplet is insufficient to break the the water film between the bubble and the droplet [31].

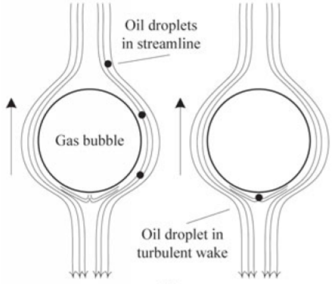


Figure 2.3: Hydrodynamic capture of oil droplets in the wake of rising gas bubble [31]

2.1.3 Gas Bubble Clusters - Buoyant Mat

Flotation process for oil with negative spreading co-efficient or suspended solids, results in forming a bridging structure with a cluster or a ”mat” of bubbles making multiple point attachments with the oil droplets [34]. The formed mat sweeps the droplets with a much wider diameter than a single bubble thereby effectively increasing the efficiency of the process [31, 34]. Figure 2.4 represents the buoyant mat mechanism. This mechanism is observed when high ionic composition or stabilizing chemicals are present in water that hinders bubble coalescence making bubbles attach without forming larger bubbles [31, 34]. Cluster formation is also promoted by high density of finely dispersed oil-droplets and bubbles [34, 31].

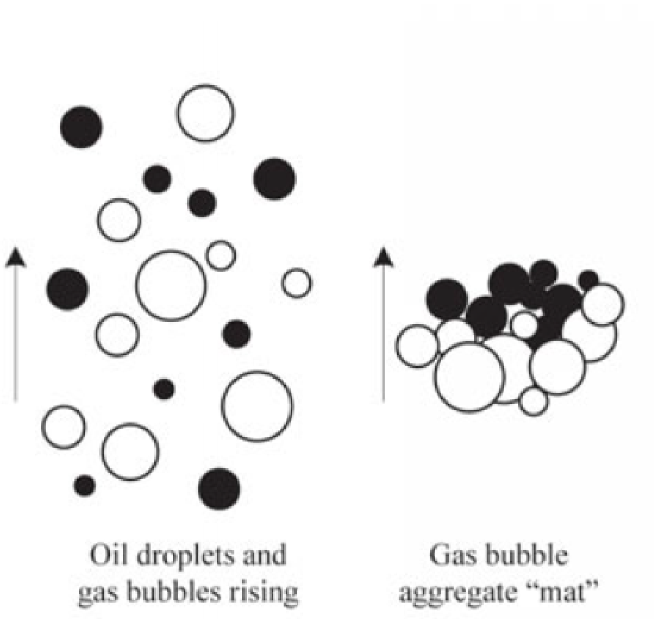


Figure 2.4: Gas bubble clusters forming buoyant mat [31]

2.1.4 Gas Bubble Nucleation

Gas bubble nucleation mechanism is explicit for dissolved gas flotation [34]. Like a normal DGF process, the hydrocarbon phase is saturated with dissolved gas, and dissoluted after the fluids enter the flotation column [31]. When pressure is reduced to a large extent inside the flotation column, gas bubbles start nucleating on the surface of the liquid droplet with sufficient effervescence [34]. The nucleated species grows in diameter slowly, as shown in Figure 2.5. The nucleated bubbles come in contact with each other to form larger bubbles. The formed bubbles attach and encapsulate the droplets depending upon the spreading co-efficient between the gas and oil [31, 37].

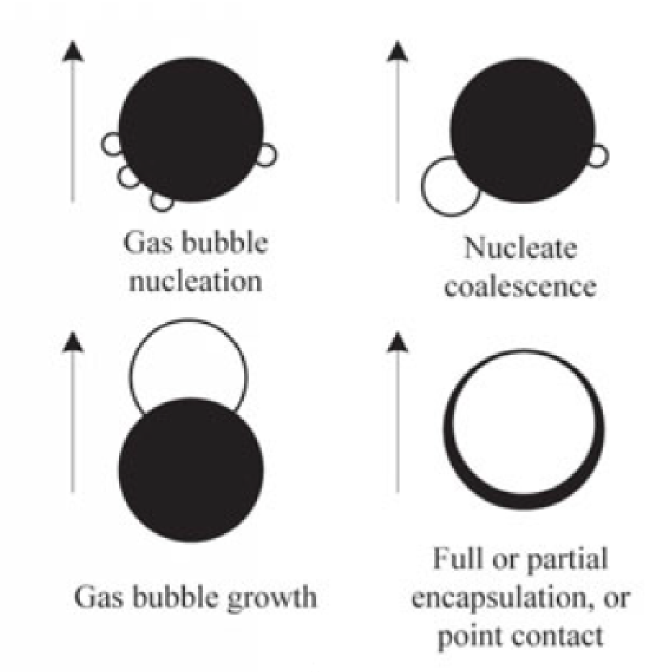


Figure 2.5: Nucleation and growth of gas bubble on the surface of an oil droplet [31]

2.2 Factors influencing Bubble-Oil Interaction

Oil-water interaction is influenced by a plethora of parameters, and that influences separation uniquely owing to different underlying phenomena that causes it. This section discusses some of the important factors influencing flotation process.

2.2.1 Nature of Crude

Crude oil is a complex mixture of various organic compounds and hydrocarbons. Understanding the nature of crude and various hydrocarbon fractionation is important to analyze its influence in the separation process. Saturates, Aromatics, Resins, and Asphaltenes (SARA) is measured for crude oils, as they differ for different crudes. Asphatlenes and resins are highly surface active components, so at interfaces they influence film thinning and rupture. Induction time and coverage time values helps in understanding the influence of surface active components in crude [12]. The time required for film thinning and rupture, when bubble and droplet are in contact is called induction time and the time required for the droplet to spread on the droplet surface is called coverage time [12].

Table 2.1: Induction and coverage time in synthetic brine [12]

Crude Oil	Induction time (s)	Coverage time (s)
A	8.00 ± 3.04	0.65 ± 0.15
B	8.75 ± 3.99	2.85 ± 0.91
C	1.01 ± 0.34	5.14 ± 1.16
E	4.11 ± 1.47	1.09 ± 0.33
F	3.28 ± 1.31	1.03 ± 0.38
G	4.79 ± 2.01	5.34 ± 1.20
H	6.34 ± 2.21	1.08 ± 0.54
I	3.84 ± 1.22	2.14 ± 0.95

Induction and coverage times for various crudes are listed in Table 2.1. It can be noted that they vary from crude to crude. The most influential parameter in the variation between induction and coverage times from crude to crude is the fraction of polar components present. Film thinning and rupture becomes difficult with high induction times, so the attachment efficiency is affected to a great extent [12]. Coverage time depends on the spreading co-efficient between the oil-droplet and bubble, and it increases with increase in viscosity. High coverage time is not favoured for flotation as it could detach the droplet from the bubble with flotation hydrodynamics [37, 12]. Low induction and coverage times are required for maximum attachment and separation efficiency [12].

2.2.2 Brine Composition

Brine composition influences the nature of bubble and droplet bubble interactions. It can alter the surface charge present on the droplet and bubble [37], which affects bubble sizes, spreading co-efficient and CMC [26]. High salt concentrations in brine affects ionic surfactants in droplet by modifying the charges in the hydrophobic part of the molecule by ion exchange, this phenomena influences the interfacial tension and interactions between bubble and oil [26]. Presence of multivalent ions in the brine effectively compresses the electrical double layer, this decrease in electrostatic stability favours film thinning and rupture [37, 26]. Strickland *et al.*[40] investigated the influence of salinity on bubble sizes and observed a decrease in bubble sizes for increase in salinity up to 3% and the sizes remained constant for salinity levels from 3-20% [40]. Figure 2.6 is a plot of bubble sizes against salinity.

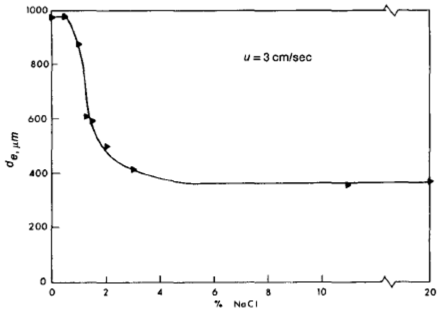


Figure 2.6: Plot of bubble diameter as a function of salinity [40]

2.2.3 Spreading Co-efficient

Spreading co-efficient plays a vital role, once the water film between the bubble and droplet ruptures and the droplet attaches itself to the bubble.[31] Spreading co-efficient(S_o) is given by the equation,

$$S_o = \gamma_{wg} - \gamma_{ow} - \gamma_{og} \tag{2.1}$$

Positive values of spreading co-efficient indicates that the oil spreads on the surface of the bubble and encapsulates the it. This can be observed when the interfacial tension between water-gas is larger than the sum of the interfacial tensions of oil-gas and oil-water. Positive S_o values often result in full encapsulation as discussed in Section 2.1.1 [31]. Negative spreading co-efficient values results in oil droplet having a finite contact angle with the gas and water interface, so a point attachment is observed in such cases [31, 37]. Spreading co-efficient is an indirect measure for the strength of attachment [35, 37]. High salinity, small bubble sizes, large droplet sizes increases spreading co-efficient, whereas presence of impurities in gases reduces interfacial tension between gas and water subsequently decreasing spreading co-efficient [37, 31].

2.2.4 pH

Oil droplets dispersed in water and bubbles acquire a negative charge on the surface, which can be influenced by pH [37]. Varying pH significantly changes the surface charges of the droplets and bubbles. Experimental investigation of Li Xiao-Bing *et al.* [25] on the effect of pH with separation efficiency for a dissolved gas flotation system is shown in Table 2.2. It was noted that pH affected separation efficiency to a large extent, and the optimal pH for maximum separation was observed to be between pH 6 - 9 [25, 37].

Table 2.2: Effect of pH value on oil removal [25]

pH	3	5	6	7	9	10
Oil removal (%)	64.1	76.3	77.0	77.5	78.6	75.2

2.2.5 De-emulsifiers and flocculants

Surface active agents like surfactants and polymers modifies the interfacial properties of colloidal systems [37]. Current industrial flotation process uses ionic surfactants for oily-waste water treatment. These components help tailor flotation process efficiency by the following steps[26]:

- Modifying the charge on the oil droplets
- Flocculation by anchorage and bridging

For optimum results, addition of primary coagulant at the beginning of the process is favoured. Coagulants are highly charged cations with low molecular weight, which help neutralize the negatively charged bubble and oil droplet surface [35]. The effect of pH also has a significant effect on the surface charges of the floating species as discussed in Section 2.2.4, so specifying optimal pH range is important [1]. Table 2.3 lists common industrial coagulants used in flotation systems and their optimal operational conditions [35, 37].

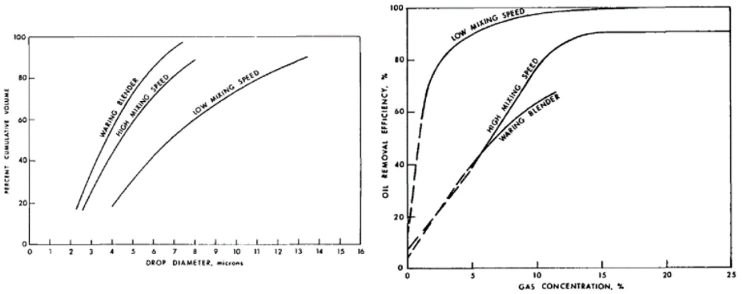
Table 2.3: Coagulants used in Flotation System [35]

Coagulant type	Optimal dosage (mg/L)	Optimal pH	Influent concentration (mg/L oil)	Removal efficiency
Aluminium Sulphate [1]	100	8	1630	99.3%
Ferric Sulphate [1]	120	7	1630	99.94%
Ferric Chloride [15]	500–700	8.41 ± 0.15	169.7 ± 17	73 ± 5%
Alum [15]	600–800	6.93 ± 0.2	169.7 ± 17	78.59 ± 0.8%
Ferrous Sulphate [15]	700–1000	8.9 ± 0.2	169.7 ± 17	72 ± 4.2%
Aluminium Sulphate [23]	50	4	500	93%
Alum [30]	800–1400	8-10	–	99%
Ferric Chloride [52]	100	6	500	>95%

Separation efficiencies can be further enhanced by adding high molecular weight (approximately 2000[26]) ionic polymers. The polymers bridge and attach to nearby bubbles and droplets forming flocs which rise effectively to the surface of water enhancing efficiency of the process [26, 37].

2.2.6 Size Distribution

Variation of mixing speed yields in samples with different drop-size distribution. Strictland *et al.*[40] investigated the flotation efficiencies for oil-water emulsions by varying the mixing speed for emulsion preparation. Figure 2.7 shows plots of drop diameter variation for different mixing speeds and oil removal efficiency against gas concentration for samples prepared with different mixing speeds. Comparing the results from the two plots, oil removal efficiency increases with increase in drop-size. The sample prepared with the lowest mixing speed had the highest drop-sizes and highest oil removal efficiency [40].



