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DOMENIUL FUNDAMENTAL – ȘTIINȚE INGINEREȘTI
DOMENIUL DE DOCTORAT – MINE, PETROL ȘI GAZE

TEZĂ DE DOCTORAT

MODELAREA ȘI OPTIMIZAREA

PROCESELOR DE DEZEMULSIONARE A

ȚIȚEIURULOR GRELE

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MODELING AND OPTIMIZATION OF HEAVY
OIL DE-EMULSIFICATION PROCESSES

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Scope of work

The project's scope is studying the water-oil emulsion and heavy oil demulsification. Also the *work focus on the mathematical modeling desalting in order to optimize of desalting operation in an existing production unit of one giant Iranian oil field. The capacity of production unit is 75,000 BPD.* After separation and desalting processing, the produced oil specification meets 0.1 % water (BS&W) and salt (12 PTB). The feed of unit production is heavy oil with API 15-20.

Because of some operating problem such as dehydration high temperature (110 C°), high gas flaring and so one, the development of desalting modeling is very important to identify operating parameter effect on desalter. Generally, the oil desalter temperature is between 60- 80C° in most of production unit. Therefore, the mathematical model developed to predict the parameter changes effect on desalter with consideration to meet previous spesification. Besides the modeling, the demulsification has investigated by using some experimental test Data (such as temperature dehydration laboratory test, demulsifier test, and the demulsifier type). Also, based on experimental lab test data, the amount of demulsifier has optimized. The mathematical modelling of desalter has done based on population balance theory and the model tuned by field operation data. Therefore, the effect of operating parameter on dehydration efficiency have studied on the model. The mathematical model also has written by MATLAB software.

Then the electrostatic desalter process has simulated by HYSYS software. Finally based on the mathematical modelling and HYSYS simulation, the best operating conditions with consideration oil water specification and maximum oil recovery have achieved.

Based on the result of the case study and field operation data, the model's accuracy shows good result. Also the theory of water oil emulsion and heavy oil demulsification method reviewed.

Based on the project scope, the following stages have been done:

- ✓ *Crude oil water emulsion and demulsification theory.*
- ✓ *Heavy oil demulsifiaction methods.*
- ✓ *Optimization of demulsifire dosage based on Lab test and Software (Qualitec-4).*
- ✓ *Develop Desalter Mathematical modeling based on population balance (By Matlab).*
- ✓ *Oil production Unit Modeling by HYSYS software and tuning mathematical model with operation data.*

Chapter 1

Theoretical Aspects Regarding Crude Oil-Water Emulsions and Demulsification

1- Theoretical Aspects Regarding Crude Oil-Water Emulsions and Demulsification

In our daily life, emulsions play a significant role. Due to their common presence in most fact of our daily consumption, the emulsion is excellent practical importance. Those used in foods, cosmetics, pharmaceuticals, and agricultural products are some known emulsions. However, oil and water emulsions are among challenges closely related to the oil field production and refinery. Crude oil has very seldom produced alone. It has typically associated with water, which causes several many problems during exploration.

1.1- Water Oil Emulsion Nature

Emulsions have presented in the form of drop as a heterogeneous liquid composed of immiscible liquids that have dispersed in another liquid. Generally, an emulsion includes two phases:

- 1- Continuous phase, in which the liquid has distributed.
- 2- Dispersed phase, in which consist dispersion droplets.

1.2- Petroleum Emulsion

Oil production has commingled with the continuous formation of water production from petroleum reservoirs. Usually, water production rates are relatively low in its early life, while the produced water can be high as 90% or more, in the end, the well's lifetime. Water / oil emulsification can happen in the reservoir or process equipment such as chokes, pipeline system, separators and pumps.

1.3- Properties of Emulsions

The stability of an emulsion is determined by adsorbed structures at the interface of the two liquid phases that stabilize the surfaces of oil-water.

1.3.1- Viscosity of Emulsions

- ***Bulk Viscosity***
The viscosity of emulsion may be actually more significant than even the oil or the water viscosity because emulsions have non-Newtonian behavior.
- ***Interfacial Viscosity***
The viscosity described above has restricted to the bulk emulsion viscosity.

1.4- Type of Emulsion

Emulsions have characterized as colloidal process in which one liquid's thin droplets have distributed into some other liquid where the two liquids often are immiscible.

Oil and water emulsions have categorized into the following:

- Oil in water emulsions (O/W)
- Water in oil emulsion (W/O)
- Variety of emulsions (W/O/W) or (O/W/O)

1.5- What Cause Crude Oil Emulsion to Form

As the oil and water move into surface, there is adequate mixing. Where an emulsifying agent or emulsifier is available, Crude oil emulsions have formed.

