Division of Engineering, Science and Computing
Department of Chemical Engineering

Developing a Water Treatment System for Subsea Gas Processing Plant

Dana Honer Badi M. Nazhat

This thesis is presented for the degree of
Master of Engineering
of
Curtin University of Technology

August 2006

Declaration

This thesis contains no material, which has been accepted for the award of any other degree or diploma in any university.

To the best of my knowledge and belief, this thesis contains no material previously published by other person except where due acknowledge has been made.

Signature……………………………..

Date………………………

ABSTRACT

The petroleum industry is currently moving to meet the ever-rising demand for oil and gas production. As onshore fields become depleted and decline in production, exploration and production companies have started venturing further offshore. To support this activity, there is need for new subsea production technologies to develop deepwater and ultra deepwater fields.

Woodside Hydrocarbon Research Facility (WHRF) at Curtin University of Technology is working on natural gas dehydration processing using gas hydrate technology. Through the studies, a novel gas dehydration process has been developed and now proposed for subsea application. Natural gas dehydration processes generate both a treated dry gas stream and a waste stream of condensate consisting of both hydrocarbons and water. This condensate can be reinjected to the reservoir formation but this is not always economic or practical. Availability of an alternative means of treatment and disposal of the condensate would be advantageous. This study aims to investigate and to provide a basis for the design of such an alternative scheme by constructing a floating separator for the treatment and disposal of waste condensate from subsea dehydration stage.

A model was developed to simulate the process of evaporation of condensate from the proposed floating separator. The calculations were performed taken into account zero wind speed and an ambient temperature around 34 °C. The simulation results showed that condensate skimming time was found to be 15 days for flowrate (Q_{in}) of 100 bbd associated with specific separator diameter and total height dimensions. By considering the ratio of diameter to total height of 2.5, the floating separator was designed to enhance the evaporation rate and to get overall structure stability due to the mechanical restrictions that might be encountered in the sea.

ACKNOWLEDGEMENTS

I would like to express my gratitude and deep thanks to my supervisor, Dr. David Pack for his continuous help, valuable suggestions and advice, and great support throughout his supervision of this research. In short, without his kind help, this work would not have come to light.

I would like to thank Prof. Robert Amin for his assistance and patience along with my work and his appreciable remarks and generous encouragement.

My great gratitude to Alan Jackson for his valuable assistance and comments in laboratory works, which were of great importance and value in the completion of this research. My thanks also go to Dr. Nimalan Gnanendran for his assistance at the beginning of the research.

My appreciation goes to Core laboratory staff for providing condensate samples.

I am indebted to Amir Kurdi for his help and assistance that presented to me.

I also take this opportunity to extend my sincere appreciation to my beloved family back home including my father Honer, my mother Humaima, my brother Delair and my sister Daniya in Baghdad and Kurdistan for their tremendous support, understanding and being proud to finish the research.

TABLES OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

Symbols

A	Evaporation area
$A, B, C, D, E \text{ and } F$	Constants depend on the curve fittings
C_s	Concentration of the evaporating fluid
D	Diameter of the floating separator (m)
d	Diameter of the spill
d_m	Droplet diameter (µm)
D_{50}	Oil droplet diameter for which is valid: 50 vol. % of all oil droplets have a smaller diameter
F_b	Buoyant force
F_d	Drag force
F_g	Gravitational force
h	Layer thickness
H_{accum}	Maximum height of the floating separator that condensate layer can reach for specific diameter (m)
h_l	Height loss rate (ml/hr)
H_t	Total height of the floating separator (m)
K	Mass transfer coefficient of the evaporating fluid
K_{ev}	Atmospheric stability
M	Molecular weight of the component
P	Vapor pressure
Q_{accum}	Condensate accumulation rate (bbd)
Q_{evap}	Condensate evaporation rate (bbd)
Q_{in}	Flowrate (bbd)
r	Empirical exponent assigned values from 0 to 2/3

S_c	Schmidt number
$S_{L/S}$	The spreading coefficient
T	Time (hours)
T_{accum}	Condensate skimming time (days)
T_u	Turbulence factor
U	Wind speed (m/s)
V_{accum}	The accumulated volume available for condensate layer to be filled in the separator (m^3)
X	Pool diameter or the scale size of the evaporation area
Y	Cumulative evaporated percent (%)

Greek Symbols

ß	Meterological constant
$\Delta\rho$	Density difference between the continuous and dispersed phase (lb/ft^3)
θ	Evaporative exposure
μ	Viscosity of the continuous phase (cP)
µm	Micrometer
γ_{SV}	Solid-vapor interfacial tension
γ_{LV}	Liquid-vapor interfacial tension
γ_{SL}	Solid-liquid interfacial tension
u	Settling or terminal velocity (ft/s)

Abbreviations

API	American petroleum institute
BAT	Best available technology
bbd	Barrel per day
BTEX	Benzene, oxygen, ethylene and xylene
COD	Chemical oxygen demand

CPI	Corrugated plate interceptor
EIF	Environmental impact factor
GAC	Granular activated carbon
GAC-FBR	Granular activated carbon fluidized bed biological reactor
GRI	Gas research institute
G-force	Centrifugal force
MIC	Microbial influenced corrosion
MPPE	Macro porous polymer extraction
OSPAR	Oslo-Paris commission
PAH	Polycyclic aromatic hydrocarbon
PECT	Performance enhancing coalescence technology
PPI	Parallel plate interceptor
SNGH	Synthetic natural gas hydrate
sp.gr.	Specific gravity
USA	United States of America
USEPA	United States Environmental Protection Agency
UWA	University of Western Australia
WAF	Water accommodated fraction
WHRF	Woodside Hydrocarbon Research Facility

CHAPTER 1

INTRODUCTION TO THE RESEARCH

1.1 Introduction

As petroleum reserves become increasingly depleted in onshore fields, the oil industry is moving towards offshore field developments. This is coincident with the rapidly increasing demand for fuel. The escalating demands on the petroleum industry and the increase in the cost of petroleum fuel will lead to future exploration and production using deep-water sub sea production technology. This research focuses on gas processing technology and its waste treatment.

For gas transported from offshore production fields, the existence of water in the gas stream leads to many problems, one of which is hydrate formation in the gas transportation pipelines. Excessive hydrate build up may block the flow of the gas in the system, resulting in an increase in the pressure in the pipeline. This can potentially lead to serious operational problems and cause extended shutdowns of the gas pipelines. The Woodside Hydrocarbon Research Facility (WHRF) at Curtin University has developed a novel method for gas dehydration using gas hydrate formation as a separation process. Abu El Ela (2004) has found that it is beneficial in using gas hydrates for gas dehydration. Application of this technique resulted in the problem of gas hydrate formation during gas transportation being solved.

The possibility of sub-sea dehydration of gas would have a significant positive economic impact by eliminating pipeline corrosion problems associated with water and thus reducing pipeline costs. The major cost reduction would be through avoiding expensive materials for the pipe to ensure corrosion does not occur. Thus, the treatment of sub sea gas processing condensate / water system becomes crucial.

Implementing offshore produced water treatment equipment can be challenging because offshore facilities do not have abundant space, are weight limited and are costly to construct and maintain. In addition, offshore environments can be remote and typically harsh; equipment and processes that operate there must be designed for such conditions. Alternative treatment processes could have very definite benefits, if this water could be treated and disposed to the sea within the environmental limitations.

1.2 Statement of the Problem

Water produced with the gas flows from wells and is subsequently separated from the gas phase contains high amounts of small oil droplets and high percentages of dissolved hydrocarbons (Callaghan & Baumgartner 1990; op ten Noort, Etten & Donders 1990; Hansen & Davies 1994). The removal for these two factors is difficult.

Special equipment is needed to remove the smallest oil droplets, because settling velocities are very small due to the low buoyancy force. The treatment for removal of the dissolved compounds is an expensive process because of the weight, space and high-energy requirements. Moreover, water treatment equipment has to be located close the producing wells within the offshore environment. This is a distinct disadvantage due to the space and weight requirements and the fact that platform construction costs under offshore condition are very high. Offshore structures are designed to resist severe weather and corrosion environments and withstand wave motions and sea currents. Process equipment requires a large space and represents significant weights on the structure.

Due to the increasingly stringent environmental legislation applicable to the disposal of water to the sea environment (high oil content), the produced water has been reinjected to avoid discharging above acceptable limits into the sea.

Current technologies permit acceptable conditioning of produced water; for example, produced water reinjection has been demonstrated to reduce both dispersed oil in the water level below legislation limit and aromatic oil components in water phase. On the other hand, there are drawbacks such as:

- Need to have a suitable injection zone;
- Reinjection can be very energy intensive due to high pump pressure requirements;
- Difficult to meet performance standard in the portion of produced water being discharged, and potential high capital cost/expenditure and operating/maintenance expenses;
- The risk of generating hydrogen sulphide (H_2S) which can cause reservoir souring due to bacteria effect;
- The presence of undesired dissolved gases, primarily carbon dioxide and hydrogen sulphide intensify the corrosion problems;
- The water has to be filtered with added chemicals in order to prevent the formation of bacteria and corrosion. Filters require regular cleaning because of the deposition of salts and paraffins in tubing and lines. Filters are important to remove suspended oil droplets that may impair injection of water to the formation and effectiveness of injection operations;
- Chemicals are difficult to store and transport to the offshore fields; and
- As petroleum production continues for a particular well, higher amounts of produced water can be expected (water cut). In this case, produced water reinjection can become expensive.

It can be seen that constructing conventional equipment for treatment and reinjection is not the optimum alternative to dispose of the produced water and effluent from dehydration plant and presents many drawbacks.

An alternative scheme for separation and disposal of water is presented in the following section.

1.3 Scheme for Treatment of Dehydration Effluent

Figure 1.1 shows the conceptual produced water treatment schematic diagram for a subsea gas processing plant. The work described in this thesis is an integral part of the subsea natural gas treatment system.

A hydrocyclone is proposed to remove the greatest part of produced water at around 98 % of the total produced for reinjection. The gas dehydration plant is designed to receive around 2 % of the total produced water together with the water saturated gas stream. The floating separator has been designed to accommodate the liquids produced by the gas dehydration plant.

The application of the water treatment technology, as outlined in this thesis, to subsea gas processing demonstrates considerable promise. This technique depends on constructing a treatment system that can float on the sea surface. Within this treater, condensate and water would be separated within a specific retention time.

Water passes for the separator directly into the sea. Condensate is partially evaporated to the atmosphere. The remainder accumulates and must be removed periodically for disposal.

The design of the floating separator system relies on gravity separation that depends basically on density difference. Conventionally, chemicals have been used to solve oil and water separation problems, these chemicals are called de-emulsifiers. Under offshore conditions, de-emulsifiers are hard to apply.

Produced water has different compositions and can contain salts in various concentrations. It has an average salinity of approximately 3.5 % and can go up 30 % as reported by Ayers & Parker (2001, p. 11) and Alaee, Whittal & Strachan (1996, p. 1161). The effect of salinity in produced water leads to an increase the density difference between oil and water. The impact of salinity concentrations has been studied previously as a separation process (Mohamed, El Gamal & Zekri 2005). This study revealed that salty concentrations can lead to an enhanced separation process, without the need for any chemicals to be applied.

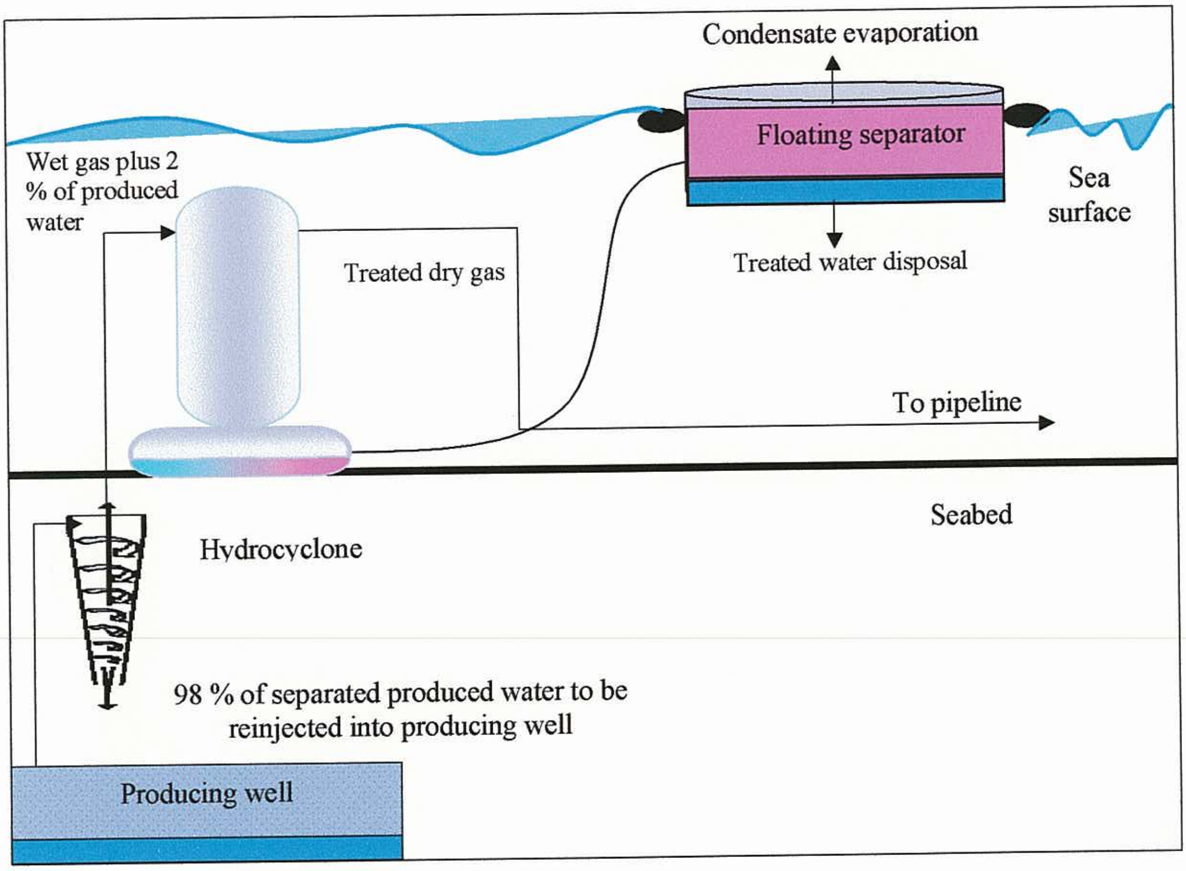


Fig 1.1- Conceptual produced water treatment diagram for a subsea gas processing plant.

1.4 Objective of the Research

This research has two main objectives:

1. The main objective is to develop a reliable simple water treatment system using a novel sub sea gas dehydration plant. The development involves determination of the operational requirements for a floating separator capable of operating for long periods of unattended operation in a harsh and remote marine environment.

2. A secondary objective is to investigate the possibility of utilizing other means such as evaporation to get rid of light hydrocarbon condensate to the atmosphere. Evaporation depends on wind speed and temperature effect.

1.5 Thesis Outline

This thesis explains the idea and the theory of the proposed separation and evaporation technique and the optimization of the floating separator operational and design parameters.

The thesis is subdivided into six chapters: These chapters are organized in a logical order to reflect the progress in achieving the above-mentioned objectives.

- Chapter 1 presents the introduction, statement of the problem, the scheme proposed for treatment of dehydrator effluent, objective of the research and finally the thesis outline.
- Chapter 2 contains a literature review on the dispersed compounds, dissolved compounds, an explanation on the existing produced water treatment equipment being applied in the offshore environment and evaporation models for oil spills.
- Chapter 3 presents the description of the experimental work and methodology that were conducted to achieve the objective of this study followed by the results and discussions.
- Chapter 4 presents a simulation model for the evaporation process.
- Chapter 5 discusses and analyzes the results thoroughly in terms of wind speed and tank diameter size.
- Chapter 6 concludes with a summary of the research findings and outlines recommendations for future research in this area.

The relevant information outside the main chapters is given in appendices to the thesis. Finally, the literature cited in this thesis is given in the references.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Since reinjection of produced water has proved to be problematic to the petroleum industry, investigations are now being increasingly undertaken into the use of alternative methods to dispose of produced water. As onshore petroleum reservoirs are becoming more depleted and the world demand for energy requires exploiting more adverse locations and environments, the focus for petroleum production has been moving offshore. Offshore production presents unique problems and subsequently generates high costs. This location makes it more difficult to reinject the water. The problems associated with produced water and its treatment in the offshore environment has attracted considerable interest.

The literature review is divided into four main headings and provides critical explanation and description of the researcher's studies regarding the dispersed and dissolved compounds associated with the disposal of produced water. Section 2.2 deals with dispersed compounds and issues regarding the emulsion's stability, water quality considerations and treatment equipment. Section 2.3 addresses dissolved compounds, dissolved compounds solubility and the removal of dissolved compounds. Section 2.4 looks into evaporation models.

2.2 Dispersed Compounds

Dispersed compounds are defined as the small droplets that are dispersed either in oil or in water. Dispersion normally does not occur in the produced formation but is formed because of the agitation that occurs to both oil and water layers during production.

2.2.1 Emulsion Stability

There are two types of emulsions usually formed. These can exist either as a normal emulsion, where water droplets are dispersed in the continuous oil phase, or as a reverse emulsion where oil droplets are suspended in the continuous water phase, as shown in Figure 2.1.

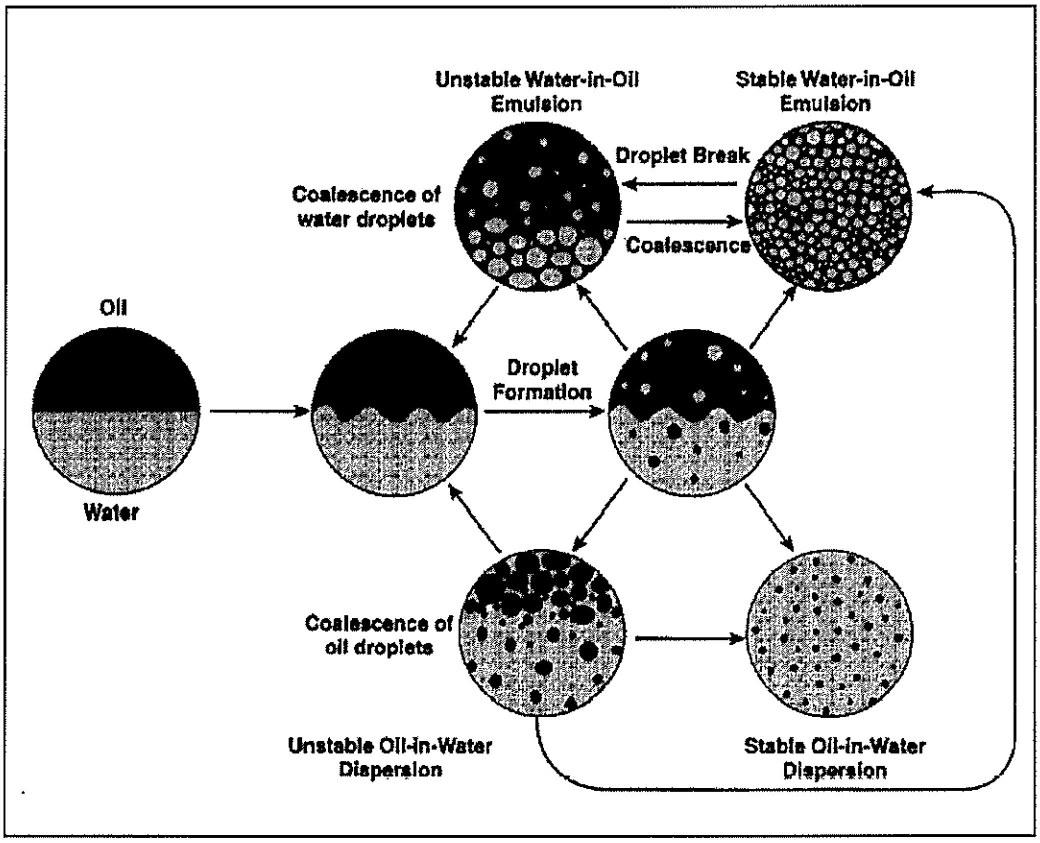


Figure 2.1- A schematic diagram of the formation of stable and unstable emulsions (Nordvik et al. 1996).

Stability of an emulsion can be defined as the relative difficulty of separating it into two phases. Emulsions can be stable when the disperse phase droplets do not coalesce over time. They are not thermodynamically stable and can be separated if sufficient time is given. However, a very stable emulsion, known as a tight emulsion, is unable to resolve itself in a defined time period without some form of mechanical or chemical treatment.

Table 2.1 shows that emulsion stability ranges from very weak to very strong depending on the droplet diameter size (μm).

Droplet size has a great effect on emulsion stability, which in turn affects produced water treatment equipment. However, this section looks into emulsion stability and the issue of produced water treatment equipment is discussed in Section 2.2.3. The finer the droplets dispersed in an emulsion, the more stable it is.

Table 2.1- Emulsion Stability with Droplet Size (Liquid-Liquid Coalescer Design Manual 2003, p.5)

Separation time (minutes)	Emulsion stability	Droplet size (μm)
< 1	Very weak	> 500
< 10 minute	Weak	100-500
Hours	Moderate	40-100
Days	Strong	1-40
Weeks	Very Strong	< 1

Turbulent flow, caused by agitation, forces the oil and water droplets to interfere and disperse one in the other as tiny spheres or droplets which are stabilized by emulsifying agents (Abdel-Aal, Aggour & Fahim 2003, p. 140).

The emulsifying agents (emulsifiers) are usually complex molecules, often having a hydrophilic (water-loving) group at one end and a hydrophobic (oil-loving) group at the other, as shown in the Figure 2.2. Sullivan & Kilpatrick (2002, p. 1) reported that there are two main categories of the surface-active molecules in the crude: asphaltenes and resins. Asphaltenes are flat sheets of condensed polyaromatic hydrocarbons interconnected by sulphide, ether, aliphatic chain and naphthenic ring linkage. Resins are structurally similar to typical surface-active molecules. One end is hydrophilic, with polar functional groups; the other is hydrophobic, consisting of alkyl chains, as shown in Figure 2.3. The dielectric characteristics of water and oil cause emulsified oil droplets to carry negative charges. A stabilizing film has an affinity for both water and oil that enables the emulsifiers to overcome the natural forces of coalescence. Stabilization occurs because the solid and finely dispersed solids materials such as sand particles absorbed at the oil / water interface tend to reinforce the interfacial film. Therefore, the dispersed droplets cannot coalesce because of the interference, or blocking effect of the solids, as shown in Figure 2.4. At the Arun field located in the Aceh Province on the northern coast of Sumatra, Indonesia, it was found by Madian et al. (1994) that the emulsification was due to the presence of fine bubbles of carbon dioxide such that the emulsified hydrocarbon was very stable, as evidenced by the persistent milky color of the water.

Researchers such as op ten Noort, Etten & Donders (1990), Callaghan & Baumgartner (1990), Bansal & Caudle (1998), Finborud, Faucher & Sellman (1999) and Mohamed, El Gamal & Zekri (2003; 2005) discussed and reviewed the factors that can contribute to emulsion stability noting that factors such as salinity, ratio of aromatic to aliphatic, corrosion inhibitor, high-pressure drop and chemicals enhance the emulsion stability.