(a) (b)

Figure 2.7: Influence of mixing speed, (a) Plot of cumulative volume percentage against drop diameter (b) Plot of oil removal efficiency [40]

2.2.7 Initial Oil Concentration

Li Xiao-Bing *et al.*[25] studied the influence of initial oil concentration on oil removal efficiency and residual oil concentration for dissolved air flotation. Figure 2.8 shows plot of residual oil concentration against dissolved air pressure for various initial oil concentrations. It was observed that the oil removal efficiency of 70.4%, 69.7%, 70.6%, and 71.0% achieved corresponding to initial oil concentrations of 51.0 mg/L, 100.5 mg/L, 150.9 mg/L, and 201.2 mg/L were similar, but the residual oil concentrations varied significantly.

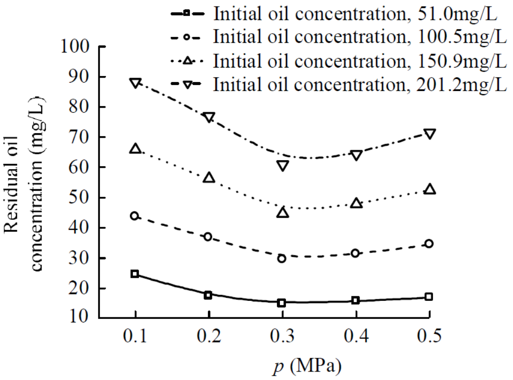


Figure 2.8: Influence of initial oil concentration [36]

2.2.8 Bubble Size

In induced gas flotation systems, spargers were used for generating bubbles required for the separation process and influences the bubble size distribution in the system. Pore size distribution is a primary factor which influences the bubble size distribution through a sparger. The work of Schäfer *et al.* [36] compared initial bubble size distributions of three spargers of different pore size distributions are shown in Figure 2.9. Sparger with the smallest average pore diameter produced the smallest bubbles. Moosai *et al.* [26] suggests that maximum separation efficiency for the system can be achieved for smallest bubble sizes and largest droplets.

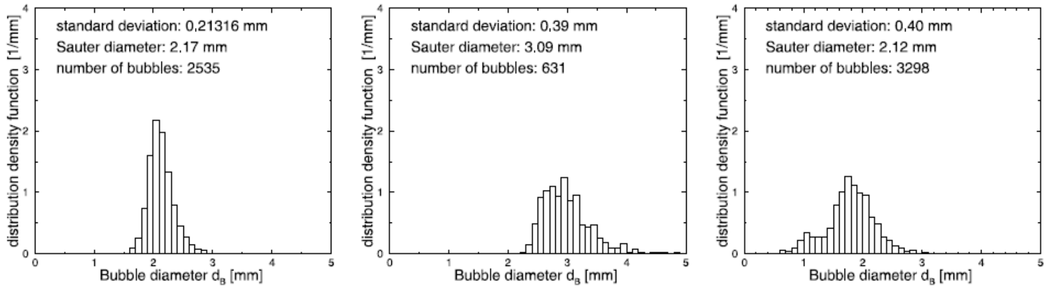


Figure 2.9: Comparison of initial bubble size distribution of capillary sparger ($d_{sp} = 150\mu m$), ring sparger($d_{sp} = 400\mu m$) and porous BRANDOL sparger($d_{sp} = 50\mu m$) with N_2/water system[36]

2.2.9 Flow Regime

The swarm of rising bubbles can be classified into three flow regimes depending upon the flow rate and size distribution of the bubbles as homogeneous regime, heterogeneous regime and slug flow. In homogeneous regime, uniform bubble distribution can be observed and the regime ranges from 0.03-0.08 m/s depending on the system [51]. In heterogeneous regime, due to high flowrates and turbulance created increased coalescence and large bubbles were observed. If diameter of the flotation column is small, slug flow is observed for higher velocities. In this regime extremely large bubbles were formed and were stablised by the column wall [51, 37]. Figure 2.10 shows different flow regimes discussed for a bubble-liquid system [51, 37].

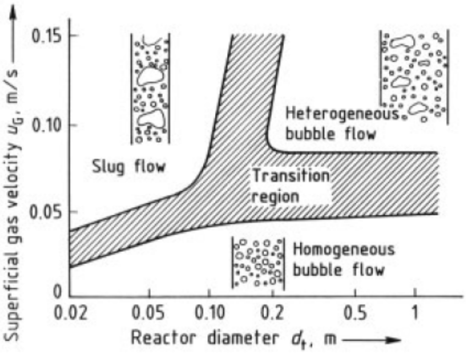


Figure 2.10: Influence of type of sparger [51]

2.2.10 Type of Gas

Interfacial interactions of the gas with water and oil is very important as discussed in Section 2.2.3. Methane is used for most industrial oil-water separation due to its availability and low interfacial tension with oil when compared with other gases, thereby favouring spreading. Nitrogen and carbon dioxide were other commonly used gases for flotation. Air oxidizes with oil forming a sticky mass, so it is generally not used for flotation process [26, 37].

In IGF process, the wettability of the gas with the material of the sparger can influence the size of the bubbles generated. Figure 2.11, Schäfer *et al.* [36] compares the initial bubble diameters with nitrogen gas formed with polyethylene spargers without(left) and with(right) sputtered gold layer. The sparger with the gold coating wets the surface better and a smaller contact angle was made by the gas with the surface, thereby forming smaller bubbles in the process [37, 36].

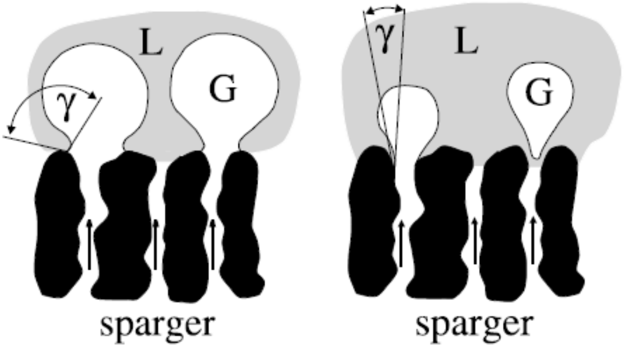


Figure 2.11: Influence of contact angle on initial bubble diameter [36]

Chapter 3

Materials and Method

3.1 Materials

3.1.1 Crude Oil

Three types of crude oil were studied and were denoted by B, E and F. Some of the important physico-chemical properties are listed below.

Table 3.1: Physico-Chemical data for the Crude oil B, E & F []

	B	E	F
Density (20°C, g/cm^3)	0.841	0.831	0.822
Viscosity (20°C, cP)	14.2	8.3	7.5
Saturates (wt%)	84.0	74.8	78.5
Aromatics (wt%)	13.4	23.2	18.9
Resins (wt%)	2.3	1.9	2.5
Asphaltenes (wt%)	0.3	0.1	0.1
Resin/asphaltenes	8	19	25
TAN (mg/g)	<0.1	0.5	0.1
TBN (mg/g)	1.0	0.4	0.6

De-emulsifer of concentration 200 ppm was added to the crude. Demulsifiers changes the chemistry of the crude, so influence of type of crude will not be discussed in this thesis.

3.2 Preparation of Brine

The brine was prepared by dissolving analytical grade of NaCl (99.5%, Merck, Germany) and $CaCl_2.2H_2O$ (99.5%, Fluka, Czech Republic) in water provided by Millipore ultrapure water system. Two compositions of brine were prepared, one with and other without divalent cations (Ca^{2+}). The ionic strength was kept constant in both brine solutions.

Table 3.2: Ionic composition of brine solution

	Concenration (g/L)	
Ion	Brine without divalent cations	Brine with divalent ions
Cl^-	35	36.87
Na^+	35	32.236
Ca^{2+}	0	2.317

3.3 Preparation of Synthetic Produced Water

Synthetic produced water emulsions were prepared by dispersing weighed amount of crude oil in the 80 ml of prepared brine at a specified pH, using Ultra-Turrax at a specified mixing speed for 4 minutes. The emulsions were prepared in two parallels. A small sample of the prepared produced water emulsion was immediately transferred into a glass cuvette and was taken to the microscope for further analysis.

3.4 Experiments

3.4.1 Gravity

Gravity experiments were conducted in the same cell designed for gas flotation. The prepared produced water of 70 ml volume, was poured into the cell and was let to separate under the influence of gravity for 2 minutes. Sample of 25 ml was collected after the separation time from about 3 cm from the bottom of the cell from which 20 ml was transferred to a schott bottle for measuring the oil concentration present using UV-Vis spectrometer. The remaining sample collected after separation was transferred to a cuvette and was taken to the microscope to determine the drop-size distribution of the sample after separation.

Design of Experiments

Gravity experiments were conducted for all three crudes, Crude B, E and F as shown in Figure 3.1. Experiments were conducted for two brine solutions at pH 6. Two different oil concentrations were experimented for sample with brine containing no divalent ions. For samples containing initial oil concentrations of 250 ppm, mixing speeds of ultra-turrax was varied.

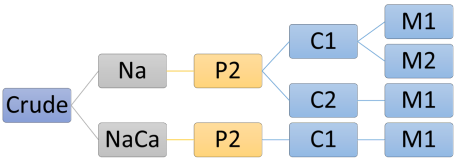


Figure 3.1: Design of experiments for gravity experiments

Na - Brine without divalent ions
NaCa - Brine with divalent ions
P2 - Brine solution at pH 6
C1 - Initial oil concentration - 250 ppm
C2 - Initial oil concentration - 500 ppm
M1 - Mixing Speed - 15000 rpm
M2 - Mixing Speed - 10000 rpm

3.4.2 Gas Flotation

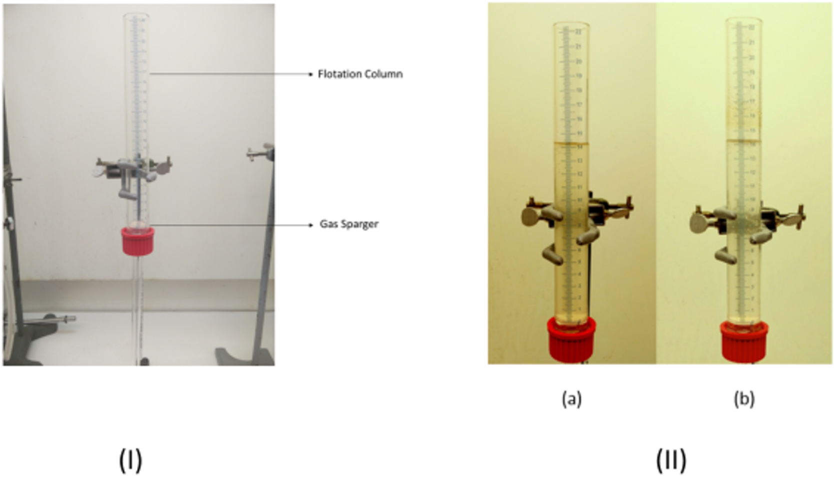


Figure 3.2: (I) Flotation Cell, (II)(a) Produced water sample before separation (b) Produced water sample after separation

The flotation cell used was designed of type induced gas flotation. It was a glass column of diameter 2.5 cm and height 25 cm as shown in the Figure 3.2. The synthetic produced water sample of volume 70 ml was filled into the cell and gas of constant flow-rate, 120 mL/min was introduced at the bottom of the column through a porous glass sparger. After 2 minutes of separation time, 20 ml of sample was collected by a pipette. Sampling point was about 3 cm from the bottom of the column. Figure 3.2 shows flotation before and after separation.

Design of Experiments

Flotation experiments was designed to study the influence of various parameters. Depending on how they influence the flotation process, the parameters were grouped into pre-separation and process parameters. Type of crude, pH of brine, initial oil concentration and mixing speed were grouped under pre-separation parameters and Type of sparger and gas used were grouped under process parameters. Spargers SP1 and SP2 mentioned in the design of experiments were porous glass spargers with pore size distribution in the range of 9-15 μm and 15-40 μm respectively.