1.6- Role of Emulsifying Agents

Water / oil emulsions include specific organic and inorganic component mixtures. The material that is present with oil and water are considered emulsifying agents. The emulsifying agents can create a structure at the droplets surface that causes weak interfacial tension and powerful interfacial film

1.7- Source of Water Oil Emulsion in Oil Field

Water is always available at the end of the reservoir and causes pressure on oil reservoir. When the oil production goes up, the existing water moving with the oil to the surface. Three significant categories found in both theory and operation as following:

1.7.1- Primary Causes

The oil reservoir always has oil and water. In the earlier field life, the reservoir produces water.

1.7.2- Secondary Causes

Many potential source of water produced in oil wells that are those of unexpected failure in producing oil.

1.7.3- Tertiary Causes

Many sources of water penetration are also presented, caused by later technology or enhanced oil recovery.

1.8- Oil Field Emulsion Characteristics and Physical Properties

Oil emulsions have classified by variety of properties such as following:

- Emulsion appearance and color
- Base sediment and water (BS&W)
- Emulsion water drop size
- Emulsion viscosities

1.9- The Parameters Effect on Emulsion

The summarized parameters that can be affected by emulsion as following:

- ✓ **Type of emulsifying agent**
- ✓ **Droplet size**
- ✓ **Water content**
- ✓ **Oil Viscosity**

1.10- Emulsion Stability

Because of small drop size and the availability of an interfacial layer around the water drops, the stability is a result.

1.10.1- Interfacial Films

The oil emulsions are stabilized at the oil/water interface because of forming layer around the water droplets. The films have classified into two categories based on their mobility:

- ✓ **Rigid, or Solid, Films**
- ✓ **Mobile, or Liquid, Films**

1.10.2- Interface Steric Stabilization

The existence of particles at interfaces cause rising the repulsive surface forces which stabilize the emulsion based on thermodynamic.

1.10.3- Interface Electric stabilization

Electrical double-layer repulsion or charged stabilization by polymers and surfactants can stop the drops from coming into interface. Surfactants, polymers or adsorbed particles may generate an interfacial film that is mechanically strong and elastic and cause as an obstacle to aggregation and coalescence.

1.11- Factors Affecting Stability

The essential parameters which impact the stabilization of emulsion are as the following:

1.11.1- Heavy fraction in Crude oil

The Fraction of heavy crude Oil acknowledged which the naturally present emulsifiers (or stabilizers) have distributed in the high boiling point of crude oil polar fraction. That include as following:

✓ **Asphaltenes**

Due to their reasonable surface-active bond, the asphaltenes remain at interface of the oil-water.

✓ **Resins**

The resins influence in stabilizing emulsion and tend to associate with asphaltenes

✓ **Waxes**

Waxes is the high-molecular-weight paraffin component in the crude which crystallizes when the oil is cooling under the cloud temperature. However, adding a small dosage of asphaltenes to wax-containing oils can have formed a stable emulsion.

1.11.2- Solids

The small solid particles contained in the crude have able to stabilize emulsions. Some factors such as the particle size, interactions of particle and the particle wettability have to effect in stabilizing emulsions.

1.11.3- Temperature

Emulsion stability can greatly have influenced by temperature. Temperature changes the physical oil, water and interfacial films properties, and solubility of surfactant in the oil and water that impact the emulsion stability. The most significant temperature impact is on the emulsion's viscosity that it can have decreased as temperatures increase.

1.11.4- Droplet Size

Generally, emulsions have a droplet size distribution instead of a set droplet size. The emulsions with smaller sized droplets would usually be more stable.

1.11.5- PH

Water – phase PH has an important impact on the emulsion stability. The organic acids, asphaltenes with ionizable groups and particles are in the tight emulsion film.

1.11.6- Brine Composition

The structure of brine also has an important influence on the stabilization of emulsions. The PH changes from about 10 to about 6 and 7 for pure water and the brine solution.

1.12- Emulsions Prevention

When the oil is produced, the emulsion can prevent the formation of the emulsion by removing all water from the oil or preventing all agitation of suitable fluids. Still, since all these are possible or almost, the emulsion can have formed from several wells must be expected. The weak operation often, however, improve emulsification.

1.13- *Effect of Emulsion on Surface Facilities*

The water separation from crude oil has always been an important aspect of crude oil process. For the significant aspect such as Corrosion, scale accumulation and catalyst Poisoning, the salts and water must have eliminated in operation.