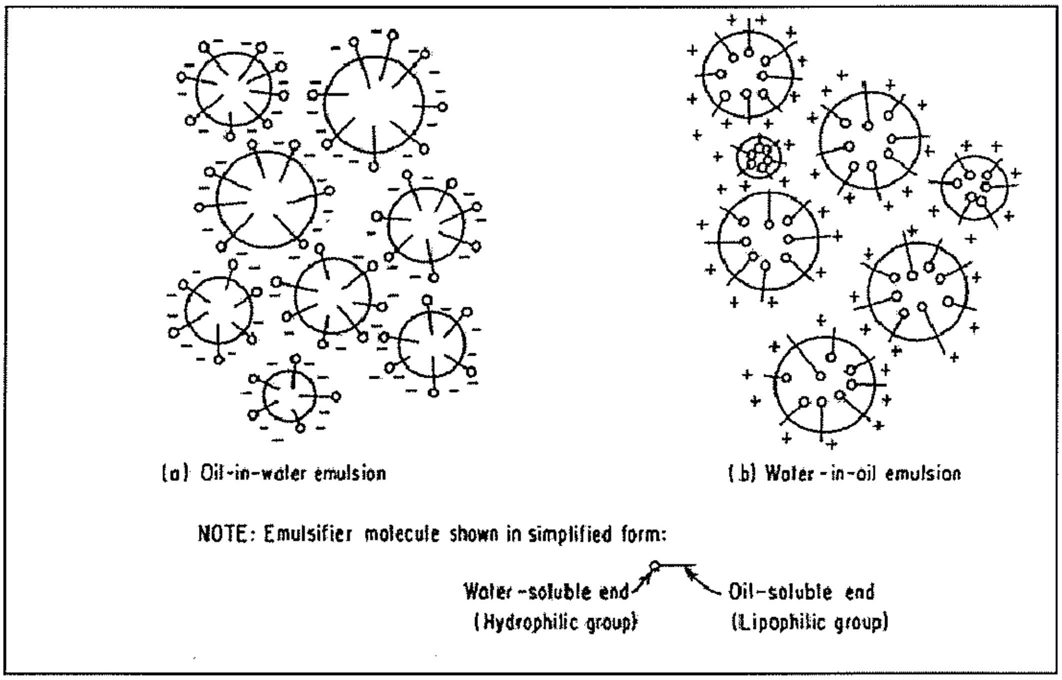


Fig. 2.2- Schematic of different emulsion systems (Kemmer 1988).

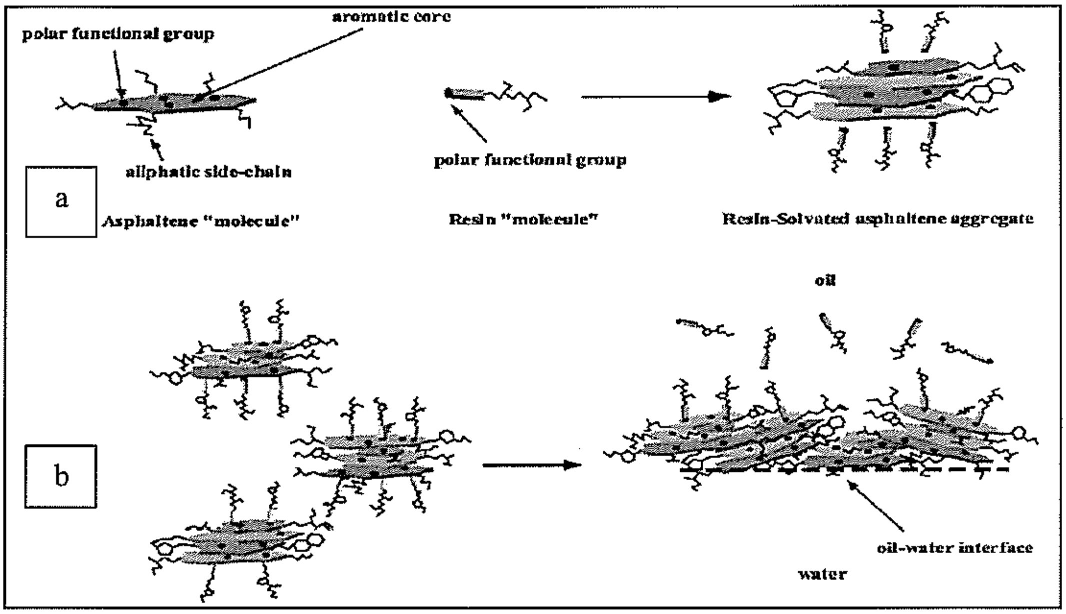


Fig. 2.3 (a)- Resin-asphaltene association to form a colloidal aggregate. Resins solvate asphaltene aggregates through polar functional group interactions. (b)- Resin-asphaltene aggregate association to form an interfacial film. Primary asphaltene aggregate cross-link to form a rigid, viscoelastic structure at the oil / water interface (Sullivan & Kilpatrick 2002, p. 2).

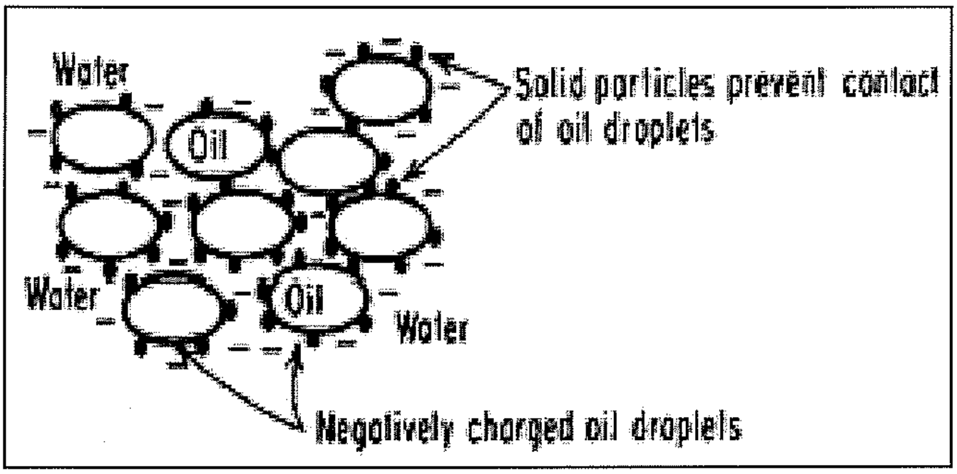


Fig. 2.4- Physical emulsion stabilization by finely divided solids, illustrated with oil / water emulsion (Kemmer 1988).

Produced water from gas fields consists of finely dispersed aliphatic hydrocarbon with extremely tiny droplets and aromatic hydrocarbons dissolved in the water phase. op ten Noort, Etten & Donders (1990) and Callaghan & Baumgartner (1990) claimed that produced water from gas fields can prove difficult to treat, particularly where the water salinity is low and the oil or condensate contains large quantities of light aromatic compounds. This encourages the formation of very fine, stable dispersed oil droplets with a weak chance for oil to agglomerate. At offshore gas production platform P/6A, it was found that because the ratio of aromatic to aliphatic hydrocarbon is relatively high, the aromatic hydrocarbons tend to keep the dispersed hydrocarbon in suspension. This renders it difficult to separate out the dispersed hydrocarbons by means of gravity and coalescence (op ten Noort, Etten & Donders 1990).

The effect of salt in reducing emulsion stability has been researched in detail by Mohamed, El Gamal & Zekri (2005). Mohamed, El Gamal & Zekri (2005) reported that salt can have an effect on the internal energy and increase the separation rate for oil and water system. Finborud, Faucher & Sellman (1999, p. 3) mentioned that when the salinity is low, the droplet electrostatic charge is high, thus preventing coalescence. The oil negative electrostatic charge is influenced by salt concentration. When the salinity is high, at about 2.5 % or more, the electrostatic charge is low and therefore conditions for coalescence exist.

It was observed by Callaghan & Baumgartner (1990) and op ten Noort, Etten & Donders (1990) that the existence of corrosion inhibitor and high-pressure drop during production enhanced stability. Both of these factors create stable dispersions of condensate droplets in the process water discharged from gas production platforms. Rye & Marcussen (1993) stated that the high pressure drop was shearing the oil droplets into smaller droplets in the Tyra gas field in the Danish part of the North Sea. As well, mechanical devices such as flow restrictions in pipes, valves, pumps and other devices can constrain flow or induce turbulent flow.

2.2.2 Water Quality Considerations

Two organizations, the Oslo-Paris Commission (OSPAR) and the United States Environmental Protection Agency (USEPA), established significant regulations for produced water discharges in March 1993. The work of these two organizations is felt to be the most influential and appropriate when considering regulations of produced water discharges as a result of the Best Available Technology (BAT) effluent limitations for offshore. The regulations are largely based upon the performance capability of oil / water gravity separation technologies, followed by gas flotation or a hydrocyclone to remove oil and grease. Table 2.2 shows produced water treatment standards.

Table 2.2- Produced water treatment standards

(Ayers & Parker 2001, p. 47).

Country	BAT	Effluent Limits
US	Gas flotation	29 mg/l monthly average. 42 mg/l daily maximum.
UK	Gas flotation Hydrocyclone	40 mg/l monthly average. 30 mg/l annual average.
Norway	Gas flotation Hydrocyclone	40 mg/l monthly average. The same as above.
Canada	Not stated	40 mg/l monthly average. 80 mg/l two day average.

Australian Regulatory Requirements 1999 require oil and gas production facilities to have 50 mg/l as a maximum at any one time and average less than 30 mg/l during each period of 24 hours (Cobby 2004, p. 2). While, Arnold & Stewart (1999, p. 230) stated another worldwide produced water effluent oil concentration limitations as follow:

- 15-25 mg/l for Indonesia;
- 29 mg/l for USA;
- 30 mg/l for Ecuador, Colombia, Brazil, Argentina, Venezuela, Malaysia, Middle East, North sea and Australia; and
- 50 mg/l for Nigeria, Angola, Cameroon, Ivory Coast and Thailand.

2.2.3 Produced Water Treatment Equipment

As produced water leaves the primary separator, it goes through a series of treatment equipment to reduce the oil concentration in the water continuous phase for final discharge. Investigations into the results of dispersed oil concentrations have produced varying results. Abdel-Aal, Aggour & Fahim (2003, p. 220) noted that the dispersed oil concentration ranges from 1000-2000 mg oil per liter of water, whereas Ayers & Parker (2001, p. 40) stated a range between 100-2000 mg/l. The primary separation can easily remove amounts of free oil and free water when the retention time within the separator is sufficient. The separation is based on the difference between the specific gravity of oil and water and the coalescence of oil droplets that depends on the diameter size. The remaining part is tiny oil droplets remaining in the water continuous phase and small water droplets remaining in the oil continuous phase. However, in this literature, the discussion is related to tiny oil condensate droplets in the water continuous phase.

The tiny oil droplets need longer retention time to allow gravity settling. A range of produced water treatment equipment provides means of separation. Figure 2.5. summarizes the application of various water treatment equipment according to specific droplet size. The effect of droplet size on the selection of specific treatment equipment is also stated by Arnold & Stewart (1999, p. 195).

Knowledge of the oil droplet size is crucial in the selection of the most effective separation equipment. As produced water effluent transfers to the next equipment stage, the oil droplets become smaller in size and therefore need longer settling time. However, the long retention time for gravity settling of small oil droplets becomes impractical. The removal of smaller droplets is complicated because of the low ratio of buoyancy force and rising velocity to the drag force. Thus, other means of separation are used, such as a coalescer that works on reducing the distance that the droplets need to rise and coalesce or other centrifugal separation to separate small droplets.

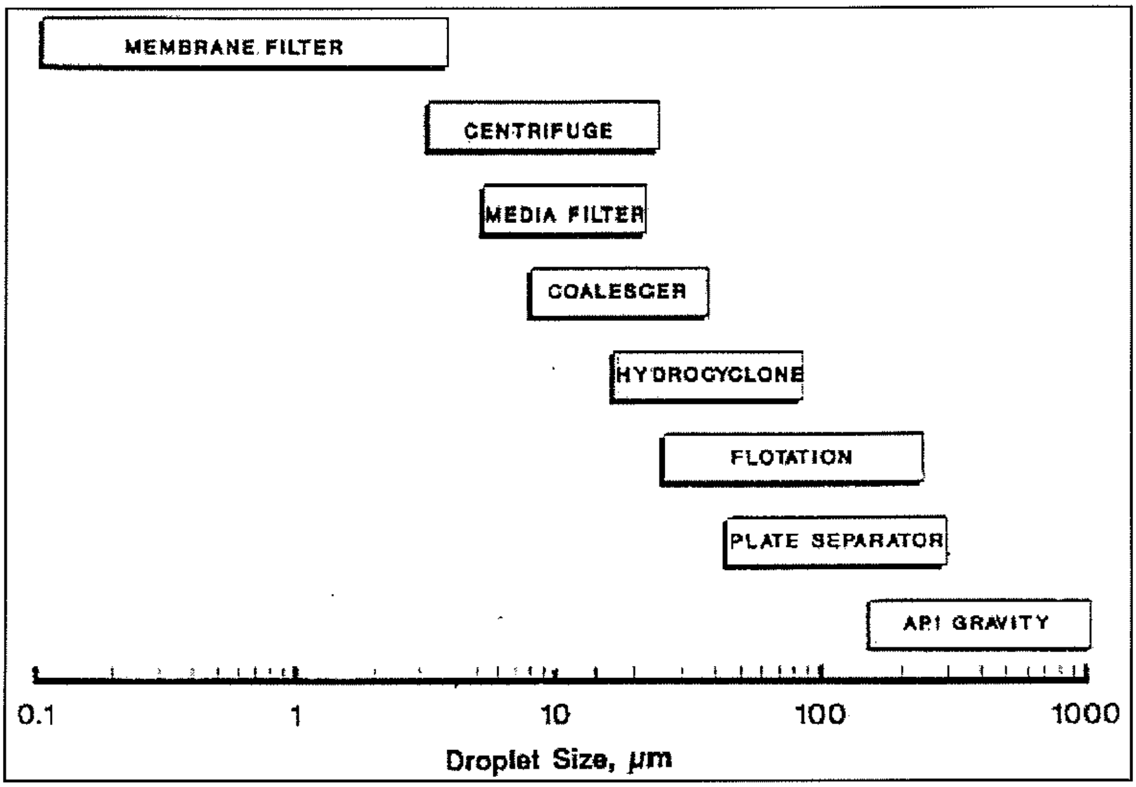


Fig. 2.5- Typical range of droplet size removed by various types of de-oiling equipment (Callaghan & Baumgartner 1990, p. 8).

Condensate droplets are extremely small. op ten Noort, Etten & Donders (1990) reveal that in an analysis of the particle size distribution, about 90 % of the droplets from gas fields have a particle size smaller than 10 µm. Details of the observed particle size distribution are shown in Figure 2.6. These findings are in agreement with those of Callaghan & Baumgartner (1990). Callaghan & Baumgartner state that that all droplets larger than 6-8 µm must be removed to meet the specified hydrocarbon limit for most of the gas platforms studied. Details of these findings are shown in Figure 2.7. This was also confirmed by Rye & Marcussen (1993) in the Tyra gas processing field in the Danish part of the North Sea. The following is a description of the typical produced water treatment equipment used offshore.

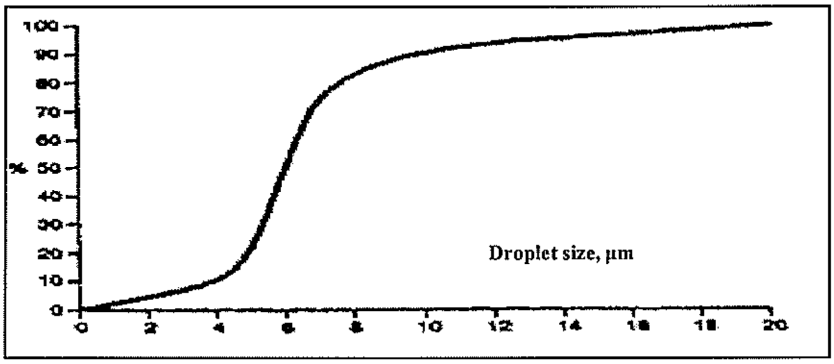


Fig. 2.6- Cumulative particle size distribution (op ten Noort, Etten & Donders 1990).

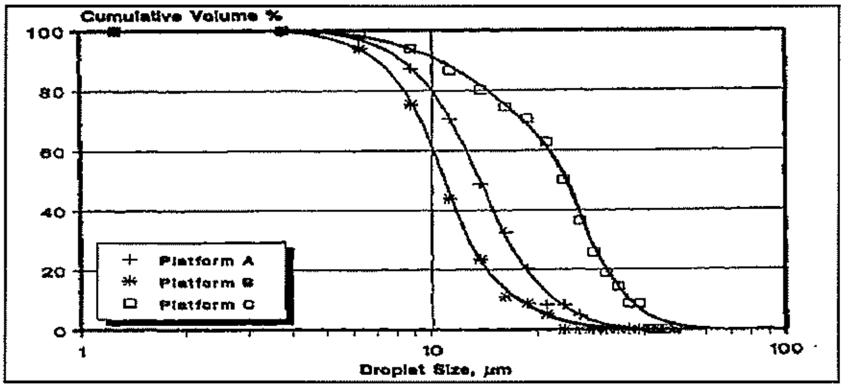


Fig. 2.7- Measured condensate droplet size distribution for platforms A, B and C (Callaghan & Baumgartner 1990).

2.2.3.1 Gravity separators

A gravity separator is the simplest form of produced water treatment equipment. It is a simple vessel with enough capacity to allow adequate retention time to permit separation of free oil and water under the effect of density difference and coalescence of oil droplets. Gravity separators allow droplet diameter of 150 µm to settle as the smallest droplet size.

2.2.3.2 Plate Separators

There are mainly two types of plate separator: the parallel plate interceptor (PPI) and the corrugated plate interceptor (CPI). They are basically gravity separators that contain a pack of tilted parallel plates spaced a short distance apart and inclined at an angle of 45 degrees. The plates are arranged and installed inside an American Petroleum Institute (API) separator such that oil droplets in the produced water passing through the pack only need to rise a short distance before striking the underside of one of the plates, as shown in Figure 2.8. On the plates, oil droplets coalesce into larger droplets and rise easier.

CPI uses a similar principle with corrugated plates surface. The plate operates in an inclined position. The operation of the CPI is shown in Figure 2.9. Once again, the oil collects and coalesces on the plates and the oil rises upward in the top of the corrugations and flows tangentially up the plates. The main advantages of this system, is that it is much smaller than a gravity separator with the same efficiency. In addition, high fluid velocity has a negative impact on the efficiency.

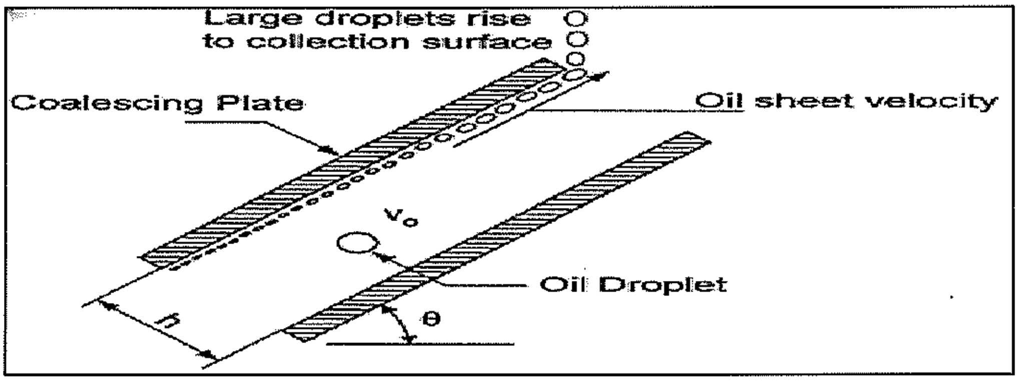


Fig. 2.8- Parallel plate interceptor.

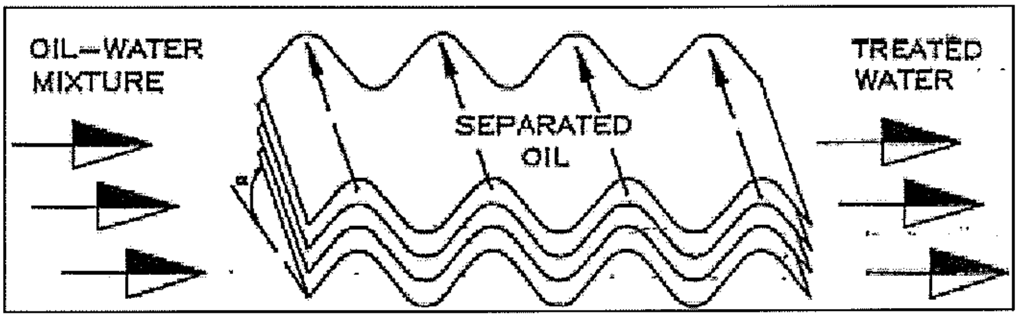


Fig. 2.9- Corrugated plate interceptor.

2.2.3.3 Flotation Units

A flotation unit works by introducing small bubbles into the water being treated. The gas bubbles acquire a small electric charge, opposite to that of oil droplets and this causes the gas and oil particles to be attracted together. Once oil droplets attach to gas bubbles, the density difference between oil and water become higher and oil droplets will rise to the surface and be recovered as froth.

According to Georgie, Bryne & Kjaerland (1992, p. 228) and Bansel & Caudle (1998), there are a number of interferences that can affect the performance of flotation system, these are:

- Variable flow interference: A variable flow leads to upset shock loads. Thus, a surge vessel upstream of the flotation unit is important to adjust flowrate fluctuations as it requires a steady constant feed; and
- Chemical interference: Chemicals are usually used to break the emulsion formed. Therefore, the use of optimum emulsion breaker and its dosage is very important to avoid creating stable emulsion or stabilize oil droplets in the water phase. As well, the location of the injection point is greatly influenced by the chemistry of the fluid treated and the chemical aid used.

2.2.3.4 Hydrocyclones

Hydrocyclones have become especially popular since their introduction during the 1980s (Grini, Hjelsvold & Johnsen 2002, p. 2). They have been deployed for oil / water separation on a large number of facilities in the UK sector of the North Sea. This technology is now considered to be the most suitable for offshore applications.

Hydrocyclones induce a centrifugal rotating motion to the produced water in order to amplify the effect of gravity by several orders of magnitude to separate oil from the water. Figure 2.10 shows the oil and water flow in a hydrocyclone. Hydrocyclones can provide significant savings in weight and space compared with the gravity skimmers and flotation units.

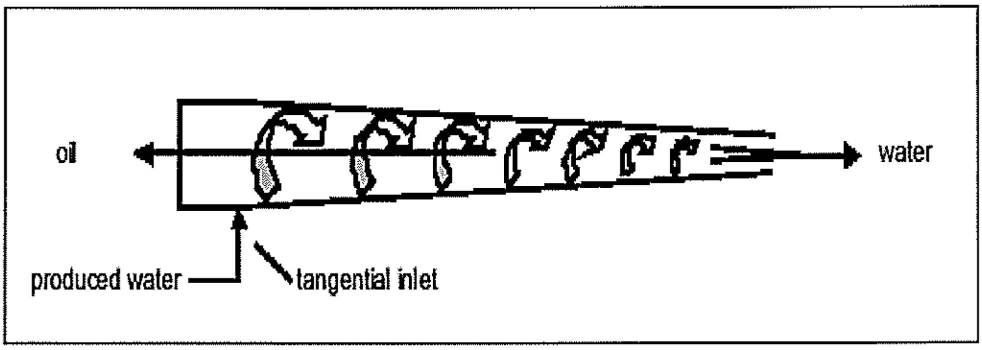


Fig. 2.10- Oil and water flow in a hydrocyclone.

There are two important parameters that have to be taken into account for separation of oil and water in a hydrocyclone system, they are:

- Oil droplet size; and
- Flowrate.