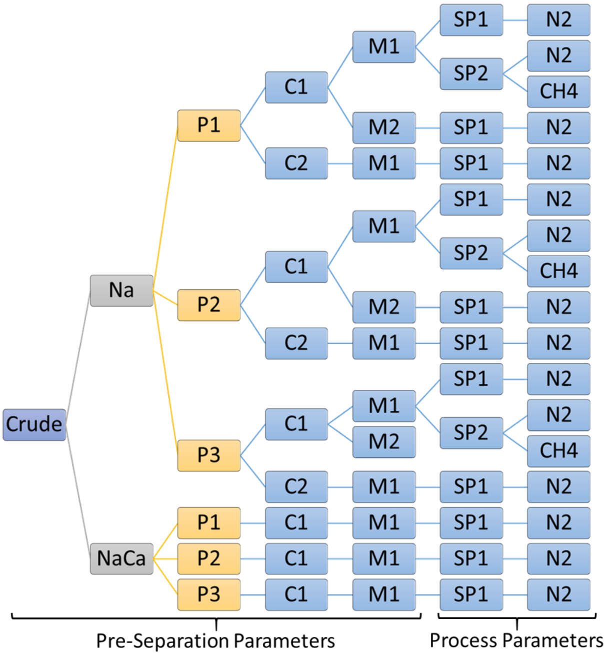


Figure 3.3: Design of experiments for gas flotation experiments

Crude - Crude B, E or F
Na - Brine without divalent ions
NaCa - Brine with divalent ions
P1 - Brine solution at pH 4
P2 - Brine solution at pH 6
P3 - Brine solution at pH 10
M1 - Mixing Speed - 15000 rpm
M2 - Mixing Speed - 10000 rpm

C1 - Initial oil concentration - 250 ppm
C2 - Initial oil concentration - 500 ppm
SP1 - Sparger with porosity grade 4
SP2 - Sparger with porosity grade 3
N2 - Nitrogen as flotation gas
CH4 - Methane as flotation gas

3.4.3 Microscope

Microscope was used to capture produced water sample images to measure its droplet size distribution. Images of the sample were taken using Nikon LV 100D microscope. Microscope was focused on the upper part of the cuvette containing freshly sampled produced water. Ten images were taken for each sample and the drop sizes were measured using the software ImageJ.

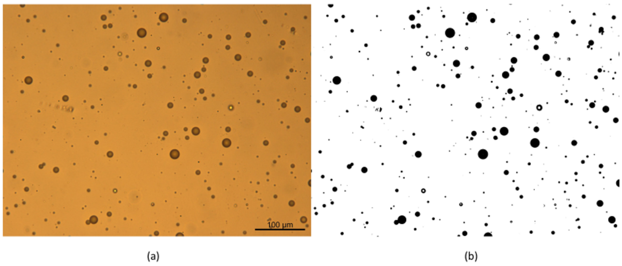


Figure 3.4: (a) Sample image from microscope (b) ImageJ software processed image for measuring droplet area

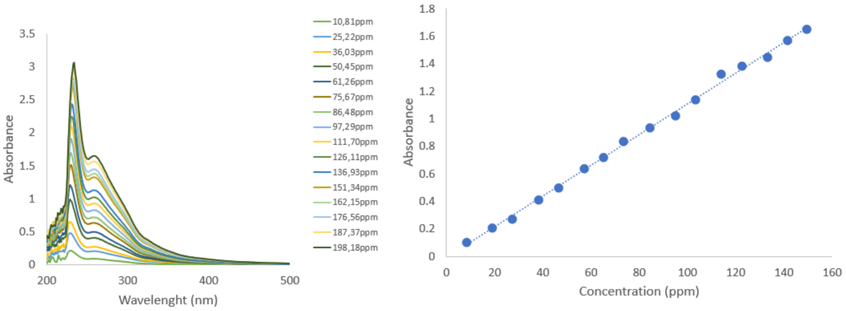
Binary image segmentation was used to process the image. The software calculates the area occupied by each droplet. A MATLAB code written by the author calculates the sauter mean diameter (d_{32}) of the droplets and the standard deviation. Sauter mean diameter of the droplets was calculated by the Equation 3.1 and SD was calculated using 68-95-99.7 rule.

$$d_{32} = \frac{\sum_1^n D_i^3}{\sum_1^n D_i^2} \tag{3.1}$$

where D_i is the geometric mean diameter calculated for $i^t h$ species

3.4.4 UV-Vis Spectroscopy

UV-Vis Spectrometer was used to calculate the oil concentration present in each sample after separation by measuring their absorbance values. The sample collected after separation was completely mixed with dichloromethane to extract the crude from the sample. Organic phase was separated from the mixture through a separation funnel. Ultra-violet spectroscopy was used to determine the amount of crude oil present in the sample, by using the absorbance value at 259nm and pre-made calibration curves data for each crude oil dissolved in dichloromethane. Figure 5.15 shows the UV spectra and calibration curve for Crude B. Oil concentration of the sample was determined by averaging the oil concentrations measured at three different dilutions for the same sample.



(a) (b)

Figure 3.5: (a) UV spectra of known oil concentration in Dichloromethane for Crude B (b) Obtained calibration curve

With the initial and final amounts of crude oil in the emulsion, the Oil Removal Efficiency (ORE) was calculated by the Equation 3.2. The average value of two repeated experiments with standard deviation was reported for ORE.

$$ORE = \frac{(C_i - C_f)}{C_i} \tag{3.2}$$

where,

C_i	Initial oil concentration (ppm)
C_f	Oil concentration after 2 min of separation time (ppm)

Chapter 4

Results and Discussion

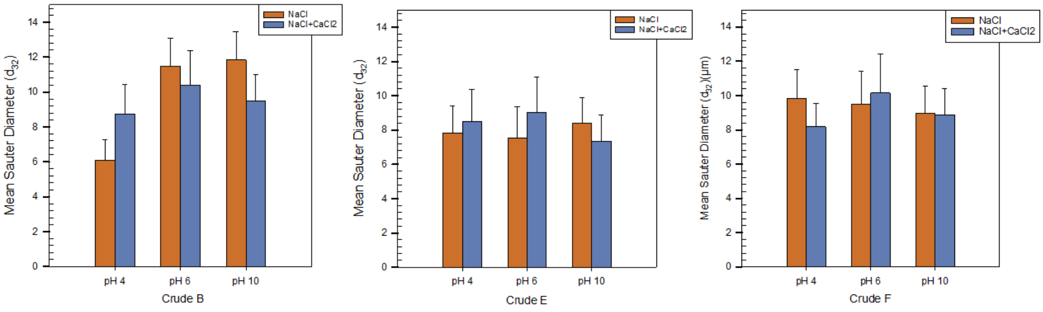
Summary of results obtained from the experiments conducted and detailed inferences are discussed in this chapter. The first part of the chapter presents the results of droplet sizes measured which is followed by gravity and gas flotation process. The final section compares the efficiency of gravity and gas flotation methods for oil removal.

As discussed in previous chapter 3.4.2, the parameters varied in this study were grouped into two categories, pre-separation parameters and process parameters. Droplet sizes dispersed in crude oil and gravity separation process were only influenced by pre-separation parameters. Flotation process on the other hand was influenced by both pre-separation and process parameters.

4.1 Droplet Size Distribution

Droplet size distributions help in understanding the nature of the colloidal system and is influenced by parameters like brine composition, pH, etc. The effect of each parameter over droplet sizes were determined.

4.1.1 Effect of Brine

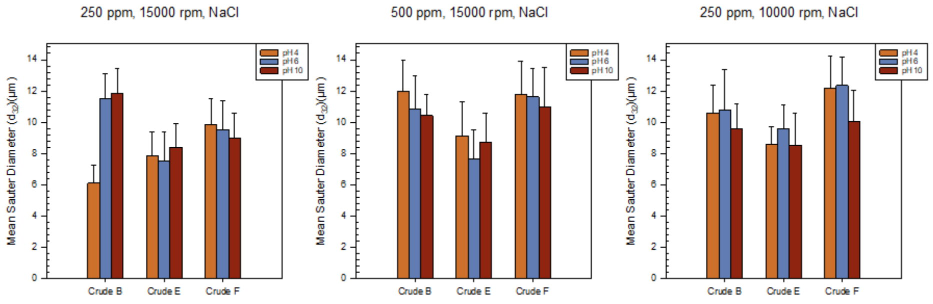


(a) (b) (c)

Figure 4.1: Sauter mean diameter for samples with varying brine composition

Droplet size measurements for produced water samples prepared with different brine compositions with crudes B, E, and F at three different pHs of 4, 6, and 10 is represented in Figure 4.1. The mixing speed and initial oil concentration were constant at 15000 rpm and 250 ppm respectively. The presence of divalent ions in produced water, favours coalescence by minimizing the electrical double layer on the droplet surface. It can be observed that this holds true for most cases in the system with pH10 being an exception. Droplet sizes of crude B and E at pH 10 have significantly reduced from 11.85 μm and 8.39 μm to 9.47 μm and 7.33 μm respectively. In crude F, pH 4 had a decrease in droplet size from 9.84 μm to 8.18 μm.

4.1.2 Effect of pH



(a) (b) (c)

Figure 4.2: Sauter mean diameter of three different sample sets

When the influence of pH over droplet sizes was studied, no definitive trend was observed. Droplets sizes of Crude B can be considered for this case. For samples with 250 ppm initial oil concentration and 15000 rpm mixing speed, the droplet sizes increased with increase in pH as shown in Figure 4.2 (a). For the same crude with higher initial oil concentration (500 ppm) shown in Figure 4.2 (b), a completely reverse trend was observed. The observed irregularity was different for different crudes as well. No literature evidence was available for these observations and with the available data, the cause for irregularity is difficult to speculate.

4.1.3 Effect of Initial Oil Concentration

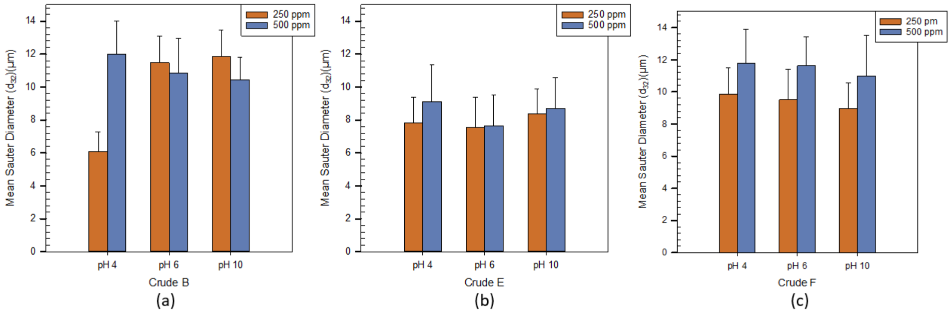
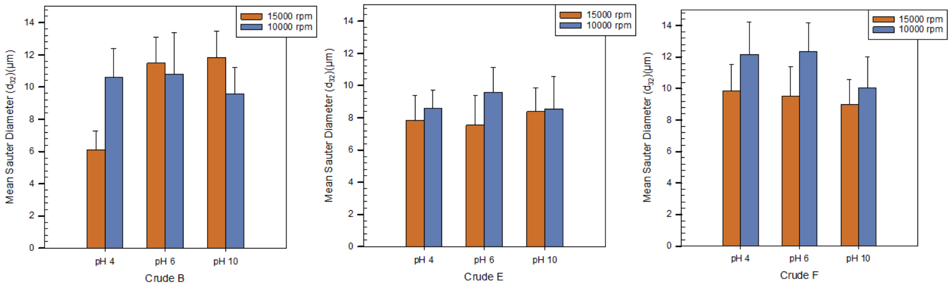


Figure 4.3: Sauter mean diameter for samples with varying initial oil concentration

Experiments were conducted with two different initial oil concentrations of 250 and 500 ppm at mixing speed 15000 rpm with NaCl brine. From Figure 4.3, it can be observed that, there was an increase in droplet size for increase in initial oil concentration. With increase in concentration, the number of droplets dispersed in the continuous phase is more, which increases the encounter frequency and coalescence of oil droplets in the system, resulting in the observed trend of increase in size. Crude B at pH 10 was an exception to this norm, as its decreased with increase in initial oil concentration. Crude B has the highest TBN value and viscosity among the three crudes used, the basic environment might have influenced the surface active basic compounds to alter the surface charge of the droplet, this combined with high viscosity values might have prevented the coalescence of droplets.

4.1.4 Effect of Mixing Speed



(a) (b) (c)

Figure 4.4: Sauter mean diameter for samples with varying mixing speed

Two different mixing speeds of 15000 and 10000 rpm were used for its possible influence over the droplet size distribution. Mixing speed indirectly corresponds to the energy input given to the colloidal system. Generally. high mixing speed corresponds to high energy input to the system which effectively disperses oil in brine solution, resulting in a stable emulsion with smaller droplets. The same can be observed for most the sample crudes in Figure 4.4.

4.2 Droplet size distribution before and after separation

Crude at pH 6 was selected to study this effect.Figure 4.5 is a plot of mean sauter diameter of droplet sizes before and after separation of crude B experiments. It can be noted that the droplet sizes before separation for crude B was almost the same in all cases, if the values are considered with their standard deviations. The sizes after separation differ based on the method of separation used. For gravity separation and gas floation, smaller droplets were observed post separation. Gravity separation had exceptions in experiments involving 10000 rpm (lower mixing speed) and 500 ppm (higher initial oil concentration). The sampling point for the experiments were at 3 cm above the base of the cell. At this point the larger droplets easily tend to rise to the surface of water, compared to the smaller droplets. The droplets left in the cell are so small that they are unaffected by both gravity and gas flotation. For experiments at low mixing speed, easy emulsification takes place, in which the emulsion is broken by fast coalescence. The droplets coalesce in the process forming larger droplets. Similar trend was also observed in experiments with higher concentration.