1.14- *Water Oil Demulsification*

1.14.1- *Emulsion Break Down appreciate*

Generally, three item can have affected the emulsions breakdown rate. These are as following process:

- ✓ **Flocculation**
- ✓ **Coalescence**
- ✓ **Phase separation**

1.14.2- *Demulsification methods*

Based on the demulsification process, the methods as the following table have used:

<u>Destabilization</u>	<u>Coalescence</u>	<u>Gravity Separation</u>
Heating	Heating	Heating
Chemical	Agitation	Gravity settling
Distillation	Coalescing plates	Centrifugation
	Electrostatic field	
	Water washing	
	Filtering	
	Fibrous packing	
	Retention time	
	Centrifugation	

Table 1- Process for Demulsification Methods

1.14.2.1- *Heating*

Heat decreases the oil's viscosity and emulsifier effect which helps the water droplets collide and settle very easily. Also applying heat will increase density varieties. A considerable loss of light hydrocarbons with a low boiling point will result in heating. Optimizing of an emulsion heating will be of great value to water separation if managing correctly. The emulsion processing can be economical using lower heat and suitable chemical, some agitation and equipment installation space.

1.14.2.2- *Chemical Demulsifiers*

Demulsifiers are the chemical substance which has commonly used to destabilization. This help in the crude emulsions coalescence. Four actions which done by chemical demulsifier as following:

- ✚ ***Oil/Water Interface Strong Attraction***
- ✚ ***Flocculation***
- ✚ ***Coalescence***
- ✚ ***Solids wetting***

1.14.2.3- *Agitation*

Agitation or turbulence has required to forming a crude-oil emulsion. However, the turbulence should be managed.

1.14.2.4- Coalescing Plates

The baffle plates designed and placed in the vessel can help demulsification by spreading emulsion uniformly and creating moderate agitation that allows coalescing the droplets by causing to collide.

1.14.2.5- Electrostatic Coalescence

The dispersed tiny water droplets in the crude may have coalesced by considering electrical field with high-voltage for the water-in-oil emulsion.

1.14.2.6- Water Washing

The efficiency of water wash will be more if the demulsifier destabilize the emulsion and also the water heat.

1.14.2.7- Filtering

A filtering material with the right pore-space size and the appropriate ratio of pore space to total area will be used to filter out the dispersed water drops of an oil emulsion.

1.14.2.8- Fibrous coalescing Packing

A coalescing pack is a portion or compartment in an emulsion-treatment vessel filled with a water-wetted material, allowing to coalesce of the water into more massive droplets in the emulsion.

1.14.2.9- Settling by Gravity

The oldest, easiest and most commonly method for processing crude emulsions is Gravity settling. The oil and water density gradient allows the water to settle by gravity in the oil.

1.14.2.10- Retention Time

Coalescence will occur in a gravity settler, but the rate of interaction of water drops will be low due to the tiny forces at work, and colliding drops hardly to make coalesce quickly.

1.14.2.11- Centrifugation

An emulsion can be broken by centrifugal force and cause oil and water separation due to the density differential between oil and water.

1.14.2.12- Distillation

It's possible that distillation was used to extract water from crude-oil emulsions. Water can be distilled together with lighter oil fractions and then separate by using appropriate methods. Lighter oil fractions have typically returned to crude oil.

Chapter 2

Demulsification Methods of Heavy Oils Used in Oil Fields

2- Demulsification Methods of Heavy Oils Used in Oil Fields

The emulsion affects the reservoirs' ability to produce fluids into the well and change wettability, increases the fluid's viscosity and provides nucleation sites for further deposition. Because of increasing development of heavy and extra heavy oil, compare to separation for conventional oil fields, separation operations are becoming more difficult.

2.1- Oil Demulsification

Three factors of oil demulsification is considered as following:

- Oil produce amount and velocity at that this separation appears
- The remaining water in the crude after the separation has been done
- separated water quality for disposal

2.2- Heavy Oil Demulsification

High capital costs and increased operational costs also require successful water removal from heavy oil, affecting both upstream and downstream desalting operations. To minimize these cost, new technologies of electrostatic dehydrator have the potential to meet a significant effect.

2.3- Destabilizing Heavy Oil Emulsions

Destabilizing or breaking emulsions are also strongly related to the deletion of interfacial layer. Parameters effecting the interfacial layer have explained in oil emulsions Stability. This parameter which increase or accelerate the breaking of emulsion have mentioned here.