Oil droplet size is critical to the hydrocyclone separation process. Grini, Hjelsvold & Johnsen (2002) stated that a hydrocyclone design can separate droplets down to a certain size, typically in the region of 15-20 µm. According to van Den Broek, Plat & van der Zande (1998), there is a marked influence of the oil droplet size on the separator efficiency. For D_{50} values of 55, 40 and 35 µm (D_{50} is oil droplet diameter for which is valid: 50 vol. % of all oil droplets have a smaller diameter), the efficiency is relatively high. This efficiency decreases to about 70 % and about 50 % for D_{50}'s of 25 µm and 15 µm, respectively. This is in agreement with Rye & Marcussen (1993) when they explained how hydrocyclone efficiency dropped dramatically due to the variation of droplet size down to very small droplets. op ten Noort, Etten & Donders (1990) in their experiment stated that oil droplets less than 10 µm are not effectively removed. It was observed that the relatively small droplet size has a negative impact on the efficiency. Thus, an improvement was achieved by increasing the oil droplet size. This technology was patented by Opus Plus Ltd (formerly Orkney Ltd) and was called Performance Enhancing Coalescence Technology (PECT), also known as Mare's Tail. A technology of installing a fiber-based coalescer has been used before and placed upstream of hydrocyclones. The purpose of this technology is that the small droplets will coalesce on the media into larger ones and reduce the population of smaller oil droplets, thus improving the removal efficiency of the hydrocyclones. It was found that the downstream hydrocyclone performance was improved by 40 % and the dispersed oil content was reduced by 65 % down to a concentration of approximately 25 mg/l independent of inlet concentration (Knudsen et al. 2004, p. 4).

Flowrate has an effect on the hydrocyclone operation. On one hand, if flowrate is low and variable, a buffer tank can be used to build sufficient volume to operate with high flow rate to promote the coalescence (Knudsen et al. 2004). On the other hand, if flowrate is high, one hydrocyclone will be insufficient to separate oil droplets.

2.2.3.5 Filters

Filters have been used to trap oil droplets such that water is forced to flow through a bed of porous medium, normally sand. The disadvantage of this system is the strong possibility of clogging the filter media. To avoid clogging, at least two filters have to be placed in parallel. Once one filter gets plugged, the flow is directed to the other and the clogged filter is backwashed. The backwashed water has to be treated.

2.2.3.6 Centrifuges

A centrifuge is usually applied as a polishing step when a discharge limit cannot be achieved.

A centrifuge meets the requirements of safety and maintenance and is of a suitable size for offshore installations. A centrifuge allows for better separation of smaller oil droplets than does a hydrocyclone, although the energy consumption is higher. Figure 2.11 shows the working principle for a centrifuge.

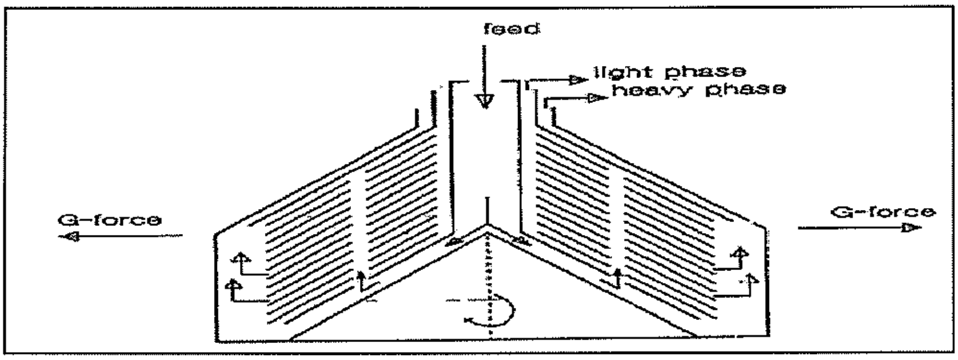


Fig. 2.11- Work principle for a centrifuge.

Oil / water separation is based on centrifugal force (G-force) and the difference in specific gravity of oil and water. It was found by op ten Noort, Etten & Donders (1990) that centrifuges have the capability to reduce the oil concentration below 1.0 mg/l and have been effective in removing tiny aliphatic (dispersed) condensate at the offshore gas production platform P/6A in the Dutch continental shelf.

Flowrate is an important factor that can affect centrifuge performance. Rye & Marcussen (1993) stated that the droplet size distribution changes did not have any effect on the separation efficiency down to a very small droplets on the Tyra gas field in the Danish part of the North Sea and found that the application of centrifuge technology was environmentally acceptable, as well as being a very effective way of treating produced water that contains small condensate droplets. They claimed also that oil droplets distribution was found to be smaller than was initially expected, even though it was treated down to 10-20 mg/l. As mentioned by van den Broek, Plat & van der Zande (1998), the lower droplet size removal can be achieved by decreasing the flowrate for example, 5, 6 and 8 μm droplet size removal correspond with low flowrates. Moreover, van den Broek, Plat & van der Zande (1998) noted that in some cases 2 μm size have been reached, and much lower values than this can be realized with extremely low flowrates. However, in this case it can make such a separation unattractive and impractical. It is worth mentioning that van den Broek, Plat & van der Zande made his results based on assumption of assigning dimensions and derivation not on field practice.

2.2.3.7 Membranes

The work principle depends basically on entrapment of the small droplets and accumulating them in the membrane wall while allowing for water to pass.

In 1990, micro filtration membranes were investigated by op ten Noort, Etten & Donders (1990) for oil removal and were found to have potential for removing the oil / condensate droplets down to 0.1 µm from the water to very low concentrations. These results indicated that the micro filtration membrane was highly suitable for the offshore gas production platform P/6A. The oil concentration did not have an effect on the membrane fouling and showed the best capacity behaviour over time and the least susceptibility to fouling. This test, however, should be subjected to longer term testing to establish the true performance.

The use of membrane technology for offshore application is not considered as viable due to the practicality, operability, maintenance and reliability issues, other issues for considerations are:

- It is expected that this equipment would require frequent shutdown for maintenance and intensive supervision is required; and
- In addition, it will create a waste stream that can generate additional problems in processing.

2.2.3.8 Conclusion

In conclusion, on the basis of this information, produced water treatment technique proves to have only limited success for removing tiny dispersed droplets. The size and distribution of condensate droplets are of a character that conventional treatment would have difficulties in separating efficiently.

2.3 Dissolved Compounds

There are two types of dissolved hydrocarbons found in the water phase:

1. Benzene, toluene, ethylbenzene and xylene (BTEX); and
2. Polycyclic Aromatic Hydrocarbon (PAH).

BTEX compounds are the most abundant hydrocarbons in produced water. These compounds are very soluble in the water (Tsonopoulos 2001). They are unsaturated closed rings. They are not easily removed from produced water and therefore are typically discharged with it.

Polycyclic Aromatic Hydrocarbons (also called polynuclear aromatic hydrocarbons) include medium to higher molecular weight hydrocarbons (C6 to C15). Naphthalene is the dominant compound of PAH. They are soluble in water at low concentrations, but are not as soluble as lower molecular weight hydrocarbons.

2.3.1 Relation between Dispersed and Dissolved Compounds

"Is the concentration of BTEX and PAH compounds affected by the traditional removal of oil dispersed droplets? " The answer is addressed below.

Hydrocarbon compounds' solubility in produced water ranges from high solubility for BTEX to low solubility for PAH. It is necessary to quantify the amounts of dissolved BTEX and PAH that can be either in the oil phase or in the water phase. The ratio of these amounts is termed "the partition coefficient". It was thought previously that the main part of the aromatic components is dissolved in the water phase (Utvik 1999). This means alkylated phenols and PAHs are in the water soluble fraction or in the water accommodated fraction (WAF). However, recent systematic studies done by Descousse, Monig & Voldum (2004), Faksness, Grini & Daling (2004) and Callaghan & Baumgartner (1990), have shown that the major part of the heavier PAH, C4-C5 phenols and C6-C9 phenols are present and dissolved in the oil phase because they are considerably less soluble in water.

It was found that the technologies, which enhance the removal of dispersed oil, also remove a large fraction of PAH from the produced water together with the dispersed oil. This is provided that PAH is part of the dispersed oil and not dissolved in the water phase. Most of the PAH is part of the dispersed oil; for example, at a concentration of 25 mg/l of the dispersed oil, more than 75 % of the 2 and 3 ring PAH and more than 90 % of the PAH with more than 4 rings are part of the dispersed oil (Grini, Hjelsvold & Johnsen 2002). This was confirmed by Descousse, Monig & Voldum (2004) in the Ekofisk field and Ekins, Vanner & Firebrace (2005) by noting that the heavier aromatic compounds such as C6-C9 phenols, 2-3 ring and 4-6 ring PAH are dissolved mainly in the oil phase as they are considerably less soluble in water, and can be removed with the dispersed oil. These results are similar to those found for other fields in the North Sea (Statfjord B, Gullfaks C).

Callaghan & Baumgartner (1990) have concluded that the residual aromatic contents may be dispersed or dissolved in water. This was demonstrated in the two following case studies; one with high aromatic content (there were glycol overheads such that 65-70 % of the total hydrocarbons present were dissolved in the water) and the other with low aromatic content (there were no glycol overheads such that 75 % of the hydrocarbon was aliphatic and more than 90 % of the total hydrocarbon was found to be dispersed and consequently the residual aromatics compounds were primarily dispersed).

The concentration of dissolved compounds, especially BTEX and C0-C3 phenol, is independent of the concentration of dispersed oil in the water phase. It was found by Faksness, Grini & Daling (2004) that when the concentration of dispersed oil is reduced from 40 to 20 mg/l (50 % reduction), the concentration was reduced by 60 % of C4-C5 phenols and by 45 % for the 4-6 ring PAH and C6-C9 phenol from Statfjord B field. No significant decrease in the C0-C3 phenols concentration was found. The same result was found in the Gullfaks C field, but with the percentage reduction of the 2-3 ring PAHs and the 4-6 ring PAHs appearing to be more strongly associated with the dispersed oil, while the relative reduction for the C6-C9 phenols was noted as being lower. As oil concentration is reduced down to 5 mg/l, the results show more reduction as shown in figure 2.12.

As mentioned previously, the produced water treatment equipment can remove the dispersed oil only with specific droplet diameter, not the soluble compounds; thus, most of the petroleum hydrocarbons remaining after treatment are low molecular weight aromatics hydrocarbons that are dissolved in the produced water (Neff & Saucer 1996). It can be seen that BTEX, C0-C3 phenols and low molecular weight PAHs cannot be removed or affected by the traditional removal of dispersed oil droplets, as they are dissolved in the water phase.

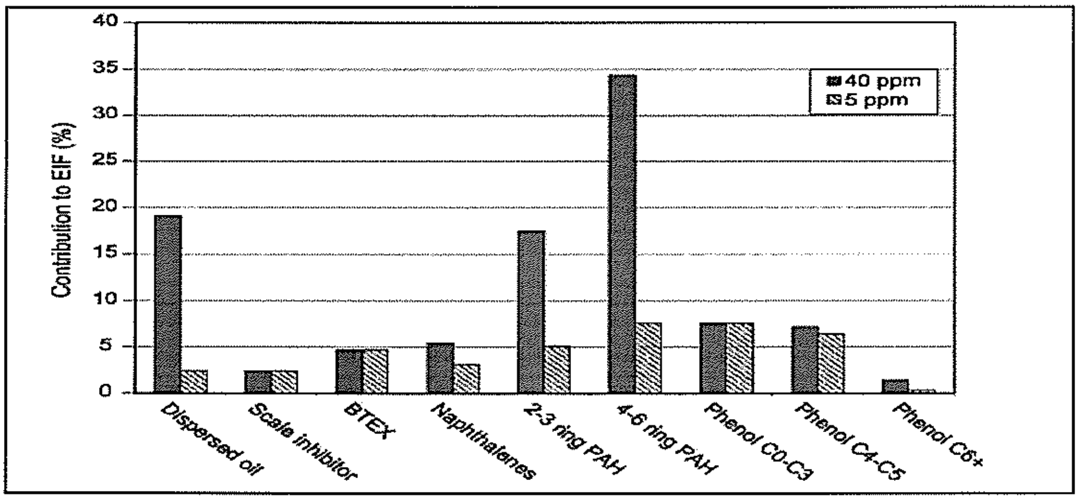


Fig. 2.12- The effect of oil concentration reduction from 40 mg/l (gray bars) down to 5 mg/l (shaded bars) on the chemical composition as contribution to environment impact factor (EIF) on the Gullfaks C field (Faksness, Grini & Daling 2004).

2.3.2 Dissolved Compounds Solubility

Waldie et al. (1998, p. 563) reported that salt has an effect on reducing the solubility of BTEX compounds. Table 2.3 shows the difference in solubility of lower molecular weight aromatics (BTEX) in distilled and seawater sample.

Table 2.3- Solubility of Lower Molecular Weight Aromatics (BTEX) in Water at Atmospheric Pressure and 25 C, mg/l (Waldie & Harris 1998, p. 563).

Composition	Distilled water	Sea water (3.45 %)
Benzene	1700	/
Toluene	535	379
Ethylbenzene	161	111
o-Xylene	171	130
m-Xylene	146	106

Thus, it can be expected that salt can have an effect on hydrocarbon solubility in water phase.

2.3.3 Removal of Dissolved Compounds

Researchers such as Place (1991), Median et al. (1994), Hansen & Davies (1994), Seybold et al. (1997), Miller et al. (1997), Pars & Meijer (1998), Georgie, Sell & Baker (2001) and Ayres & Parker (2001) investigated and looked into different ways of removing the dissolved hydrocarbon from both oil and gas produced water.

The technologies for removing soluble components from produced water have not been fully assessed or utilized offshore. Most options available would involve the use of other chemicals and solvents and additional power as well as producing a concentrated waste stream. All these technologies would add significantly to the cost, weight and space requirements of produced water treatment. The following provides a brief description for some of the removal processes.

Place (1991) describes acidification process as a proven technology to remove dissolved compounds. Although, he presented an overview about oil field brine, it could be taken as a reference. Acidification depends basically on amounts of acid being added to the produced water in order to reduce the pH to about 2-3 and then precipitate the dissolved oil (organic acids) from the water. This aids in coalescing the suspended oil. Some of these organic acids are water-soluble and do precipitate in time to be removed from the water. But, even when the acids precipitate, they frequently occur as very small droplets that treatment equipment does not remove. The operating cost for such a system is expensive. It requires certain quantities of acids such as hydrochloric acid to sufficiently lower the pH and the same quantity of caustic to neutralize.

Madian et al. (1994) provided an explanation for the use of bacteria for removing the dissolved compounds. It is regarded as expensive and due to a long retention time, it needs a large space for bacteria to degrade the dissolved compounds. It has been found that highly acidic water causes disruptions to the microbial biomass stability and thus has an effect on the bacterial colony. In addition, there is a high power requirement for the oxidation ponds, and a need for sludge settling and recirculation. Madian et al. did not take into account microbial influenced corrosion (MIC). MIC occurs as microorganisms attached to a metal surface or embedded in a gelatinous organic matrix (the biofilm). It refers to the undesirable formation of deposits on metal surfaces and affects the interaction between metal surface and the environment (Videla & Characklis 1992).

Exxon Mobil Production Company's Las Flores Canyon onshore facility in Southern California uses bacteria media as anaerobic treatment to remove dissolved compounds from oil field. The water treatment is located onshore. The treatment facility receives water via a pipeline from three offshore platforms located between 10-15 miles from the facility. The plant processes approximately 30,000 bbd through an onshore anaerobic biological treating system and returns the treated produced water offshore for discharge. It removes over 90% of the dissolved organic material. It requires about a two-day retention time, which is uneconomical offshore (Ayers & Parker 2001, p. 42).

In an extensive research into potential technologies for the removal of dissolved components for both oil and gas fields, Hansen & Davies (1994) explored six technologies. The selected technologies were based on an oil field produced water design flowrate of 875 m^3/hr (130,000 bbd) and a gas field produced water flowrate of 6.7 m^3/hr (1000 bbd). These flowrates were selected as typical for the Norwegian sector of the North Sea. The findings by Hansen & Davies are based on a theoretical review of the selected technologies and not specific field conditions, therefore their results are taken as being indicative of the technology performance.

These six technologies are:

1. Ion exchange;
2. Wet air oxidation adsorption;
3. Adsorption on synthetic zeolite;
4. Membrane filtration;
5. Air (and other gas / vapour) stripping; and
6. High rate biological treatment.

1. Ion exchange is basically an immobilized resin bed used for absorbing the charged ions. Ion exchange produces high concentrations of the absorbed ions that are removed by using regenerant solutions such as hydrochloric acid. A media filter has to be used to control fouling or blocking because of dispersed oil and solids. It was found to be the most promising technology presently available to remove dissolved inorganic heavy metal from produced water. The limiting factors for this process are that it doesn't take into account the ultimate disposal for hydrochloric acid regeneration.
2. Wet air oxidation adsorption with regeneration of carbon is a method of using activated carbon to remove dissolved organic compounds from produced water. In gas fields, wet air oxidation could be used without the activated carbon adsorption step. This is because it depends on the quantity of chemical oxygen demand (COD) that allows the system to be self-sustaining without any concentration step. Two reactor vessels would be required to ensure near complete oxidation of all contaminants. The adsorption process depends on a continuous moving bed of granular activated carbon. The wet air oxidation converts hydrocarbon to water and carbon dioxide and oxidizes most other organic and inorganic matter. When the process was evaluated, wet air oxidation appeared to be more applicable for removing almost all dissolved organic compounds in gas fields.
3. Adsorption on synthetic zeolite has been used as hydrophobic zeolite pellets to adsorb dissolved organics from produced water in a fixed bed design. Upstream pretreatment is important to reduce the blockage effect. Regeneration of the zeolite bed after adsorption has to be done periodically up to 5 times per year.

4. Membrane filtration has been used to remove dissolved compounds from produced water for both oil and gas fields in the Norwegian sector of the North Sea. This process contains basically a hollow fiber membrane comprising regenerated cellulose on a highly porous substructure. The membrane separation system is operated as a cross flow membrane filter to reduce the possibility of clogging. This operation allows only 20-25 % of the water flowing through the membrane to be filtered in one pass. The remaining water, about 4-5 times the feed flowrate, is mainly recycled to the feed. Although the system has 90 % aromatic (BTEX) removal, it has removal efficiency only 10 % and 15 % for naphthalene and phenol, respectively. There is need to use a strainer or hydrocyclone as a pretreatment step. In addition, high pressure is required to feed the water.
5. Air stripping has been employed as a means to transfer a volatile component in a liquid mixture from the liquid phase to the gas phase. Air, nitrogen, natural gas or steam can be used as the stripping gas / vapour. The temperature of gas and liquid phase governs the rate of removal of volatile components from liquid to gas phase. Produced water temperature has great effect on the process; the efficiency is reduced if the produced water is cooled. Scale formation may prove problematic.
6. Bacteria has been claimed to remove the dissolved compounds. In case of aerobic treatment, it can realistically be considered for offshore produced water treatment. It preferentially removes up to 77-90 % of fatty acids, which are the main contributor to organic loading and the total organic carbon discharged. However, rapid variation in flowrate (fluctuation) should be avoided so as to maintain an optimal bioculture loading in the reactor. This process needs cooling water pumps and a biological oxidation unit with a sludge separation unit.

Hansen & Davies did not take into account retrofitting of such process for use offshore into a larger number of existing platforms, such that; they are expensive, need high power requirements, occupy large spaces and are heavy. Power, weight and size involvement requirement are shown in Table 2.4 and 2.5, respectively. Moreover, in the case of total removal efficiency, two or more systems might be required in series if total removal of dissolved components were to be required. However, Hansen & Davies (1994, p. 188) reported that offshore testing known to be underway includes:

- A steam stripping system on gas platforms in the Dutch sector of the North Sea. It has been operated since mid-1992 in K6 gas production platforms;
- Air stripping trials and membrane filter trials on the Dutch sector of the North Sea and being conducted by operators to investigate disposal options for the contaminated air;
- Membrane filter on gas platforms on the British sector of the North Sea. Although it was only reported for a very short period of time, results have demonstrated that on Shell's Indefatigable gas field, the membranes have removed between 50 and 80 % of the aromatic hydrocarbon and up to 99.8 % of the aliphatic in the produced water; and
- Other membrane filtration trials have been conducted in the North Sea and in the in Gulf of Mexico.

Table 2.4- Power Consumption Estimates (Hansen & Davies 1994).

Process	Power consumed (oil field), kW	Power consumed (gas field), kW
Ion exchange	154	2.1
Activated carbon/ wet oxidation	751	Not applicable
Zeolite adsorption	598	7.3
Membrane filtration	1375	17.5
Air stripping	240	2.4
Biological treatment	738	24.9
Wet air oxidation	Not applicable	32

Table 2.5- Weight and Space Requirement Estimates (Hansen & Davies 1994).

Process	Wet weight oil field, ton	Wet weight gas field, ton	Size oil field, m^2	Size gas field, m^2
Ion exchange	443	15.2	310	45
Activated carbon/wet oxidation	610	Not applicable	200	Not applicable
Zeolite adsorption	420	21	200	36
Membrane filtration	250	16	200	4.5
Air stripping	39	5	90	12
Biological treatment	300	4.7	140	40
Wet air oxidation	Not applicable	11	Not applicable	9

A composite process to reduce the organic loading rate has been demonstrated in Wyoming in 1995-1996 at the Gas Research Institute (GRI) for a natural gas produced water treatment plant at Lysite. The process is called the granular activated carbon fluidized bed biological reactor (GAC-FBR) (Seybold et al. 1997; Miller et al. 1997). It is basically a combined biological process using a fixed microbial film, which biologically mineralizes the dissolved organic compounds. The use of an adsorptive biomass carrier in the form of granular activated carbon (GAC) affords the process robustness. The adsorptive capacity of the GAC carrier particles serves as an effective organic loading system. Both processes have been used in a series aerobic (using air) and anaerobic (nitrate or sulfate as electron acceptor). The removal efficiency of BTEX was found around 98 to 99.9 %.

Pars & Meijer (1998) invented the Macro Porous Polymer Extraction (MPPE) process. This technology has been evaluated and verified during 1996 for treatment of offshore process water by the Orkney Water Technology Center in Harlingen, Netherlands. MPPE is based on vapour-liquid equilibrium and utilizes two proven technologies through two columns: liquid-liquid extraction and steam stripping with an innovative medium (the MPPE particles). Due to the difference in the boiling point of both produced water and light hydrocarbons, hydrocarbon components can be easily separated. They allow continuous operations with simultaneous extraction and regeneration. The system could be used for offshore oil and gas production facilities. This system has a remarkable effect on reducing the BTEX concentration of approximately 800 mg/l to 5 mg/l. The presence of dispersed oil with a concentration of 150 mg/l did not affect the performance of the unit. There are several critical operational parameters that have to be taken into considerations; for example, the system has a high space, steam, electrical power consumption, weight requirement and is therefore suitable only for low volume and MPPE particles can degenerate over time and need replacement.

Hydrocyclones have been used as a potentially single stage process for both dispersed and aromatic removal by Statoil through a process called C Tour. Statoil has taken into account the potential to treat large amount of water, low weight, height and footprint. The

C Tour process has been performed on the Statoil Statfjord on SFB platform (Grini, Clausen & Torvik 2003). The injected gas condensate acts as an extraction-solvent that enhances the removal of dispersed oil up to 90 % compared with a standard process without condensate injection. C Tour basically uses a solvent that extracts the dissolved hydrocarbons from the water phase. The hydrocarbons are then removed in the hydrocyclone. This technique reduces the concentration of dispersed oil by 50-70 % as well as making the dissolved organic content disperse so that it can also be removed in the hydrocyclone. The trials by Grini, Clausen & Torvik (2003), noted that the removal efficiencies with condensate injection produced the following:

1. An average 98 %, of PAH;
2. C6-C9 phenols approximately 95 %; and
3. C4-C5 phenols up to 55 %.

Small scale tests carried out in a laboratory have been very promising. However, the last test has yet to be evaluated on a full-scale basis on the Statjford field. Finding a suitable application for it offshore may be very challenging. Other limitations are:

- Only a specific grade of gas condensate will suffice as the solvent; and
- The solvent increases the concentration of BTEX compounds in the produced water stream by about 40 % from approximately 10 mg/l to 14 mg/l over the hydrocyclone.