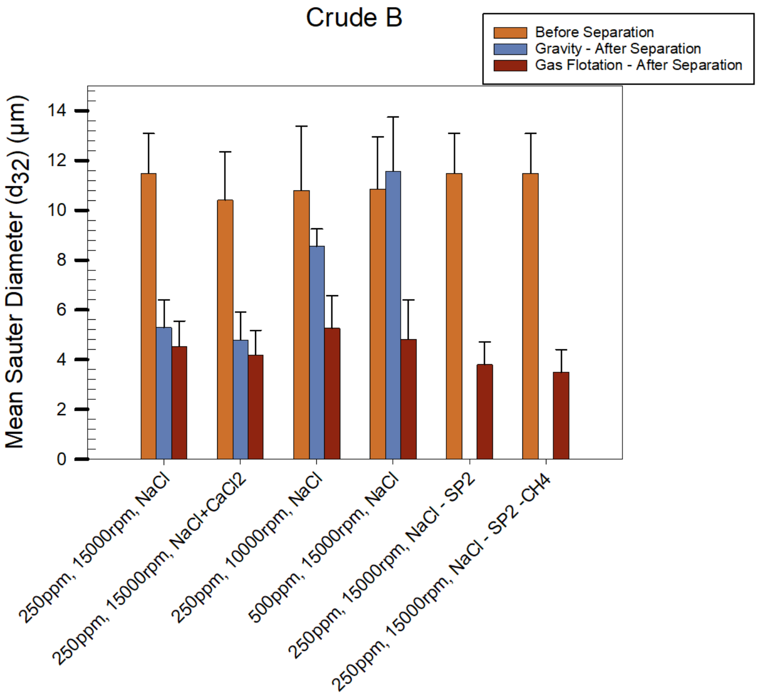


Figure 4.5: Sauter mean diameter for all samples of crude B before and after separation at pH6

Figure 4.6 represents mean sauter droplet diameter bfeore and after separation for all experiments with crude E. The results for crude E is a similar to that of crude B.

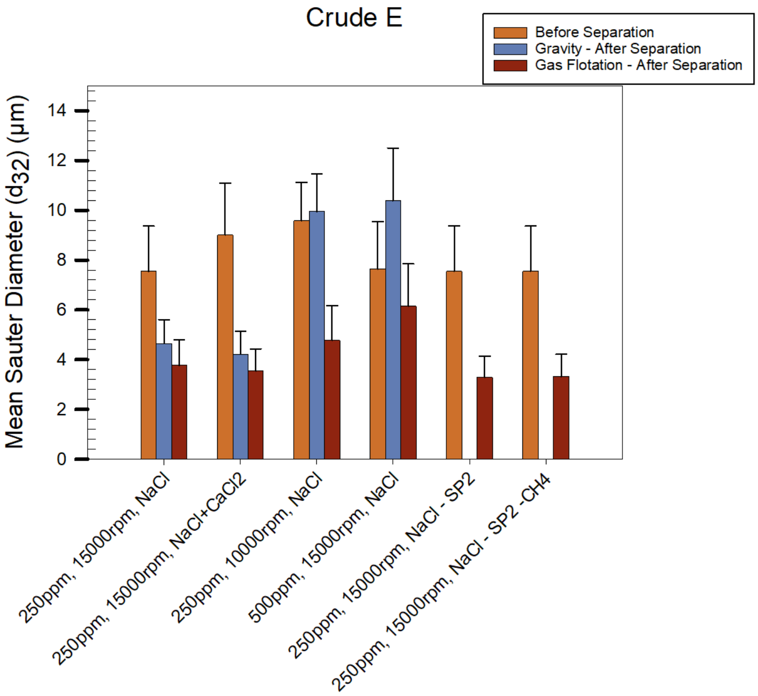


Figure 4.6: Sauter mean diameter for all samples of crude E before and after separation at pH6

A plot of all drop size measurements before and after separation data is shown in Figure 4.7. The data of post gravity separation droplet diameter for crude F is almost equal in all cases and the value is slightly higher than the pre-separation data. This could be due to the fact that crude F is the lightest of the considered crude and has the least viscosity among the three crudes, so high coalescence rate could have yielded such observed results in this case.

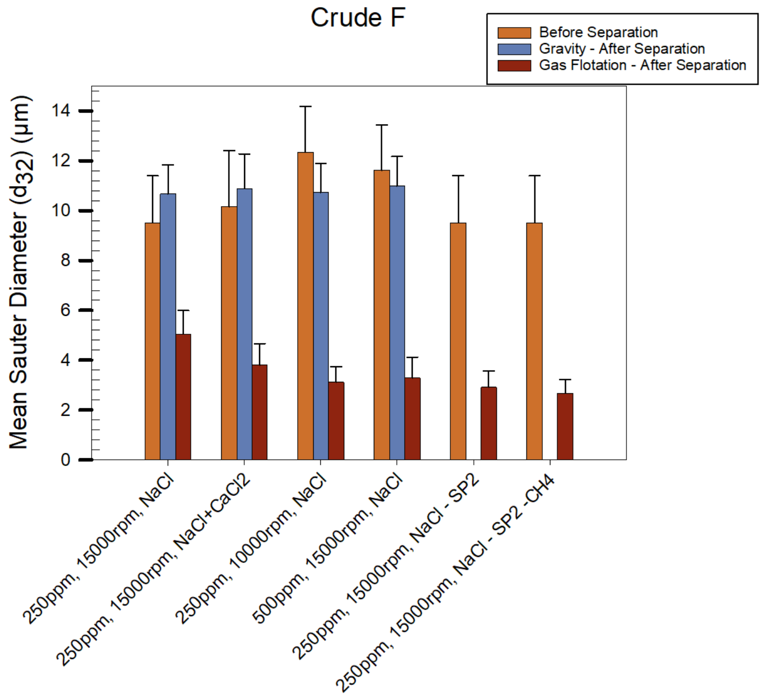


Figure 4.7: Sauter mean diameter for all samples of crude F before and after separation at pH6

In all three cases, post gas flotation droplet diameters of experiments with sparger SP2 for nitrogen and methane gas had the least values. The sparger SP2 has higher pore size than the sparger SP1, so larger bubbles were formed in the former than the latter. The reason for the observed trend could be due to the mechanism, hydrodynamic capture of oil droplets mentioned in Section 2.1.2, which explains the effectiveness of large bubbles removing droplets of the smallest sizes.

4.3 Gravity Separation

Just like droplet size distributions, gravity separation was also influenced only by pre-separation values. All gravity separation experiments were done at pH6.

4.3.1 Effect of Brine

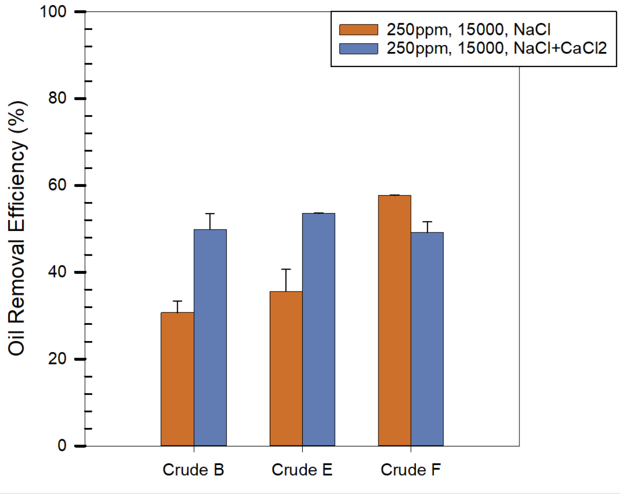


Figure 4.8: Effect of brine on oil removal efficiency of gravity separation

The effect of brine on the separation efficiency was studied by comparing the results of separation efficiency of two brine compositions considered in this project. Other parameters like initial oil concentration and mixing speed were kept constant. Figure 4.8 is a plot of oil removal efficiency against three different type of crudes with two different brine composition. For brine without divalent ions, crude F showed the highest separation efficiency of 57.653±0.11 and, for brine with divalent ions crude E had the highest efficiency of 53.513±0.08. The separation efficiency of crude B and crude E increased with the presence of divalent ions. The divalent ions suppresses the electrical double wall around the droplet thereby promoting coalescence and increase in droplet diameter. The separation process follows stokes law, which is given by,

$$v = \frac{g d_p^2 (\rho_l - \rho_p)}{18\mu} \tag{4.1}$$

where,
v – Terminal velocity (m/s)
g – Gravitational acceleration (m/s^2)
d_p – Bubble/droplet diameter (m)
ρ_l – Density of the continuous phase (kg/m^3)
ρ_p – Density of bubble/droplet (kg/m^3)
μ_l – Viscosity of the continuous phase (kg/ms)

From equation 4.1, increase in droplet diameter increases the terminal velocity of settling, thereby enhancing separation. It is to be noted that the increase in droplet diameter in crude F, did not improve the separation efficiency in the presence of divalent ions.

4.3.2 Effect of Initial Oil Concentration

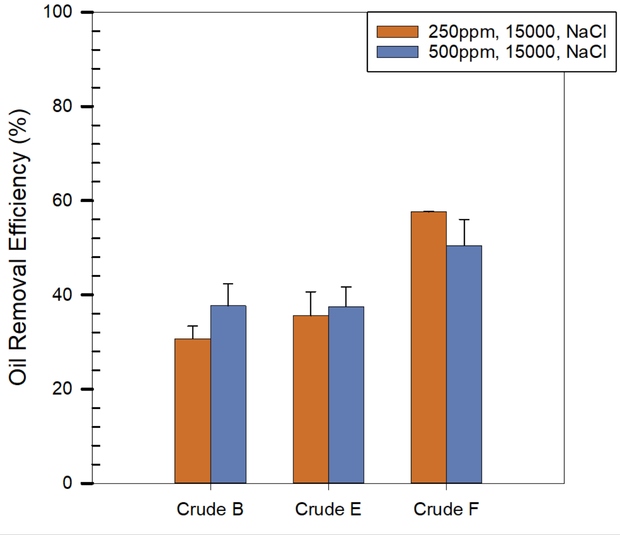


Figure 4.9: Effect of initial oil concentration on oil removal efficiency of gravity separation

Experiments were conducted to determine the influence of initial oil concentration on the efficiency of gravity settling process. Two initial oil concentrations of 250 ppm and 500 ppm were considered, and having all other parameters constant. The experiments were conducted for all three types of crude. Figure 4.9 shows the effect of initial oil concentration over oil removal efficiency for three different crudes. It can be inferred that crude B had a slight increase in separation efficiency, crude E had no effect and Crude F showed slight decrease in the oil removal efficiency. The minimal increase in the oil removal efficiency for crude B and E can be associated with the increase in the droplet diameter post separation as shown in Figure 4.5 and 4.6 respectively. Higher concentrations are associated with high number of droplets dispersed in water, these droplets can easily coalesce forming larger droplets, which rise to the surface of the water more effectively, but in most systems higher initial oil concentrations result in higher residual oil in the left

4.3.3 Effect of Mixing Speed

Tests to determine the influence of mixing speed on gravity separation efficiency were designed for two different mixing speeds of 15000 rpm and 10000 rpm with brine containing no divalent ions (Pure NaCl brine) and constant oil concentration of 250 ppm. Figure 4.10 shows the plot of oil removal efficiency against type of crude used.

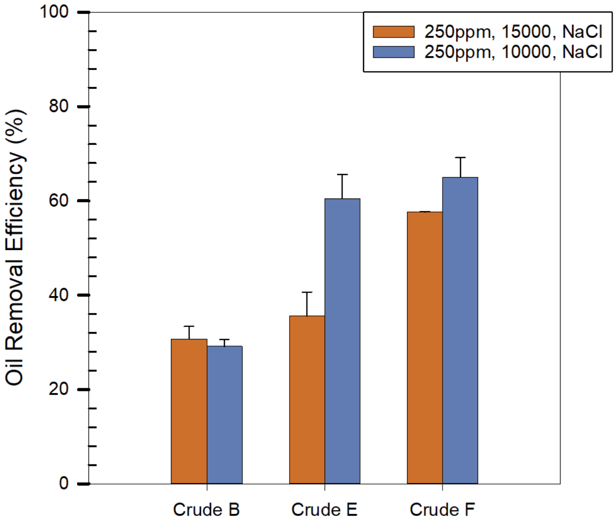


Figure 4.10: Effect of mixing speed on oil removal efficiency of gravity separation

A trend of increasing oil removal efficiency is observed for decrease in mixing speed. This could be associated with increase in the droplet size before separation at lower mixing speed as shown in Figure 4.4. Larger droplets rise to the surface at a higher rate than its smaller counter parts which is given by stokes equation 4.1.

All the data obtained from gravity separation method, was plotted against its respected residual oil concentration as shown in Figure 4.11.