2.3.1- Temperature

The consequences of a temperature increase for demulsification as following:

- Decrease the oil viscosity.
- Increases the water droplets mobility.
- Increases the water droplets settling rate.
- Increases collisions of droplet and support coalescence.
- Due to expansion of water and increase film drainage and coalescing, the film on water droplets will be a rupture.
- Increases the fluids densities difference that further increases the separation.

2.3.2- Agitation

Generally, the emulsion stability will reduce with decreasing agitation and shear. Also increasing crude oil shearing should have prevented or minimum if possible.

2.3.3- Retention Time

Increasing the residence time improves the efficiency of separation and decreases the crude oil's residual amount of water. Additionally, rising retention time means the higher costs of separator and equipment.

2.3.4- Solids/ particles removal

Presence of solids cause to stabilize emulsions, mainly if the solids available as tiny or when both of oil and water moistens them.

2.3.5- Emulsifying Agents Control

Since emulsifying agents are essential for stabilization emulsions, the agent's control can be allowing for emulsion destabilization and also resolution.

2.3.6- Retrofitting

Through the retrofitting existing equipment, the water separation can have achieved with high efficiency. Usually, emulsion issue increase because of field aging, unsuitable design, increased water cuts or any other reasons after the separation equipment has installed.

2.4- Mechanisms Involved in Heavy Oil Demulsification

Heavy oil demulsification is also a two-stage process that at the beginning and second steps are flocculation (aggregation, accumulation, or coagulation) and coalescence.

- ✓ *Flocculation or Aggregation*
- ✓ *Coalescence*
- ✓ *Sedimentation or Creaming*

2.5- Methods of Heavy Oil Emulsion Demulsification

This process for heavy crude oil demulsification has carried out by any or a variety of standard methods as the following:

- Considering chemical demulsifiers
- Raising the temperature of emulsion
- Considering electrostatic fields which improve coalescence
- Decrease the flow velocity which able oil, water, and gas separation by gravity. This has usually done in huge separators and desalters.

The demulsification techniques are as following:

2.5.1- Thermal methods

Heating decreases the viscosity of oil and rise the amount of water-settle down. High temperatures cause destabilization of the rigid films due to decrease interfacial viscosity, especially for heavy crude oil. The cost-efficiency of applying heating should have controlled towards the followings:

- higher processing time (huge separator)
- Chemical costs
- Losing light oil and a resulting reduced price of oil production
- electrostatic electrode installation costs

2.5.2- Mechanical Methods

There is a large range of industrial devices accessible for oilfield demulsification

2.5.2.1-Free-Water Knockout Drums

The free water of crude oil separate in free-water knockout drums.

2.5.2.2-Three-Phase Separators or Production Traps

To separation, a mixture of oil, water, and gas, three-phase separators have considered.

2.5.2.3-Desalters

Efficiency has improved by a proper modulation of operation parameters such as following:

- Operation temperatures
- Interface level
- Chemicals for treating
- Wash-water amount and location of injection
- Mixing valves settings

2.5.3- Electrical Methods

For emulsion treatment, electrostatic grids have usually used. As an electrostatic field is subjected to a nonconductive liquid (oil) which contains a conductive liquid (water), one of three physical process lead to the combination of the water droplets and improve the dehydration efficiency.

2.5.4- Chemical methods

Adding demulsifiers is the most common emulsion treatment method. These chemicals have formulated to neutralize the emulsifying agents' stabilizing effect.

2.5.4.1-Chemical selection

For demulsification, chose of the correct demulsifier is critical. The detailed approach for choosing the suitable demulsifier chemicals contains the following steps.

- The crude oil and contamination characterization are the crude oil API gravity, type of oil and brine and composition, salts content and its type, inorganic solids and etc.
- Operational data evaluation includes production rates, operating pressures and temperatures, equipment capacity and specification, chemical injection facilities and etc.
- Emulsion-breakage performance assessment: past experiences and operation data include oil, water, and solids during various tests; operating costs; composition and performance and etc.

2.5.4.2-Mixing/agitation

The demulsifier must come into contact with the emulsion and move through the oil-water interface in order to be efficient. To blend the chemical with the emulsion, there must be enough mixing or agitation. To prevent re-emulsification, agitation should be held to a minimum once the emulsion has dissolved.

2.5.4.3-Dosage

Managing standard or normal dosage rates for demulsification is very difficult due to the followings issues:

- Available demulsifier chemicals have a wide variety.
- Crude with different types have handled.
- Variations in product qualities
- Choice of separation equipment

2.5.4.4-When Injection Has Not Recommended

The chemical normally injected into a coupling welded on the pipe side, although this has not recommended where flow rates are less than 3 ft/sec or whenever the laminar flow has observed.