2.4 Evaporation Models

A number of studies have been done to estimate the oil evaporation rate from oil spills under a variety of environmental conditions (Yang & Wang 1977; Stiver & Mackay 1984; Stiver, Shiu & Mackay 1989; Riazi & Edalat 1996; Riazi & Al-Enezi 1999; Reed et al. 1999; Barker & BuFarsan 2001; BuFarsan et al. 2002; Fingas 1995; 2004). Different models were developed according to specific parameters and various approaches were investigated to quantify the oil spill losses to the atmosphere.

Oil spill modeling initially applied calibrating equations originally developed for water evaporation. The results from water evaporation researchers were subsequently used by oil spill modelers to predict and describe oil and petroleum evaporation. Much of the pioneering work for the water evaporation rate was performed by Sutton (1934). Sutton proposed the factors where the evaporation rate depends on mass transfer coefficient (K), concentration of the evaporating fluid (C_s), wind speed (U), evaporation area (A), Schmidt number (Sc) and the empirical exponent (r). Sutton expressed the turbulence as a combination of the wind speed and the Schmidt number that relates the diffusivity of a particular gas in the air. The Schmidt number is the ratio of kinematic viscosity of a gas over the molecular diffusivity of the gas in the air and was thought of as representing the molecular diffusivity of the evaporating substance in air.

For oil, as a multi component fluid with composition varying from source to source, the case is different and a more complex relation (logarithmic) will exist for the evaporation rate because of the depletion of more volatile components. More extensive studies on the evaporation of water have been developed to express the oil evaporation (Fingas 1995, p. 3). The average boiling points of successive fractions were used as the starting point to predict the overall vapor pressure. The evaporation time was a function of layer thickness (h), diameter of the spill (d), atmospheric stability (K_{ev}), meterological constant (ß), wind speed (U), vapor pressure (p) and molecular weight of the component (M). After that, the equations used to estimate the hydrocarbon evaporation were corrected by using the evaporation rate for cumene (Fingas 2004, p. 2). It was found that the difference in constants was related to the enthalpy differences between water and cumene. Data was used to correlate the gas phase mass transfer coefficient as a function of wind speed, pool size and the Schmidt number.

The difficulty of a multi-component system is primarily that of expressing the liquid vapor pressure as a function of its changing composition. As a liquid evaporates, the more volatile materials are lost preferentially and the mixture's total vapor pressure falls.

2.4.1 Evaporation Losses Computation Methods

Two main methods are currently used to compute evaporation rate and changing in vapor pressure. Both methods use a similar mass transfer concept, expressing a mass transfer coefficient as a function of wind speed, vapor pressure, spill size and temperature (Fingas 1995, p. 3; Sebastiao & Soares 1995, p. 124). They are:

1. The pseudo-component approach, which consists of a selected set of hydrocarbon components grouped by molecular weight or by boiling point fraction. Crude oil is modeled as a relatively small number of discrete, non-interacting components. Each pseudo-component is treated as a single substance with an associated vapor pressure and relative mole fraction. The total evaporation rate of the slick is the summation of the individual rates.
2. The analytical approach, by which vapor pressure is computed as a function of the temperature and the amount evaporated. In this approach, Stiver & Mackay (1984) relate fraction evaporated to the evaporative exposure termed as θ. The unique aspect of this approach is that it simply permits the results from a variety of laboratory evaporation experiments to be easily extrapolated to actual environmental conditions. The evaporative exposure is a function of time, oil slick thickness and wind speed. The oil is treated as a single substance with a vapor pressure that varies with the fraction evaporated.

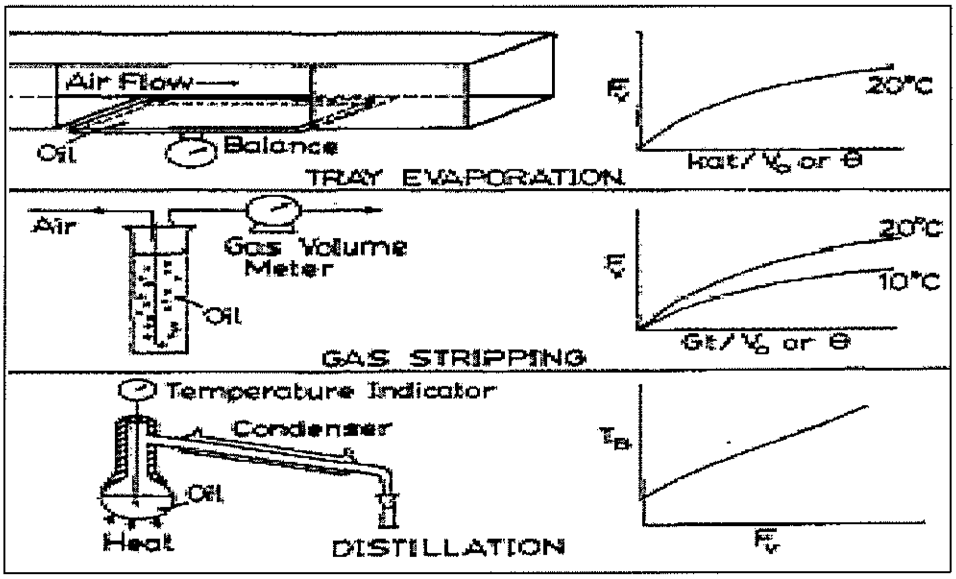


Fig. 2.13- Schematic diagrams of evaporation experiments: surface evaporation (top), gas stripping (middle) and batch distillation (bottom) (Stiver & Mackay 1984).

2.4.2 Effect of Temperature and Wind Speed on Evaporation Losses

"Is it possible to use the effect of temperature and wind speed in an offshore environment as a means to remove the oil waste and change its composition?". The answer is addressed below.

Yang & Wang (1977) developed a numerical model depending on a psuedo-component approach to predict the changes in oil characteristics, specific gravity and percentage weight remaining of oil on water. Different simulated temperature and wind speed conditions were applied such that temperature ranged from 14, 21 and 26 °C and wind speed ranged from 0.71, 1.54 and 3.2 m/s. Wind speed device was placed 10 cm above the oil layer. It was observed that the temperature and wind speed are of paramount effect in the early stage of evaporation up to around 50 hr for No.2 fuel oil (0.8472 sp.gr.).

Stiver, Shiu & Mackay (1989) conducted a theoretical treatment for the evaporation rate for specific hydrocarbons from crude oil spills. They found that it was possible to predict the evaporation time in an evaporating oil spill and consequently they were able to determine the fraction evaporated for a particular exposure. They also found that on the basis of the weathered oil's initial boiling point, θ can be calculated. From this environmental exposure, the fraction remaining of any component and thus the composition of the fresh oil, can be estimated.

Riazi & Edalat (1996) presented a mathematical model based on a pseudo-component approach to predict the rate of oil evaporation and dissolution for an oil spill. It was found that the rate of dissolution under normal sea surface conditions is about 0.1 % of the rate of evaporation. This result was agreed by Robotham & Gill (1989, p. 53). Riazi & Edalat conducted a model on two different samples: a crude oil from Ahwaz oil fields in Iran and a home kerosene produced at the Tehran Refinery. Results showed that an oil spill floating on the seawater surface may completely vaporize within a few days at temperature of 40 ° C for Ahwaz crude oil with a density of 0.875 gm/cc. In 1999, Riazi & Al-Enezi developed an accurate semi-analytical and general model to estimate the amount of oil disappearing from an oil spill floating on a sea surface. The oils applied were Kuwait crude oil (alkanes) and Kuwait petroleum products (naphtha, kerosene, diesel fuel and gas oil). This model takes into account the sedimentation as well as evaporation and dissolution. For estimation of solubility under different temperature, salinities and for different oils, an empirical correlation was derived. Riazi & Al-Enezi determined the evaporation mass transfer coefficient (K), which depends on wind speed, molecular weight and temperature based on the rate of oil disappearance for the four petroleum fractions studied.

Barker & BuFarsan (2001) investigated the evaporative losses from the surface of oil lakes of Southern Kuwait. Four temperatures 25, 30, 40 and 50 °C were used with three airflows 25, 50 and 100 ml/min on a Kuwait crude oil (from Burgan field) and a Venezuelan crude oil. The compositional changes were monitored by taking samples periodically for gas chromatographic analysis. Wind speed was calculated as volume per time (ml/min) not as speed units (m/s). Laboratory simulation experiments shown that evaporation is initially rapid but the rate of weight loss decreases until only approximately two-thirds of the oil remains. Evaporative losses produced a residual crude oil that has increased density and viscosity with devolatilized surface skin that acts as a protective layer inhibiting further evaporation. The original oil used in the experiments had a density of 0.876 gm/cc. This density was noted to increase up to 0.893, 0.904 and 0.922 gm/cc as oil weight was lost by evaporation of around 12.9, 20 and 30 %, respectively. The same result for evaporation rates was found by BuFarsan et al. (2002) on the same oil sample.

Fingas (2004) concluded that oil evaporation is not strictly boundary-layer regulated from an experiment set up. It was reported that:

- Temperature is the most important environmental consideration; and
- Wind speed is not that important.

Fingas found that the evaporation rate of several oils with increasing wind speed does not change significantly except for the initial step over the level zero wind. Wind speed had limited effect on the evaporation rates for oils and even the light product, gasoline and water. Therefore, it would appear to indicate that the oils used are somewhat boundary-layer regulated, but only to the degree that effect is seen in moving from 0 m/s to 1 m/s and not thereafter.

Sebastiao & Soares (1998) found that the pseudo-component approach gave results much closer to the experimental points than did the evaporative exposure simulation. Since the evaporation process represents a significant loss of volume during the first hours after spillage, such a difference leads to a significant variation in the predicted volume remaining in the oil slick. However, it should be noticed that the oil composition was based on average percentages for a light crude oil. Reed et al. (1999, p. 8) came to the same above conclusion that the extended analytical method in general predicted significantly larger evaporative losses than his own pseudo-component model.

To summarize, there are many and different approaches that have been considered in relation to oil evaporation. Although there is debate about the effect of temperature and wind speed on the evaporation rate, some researchers have found that both temperature and wind speed play a significant part in the ocean offshore environment on the removal of light oil layers into the atmosphere.

CHAPTER 3

EXPERIMENTAL WORK

3.1 Introduction

In the offshore oil and gas platforms, space, power and weight requirements are of major concern. Thus, the subsea collection and processing of hydrocarbon fluids is gaining favor. The sub sea environment presents many challenges, one being the possibility of disposing of produced water. The effective disposal of water and the accumulation of condensate is the area of investigation for this experimental work. The idea of collecting amounts of condensate that can be separated above a salt water layer within an open tank (floating separator) situated on the sea surface, with the condensate evaporated under the action of wind speed and temperature is proposed as being a viable solution.

The chapter covers two experiments: firstly, to determine the time needed for dispersed condensate to float on the water surface, and secondly, to determine the condensate column evaporation losses and its change in density with time. Moreover, the methodology, sample handling, results and discussions have been thoroughly investigated.

3.2 Experiment 1: The Effect of Salinity on Condensate / Water Column and Separation Percent on Condensate Water System in terms of Time.

3.2.1 Methodology

The procedure observed for the experiment is as following:

1. Filtered water was taken.
2. Salts were prepared.

3. Graduated measuring flask was taken and 100 ml of water and 100 ml of condensate were poured in it and closed by stopper. Condensate composition brought from Core Laboratory (Appendix A).
4. Mixing was achieved around 48 hours by using a rocking machine to make dispersion of both condensate and water droplets in each other. Mixing achieved under controlled room temperature conditions (Appendix B).
5. Separation process was observed by taking the sample on a stable platform. Condensate / water column heights with time were recorded.
6. Each recorded observation represents the amounts of condensate / water separated at that time.
7. The reading times were selected as: 0, 3, 6, 12, 15, 18 and 21 min.
8. Preparation of salty water: 5 % salt concentration is added to 1000 ml of filtered water (concentration by weight 50 gm salt/ 1000 gm water) in a cylinder with a capacity of two liter. This 5 % salt concentration solution was then used to derive diluted samples of 1 %, 2 % and 3 %.

3.2.2 Sample Handling

1. In the beginning, 100 ml of water was added in the mixing cylinder then by using a syringe (60 ml capacity), 60 ml of condensate was poured to the water followed by 40 ml. This mixture represents the “produced water” for the test.
2. After mixing was achieved, the cylinder is to taken out of the rocking machine and the sample is permitted to settle. The rocking machine creates a fine condensate dispersion in the water phase. This demonstrates that the high molecular weight aromatic soluble components have gone to the water phase.
3. Density of the condensate sample is 0.76 gm/cc, which is less than the whole sample density of 0.8161 gm/cc. Five samples were taken from the condensate cylinder (The cylinder was thoroughly shaken to ensure representative sample) and weighed using an electronic balance. The weight of each sample was then recorded. The condensate density was calculated by the averaging of five readings. The balance sensitivity was noted to be ± 0.1 gm. The weight of sample from the syringe divided by 10 ml (syringe volume) yield a density value.

4. The cylinder was cleaned by using a detergent with water then dried by using a clean tissue with an air compressor used to dry it. The cylinder was then inspected for cleanliness.

3.2.3 Results and Discussion

Figure 3.1 shows the effect of salinity on condensate / water separation percent in terms of time.

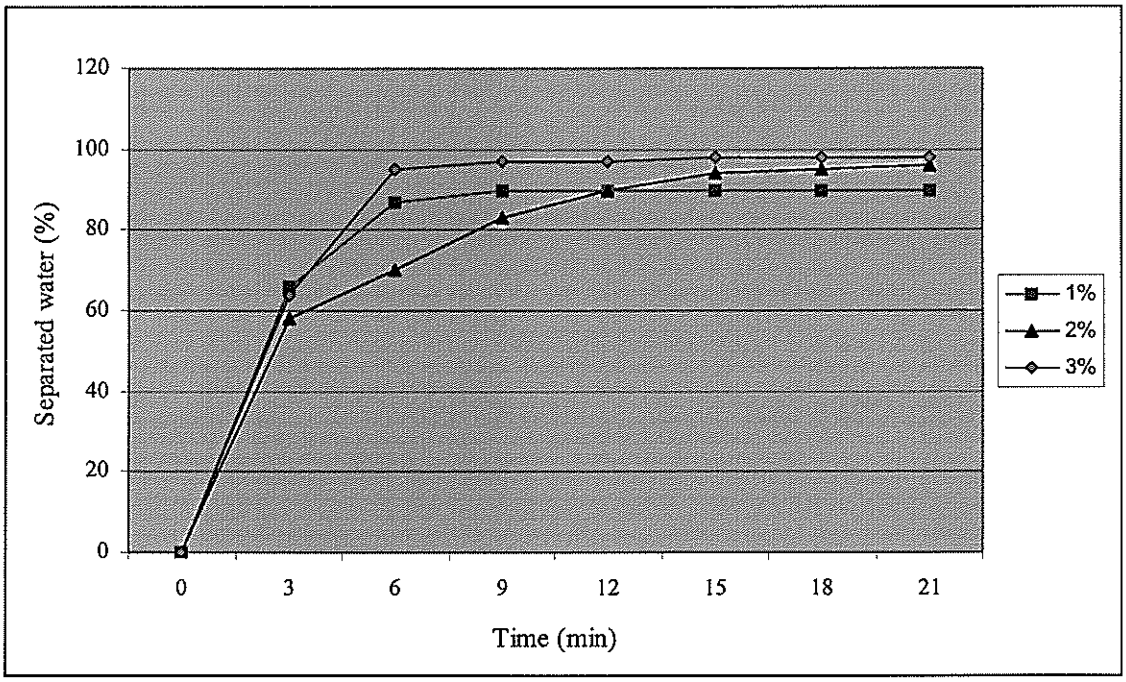


Fig. 3.1- The effect of salinity on condensate / water separation percent in terms of time.

The Figure above shows that salt concentration has a remarkable effect on separated water percent as mentioned by Mohamed, El Gamal & Zekri (2005). The results derived by Mohamed, El Gamal & Zekri (2005) are reproduced in this works as Figure 3.2, but the time is expressed in days. This variation in time compared to the work presented in this research is attributed to the oil type (diesel engine oil) with density around 0.894 gm/cc which is higher than the oil density being used in this research. This high difference in the density leads to longer separation time. Furthermore, an emulsifying agent and mechanical stirrer (2000 revolution per minute) at room temperature were used in their test.

It can be seen that there is fluctuation between 1 and 2 % salt concentration within the first 12 minutes. This fluctuation is due to that the mixing time at 1 % salt concentration was carried out at 46.5 hour. It could be also attributed to the behaviour mechanism that applies to emulsions such that a stabilizing film has an affinity for both water and oil that enables the emulsifiers to overcome the natural forces of coalescence, where the emulsion stability can be classified as weak. As well, the wettability effect was observed around the wall of the cylinder and showed a great effect on separation, therefore the condensate layer heights (levels) were taken as an average for each salt concentration, as shown in Figure 3.3. The wettability effect is discussed in detail in Chapter 4.

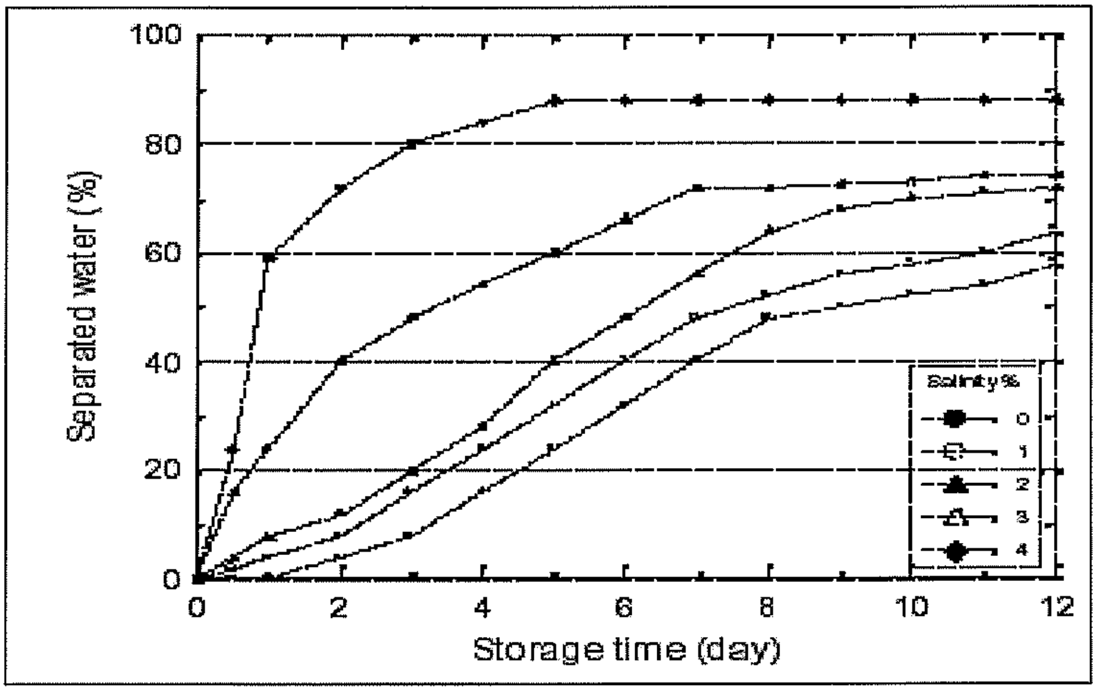


Fig. 3.2- Effect of salinity on oil / water separation percent in terms of time (Mohamed, Gamal & Zekri 2005).

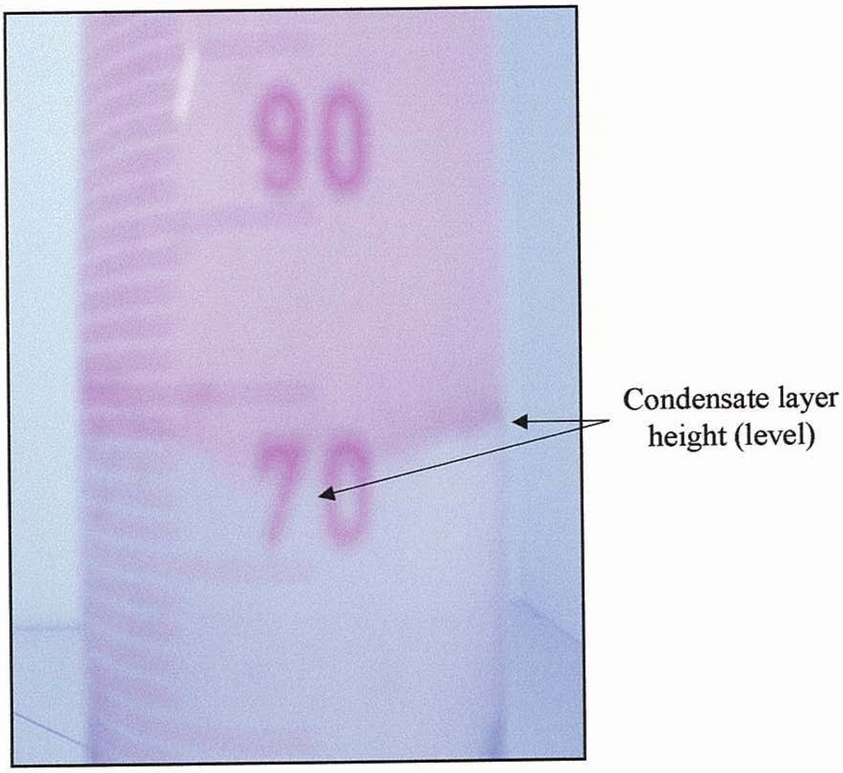


Fig. 3.3- Condensate layer height rising above water layer.

The experiments performed have demonstrated that just after generating a sample for observance of condensate / water separation, a condensate layer at the top of the liquid column begins to appear clearly. A creamy layer of condensate / water emulsion is also formed, as shown in Figure 3.4. This creamy layer observance was noticed by Mohamed, El Gamal & Zekri (2005). Varying amounts of condensate leave the water layer and reach the phase separation layer. As the condensate / water mixtures are a dispersion of oil and water droplets, commonly called an emulsion, they must be allowed to settle out.

It was seen that the rising velocity of the condensate droplets in the water continuous phase decreased as times increase. This being due to the decrease in the size of the condensate droplets remaining in the water layer.

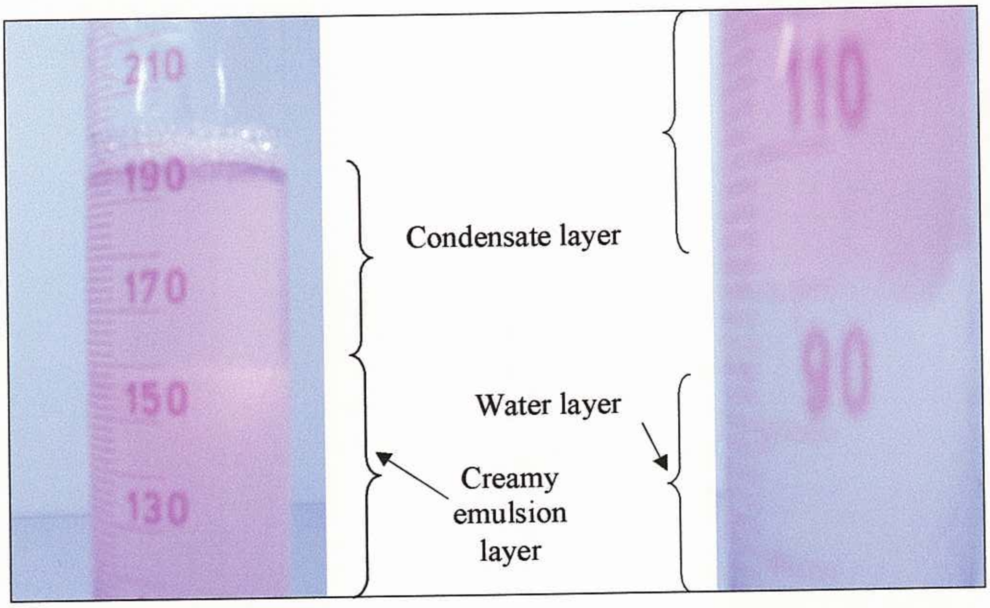


Fig. 3.4- Three consecutive layers: condensate layer, water layer and creamy emulsion layer.