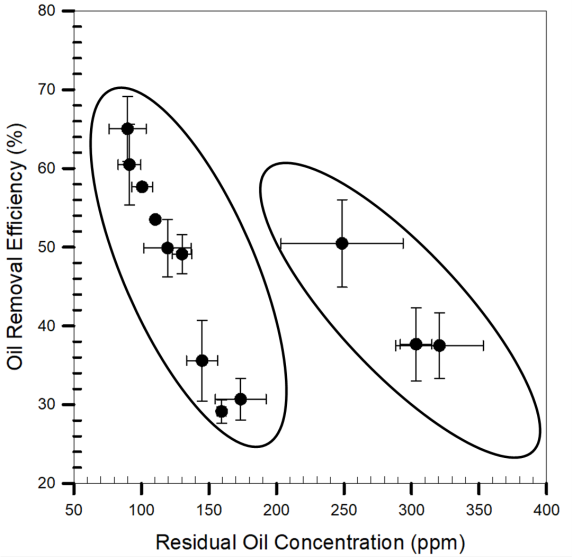


Figure 4.11: Plot of separation efficiency against residual oil concentration for gravity separation

The plot represents two distinct trends, irrespective of the type of crude used nor the parameters varied. Upon closer observation it was found that the trends corresponded to the initial oil concentration used for separation. The efficiency of the gravity separation process ranges from 29% to 65%. The data points with the highest separation efficiency was noted to be of Crude F, while Crude B had the least efficiency. Low mixing speeds and high droplet sizes characterizes the high separation efficiency.

4.4 Gas Flotation

Flotation studies were carried out to study the influence of pre-separation and process parameters mentioned on its separation efficiency. The experiments were conducted for three different crudes at three different pHs of 4, 6 and 10 respectively to study the influence of each parameter on separation efficiency.

4.4.1 Effect of Brine

Influence of divalent ions present in brine solution over separation efficiency was studied by conducting flotation experiments in brine solutions with and without divalent ions, keeping initial oil concentration and mixing speed constant in both cases. Sparger SP1 with N_2 gas was used. Figure 4.12 illustrates the oil removal efficiency for diffent crudes.

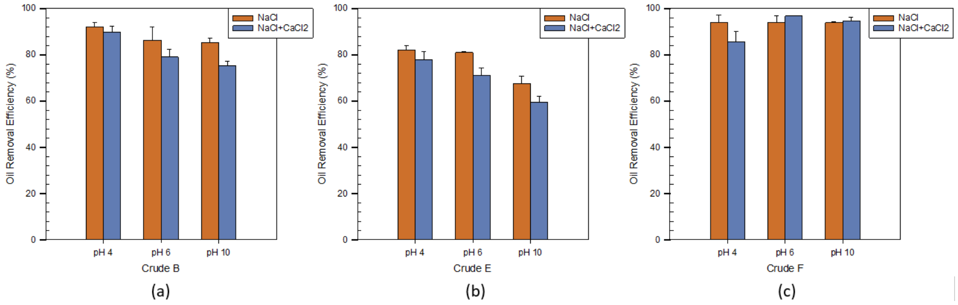


Figure 4.12: Effect of brine on oil removal efficiency of gas flotation

A general trend of reduction in oil removal efficiency with increase in pH was observed. The presence of di-valent ions also decreases the oil removal efficiency. Literature suggests that calcium reacts with surface acid groups present and alters the interfacial properties of the droplets[7]. This could be a reason for the observed decrease in trend for di-valent ions.

4.4.2 Effect of pH

All gas flotation experiments were conducted at three different pHs of 4, 6 and 10 for three different crudes. Figure 4.13 shows oil removal efficiency for two different conditions of crude B, one with a mixing speed of 15000 and other with a mixing speed of 10000.

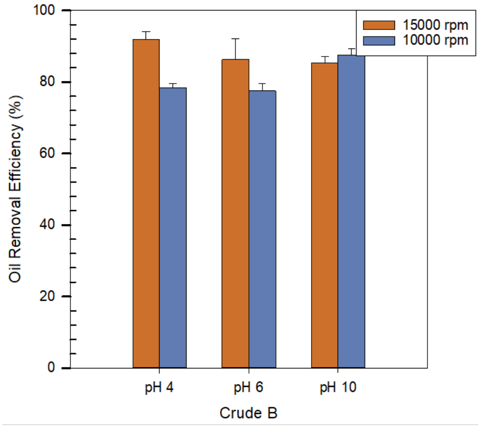


Figure 4.13: Effect of pH on oil removal efficiency of gas flotation

It can be observed from both the conditions that the trend followed by pH for 15000 rpm conditions was reversed for the 10000 rpm conditions. So, it is not possible to have a overall general trend for pH but high oil removal efficiency's were observed for low pH.

4.4.3 Effect of Initial Oil Concentration

Experiments on the influence of initial oil concentrations was studied at 250 ppm and 500 ppm by having the other parameters constant. Figure 4.14 shows the influence of initial oil concentration on oil removal efficiency.

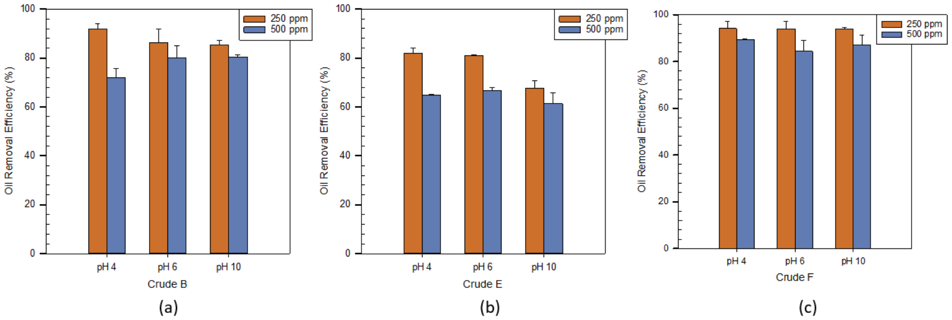


Figure 4.14: Effect of initial oil concentration on oil removal efficiency of gas flotation

Literature suggested that initial oil concentrations does not influence oil removal efficiency but has a difference in residual oil concentration[25]. In this case, a difference in trend was observed for different initial oil concentrations, with low initial oil concentrations achieving high oil removal efficiencies. This observation could be due to the inefficiency of the smaller bubbles to separate larger droplets.

4.4.4 Effect of Mixing Speed

Study on the influence of mixing speed was conducted at 15000 rpm and 10000 rpm, with initial oil concentration of 250 ppm and brine without divalent ions was used. N_2 gas was used for flotation with SP1 sparger. Figure 4.15 shows the influence of mixing sped on oil removal efficiency.

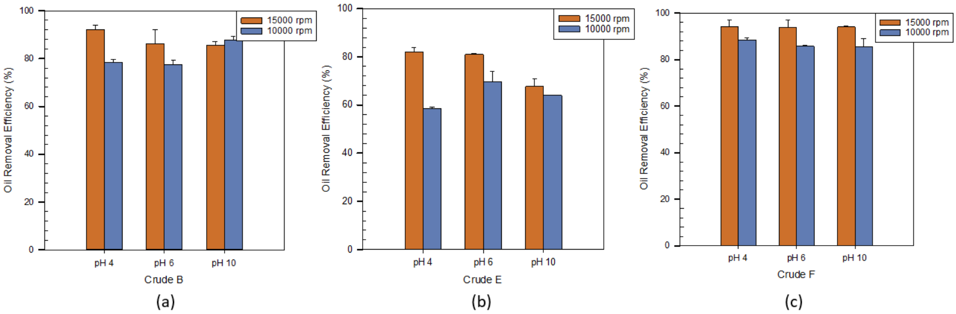


Figure 4.15: Effect of mixing speed on oil removal efficiency of gas flotation

The effect of mixing speed on oil removal efficiency could be explained with oil-droplet sizes of the before separation. Lower mixing speed produces larger droplets as shown in Figure 4.4. In contrast to gravity separation, where larger droplets had higher oil removal efficiencies, small droplets were effectively separated in gas flotation than larger droplets. Figure 4.16 shows a small illustration of the scenario considered here. The small droplets could be effectively carried by bubbles by their hydrodynamic forces which is not possible with larger droplets might be a reason for the observed trend.

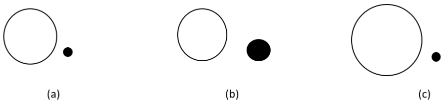


Figure 4.16: (a)Small bubble(SP1) and small droplet(15000 rpm) (b)Small bubble(SP1) and Large droplets(10000 rpm) (c)Large bubble(SP2) and small droplet(15000 rpm)

4.4.5 Effect of Bubble Size

Study of oil removal efficiency with difference in bubble sizes was conducted by using two spargers of different pore size distribution. Nitrogen gas was used in both experiments at initial oil concentration of 250 ppm in brine without divalent ions. Figure **??** shows the images of initial bubbles generated.

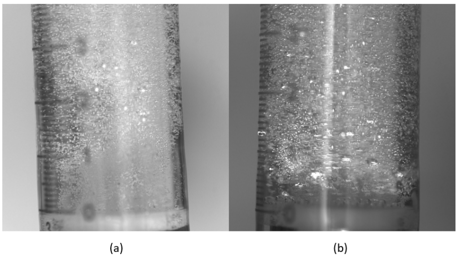


Figure 4.17: (a)Sparger SP1 (b)Sparger SP2

The size range of the bubbles are listed in Table 4.1,

Table 4.1: Bubble size range for varied spargers

SP1	0.10 - 0.42
SP2	0.12 - 0.63

Figure 4.18 illustrates the oil removal efficiency and its influence on bubble sizes.

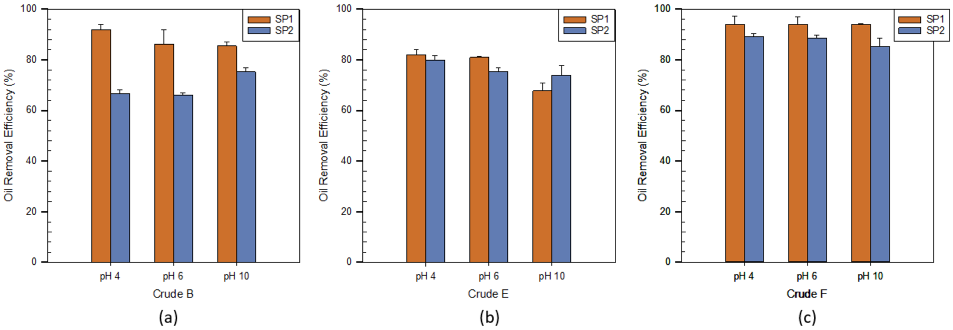


Figure 4.18: Effect of sparger on oil removal efficiency of gas flotation

A general trend of high efficiency can be observed for smaller bubble sizes. This can be explained with the illustration Figure 4.16. Smaller droplets present in the system can be pushed away by a large rising bubble due to its hydrodynamic lines of forces acting around it[28]. This phenomenon could be reason for the observed decrease in oil removal efficiency of larger bubbles.

4.4.6 Effect of Type of Gas

To determine the influence of type of gas used in flotation process, methane and nitrogen gases were tested with sparger SP2. Initial oil concentration and mixing speed of 250 ppm and 15000 rpm were used.

The bubble size range of methane and nitrogen are listed in Table 4.2,

Table 4.2: Bubble size range for gases used

N2	0.12 - 0.43
CH4	0.15 - 0.74

Figure 4.19 represents the oil removal efficiency obtained for nitrogen and methane.

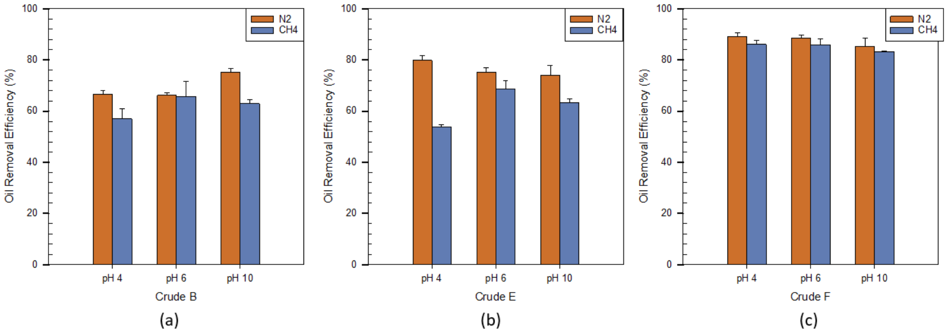


Figure 4.19: Effect of type of gas on oil removal efficiency of gas flotation

Experiments conducted with nitrogen yielded higher separation efficiency than methane. The primary reason for the observed results lie in the bubble size range of nitrogen and methane bubbles. The generation of larger methane bubbles could be due to the wettability of methane with the glass spargers used in this experiment. Literature suggests that wettability and contact angle between gas and the porous media determines the initial bubble sizes[36].

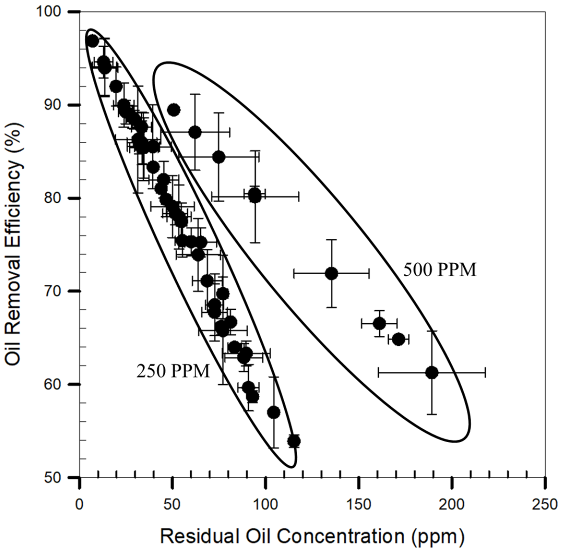


Figure 4.20: Plot of separation efficiency against residual oil concentration for gas flotation

This plot compiled all the data obtained from gas flotation. Two distinct trends were observed, irrespective of the type of crude or the parameters varied. Upon closer observation it was found that the trends corresponded to the initial oil concentration used for separation. The efficiency of the flotation process ranges from 54% to 96%. The data points with the highest separation efficiency was noted to be of Crude F, while Crude E had the least efficiency. Contradicting to the results from gravity separation gas flotation process had high separation efficiency in low initial oil concentration and high mixing speed.

Chapter 5

Conclusion

This work primarily concentrated on experimenting various parameters for the gas flotation and gravity separation process. Three different crude oils were used to prepare produced water, and a number of parameters like brine composition, pH, mixing speed, initial oil concentration, bubble sizes and type of gas used for flotation have been varied to understand the influence of these parameters on oil removal efficiency. Measured droplet sizes helped in understanding the underlying principles and mechanisms for separation.

The results from gravity separation and gas flotation compared and contrasted with each other. The former achieved a maximum separation efficiency of 65% and while the latter achieved 96% separation efficiency. The influence of type of crude was the most crucial factor in determining the separation efficiency. Crude F had the highest separation efficiency in both de-oiling methods. Lowest separation efficiency was observed with crude B for gravity separation and crude E for gas flotation. High dropsize and low mixing speed had high oil removal efficiency parameters in gravity. High mixing speed and low initial oil concentrations showed maximum efficiency in gas flotation.

5.1 Recommendations and Future Work

The addition of deemulsifier in crude, changes the chemistry of the crude. Therefore many properties of the crude could not be considered for the analysis. Determining the zeta potential of the oil droplets can help in understanding the nature of the droplets and its interaction with bubble.

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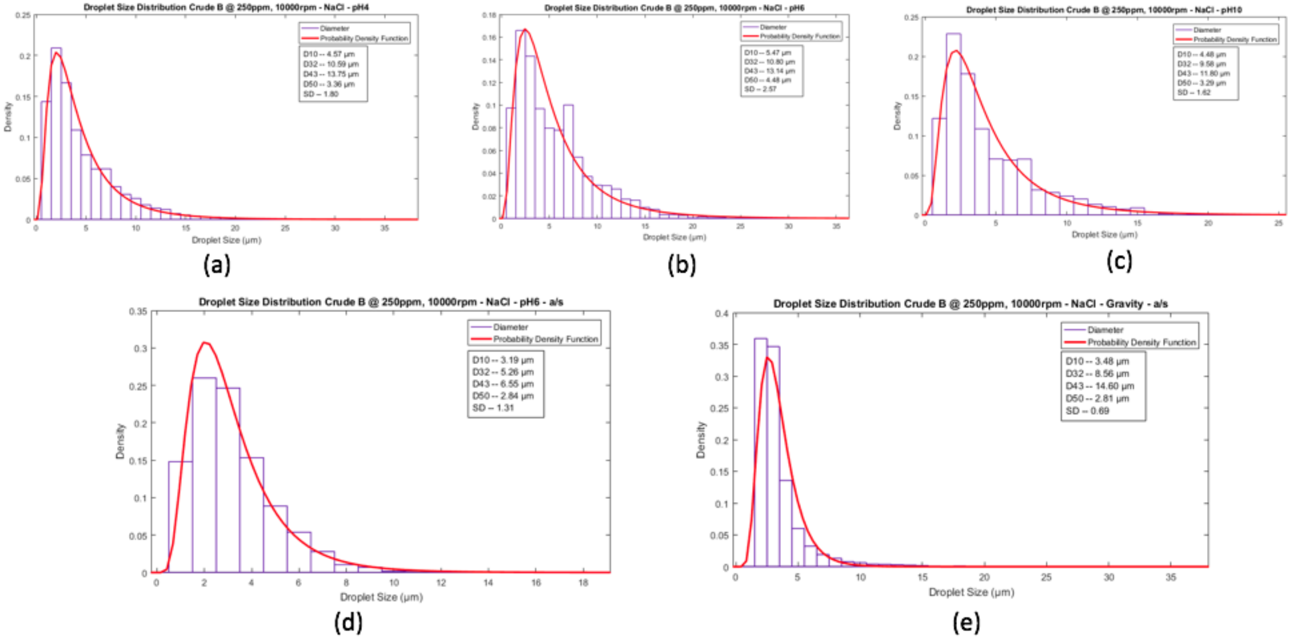
Appendix

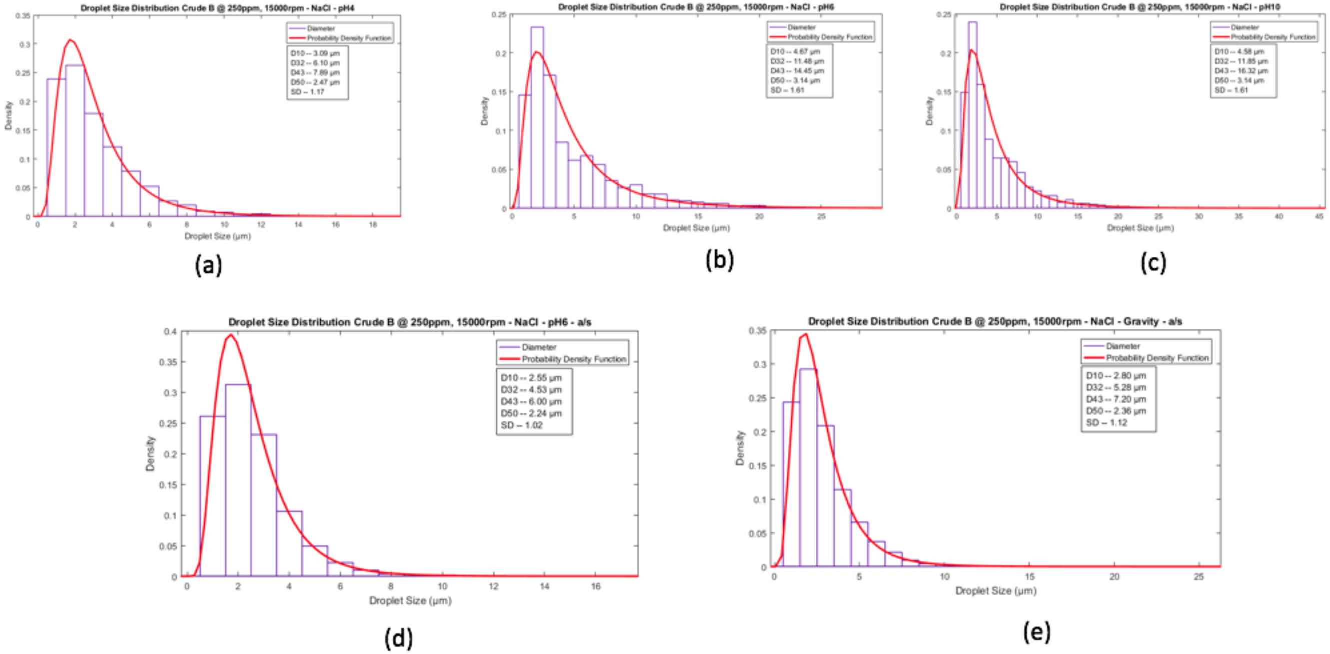
Droplet Sizes of Crude B, E and F are shown below



(a) (b) (c)

(d) (e)

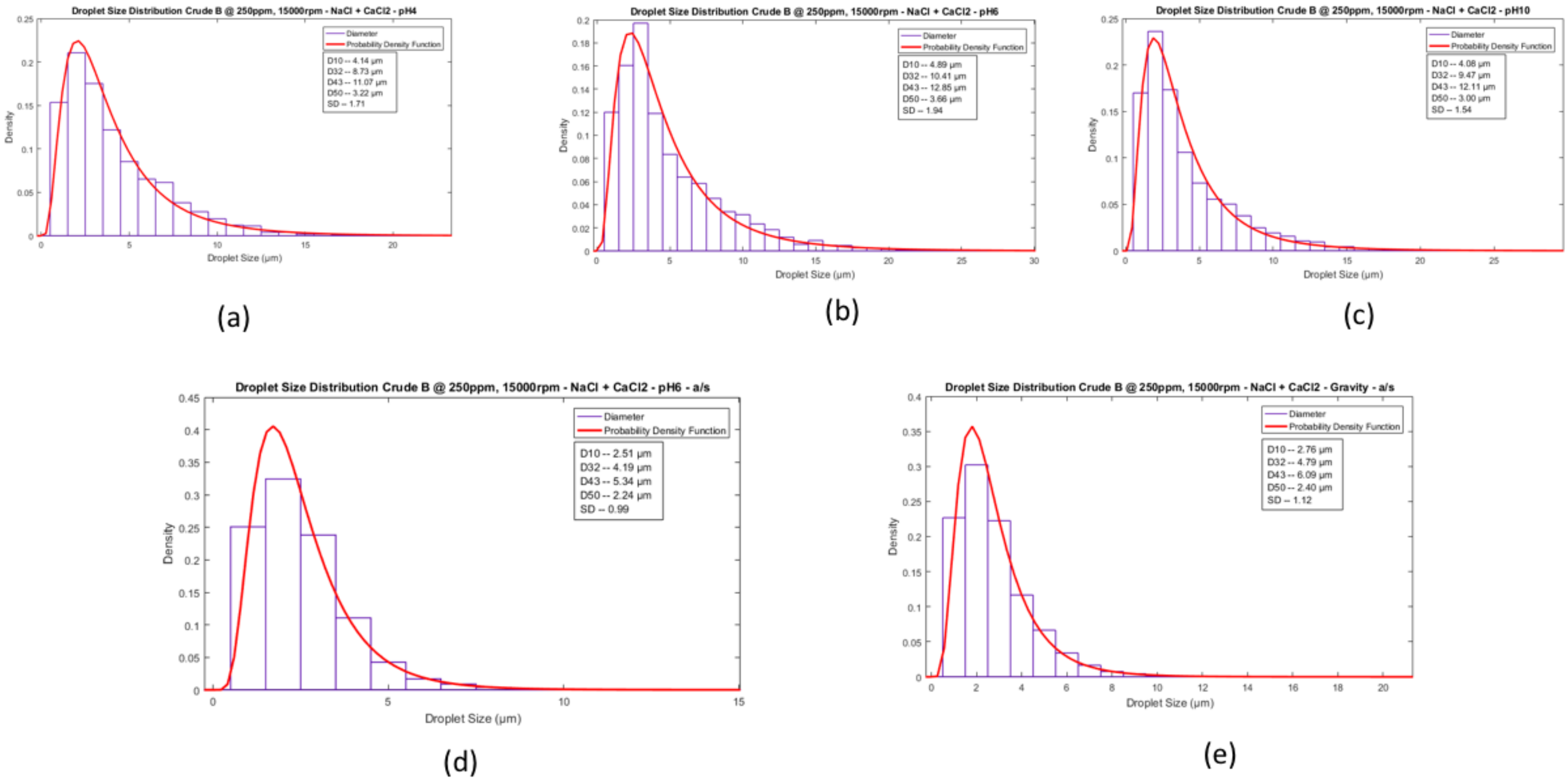
Figure 5.1: Droplet Size Distribution For Crude B @250ppm, 10000rpm, NaCl



(a) (b) (c)

(d) (e)

Figure 5.2: Droplet Size Distribution For Crude B @250ppm, 15000rpm, NaCl+CaCl2



(a)

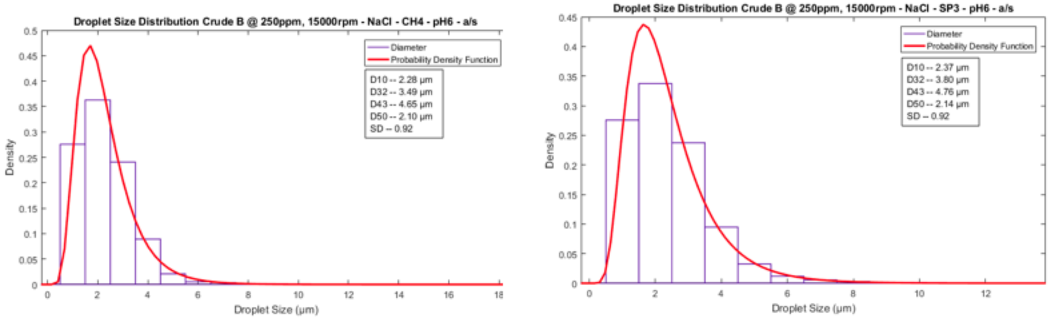
(b)