Salt destabilizes the natural emulsifiers and lowers the electrostatic repellent forces between the oil droplets. As oil droplets have a negative charge (electrostatic charge) that repels coalescence, the salinity influences the electric charge of the oil droplets, thereby having an effect on the coalescence such that when salinity is high, the electric charge is low and thus conditions for agglomeration into larger droplets exist. It was assumed that the presence of salt would suppress the electric double layer and thus causes an increase in the coalescence rate for oil / water emulsion (Mohamed, El Gamal & Zekri 2003). As salt concentration increases, the internal energy of the system increases. Consequently, the emulsions are not thermodynamically stable, and the droplets merge with each other to produce big droplets and increase the coalescence rate. Coalescence is one of the possible mechanisms of destruction of emulsions, which occurs when the energy of adhesion between two droplets is larger than the turbulent energy causing dispersion.

Another water sample (sea water) with 3.5 % salt concentration was tested. The condensate / water sample was mixed for 48 hrs then left to be separated under ambient room temperature of 21 °C. It took around 1 minute and half to finish the separation. It was found that in this second case there are two points of significance:

- There was no effect of wettability around the cylinder wall compared to the first sample prepared experimentally.
- Condensate droplet emulsified in the water phase appeared to rise as quickly as water droplets in the condensate phase. This is because of the increasing in the internal energy for the system.

3.3 Experiment 2: The Effect of Temperature and Wind Speed (Airflow) on Condensate Columns in terms of Time.

3.3.1 Methodology

The procedure observed for the experiment is as following:

1. A rectangular basin was prepared with dimensions of 20 cm height, 60 cm length and 26.5 cm width and water is added up to 19 cm height.
2. The thermometer was mounted in the basin for the duration of the experiment. The thermometer has an accuracy of ± 0.1°C.
3. A measured cylinder was fixed inside the water bath and water temperature was regulated to required temperature.
4. A sample of 125 ml of condensate was taken. It is very important to ensure that the temperature inside the measured cylinder is the same as the water bath. Therefore, the sample has to be placed in the water bath around 25 minutes prior to commencement of the experiment to ensure the required temperature stability was reached. The open end of the cylinder is closed, as shown in Figure 3.5, to ensure there is no evaporation of the condensate.
5. A fan was fixed at a specified distance, with fan axis at the centerline of the condensate cylinder to keep the simulated wind velocity on that axis.
6. The fan was switched on and airflow set to register around 1.2 m/s. Also, the temperature was recorded.
7. Once the cylinder was opened, recording the time for the first run began at t=0.

8. Water level is set of at predetermined level of 19 cm. To maintain control of the water level, the displaced water volume was limited to 150 ml.
9. For every condensate reading, 1 minute prior to taking reading, eight recordings of the wind speed from the fan by using an anemometer were recorded, as discussed later on in 3.3.2.
10. Condensate column was observed and its column loss expressed as a percentage.
11. The procedure was repeated for 2.4 m/s wind speed.

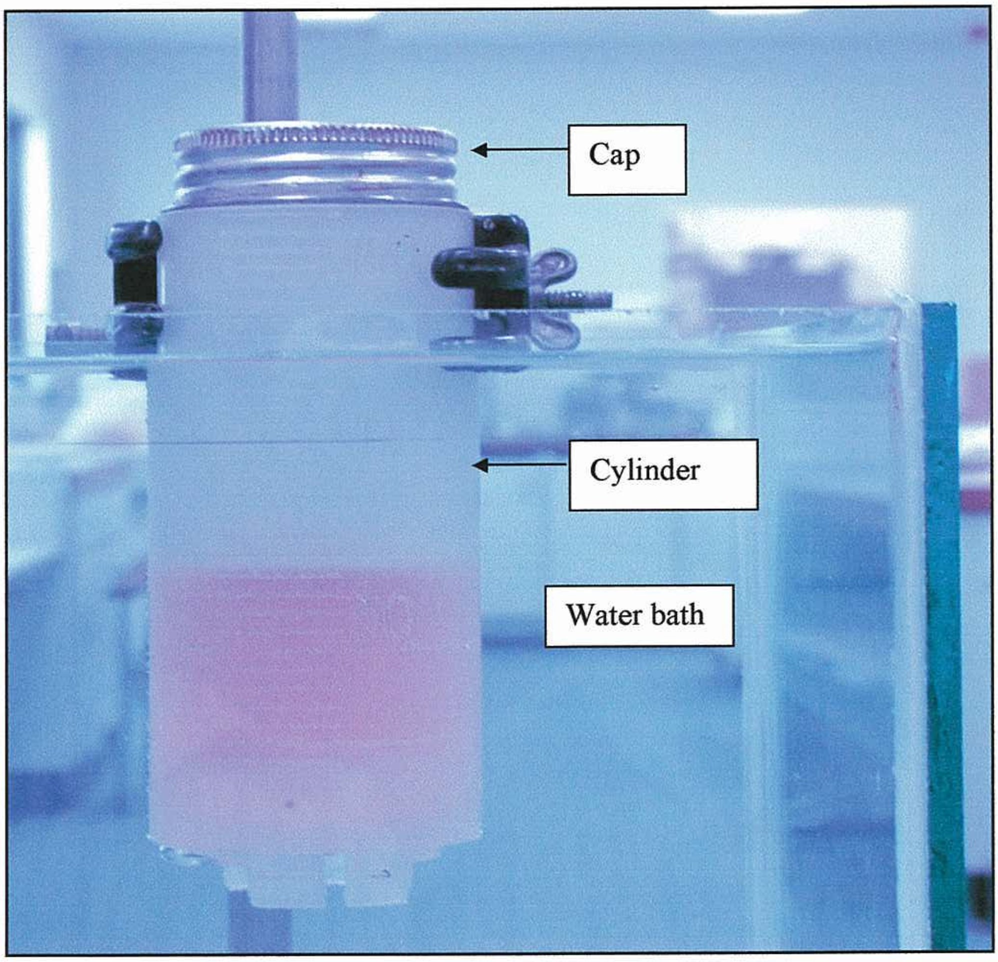


Fig. 3.5- Condensate top cylinder closed to avoid evaporation when temperature was maintained.

3.3.2 Sample Handling

Wind speed and ambient temperature were determined by using an air speed temperature anemometer, with airflow range between 0.4 - 30 m/s with an accuracy of ± 3% and temperature range – 10 to 50 °C with an accuracy of ± 0.6 °C. Anemometer readings were recorded as shown in Appendix C. Wind speed was measured at a single point, with each recorded result being derived from the averaging of eight readings. The anemometer was located at a set location with respect to the cylinder, as shown in Figure 3.6.

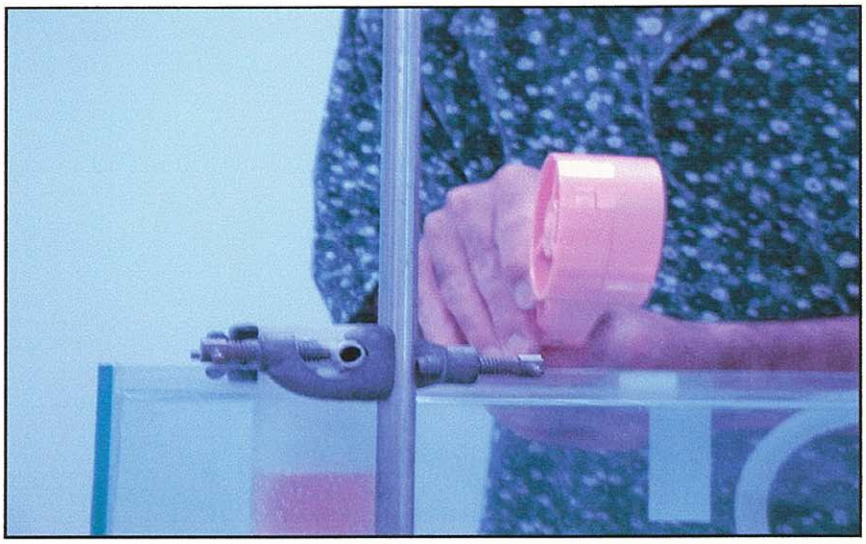


Fig. 3.6- Anemometer at fixed location.

The condensate column was observed at three hourly-intervals during the experimentation period. After six hours of evaporation within the tank, the condensate sample and container were removed from the tank for weighing. The outside was thoroughly dried. The difference between the cylinder and its content with the cap, and the cylinder and cap alone, gave the required condensate sample weight. By knowing the condensate column height, the condensate volume in the container was determined. Dividing the condensate mass value by the condensate volume, the density value was obtained for the given conditions. A balance with an accuracy of ± 0.1 gm was used.

To ensure that there was no evaporation after finishing the daily procedure, the condensate cylinder with the sample and cap was measured before beginning the next series of measurements, with the comparison made to the previous result. The majority of the values showed the same weight measurement. However, there was a notable exception for the first sample, when an error between the two readings was noted. As it was suspected that there was some degree of evaporation, the procedure was modified to have the sample and container stored in a plastic bag instead of a cap when the experiments were not being conducted. This modification appeared to resolve the problem as successive weight comparisons were in agreement, as shown below in Table 3.1.

Table 3.1- The Difference in Weight of the Cylinder, Condensate and Cap Before and After Finishing the Experiment.

Time (hr)	**Weight of Cylinder, condensate and Cap just after finishing the experiment (gm)**	**Weight of Cylinder, condensate and Cap just before beginning the experiment (gm)**
For the first sample, wind speed 1.2 m/s		
12	131.25	130.8
18	127	126.6
24	124.2	124
30	122.3	122.3
36	120.9	120.9
42	119.8	119.8
For the second sample, wind speed 2.4 m/s		
12	123.7	123.7
18	120.4	120.3
24	118.2	118
30	116.6	116.6
36	115.7	115.7
42	114.8	114.7

For the purpose of repeating the above experiment, the following changes were applied as follow:

- Three different wind speeds, 0, 1.2 and 2.4 m/s were run above the condensate sample.
- There was no water to be added for the water bath because the water surface was isolated from the room environment by a plastic cover. As a result, water level losses were very small.
- The total number of condensate evaporation readings was limited due to time constraints. However, averaged values were recorded and demonstrated good repeatability with the initial experimental results (1.2 and 2.4 m/s).
- The condensate sample was exposed for 48 hours in the water bath. The initial and final density was calculated for the three sets of experiment.
- The same cylinder and cap were used.
- Water bath and room temperature were varied as shown in Appendix C.

3.3.3 Results and Discussion

The results of the experimental work are summarized in a tabular format as shown in Appendix C, and presented graphically in Figures 3.7 and 3.8. Figure 3.7 shows effect of two different wind speeds (1.2 and 2.4 m/s) on cumulative condensate column losses percent in terms of time. Figure 3.8 shows scattering data under constant water bath temperature and three different wind speeds (0, 1.2 and 2.4 m/s). Figure 3.9 presents effect of two different wind speeds on increase condensate density with the time. Table 3.2 shows the initial and final density for the first and second runs for the three different wind speeds.

Figure 3.8 illustrates that the values of cumulative losses at wind speed of 2.4 m/s are greater than wind speed of 1.2 m/s. It was also shown that the values of cumulative losses at wind speed of 1.2 m/s are greater than 0 m/s. At the beginning, the high gradient in the evaporation is related to the flashing mechanism that occurs once the dissolved condensate-gases are exposed to atmosphere conditions.

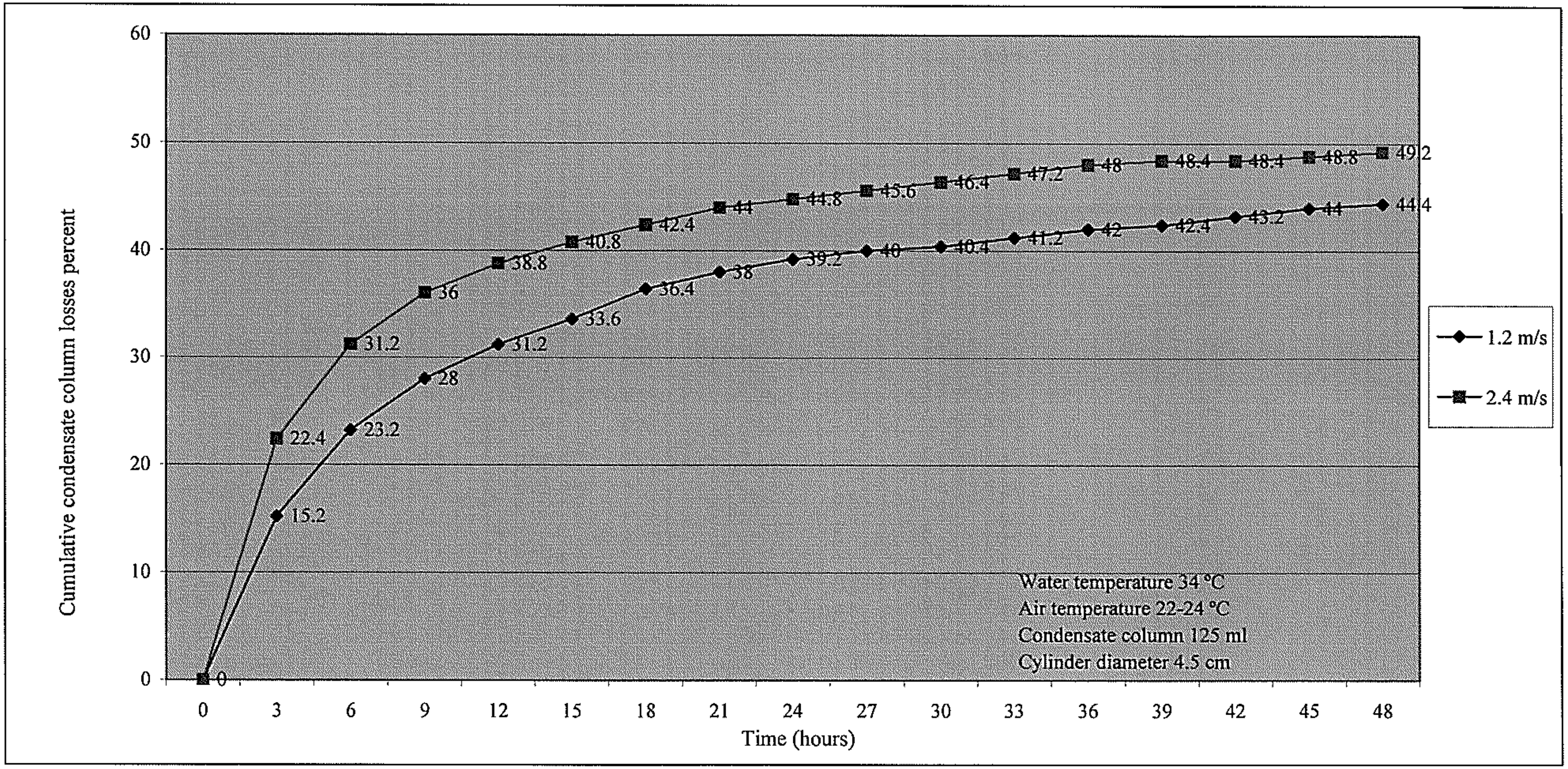


Fig. 3.7- Effect of two different wind speeds on condensate column in terms of time.

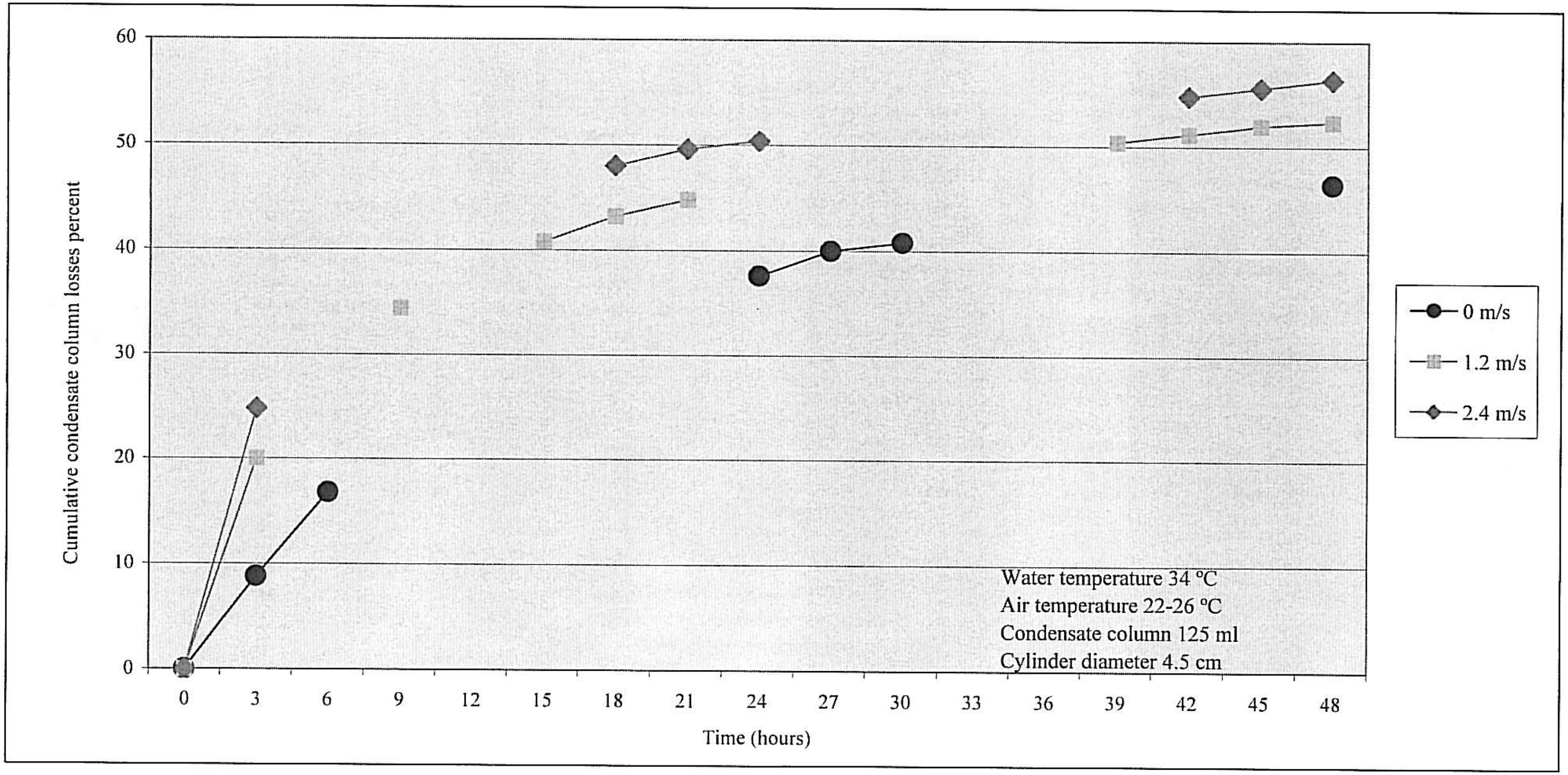


Fig. 3.8- Scattering data of three different wind speeds on condensate column in terms of time.

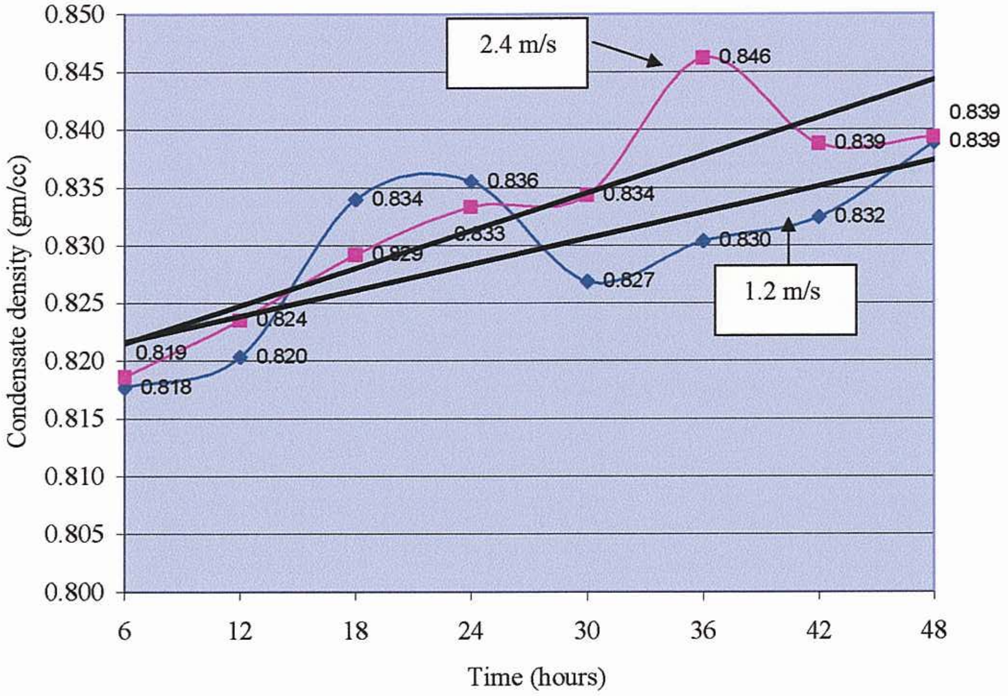


Fig. 3.9- Effect of two different wind speeds on increase condensate density with the time.

Table 3.2- The Initial and Final Density for the First and Second Run for the Three Different Wind Speeds.

Wind Speed (m/s)	Run	Initial Density (gm/cc)	Final Density (gm/cc)
0	1_{st}	0.769	0.792
1.2	1_{st} 2_{nd}	0.769 0.769	0.778 0.789
2.4	1_{st} 2_{nd}	0.768 0.768	0.801 0.805

Condensate evaporation reduces with time and both density and viscosity change with it as dissolved condensate-gases are released to atmosphere. These values decrease with time until the curve begins to flatten out at around 24 hrs. This means that as airflow increases with a constant condensate temperature, the condensate losses will correspondingly increase. Finally, after around 48 hrs, the cumulative losses converge with little fluctuation. It was found that the cumulative condensate losses percent at 0, 1.2 and 2.4 m/s, are 46.4 %, 52.4 % and 56.4 %, respectively. The above trend in condensate column losses were investigated previously by Sebastiao & Soares (1995, p. 123), Nordvik (1995, p. 22), Riazi & Al-Enezi (1999), Barker & BuFarsan (2001) and Fingas (2004).

From Figure 3.7 and Figure 3.8, it can be seen that at the beginning, the condensate column loss values are quite large. This is because the condensate layer at the top has a lower density and is more volatile compared to the next layer. This top condensate layer can be affected easily and quickly by temperature and airflow.

Figure 3.9 shows the increase in the condensate density as time increase. The individual points are from limited tests such that influence of uncertainty in density measurements is evident. Therefore; the gradient fit line for two different wind speeds was used to indicate that the condensate density is increased with the time. The change in density as evaporation time increase was conducted by Yang & Wang (1977), Barker & BuFarsan (2001), Nordvik et al. (1996) and Merlin, Cedre & Poutchkovsky (2004). Merlin, Cedre & Poutchkovsky found that density was increased from around an initial value of 0.82 gm/cc to 0.92 gm/cc after 120 hours.

From Table 3.2, the final density at zero wind speed is higher than that at 1.2 m/s. This reading is probably just a reflection of the overall uncertainty of the measurements. However, the final density readings at 1.2 and 2.4 m/s are reasonable. It is expected that as wind speed increases, the condensate column decreases and density increases with it.

CHAPTER 4

MODELING

4.1 Introduction

In this study, a simulation model (Mass Balance Model) for the process of condensate / water separation and condensate / water evaporation was developed to model the operational requirements for the floating separator to ensure that it is performing under practical condition. This model takes into account the parameters, such as wind speed and temperature that can have an effect on evaporation in terms of time. It also permits investigations to be made into the effect of wind speed and temperature on the condensate layer build up inside the separator.

A key advantage in the use of a Mass Balance Model is that the condensate evaporation and accumulation rate can be determined under the prevailing environmental conditions in terms of time for a given flowrate. The predictive model is based on the fundamentals of evaporating lighter components from the condensate layer into the atmosphere, leaving the heavier bottom condensate layer to be skimmed off. The complete construction of the simulation model, taking into account the wind speed and temperature, is described in this chapter.

4.2 Process Description

Once condensate / water mixture flows into the floating separator, two processes occur:

1. Condensate / water separation; and
2. Condensate layer evaporation.

These two processes are applicable on the sea-surface floating separator. A schematic diagram for the floating separator is given in Figure 4.1.

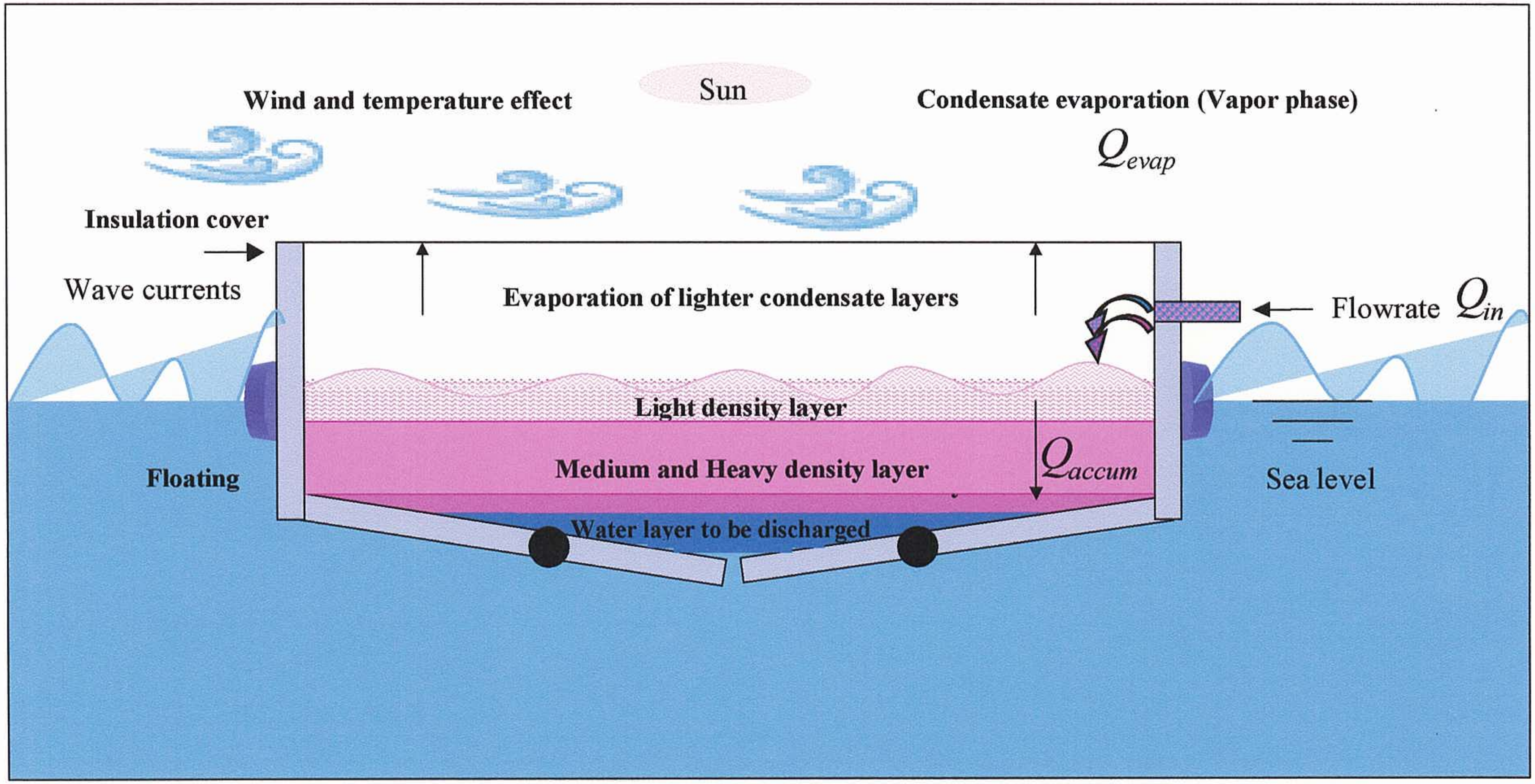


Fig. 4.1- Schematic diagram for the floating separator.

Both the condensate / water separation and evaporation processes are discussed in more detail in the following sections.

4.2.1 Condensate / Water Separation

As the condensate water emulsion enters the separator, condensate and water droplets settle. This phase separation depends on Stoke's law equation (Abdel-Aal, Aggour & Fahim 2003). The measurements units used have been directly applied from the referenced source. Therefore, some mixing of measurements units is applied, as shown below:

$$u = 2.864 \times 10^{-8} (\Delta\rho)\, d_m^{\,2} / \mu \qquad (4\text{-}1)$$

Where,

u: is settling or terminal velocity (ft/s);

$\Delta\rho$: is the density difference between the continuous and the dispersed phase (lb/ft^3);

d_m: is diameter of the droplet (μm); and

μ: is viscosity of the continuous phase (cP).

Separation of condensate and water basically depends up on density difference ($\Delta\rho$) between them. A condensate droplet, being smaller in density than the water droplet, tends to move vertically upward under the buoyant force (F_b). Water is the continuous phase exerts a drag force (F_d) on the condensate droplet in the opposite direction, as shown in Figure 4.2. Similarly, a water droplet, being higher in density than the condensate tends to move vertically downward under the gravitational force (F_g). The condensate is the continuous phase exerts a drag force (F_d) on the water droplet in the opposite direction. Both condensate and water droplet will accelerate until the frictional resistance of the fluid drag force approaches and balances F_g and F_b. The condensate and water droplet continue to rise at a constant velocity known as settling or terminal velocity. Once condensate and water droplets reach phase boundaries, coalescence of droplets takes place resulting in the production of bigger droplets.

It was noticed that there is a creamy layer of condensate / water emulsion formed. Condensate droplets in the continuous water phase leave the water; and water droplets in the condensate continuous phase leave the condensate and reach the phase separation layer. The retention time is determined to allow separation of the entrained water droplets from the condensate continuous phase and separation for the entrained condensate droplets from the water continuous phase. It was observed that in this creamy layer, condensate droplets in the continuous water phase tend to spend longer times for separation than water droplets in continuous condensate phase. Therefore, the retention time for condensate droplet is the time needed to allow for complete separation. This is because:

1. The larger size of condensate droplets that have formed in the water continuous phase, are separated more quickly than the smaller size condensate droplets. Separation is enhanced by size of the droplet diameter such that the smaller condensate droplets have buoyancy forces that diminish in magnitude. Thus, the smaller condensate droplets in the water continuous phase need more time for coalescence to produce bigger droplets. As the condensate droplets coalesce, the buoyancy force increases.

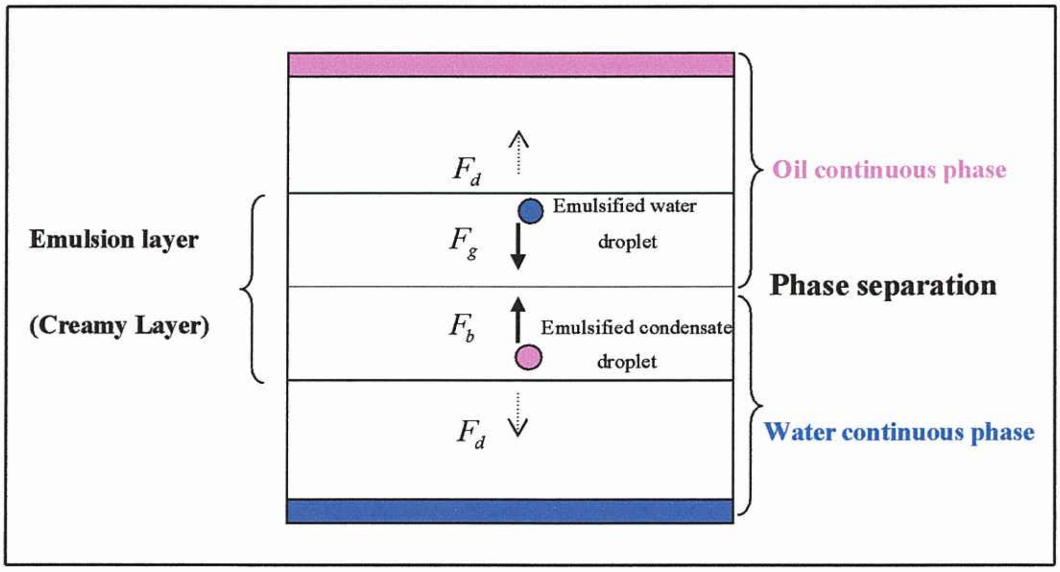


Fig. 4.2- Forces affect on condensate and water droplets.

2. It was found that the wettability of a water-wet solid surface has great effect on the movement of emulsified condensate droplets in water. The wettability of water-wet solid depends on the interfacial tension between condensate, water and the cylinder (glass) surface that is in contact with them (Kanicky et al. 2005, p. 255). The Interfacial tension is referred to the spreading coefficient ($S_{L/S}$), as shown below:

$$S_{L/S} = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} \qquad (4\text{-}2)$$

Where,

γ_{SV}: is solid-vapor interfacial tension;

γ_{LV}: is liquid-vapor interfacial tension; and

γ_{SL}: is solid-liquid interfacial tension.

In this layer, it was observed different shapes existed for creamy layer and some of them attach to the wall of the cylinder (glass). This is because the value of $S_{L/S}$ is negative. As a result, an immobile condensate layer is formed on the water-developed phase with high interfacial tension between oil and water (solid and liquid). In this case, oil droplet shape becomes flattened on the water-wet solid, as shown in Figure 4.3. It is worth mentioning that this behaviour is related to the specific cylinder diameter such that it is more pronounced with smaller diameter than bigger.

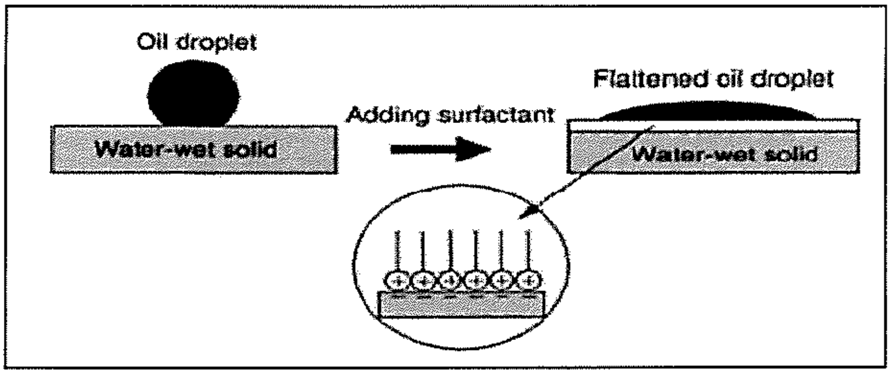


Fig. 4.3- The wettability of a water-wet solid surface in contact with an oil droplet increases when surfactant molecules adsorb on to the surface (Kanicky et al. 2005, p. 255).

However, it was found that a seawater sample does not show the same effect of wettability around the walls. The higher density difference leads to higher separation process for the condensate droplets in the water phase. It can be seen that as there was no wettability influence, the spreading coefficient is positive and the salt concentration increase the coalescence rate for condensate and water droplets.

Condensate can consist of differing compositions and contain both dispersed oil and dissolved organic compounds. Dissolved organic compounds are termed the Water Soluble Fraction or Water Accommodated Fraction (WAF). Thus, during the separation process, dispersed oil droplets move upwards and WAF will remain dissolved in the water phase to be discharged to seawater.

4.2.2 Condensate Layer Evaporation

Simulated environmental conditions for wind speed and ambient temperature were applied to the laboratory experiments. These experiments demonstrated the importance of the stratification of the condensate into various density layers. The observations have permitted a model to be generated based on a mass balance principle.

The evaporation process occurs at the condensate surface. As condensate absorbs heat, the molecules become more energetic and move around faster and enter the atmosphere as vapor phase.

At seawater level, the ambient temperature condition is regarded as the air temperature immediately above the sea surface, with the floating separator body being at the seawater temperature. However in the experiment, the water bath (around 34 °C) was always greater than that of room temperature (around 22-26 °C). This high temperature value was selected to enhance the evaporation rate of the sample.

In the experiment, flowrate of condensate was not considered. However in the model, condensate flowrate can be taken into account and related to oil evaporation rate with the floating separator volume (separator height and diameter). It is important to determine the amount of condensate accumulated above the water layers out of the amount of flowrate coming to the separator depending on mass balance equation.

The following is the description of the factors that can have an effect on condensate evaporation.

4.2.2.1 Wind Speed

Three different simulated wind speeds (0, 1.2 and 2.4 m/s) were taken into account as the air speed affect on the condensate column removal. It was noticed that the trends for the wind speed / condensate evaporation curves follow at logarithmic trend. An equation for the evaporated condensate percent in terms of time and wind speed was developed for constant temperature conditions. The equation developed from this work is as follows:

$$Y = a \times LN(T) + b \qquad (4\text{-}3)$$

Where the variables a and b are expressed in terms of wind speed, as shown below:

$$a = A \times U^2 - B \times U + C$$

and,

$$b = D \times U^2 + E \times U + F$$

Therefore,

$$Y = \left(A \times U^2 - B \times U + C\right) \times LN(T) + D \times U^2 + E \times U + F \qquad (4\text{-}4)$$

Where,

Y: is cumulative evaporated percent (%);

A, B, C, D, E *and* F: are constants depending on model parameters;

U: is wind speed (m/s); and

T: is time (hours).

In modeling the experiment, there is a correlation between Y and U. The evaporation rate for the first 9 hours is taken for simplicity as a linear relationship and is related to wind speed. The curve trend seems to be smooth at around 9 hours onwards and constant values A, B, C, D, E and F were calculated such that value of A= -0.2221, value of B= 1.1243, value of C= 12.189, value of D= -0.1902, value of E= 10.898 and value of F= -0.6878. These constants relate to wind speed within the range of investigation. Therefore the equation becomes:

$$Y = \left(-0.2221 \times U^2 - 1.1243 \times U + 12.189\right) \times LN(T) + \left(-0.1902 \times U^2 + 10.898 \times U - 0.6878\right) \tag{4-5}$$

The curve fitting for wind speed is shown in Figure 4.4.

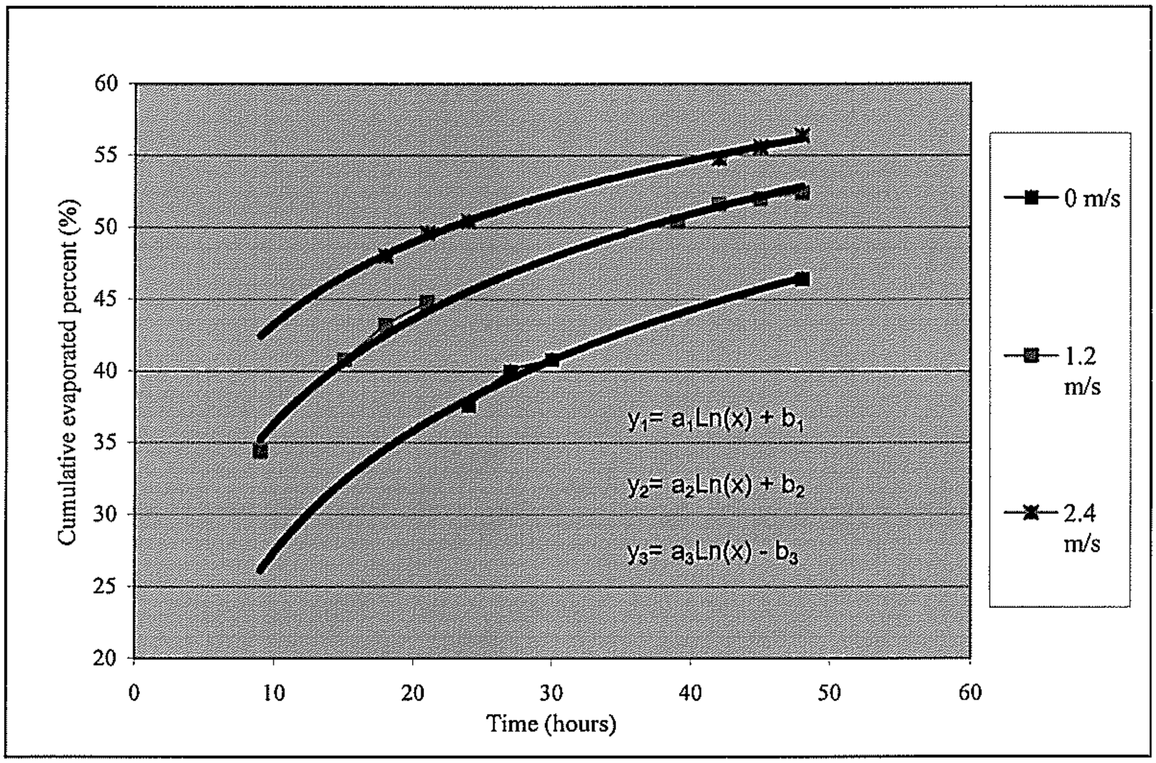


Fig. 4.4- The curve fitting for the three different wind speeds.

As condensate evaporates, the air near the surface gets humid. The vapor pressure above the surface increases till the air becomes saturated. However, in presence of wind, the vapor will disperse away and wind tends to bring dry air, thus maintain a high gradient in the vapor pressure. The vapor pressure in the atmosphere will be less than at the surface and evaporation rate enhances due to air dryness.

From the laboratory simulation studies, the predictive *Y* values for various wind speeds are shown in Figure 4.5 and tabulated in the Appendix E. The evaporation results are in good agreement with the theoretical prediction and with the data provided by Barker & BuFarsan (2001), Fingas (2004), Riazi & Edalat (1996) and Sebastiao & Soares (1995; 1998). Fingas (2004) concluded that oil evaporation is not strictly boundary-layer regulated. It can be seen that his findings are somewhat in agreement when more than 3.6 m/s is considered.

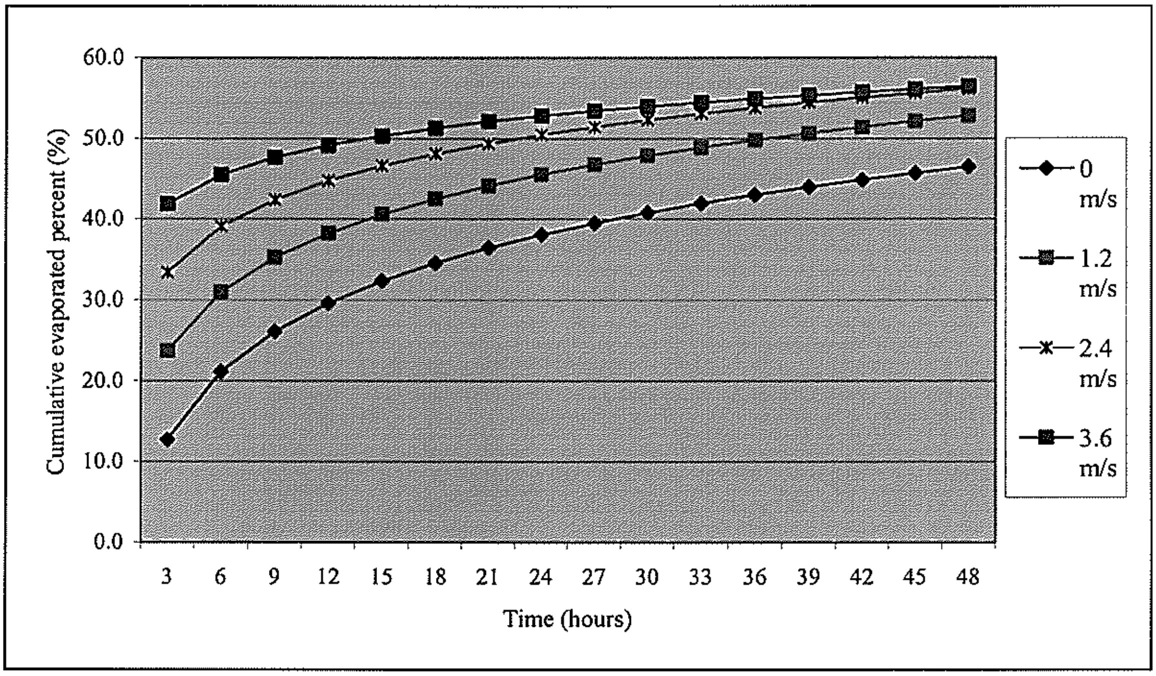


Fig. 4.5- The prediction for wind speed up to 3.6 m/s.

4.2.2.2 Ambient Temperature

The experiments have conducted with two-fixed ambient temperatures; the air temperature (simulated by the room temperature) and sea temperature (simulated by water bath temperature) to make a contribution to the condensate evaporation rate. In the simulation, it was assumed that an insulation layer would surround the separator outside perimeter to keep it at controlled temperature conditions.

4.2.2.3 Separator Diameter Size

The third parameter that has an impact on condensate evaporation is the diameter of the separator. Clearly, the larger the diameter of the separator, the greater will be the evaporation rate of condensate to the atmosphere for a given input and fixed environmental conditions.

A simple mass balance equation was developed as shown by equation (4-6). This equation takes into account the prevailing conditions of wind speed and temperature. The mass balance equation is:

$$Q_{in} = Q_{accum} + Q_{evap} \qquad (4\text{-}6)$$

where,

Q_{in} : is flowrate (bbd);

Q_{accum} : is condensate accumulation rate (bbd); and

Q_{evap} : is condensate evaporation rate (bbd).

4.2.2.4 Condensate Density and Viscosity

The condensate density and viscosity play a critical role in supporting the evaporation process. The lighter the density and viscosity, the more losses and the heavier density and more viscous the more accumulated. This trend in density is what would be expected from change in condensate physical properties.

4.2.2.5 Condensate Temperature

It is assumed that the water bath temperature that was applied in the experiment is as same as the condensate flowrate temperature.

CHAPTER 5

VIEWING AND ANALYSING THE RESULTS

5.1 Introduction

The key objective of this research is to determine the feasibility of using a floating separator and to optimize its design and operational requirements. The technical evaluation of the process including the condensate skimming time and structure stability design, are presented in the current chapter. All the calculations referenced below, have been carried out assuming constant condensate density, zero wind speed and constant ambient temperature. The results are thoroughly investigated, discussed and analyzed.

5.2 Condensate Skimming Time

As only a certain percentage of the condensate will evaporate, the remainder will accumulate and not be removed by the evaporation process. This layer will increase in height and it will be crucial, from the practical point of view to determine how long this heavier condensate can be retained within the separator before it is required to be skimmed off. Clearly, the design of the separator must be such that the retained condensate layers not be permitted to discharge overboard to the sea.

The laboratory studies clearly demonstrated that for a fixed volume of condensate that it exposed to appropriate evaporation conditions, the condensate evaporation rate displays a logarithmic trend with time. The evaporation rate becomes less and less, this leading to the increased density of the residual condensate in the container. The higher evaporation losses at the beginning is fast and high due to the dissolved gas in the condensate, but after that, the heavy compounds will show slower evaporation rates.

In the offshore operational environment, where there is a continuous flowrate of condensate into the floating separator, these heavier compounds will accumulate and occupy an increasing volume of the separator with time. This leads to the requirement to skim them off. The design criterion for the condensate skimming time (T_{accum}) is that the value of an averaged condensate evaporation rate is taken over an assumed accumulation time. This trend was stated by Sebastiao & Soares (1998).