(c)

(d)

(e)

Figure 5.3: Droplet Size Distribution For Crude B @250ppm, 15000rpm, NaCl+CaCl2



(a)

(b)

Figure 5.4: Droplet Size Distribution For Crude B @250ppm, 15000rpm, NaCl+CaCl2

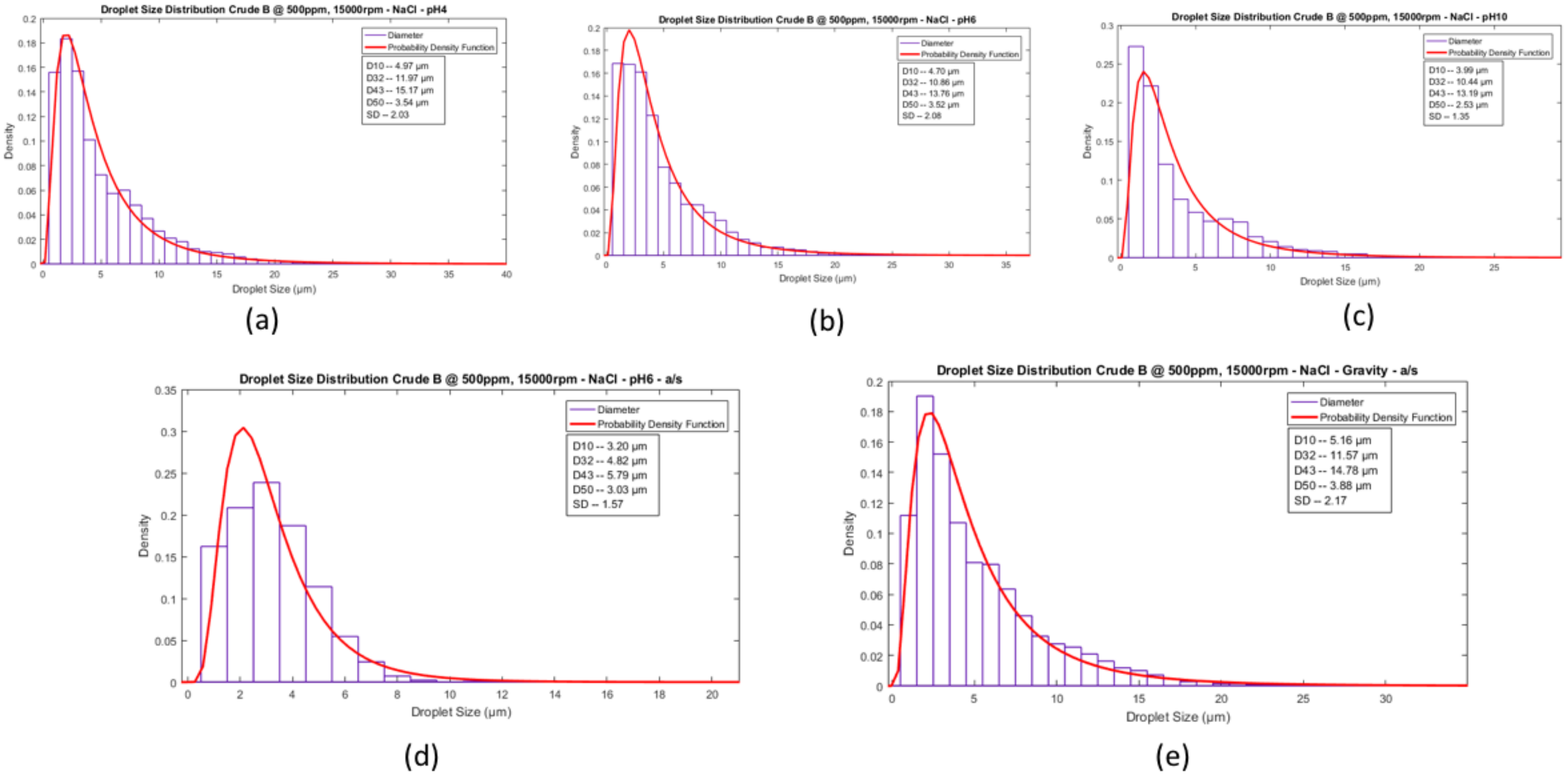


Figure 5.5: Droplet Size Distribution For Crude B @500ppm, 15000rpm, NaCl

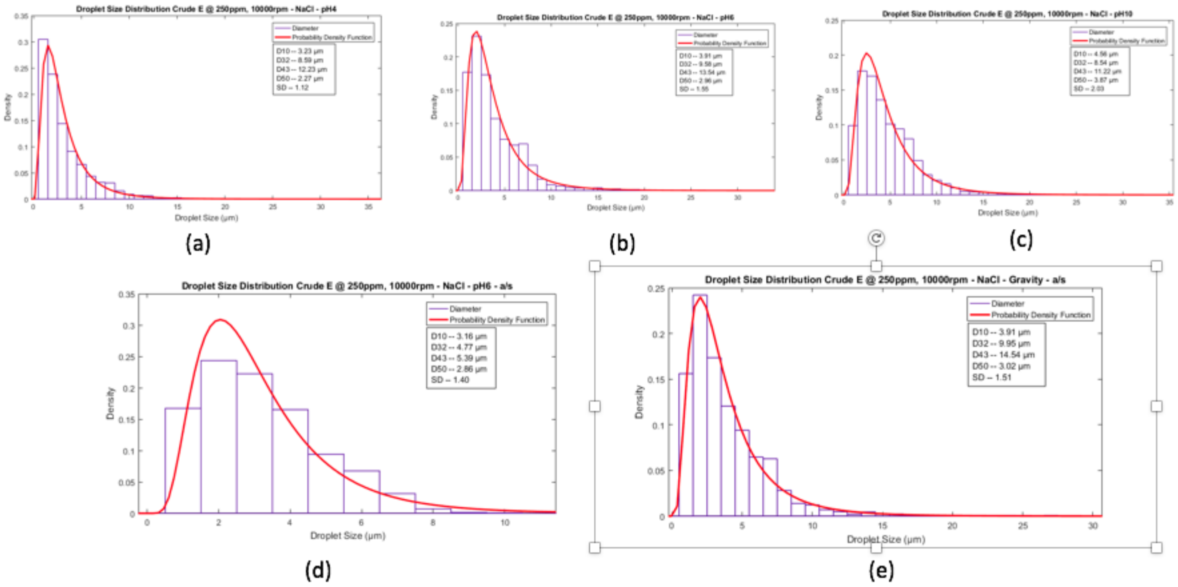


Figure 5.6: Droplet Size Distribution For Crude E @250ppm, 10000rpm, NaCl

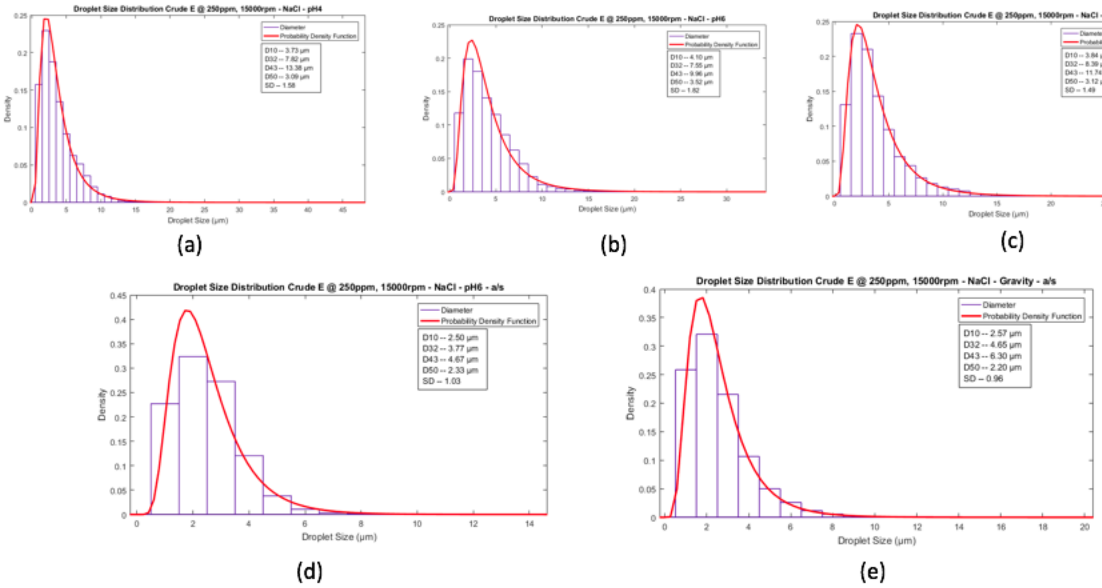


Figure 5.7: Droplet Size Distribution For Crude E @250ppm, 15000rpm, NaCl+CaCl2

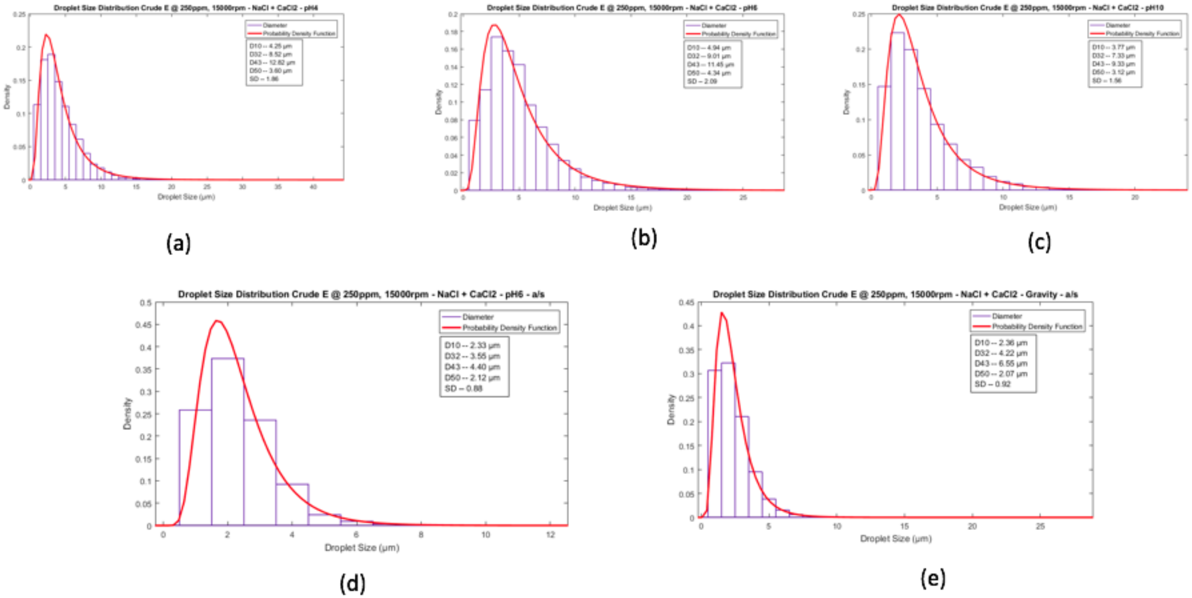
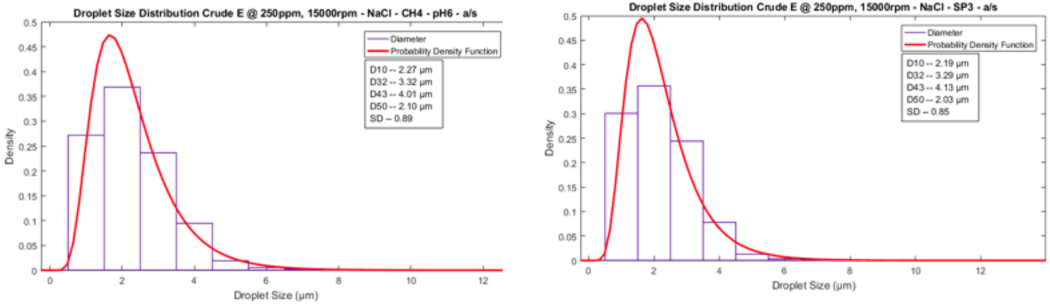


Figure 5.8: Droplet Size Distribution For Crude E @250ppm, 15000rpm, NaCl+CaCl2



(a)

(b)