The skimming time is calculated by allowing the condensate layer to fill the separator and reach maximum height (H_{accum}) for specific diameter, as shown in Figure 5.1.

By extrapolating the laboratory result curve from 48 hours into 20 days using Equation (4-5), an averaged condensate evaporation rate was able to be determined for the field conditions, as shown in Figure 5.2. The period of 20 days has been taken as a convenient period to demonstrate the effective application of the floating separator.

The derivations for conversion factors were applied for units consistency, such that;
15.89 cm^2 (diameter = 4.5 cm) is area of laboratory cylinder;
1 cubic feet (ft^3) is 28.089 liter (l);
1 barrel (bbl) is 5.61 ft^3;
1 liter is 1000 ml; and
1 m^2 is 10000 cm^2.

The simulated evaporated percent values up to 20 days were divided by a series of three hours (this period was as done in the evaporation experiment) to be converted into an evaporated percent per hour. Then, they were converted as ml height loss per hour (h_l) by multiplying them by 125, where 125 ml represents the initial total condensate height (ml) in the laboratory cylinder, To obtain Q_{evap} (bbd/m^2), the height lost values were substituted into equation (5-1).

$$Q_{evap} = h_l /(1000 ml/l \times 28.089 l/ft^3 \times 5.61 ft^3/bbl \times 15.89 cm^2) \times 10000 cm^2/m^2 \times 24\ hr/day \tag{5-1}$$

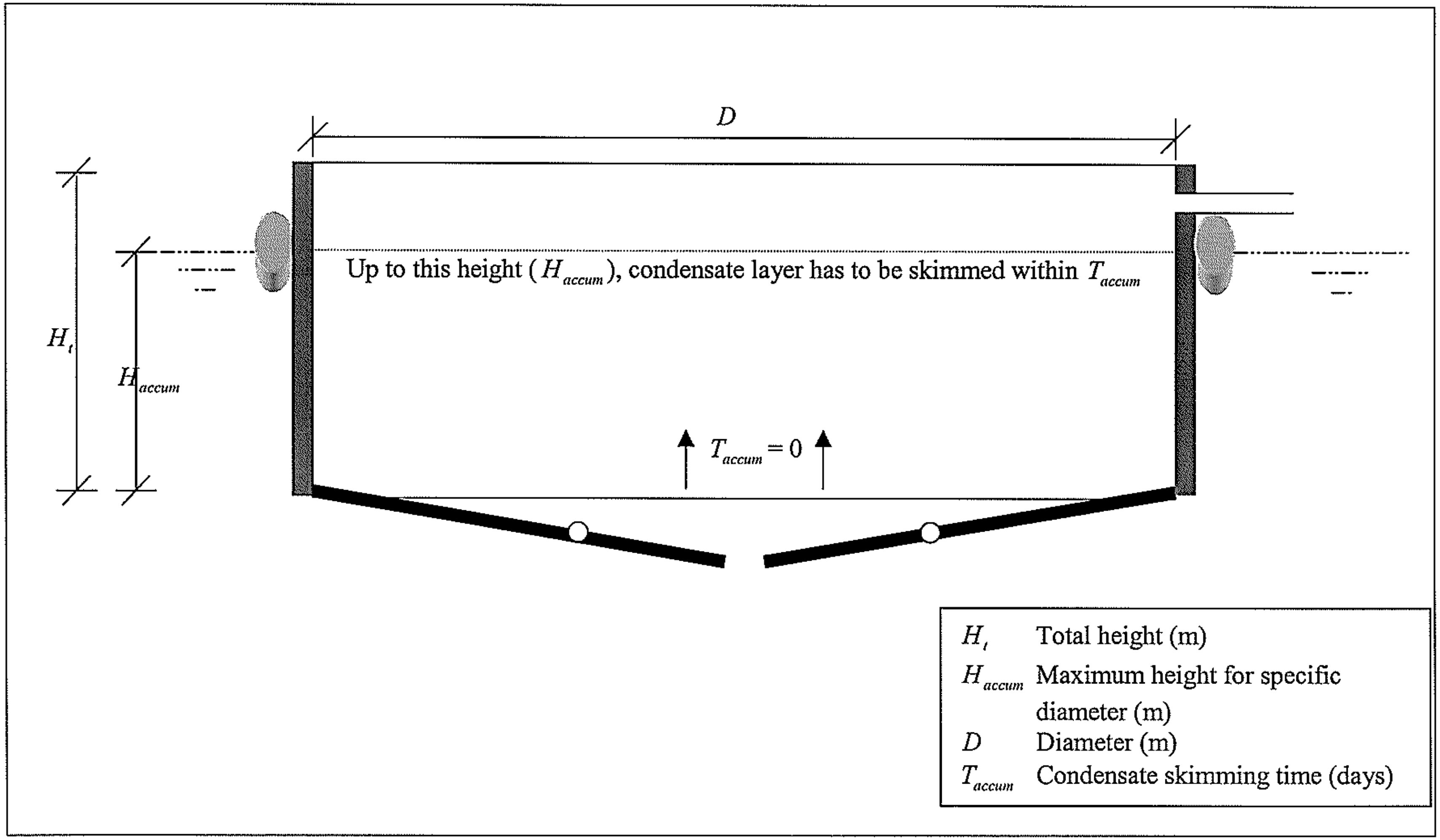


Fig. 5.1- Schematic dimensional diagram for the floating separator.

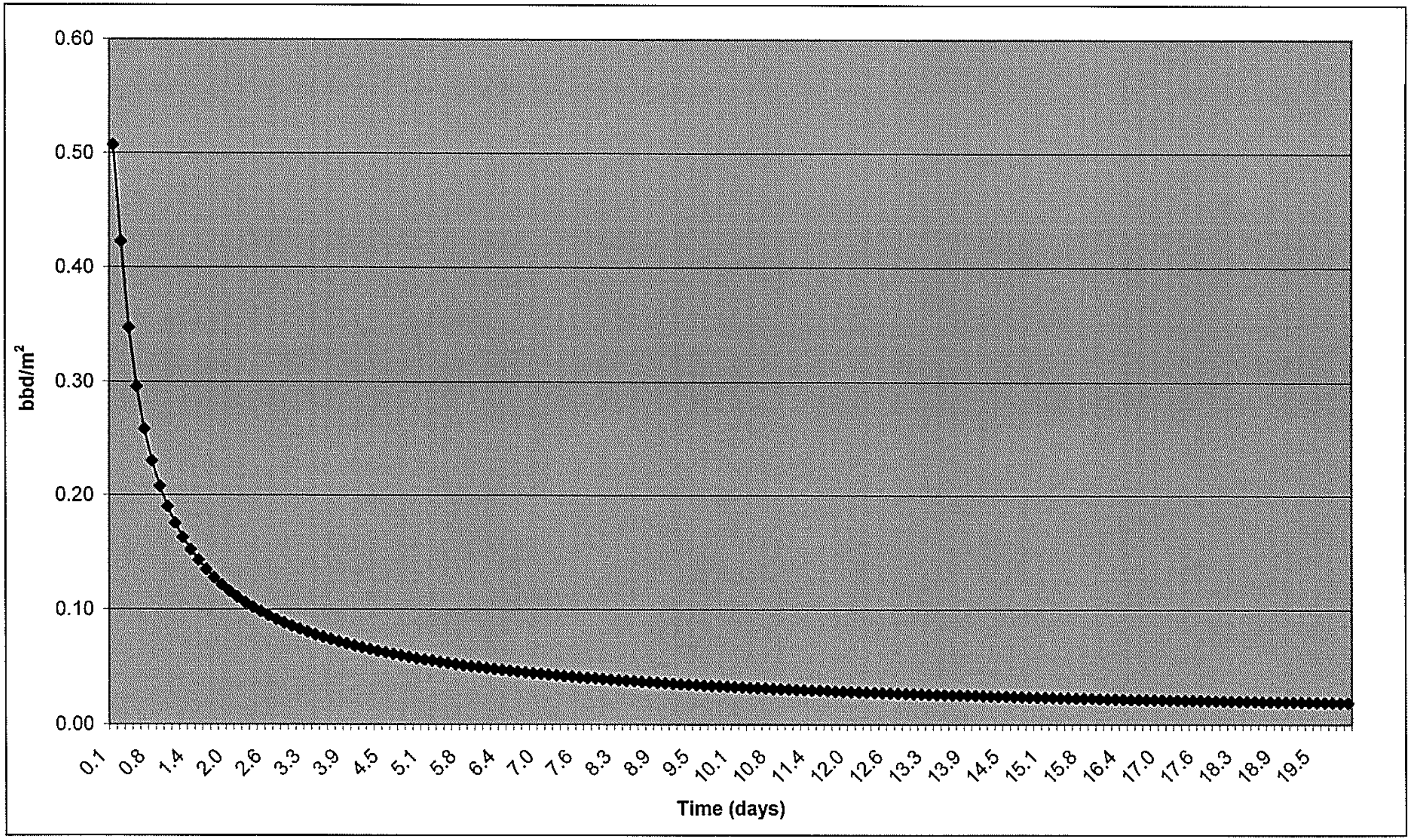


Fig. 5.2- Evaporation rates values over accumulation time

Hence, over any accumulation time, there is an average Q_{evap} value, as shown in Table 5.1.

Assume values of Q_{in}=100 bbd, H_{accum}= 6.75 m, D= 6.75 m and T_{accum}= 15 day. By applying into equation (5-2), V_{accum}=241.42 m^3.

$$V_{accum} = D^2 / 4 \times 3.14 \times H_{accum} \qquad (5\text{-}2)$$

Where;

V_{accum} : is the accumulated volume available for condensate layer to be filled in the separator (m^3); and

H_{accum} : is the maximum height that condensate layer can reach for specific diameter (m).

Accumulation rate, Q_{accum}=101.22 bbd, calculated by equation (5-3).

$$Q_{accum} = V_{accum} / T_{accum} \times 6.289 \qquad (5\text{-}3)$$

Table 5.1- Evaporation Rates Values over Accumulation Time.

Time (hours)	Time (Days)	Y	Y/hr	h_l (ml/hr)	bbl/m^2/hr (E-02)	Q_{evap} (bbd/m^2)
3	0.1	12.70	4.23	5.29	2.1139	0.51
6	0.3	21.15	3.53	4.41	1.7599	0.42
9	0.4	26.09	2.90	3.62	1.4474	0.35
12	0.5	29.60	2.47	3.08	1.2314	0.30
15	0.6	32.32	2.15	2.69	1.0757	0.26
18	0.8	34.54	1.92	2.40	0.9580	0.23
21	0.9	36.42	1.73	2.17	0.8658	0.21
24	1.0	38.05	1.59	1.98	0.7915	0.19

From the accumulation time assumed, Q_{evap} is 0.0236 bbd/m^2. By multiplying it by the surface area for chosen diameter size, it becomes 0.85 bbd.

Figure 5.2 relates to the laboratory evaporation rates values over accumulation time. This is being for a fixed single volume of condensate. The results from this graph are applied to determine the residual increase, per unit time, for the remaining condensate in the separator. As the graph demonstrates, the residual amount will increase at a defined increasing rate per day. This means that for constant flowrate and evaporation conditions at the floating separator, it will increase by a set amount for each day plus small incremental amounts for each within the skimming cycle.

By applying mass balance equation (4-6) that was developed,

$$Q_{in} = Q_{accum} + Q_{evap}$$

Q_{in} becomes 102.07 bbd. This process can be applied for different combinations of H_{accum}, D and T_{accum}.

For the evaporation process, it is crucial to have as big as possible area and as less as possible depth to achieve the greatest evaporation rate. However, as it has been realized that mechanical restrictions shall apply to a large floating tank in a marine environment, details are sought as optimize the diameter to total height ratio. This is discussed in the following section.

5.3 Structure Stability Design

To design for a certain flowrate with fixed skimming time, there are different combinations of diameters and total heights that can be taken into the design. However, there will be a limit for the ratio of diameter and total height (D/H_t).

Table 5.2 shows different combinations for a flowrate of 100 bbd with associated condensate skimming time of 15 days.

Table 5.2- Diameter and Total Height Ratio

D (m)	H_{accum} (m)	H_t (m)	Q_{in} (bbd)	D/H_t
6.75	6.75	9.0	102.07	0.75
7	6.3	8.4	102.51	0.83
7.25	5.9	7.9	103.04	0.92
7.5	5.5	7.3	102.87	1.02
7.75	5.2	6.9	103.91	1.12
8	4.9	6.5	104.4	1.22
8.25	4.6	6.1	104.31	1.35
8.5	4.3	5.7	103.59	1.48
8.75	4	5.3	102.22	1.64
9	3.8	5.1	102.81	1.78
9.25	3.6	4.8	102.97	1.93
9.50	3.4	4.5	102.67	2.10
9.75	3.2	4.3	101.88	2.29
10.00	3	4.0	100.59	2.50
10.25	2.9	3.9	102.23	2.65

Wave height associated with wind speed according to wind type has to be considered in the design of the separator in order to ensure there is no, or minimum overboard discharge to the sea, or the opposite of having the separator swamped due to waves actions for fully developed seas. Additional height must be allowed in the design calculation and then total height (H_t) can be computed. For example, US Army Corps of Engineers (1984) has recommended sea state condition for harsh environment (Reed et al. 2004, p. 31; Fingas 2004), as shown in Appendix D.

Through correspondence with Centre for Offshore Foundation Systems, University of Western Australia (UWA), it was recommended that a maximum 75 to 85 % of the separator capacity to be filled with water and condensate (M Kimiaei 2006, e-mail, 18 May). Thus, 75 % value was taken in height calculations and H_t values were calculated by dividing H_{accum} by a factor of 0.75.

It was recommended by Centre for Offshore Foundation Systems, University of Western Australia (M Kimiaei 2006, e-mail, 18 May), by having very large diameter and very small height, it might be faced with two problems:

1. Larger diameter will cause larger bending moments at the center of the bottom plate; consequently, heavier shells needed for the bottom plate thickness.
2. By having larger diameter and small height, the protection of the internal condensate from splashing sea waves could be the main problem to be encountered.

It was also advised that to get overall stability and integrity of the floating separator, a typical ration of D/H_t is 2.5 with maximum diameter about 10-12 m. Thus, in design, a value of D/H_t ratio would be taken as 2.5.

With reference to table 5.2, it can be seen that by choosing diameter of 6.75 m, total height is 9 m. D/H_t ratio is 0.75. By selecting a greater diameter, total height can be reduced and D/H_t ratio shows more stable structure. In the same time, the evaporation rate is increased for specific flowrate. However, by choosing diameter around 10.25 m, D/H_t ratio becomes 2.65, which has exceeded the accepted value of 2.5.

In summary, different diameters and heights dimensions were calculated for a specific flowrate and time period. By taking D/H_t into account, ultimate dimensions can be determined for the design of the floating separator.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary of the Research

The aim of the study was to determine the operational requirements for a floating separator capable of operating for nominated periods of unattended operation in a harsh and remote marine environment. The floating separator is an integral part of a sub-sea gas dehydration unit. The operation of the floating separator has been designed to be able to handle the commingled condensate and water that is generated through the operation of the dehydration unit. As the majority of produced water is removed by the main sub-sea located separator (hydrocyclone), which is located prior to the dehydrator, as shown in Figure 1.1, means that the amounts of produced water to be removed by the floating separator unit is a small fraction. The floating separator model developed through this study was based on treating a condensate flowrate (Q_{in}) of 100 bbd.

Within a specific retention time in the floating separator for the commingled condensate / water, the condensate droplets in the water continuous phase tend to go up and reach phase separation. Likewise, the water droplets in condensate continuous phase tend to go down and reach phase separation. Meanwhile, at the air / liquid interface of the separator, condensate (the lighter compounds that have high dissolved gas) will evaporate under the effect of wind speed and temperature and the interaction with the atmospheric environment. Evaporation will continue and change with time. The evaporation rate will decrease. This process increases both density and viscosity of the remaining condensate that resides above the water. Once the water accommodated fraction (dissolved compounds) concentrations are within environmental legislations, the water can be disposed of into the seawater. However, no specific water tests were carried out during this investigation to determine the time for acceptable water quality to be obtained.

This study essentially concentrated on investigation of the effect of wind speed and temperature on the condensate evaporation process. A mathematical model was designed to model the evaporation rate. The results from this study are thoroughly investigated, discussed and analyzed in chapter 5.

6.2 Conclusions and Key Findings

The experimental results from this work provide an analysis of the separation and evaporation processes at a variety of common parameters for a typical floating separator. Based on the experimental conditions used in this work, the following conclusions were obtained:

A. It was found that at least 12 minutes is required for separation to take place at lower salt concentrations. On the other hand, it was found that for typical seawater sample, 1 minute and half is needed for separation.

B. Through the separation process, it was found that the water droplet velocity in the condensate continuous phase is faster than condensate droplet in the water continuous phase. Thus, the condensate needs a longer time for separate than is the case for water. But, in the case of seawater, the condensate droplet velocity was the same as for the water droplet velocity.

C. A wettability effect was observed. Condensate emulsion droplets in the water phase showed different shapes of interface between condensate and water droplets and they attached to the wall of the cylinder. Because of that behaviour, average values for condensate separation were taken into account with time. However, this trend was not observed when a seawater sample was used. The higher density difference between the condensate and the water eliminated that effect.

D. It was found that there is high proportion of condensate removal to the atmosphere initially during the first hours. This is because of the high amounts of dissolved gas that tend to flash out immediately after exposure to the atmosphere.

E. At the end of the experiment, it was found that both density and viscosity of the remaining condensate increased. The change in viscosity was noted by direct observation.

F. The rate of condensate evaporation was governed by wind speed, temperature and composition.

Based on the results of the model of the process of evaporation, the following conclusions were obtained:

1. This study shows that the floating separator design is a viable technology. This technology eliminates constructing equipment with high power and weight requirements. The compact floating separator design can be installed easily on the sea surface. The major advantage of this equipment is that disposal of the liquid is cheap and effective.
2. It was found that the relationship between evaporated percent and time follows the logarithmic trend. The equation was found as:

$$Y = a \times LN(T) + b$$

The value of Y is a function of a, b and time (T). Values of a and b depends on wind speed (U).

$$a = A \times U^2 - B \times U + C$$

and,

$$b = D \times U^2 + E \times U + F$$

Therefore,

$$Y = \left(A \times U^2 - B \times U + C\right) \times LN\left(T\right) + D \times U^2 + E \times U + F$$

3. Condensate skimming time was found to be around 15 days as a continuous operation condition for flowrate of 100 bbd associated with specific separator dimensions.

6.3 Recommendations

This research reports for the first time, a simple water treatment system representing the condensate evaporation for a gas processing sub sea plant. It gives another dimension to the methodology of the condensate removal and water treatment. In order to contribute further to the development of this technique, it is suggested that further research and development be conducted. Based on the results of the present study, the direction of this research is recommended to be:

A. Condensate removal by evaporation demonstrates merit. Therefore, it is recommended to further develop the laboratory results into industrial scale applications.

B. Because this research is designed to make full use the water bath temperature to support the wind speed effect, the full range of metrological conditions needs to be modeled. This should also include anticipated maximum rainfull rate.

C. It will be useful to apply another experiment on condensate evaporation when the condensate is mixed with water to form stable water droplets in oil emulsion.

D. More studies on the mechanism of emulsifiers need to be undertaken, and in particular the way they emulsify condensate and water and the effect on retention time.

F. Since experiment conditions only simulated parts of the real field conditions, suitable scale-up criteria must be developed in order to obtain a wider set of results.

G. It is recommended that an evaporation experiment be conducted under humid conditions when the evaporation rate can become low.

H. Water removal should be studied and tested to ensure the water accommodated fraction is within the environmental legislations and to determine the time for water disposal to sea.

REFERENCES

Abdel-Aal, HK, Aggour, M & Fahim, MA 2003, *Petroleum and gas field processing*, Marcel Dekker, New York.

Abu El Ela, M 2004, *Synthetic hydrate for natural gas dehydration*, PhD Thesis, Curtin University of Technology, Perth, Western Australia.

Alaee, M, Whittal, RM & Strachan, WMJ 1996, 'The effect of water temperature and composition on Henry's law constant for various PAH's', *Chemosphere,* vol. 32, no. 6, pp. 1153-1164.

Arnold, K & Stewart, M 1999, *Surface production operations: design of oil-handling systems and facilities,* 2nd edn, vol. 1, Butterworth-Heinemann, Woburn, MA.

Ayers, RC & Parker, M 2001, *Offshore produced water waste management*, Canadian Association of Petroleum Producers.

Barker, C & BuFarsan, A 2001, 'Evaporation losses from the surface "oil lakes" of southern kuwait', *Environmental Geosciences,* vol. 8, no. 2, pp. 123-129.

Bansal, KM & Caudle, DD 'Interferences with produced water treatment for dispersed oil removal', paper SPE 46576 presented at the International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Caracas, Venzuela, 7-10 June, 1998.

BuFarsan, A, Barker, C, Wavrek, DA & AL-Sarawii, M 2002, 'Compositional changes induced by evaporation of Burgan crude oil spilled into the desert of Southern Kuwait', *Environmental Geosciences,* vol. 9, no. 1, pp. 8-16.

Callaghan, D & Baumgartner, W 'Characterization of residual hydrocarbon in produced water discharged from gas production platforms', paper SPE 20881 presented at Europec, The Hague, Netherlands, 22-24 October, 1990.

Cobby, GL 'Produced water regulatory requirements offshore Australia', paper SPE 86711 presented at the Seventh SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Calgary, Alberta, Canada, 29-31 March, 2004.

Descousse, A, Monig, K & Voldum, K 'Evaluation study of Various Produced-water treatment technologies to remove dissolved aromatic components', paper SPE 90103 at the SPE Annual Technical Conference and Exibition, Houston, Texas, 26-29 September, 2004.

Ekins, P, Vanner, R & Firebrace, J 2005, *Management of produced water on offshore oil installations: a comparative assessment using flow analysis*, UK Offshore Operators Associations and its member companies.

Faksness, L-G, Grini, PG & Daling, PS 2004, 'Partitioning of semi-soluble organic compounds between the water phase and oil droplets in produced water', *Marine Pollution Bulletin,* vol. 48, no. 7-8, pp. 731-742.

Finborud, A, Faucher, M & Sellman, E 'New method for improving oil droplet growth for separation enhancement', paper SPE 56643 presented at the SPE Annual Technical Conference and Exhibition, Houston, 3-6 October, 1990.

Fingas, MF 1995, 'A literature review of the physics and predictive modeling of oil spill evaporation', *Journal of Hazardous Materials,* vol. 42, no. 2, pp. 157-175.

Fingas, MF 2004, 'Modeling evaporation using models that are not boundary-layer regulated', *Journal of Hazardous Materials,* vol. 107, no. 1-2, pp. 27-36.

Georgie, WJ, Bryne, KH & Kjaerland, G 'handling of produced water: looking to the future', paper SPE 25040 presented at The European Petroleum Conference, Cannes, France, 16-18 November, 1992.

Georgie, WJ, Sell, D & Baker, MJ 'Establishing best practicable environmental option practice for produced water management in the gas and oil production facilities', paper SPE 66545 presented at the SPE/EPA/DOE Exploration and Production Environmental Conference, San Antonio, Texas, 26-28 February, 2001.

Grini, PG, Clausen, C & Torvik, H 2003, 'Field trials with extraction based produced water purification technologies', *Produced Water Workshop,* Organized by National Engineering Laboratory (NEL), Marriott Hotel, Dyce, Aberdeen.

Grini, PG, Hjelsvold, M & Johnsen, S 'Choosing produced water treatment technologies based on environmental impact reduction', paper SPE 74002 presented at the International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Kuala lumpur, Malaysia, 20-22 March, 2002.

Hansen, BR & Davies, SRH 1994, 'Review of potential technologies for the removal of dissolved components from produced water', *Chemical Engineering Research & Design,* vol. 72, no. A2, pp. 176-188.

Kanicky, JR, Lopez-Montilla, J, Pandy, S & Shah, DO 2002, 'Surface chemistry in the petroleum industry', in H Krister (ed.), *Handbook of applied surface and colloidal chemistry,* vol. 1-2, John Wiley & Sons, pp.251-266.

Kemmer, FN 1988, *NALCO water handbook,* 2nd edn, Mcgraw-Hill.

Knudsen, BL, Hjelsvold, M, Frost, TK, Svarstad, MBE, Grini, PG, Willumsen, CF & Torvik, H 'Meeting the zero discharge challenge of produced water', paper SPE 86671 presented at The Seventh SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Calgary, Canada, 29-31 March, 2004.

Liquid-Liquid Coalescer Design Manual 2003, Separation & Mass Transfer Products, ACS Industries, LP, Houston, Texas.

Madian, ES, Moelyodihardjo, T, Snavely, ES & Jan, RJ 'Treating of produced water at the Giant Arun field', paper SPE 27130 presented at the Second international Conference on health, Safety & Environment in Oil & Gas Exploration & Production, Jakarta, Indonesia, 25-27 January, 1994.

Merlin, FX, Cedre & Poutchkovsky, A 'Behaviour of crude oil spills: new experimental devices', paper SPE 86766 presented at the Seventh International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Calgary, Alberta, Canada, 29-31 March, 2004.

Miller, JA, Lawrence, AW, Hickey, RF & Hayes, TD 'Pilot plant treatment of natural gas produced waters to meet beneficial use discharge requirements', paper SPE 37903 presented at the 1997 SPE/EPA Exploration and Production Environmental Conference, Dallas, Texas, 1997.

Mohamed, AMO, EI Gamal, M & Zekri, AY 'Oil water emulsion stability', proceedings of the Sixth Annual U.A.E. University Research Conference, Al-Ain, U.A.E, 24-26 April, 2005, pp. ENG 28-37.

Mohamed, AMO, El Gamal, M & Zekri, AY 2003, 'Effect of salinity and temperature on water cut determination in oil reservoirs', *Journal of Petroleum Science and Engineering,* vol. 40, no. 3-4, pp. 177-188.

Neff, JM & Saucer, TC, Jr 1996, 'Aromatic Hydrocarbons in Produced Water', in M Reed & S Johnsen (eds.), *Produced Water 2: Environmental Issues and Mitigation Technologies*, vol. 52, Plenum Press, New York, pp. 163-175.

Nordvik, AB 1995, 'The technology windows-of-opportunity for marine oil spill response as related to oil weathering and operations', *Spill Science & Technology Bulletin,* vol. 2, no. 1, pp. 17-46.

Nordvik, AB, Simmons, JL, Bitting, KR, Lewis, A & Strom-Kristiansen, T 1996, 'Oil and water separation in marine oil spill clean-up operations', *Spill Science & Technology Bulletin*, vol. 3, no. 3, pp. 107-122.

op ten Noort, FJ, Etten, RS & Donders, RS 'Reduction of residual oil content in produced water at offshore gas production platform P/6A', paper SPE 20882 presented at the Europec, The Hague, Netherlands, 22-24 October, 1990.

Pars, HM & Meijer, DT 'Removal of dissolved hydrocarbons from production water by macro porous polymer extraction (MPPE)', paper SPE 46577 presented at the 1998 SPE International Conference on Health, Safety and Environment in Oil & Gas Exploration and Production, Caracas, Venezuela, 7-10 June, 1998.

Place, MCJ 'Dissolved organic compounds in produced water', paper SPE 22780 presented at the 66th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Dallas, Texas, 8-9 October, 1991.

Reed, M, Ekrol, N, Daling, P, Johansen, O, Diltevsen, MK, Swahn, I, Resby, JLM & Skogens, K 2004, 'SINTEF oil weathering model: user's manual'. Version 3.0, SINTEF Materials and Chemistry, Trondheim, Norway.

Reed, M, Johansen, Ø, Brandvik, PJ, Daling, P, Lewis, A, Fiocco, R, Mackay, D & Prentki, R 1999, 'Oil Spill Modeling towards the Close of the 20th Century: Overview of the State of the Art', *Spill Science & Technology Bulletin,* vol. 5, no. 1, pp. 3-16.

Riazi, MR & Al-Enezi, GA 1999, 'Modeling of the rate of oil spill disappearance from seawater for Kuwait crude and its products', *Chemical Engineering Journal,* vol. 73, pp. 161-172.

Riazi, MR & Edalat, M 1996, 'Prediction of the rate of oil removal from seawater by evaporation and dissolution', *Journal of Petroleum Science and Engineering,* vol. 16, pp. 291-300.

Robotham, PWJ & Gill, RA 1989, 'Input, behaviour and fates of petroleum hydrocarbons', in J Green & MW Trett (eds.), *The fate and effects of oil in freshwater*, Elsevier Science Publishers, London, pp. 41-80.

Rye, SE & Marcussen, E 'A new method for removal of oil in produced water', paper SPE 26775 presented at The Offshore European Conference, Aberdeen, 7-10 September, 1993, pp. 263-269.

Sebastiao, P & Soares, CG 1995, 'Research: modeling the fate of oil spills at sea', *Spill Science & Technology Bulletin,* vol. 2, no. 2/3, pp. 121-131.

Sebastiao, P & Soares, CG 1998, 'Weathering of oil spills accounting for oil components', in R Garcia-Martinez & CA Brebbia (eds.), *Oil and hydrocarbon spills, modeling, analysis and control,* Computational Mechanics Publications, Southampton, UK, pp. 63-72.

Seybold, A, Cook, J, Rajan, RV, Hickey, R, Miller, J, Lawrence, A & Hayes, T 'Demonstration of dissolved organics removal from produced water', paper SPE 37420 presented at the 1997 SPE Production Operations Symposium, Oklahoma. 9-11 March, 1997.

Stiver, W & Mackay, D 1984, 'Evaporation rate of spills of hydrocarbons and petroleum mixtures', *Environmental Science & Technology,* vol. 18, no. 11, pp. 834-840.

Stiver, W, Shiu, WY & Mackay, D 1989, 'Evaporation times and rates of specific hydrocarbons in oil spills', *Environmental Science & Technology,* vol. 23, no. 1, pp. 101-105.

Sullivan, AP & Kilpatrick, PK 2002, 'The effects of inorganic solid particles on water and crude oil emulsion stability', *Ind. Eng. Chem. Res.,* vol. 41, pp. 3389-3404.

Sutton, OG 1934, 'Wind structure and evaporation in a turbulent atmosphere', *Proceedings of the Royal Society of London,* vol. A 146, no. 858, pp. 701-722.

Tsonopoulos, C 2001, 'Thermodynamic analysis of the mutual solubilities of hydrocarbons and water', *Fluid Phase Equilibria,* vol. 186, no. 1-2, pp. 185-206.

Utvik, TIR 1999, 'Chemical characterisation of produced water from four offshore oil production platforms in the North Sea', *Chemosphere,* vol. 39, no. 15, pp. 2593-2606.

van den Broek, WMGT, Plat, R & van der Zande, MJ 'Comparison of plate separator, centrifuge and hydrocyclone', paper SPE 48870 presented at the SPE International Conference and Exhibition, Beijing, China, 2-6 November, 1998.

Videla, HA & Characklis, WG 1992, 'Biofouling and microbially influenced corrosion', *International Biodeterioration & Biodegradation,* vol. 29, no. 3-4, pp. 195-212.

Waldie, B & Harris, WK 1998, 'Removal of dissolved aromatics from water: Comparison of a high intensity contactor with a packed column', *Chemical Engineering Research And Design,* vol. 76, no. A, pp. 562-570.

Yang, WC & Wang, H 1977, 'Modeling of oil evaporation in aqueous environment', *Water Research,* vol. 11, no. 10, pp. 879-887.

APPENDIX A
CONDENSATE COMPOSITION BY CAPILLARY GAS CHROMOTOGRAPHY

Table A- Condensate Composition From Core Laboratory.

Component	Mol%	Weight%
Methane	0.00	0.00
Ethane	0.00	0.00
Propane	0.02	0.00
i-Butane	0.03	0.01
n-Butane	0.11	0.04
neo-Pentane	0.00	0.00
i-Pentane	0.23	0.10
n-Pentane	0.28	0.11
Hexanes	1.17	0.57
M-C-Pentane	0.54	0.26
Benzene	0.47	0.21
Cyclohexane	0.80	0.38
Heptanes	2.38	1.35
M-C-Hexane	2.85	1.59
Toluene	3.22	1.68
Octanes	4.96	3.22
E-Benzene	0.54	0.33
M/P-Xylene	2.34	1.42
O-Xylene	1.24	0.75
Nonanes	7.20	5.25
T-M-Benzene	0.94	0.72
Decanes	9.61	7.31
Undecanes	8.54	7.14
Dodecanes	8.04	7.36
Tridecanes	7.88	7.85
Tetradecanes	7.11	7.68
Pentadecanes	5.37	6.29
Hexadecanes	5.80	7.33
Heptadecanes	3.21	4.32
Octadecanes	3.23	4.61
Nonadecanes	2.37	3.55
Eicosanes	1.59	2.48
Heneicosanes	1.44	2.38
Docosanes	1.14	1.98
Tricosanes	0.86	1.56
Tetracosanes	0.79	1.49
Pentacosanes	0.63	1.24
Hexacosanes	0.53	1.09
Heptacosanes	0.44	0.93
Octacosanes	0.38	0.83
Nonacosanes	0.31	0.72
Triacontanes	0.25	0.59
Hentriacontanes	0.22	0.53
Dotriacontanes	0.18	0.46
Tritriacontanes	0.15	0.40
Tetratriacontanes	0.12	0.34
Pentatriacontanes	0.10	0.29
Hexatriacontanes plus	0.39	1.26
Totals	100.00	100.00

Measured Properties		
Whole Sample Density	0.8161	g.cc-1 @ 60°F
Whole Sample Mol.Wt.	175.8	g.mol-1

Plus Fraction Calculated Properties	Density g.cc-1 @ 60°F	Mole Weight g.mole-1
Heptanes Plus	0.8179	177.7
Undecanes Plus	0.8374	215.0
Eicosanes Plus	0.8849	342.4
Triacontanes Plus	0.9156	478.4
Hexatriacontanes Plus	0.9301	570.0

Subtotals	Mole %	Weight %
Heptanes	4.19	2.20
Octanes	11.03	6.49
Nonanes	11.32	7.75
Decanes	10.55	8.03

Notes
Calculated properties derived from Katz & Firoozabadi data.
This condensate sample is from standard stock tank.

APPENDIX B

TEMPERATURE FLUCTUATION

This appendix presents the temperature fluctuation for the condensate / water separation process.

The experiments were conducted within a laboratory with a pre-determined room temperature. The individual salt concentration experiments were conducted over differing days.

Table B- Temperature Fluctuation.

Salt concentration (Weight %)	1	2	3
Temperature (°C)	23-21	22-21	23.5-22.5

APPENDIX C

RESULTS OF THE EXPERIMENTAL WORK

This appendix presents the laboratory conditions and the results for the condensate evaporation process.

Tables C.1 and C.2 summarize all the conditions and results of the experimental work under water bath (around 34 °C) at two different wind speed 1.2 and 2.4 m/s, respectively.

Tables C.3, C.4, C.5, C.6 and C.7 summarize all the conditions and results of the experimental work at water bath temperature around 34 °C at three different wind speeds of 0, 1.2 and 2.4 m/s, respectively. Tables C.4 and C.5 show the first and second run readings for 1.2 m/s, respectively. Tables C.6 and C.7 show the first and second run readings for 2.4 m/s, respectively.

Table C.1- Effect of Temperature and Wind Speed (1.2 m/s) on Condensate Column in terms of Time.

Time (hr)	Water tempertaure (°C)	Wind speed (m/s)	Air temperature (°C)	Condensate column (ml)	Condensate column lost percent	Cumulative condensate column lost percent
0	34.8	1.16	23.1	125	0	0
3	34.8	1.22	23.6	106	15.2	15.2
6	34.8	1.13	22.2	96	8	23.2
9	34.1	1.3	22.2	90	4.8	28
12	34.8	1.36	23.2	86	3.2	31.2
15	34.2	0.88	22.3	83	2.4	33.6
18	34.2	1.18	22.8	79.5	2.8	36.4
21	34.7	1.17	22.5	77.5	1.6	38
24	34.7	1.19	22.4	76	1.2	39.2
27	34.8	1.17	22.7	75	0.8	40
30	34.8	1.21	22.7	74.5	0.4	40.4
33	34.8	1.3	22.4	73.5	0.8	41.2
36	34.8	1.24	22.5	72.5	0.8	42
39	34.8	1.23	22.4	72	0.4	42.4
42	34.7	1.23	22.5	71	0.8	43.2
45	34.5	1.19	22.5	70	0.8	44
48	34.6	1.1	23.1	69.5	0.4	44.4

Table C.2- Effect of Temperature and Wind Speed (2.4 m/s) on Condensate Column in terms of Time.

Time (hr)	Water tempertaure (°C)	Wind speed (m/s)	Air temperature (°C)	Condensate column (ml)	Condensate column lost percent	Cumulative condensate column lost percent
0	34.6	2.29	23.2	125	0	0
3	34.5	2.2	22.4	97	22.4	22.4
6	34.5	2.3	22.5	86	8.8	31.2
9	34.5	2.21	23	80	4.8	36
12	34.4	2.21	23.1	76.5	2.8	38.8
15	34.6	2.26	22.9	74	2	40.8
18	34.6	2.28	22.5	72	1.6	42.4
21	34.7	2.3	22.6	70	1.6	44
24	34.7	2.34	23	69	0.8	44.8
27	34.6	2.27	22.8	68	0.8	45.6
30	34.4	2.33	22.9	67	0.8	46.4
33	34.5	2.34	22.7	66	0.8	47.2
36	34.5	2.34	23.2	65	0.8	48
39	34.5	2.36	22.4	64.5	0.4	48.4
42	34.5	2.42	22.4	64.5	0	48.4
45	34.3	2.19	22.9	64	0.4	48.8
48	34	2.19	22.6	63.5	0.4	49.2

Table C.3- Effect of Temperature and Zero Wind Speed on Condensate Column in terms of Time.

Time (hr)	Water tempertaure (ºC)	Air temperature (ºC)	Condensate column (ml)	Cumulative condensate column lost percent
0	34.5	21.8	125	0
3	34.4	22.1	114	8.8
6	34.5	22.6	104	16.8
24	34.4	21.9	78	37.6
27	34.5	22.2	75	40
30	34.4	22.1	74	40.8
48	34.4	22.1	67	46.4

Table C.4- Effect of Temperature and Wind Speed (1.2 m/s) on Condensate Column in terms of Time (1st run).

Time (hr)	Water tempertaure (°C)	Wind speed (m/s)	Air temperature (°C)	Condensate column (ml)	Cumulative condensate column lost percent
0	34.4	1.49	23.7	125	0
15	34.3	1.27	22.9	74	40.8
18	34.3	1.21	22.7	71	43.2
21	34.3	1.24	23.4	69	44.8
39	34.3	1.2	23.1	62	50.4
42	34.3	1.29	22.4	61	51.2
45	34.3	1.42	22.4	60	52
48	34.3	1.52	22.4	59	52.8

Table C.5- The Effect of Temperature and Wind Speed (1.2 m/s) on Condensate Column in terms of Time (2nd run).

Time (hr)	Water tempertaure (°C)	Wind speed (m/s)	Air temperature (°C)	Condensate column (ml)	Cumulative condensate column lost percent
0	34.4	1.04	26	125	0
3	34.4	1.29	26.6	100	20
6	34.4	1.4	25.8	82	14.4
48	34.4	1.27	22.6	60	52

Table C.6- Effect of Temperature and Wind Speed (2.4 m/s) on Condensate Column in terms of Time (1st run).

Time (hr)	Water tempertaure (°C)	Wind speed (m/s)	Air temperature (°C)	Condensate column (ml)	Cumulative condensate column lost percent
0	34.4	2.30	22.3	125	0
3	34.4	2.40	22.2	94	24.8
18	34.4	2.16	22.4	65	48
21	34.4	2.30	22.3	63	49.6
24	34.4	2.40	22.3	62	0.8
42	34.3	2.10	22.2	56.5	54.8
45	34.3	2.15	22.1	56	55.2
48	34.4	2.28	22.7	55	56

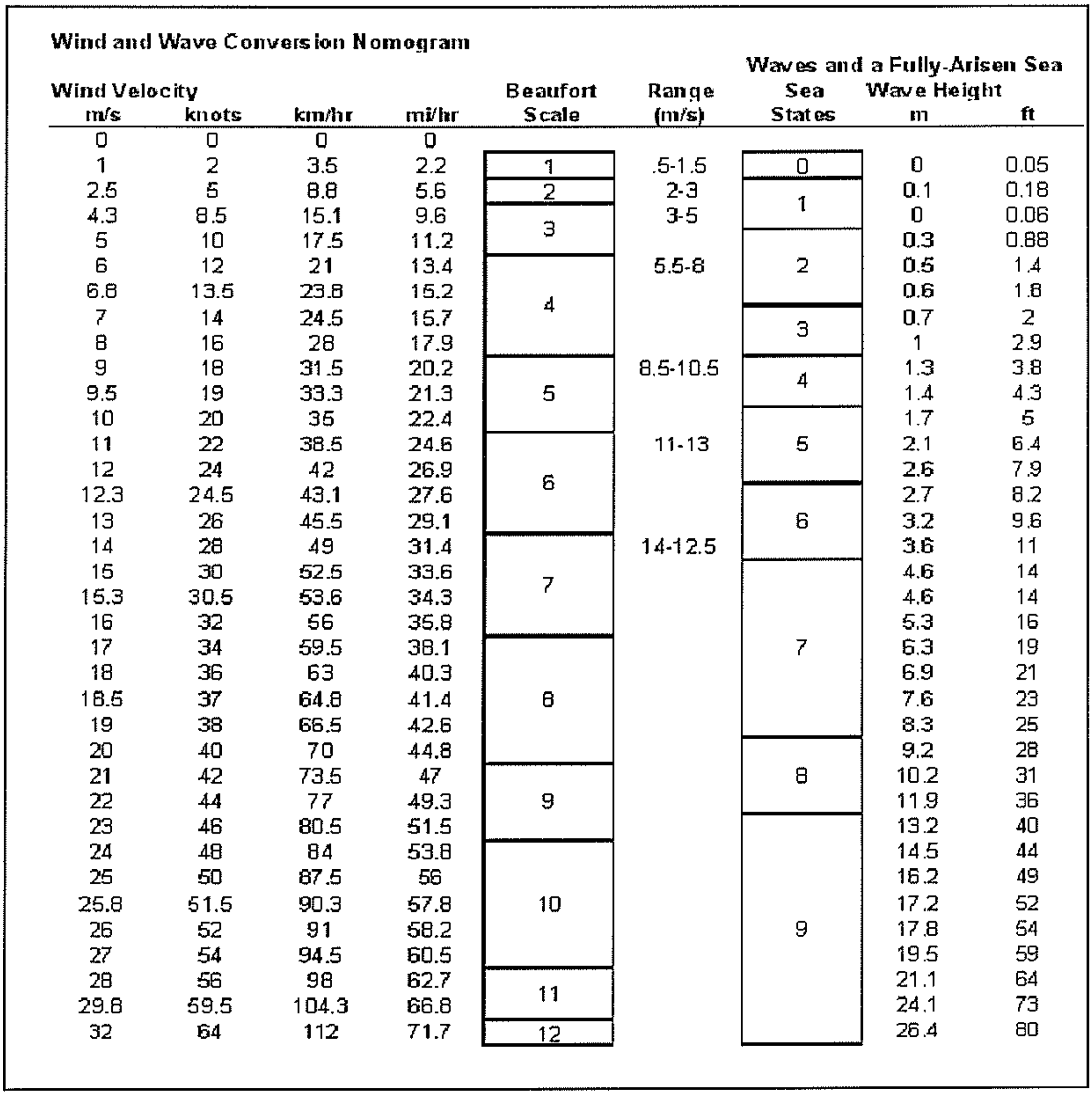
Table C.7- The Effect of Temperature and Wind Speed (2.4 m/s) on Condensate Column in terms of Time (2nd run).

Time (hr)	Water tempertaure (°C)	Wind speed (m/s)	Air temperature (°C)	Condensate column (ml)	Cumulative condensate column lost percent
0	34.5	2.24	23	125	0
3	34.5	2.14	22.4	94	24.8
45	34.5	2.18	22.9	55	56
48	34.4	2.17	25.4	54	56.8

APPENDIX D

THE RELATION BETWEEN WIND SPEED AND WAVE HEIGHT

Table D- The Relation between Wind Speed and Wave Height (Reed et al. 2004, p. 31; Fingas 2004).



Wind and Wave Conversion Nomogram

Wind Velocity						Waves and a Fully-Arisen Sea		
m/s	knots	km/hr	mi/hr	Beaufort Scale	Range (m/s)	Sea States	Wave Height m	ft
0	0	0	0					
1	2	3.5	2.2	1	.5-1.5	0	0	0.05
2.5	5	8.8	5.6	2	2-3	1	0.1	0.18
4.3	8.5	15.1	9.6	3	3-5		0	0.06
5	10	17.5	11.2			2	0.3	0.88
6	12	21	13.4	4	5.5-8		0.5	1.4
6.8	13.5	23.8	15.2				0.6	1.8
7	14	24.5	15.7			3	0.7	2
8	16	28	17.9				1	2.9
9	18	31.5	20.2	5	8.5-10.5	4	1.3	3.8
9.5	19	33.3	21.3				1.4	4.3
10	20	35	22.4			5	1.7	5
11	22	38.5	24.6	6	11-13		2.1	6.4
12	24	42	26.9				2.6	7.9
12.3	24.5	43.1	27.6			6	2.7	8.2
13	26	45.5	29.1				3.2	9.6
14	28	49	31.4	7	14-12.5		3.6	11
15	30	52.5	33.6			7	4.6	14
15.3	30.5	53.6	34.3				4.6	14
16	32	56	35.8				5.3	16
17	34	59.5	38.1	8			6.3	19
18	36	63	40.3				6.9	21
18.5	37	64.8	41.4				7.6	23
19	38	66.5	42.6				8.3	25
20	40	70	44.8			8	9.2	28
21	42	73.5	47	9			10.2	31
22	44	77	49.3				11.9	36
23	46	80.5	51.5			9	13.2	40
24	48	84	53.8	10			14.5	44
25	50	87.5	56				16.2	49
25.8	51.5	90.3	57.8				17.2	52
26	52	91	58.2				17.8	54
27	54	94.5	60.5				19.5	59
28	56	98	62.7	11			21.1	64
29.8	59.5	104.3	66.8				24.1	73
32	64	112	71.7	12			26.4	80

APPENDIX E

PREDICTIVE CUMULATIVE EVAPORATED PERCENT VALUES

Table E summarizes the predictive cumulative evaporated percent values that were developed in the simulation.

Table E- The Predictive Cumulative Evaporated Percent Values.

Time (hr)	Wind speed (m/s)			
	0	1.2	2.4	3.6
3	12.70	23.67	33.39	41.86
6	21.15	30.97	39.08	45.51
9	26.09	35.23	42.41	47.64
12	29.60	38.26	44.78	0.00
15	32.32	40.60	46.61	50.33
18	34.54	42.52	48.11	51.29
21	36.42	44.14	49.37	52.10
24	38.05	45.55	50.47	52.81
27	39.49	46.79	51.43	53.43
30	40.77	47.90	52.30	53.98
33	41.93	48.90	53.08	54.48
36	42.99	49.81	53.80	54.94
39	43.97	50.66	54.45	55.36
42	44.87	51.44	55.06	55.75
45	45.71	52.16	55.63	56.11
48	46.50	52.84	56.16	56.45