Figure 5.9: Droplet Size Distribution For Crude E @250ppm, 15000rpm, NaCl+CaCl2

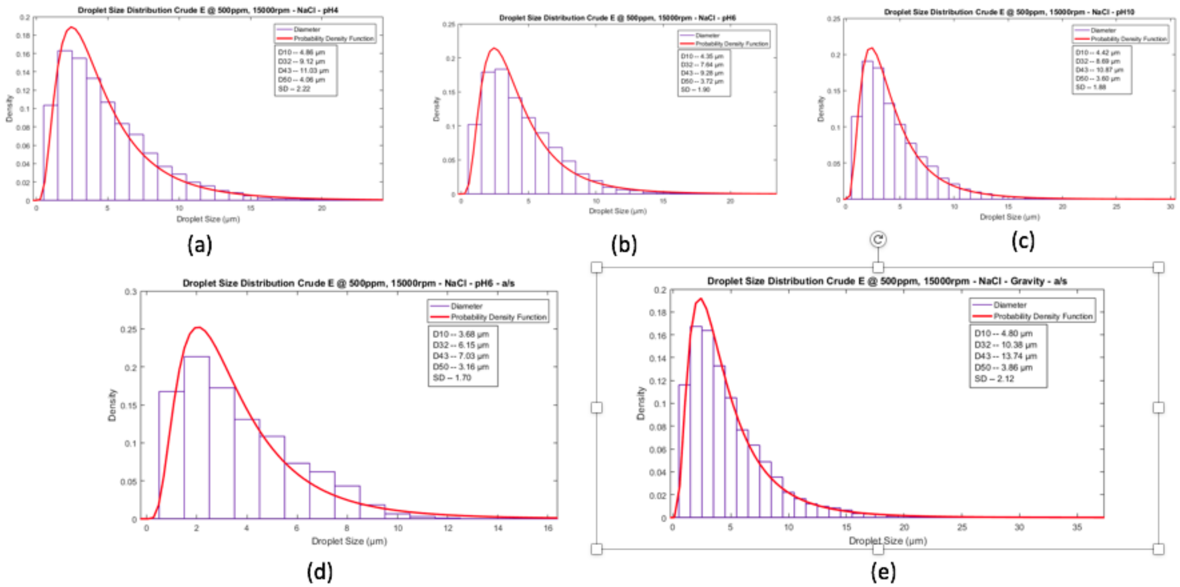


Figure 5.10: Droplet Size Distribution For Crude E @500ppm, 15000rpm, NaCl

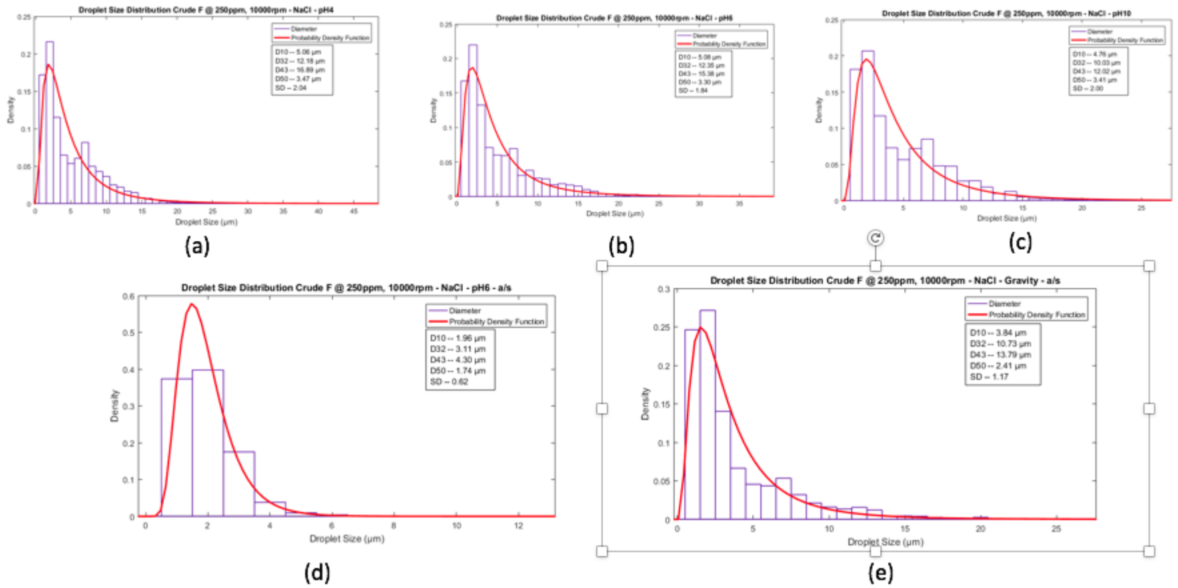


Figure 5.11: Droplet Size Distribution For Crude F @250ppm, 10000rpm, NaCl

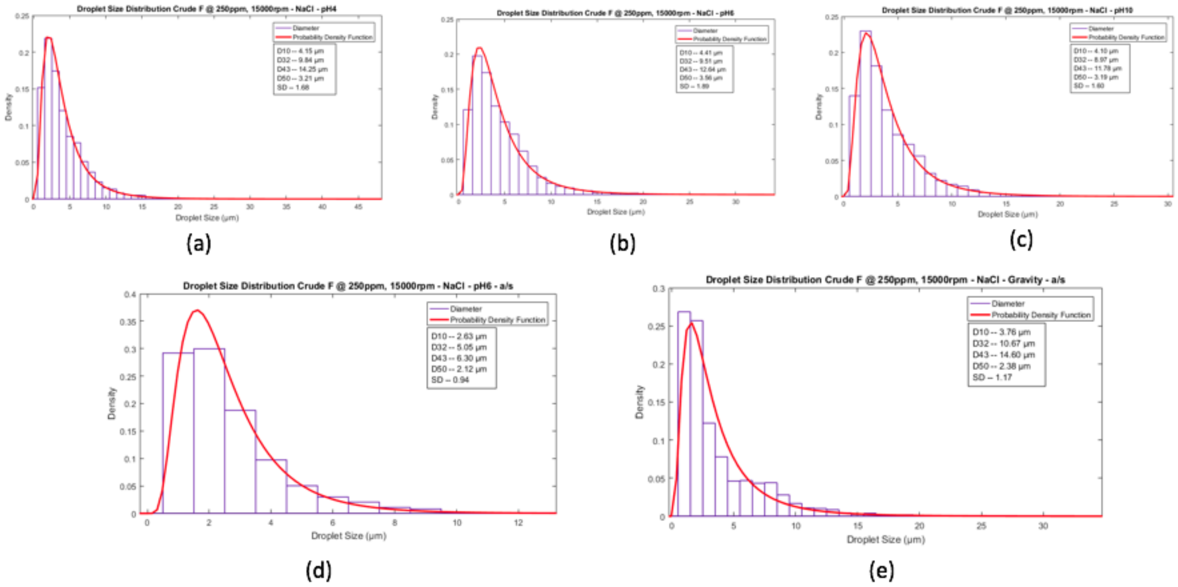
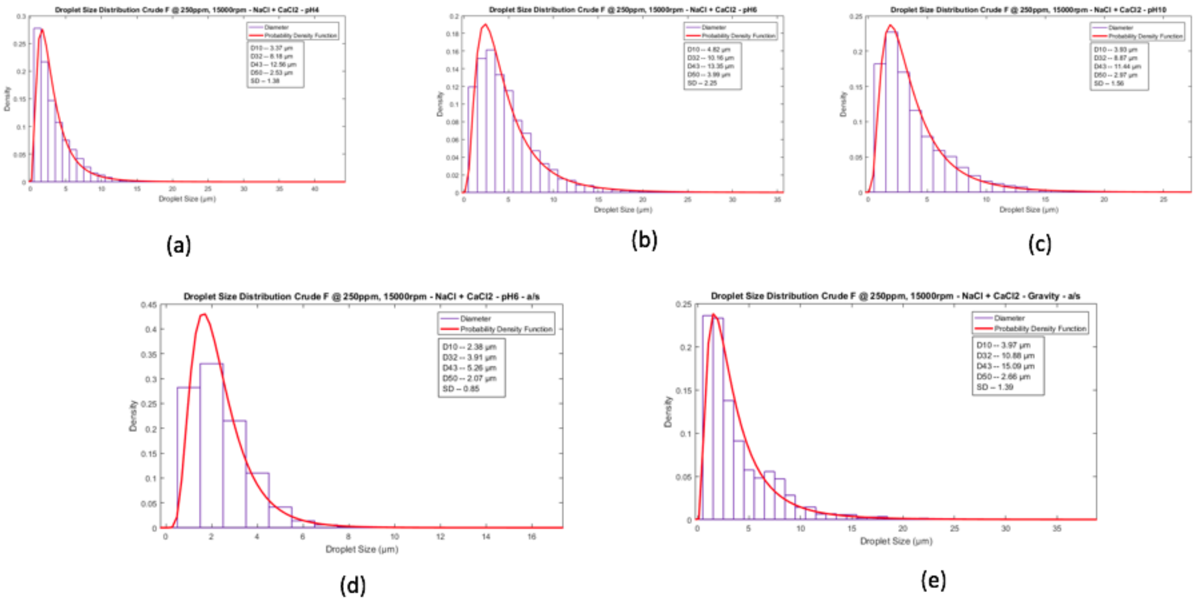


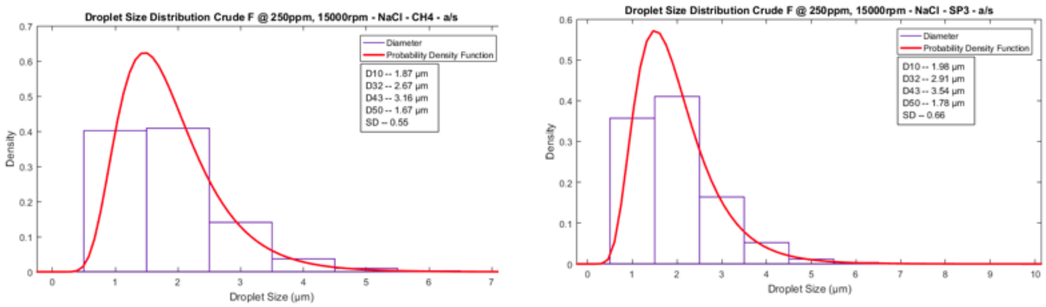
Figure 5.12: Droplet Size Distribution For Crude F @250ppm, 15000rpm, NaCl+CaCl2



(a) (b) (c)

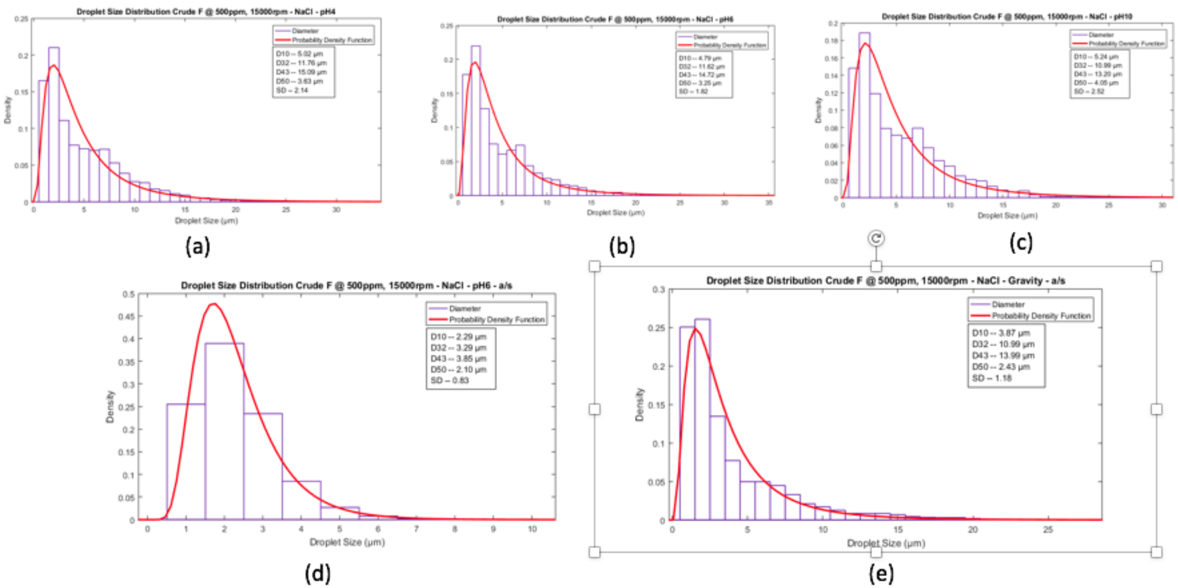
(d) (e)

Figure 5.13: Droplet Size Distribution For Crude F @250ppm, 15000rpm, NaCl+CaCl2



(a) (b)

Figure 5.14: Droplet Size Distribution For Crude F @250ppm, 15000rpm, NaCl+CaCl2



(a)

(b)

(c)

(d)

(e)

Figure 5.15: Droplet Size Distribution For Crude F @500ppm, 15000rpm, NaCl