2.5.5- Factors Affecting Demulsifier Efficiency

A number of parameter influence the efficiency of demulsifier, including:

- pH
- Temperature
- Composition of brine

- Drop size and distribution
- crude oil type

2.5.6- Chemical Demulsification Mechanisms

The demulsifier is also quite complicated. There are numerous hypotheses and assumption about the physicochemical methods for the chemical demulsifier action. The processes of adsorption and displacement and thus the effectiveness of demulsifier depends on:

- Salt content
- pH
- Temperature

2.6- Heavy Oil Demulsification Methods

For heavy crude oils, a combination of all of the above methods may have needed to achieve effective oil-water separation. A universal goal is to choose the optimum combination of techniques to minimize the costs, meet crude sales specifications, produce oil-free water, and maximize the crude value that these methods have been explained in later section completely.

2.7- Crude Oil Dehydration and Desalting Processes

Crude oil dehydration and desalting processes are all about the removal of small immiscible crude oil-water droplets. Some of heavy oil properties:

- High viscosity
- High density
- Formation water with a lower salinity
- High solids loadings
- Often high conductivity
- Low Gas / Oil ratio

The specific gravity of the formation water is a function of the amount of salt dissolved in the formation water.

2.8- Conductivities Effects on Electrostatic Desalter

The conductivity of crude oil plays an important role in the electrostatic fields' functioning inside the treaters. If the conductivity of crude oil is very strong, the electrostatic charge has a hard time hitting the scattered water droplets due to voltage decay.

2.9- Electrostatic Treater

Usually, electrostatic have vertical oil flow to up and have a few typical parts. Electrodes systems, such as a grid system made up of an array of rods, are commonly used in AC electrostatics. The AC/DC desalter have a weak AC field between the electrode plates and the grounded water phase, where it takes place to extract water. Inside the electrode area, the stronger DC field has been contained, supplies a much higher voltage gradient than the AC field, and can remove the small water drop passing through the AC field.

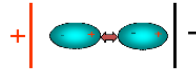
2.10- Electrostatic Forces

Water droplet in a normal dispersion of water in crude oil, coalescence occurs. That the droplets collide with enough force to pass through the coalescence barriers. Electrostatic fields generate forces

that aid in the formation of conditions conducive to increased coalescence. These forces are defined and demonstrated in the following:

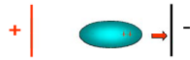
2.10.1- *Dipolar Attraction*

The electrostatic force of attraction between oppositely charged sides of water drops is known as dipolar attraction.



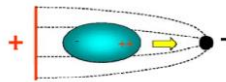
2.10.2- *Electrophoresis*

In a uniform electric field, there is an electrical attraction between the charged electrode and oppositely charged water droplets.



2.10.3- *Die-electrophoresis*

Polarized water droplets move with the displacement into the field's convergence direction in a non-uniform electrostatic field. The Electrophoretic force is the weakest of the three electrostatic forces, with about half the strength of the dipolar attraction force.



2.11- *Electrostatic Fields*

To improve the coalescence of the water droplet inside the treaters, a variety of electrostatic fields can be used. These include the following:

- alternating current field (AC)
- direct current field (DC)
- Combination AC/DC field as in Dual Polarity TM, Electro Dynamic Desalter TM and Dual-Frequency TM technologies.

2.11.1- *AC Technology*

Alternating Current (AC) technology is an oldest technology that has long been the standard for crude dehydration. It gives a 50 to 60 Hz alternating electric field to the crude oil emulsion.

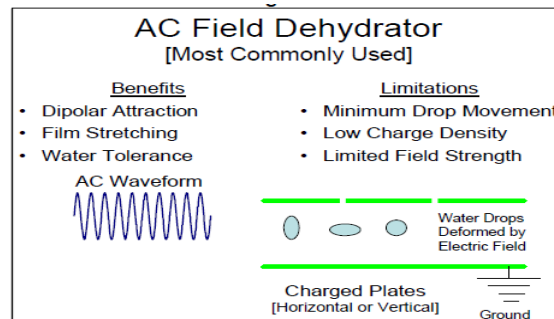


Figure 1- AC field dehydrator benefit and limitation[27]

2.11.2- *DC Technology*

DC fields were recognized as having superior coalescence early on because of their ability to use electrophoretic movement to increase the water droplet collision rate.

2.11.3- *Dual Polarity Technology*

The Dual Polarity technology is a 40-year-old technology. The electro-corrosion potential has been eliminated because the DC field only exists between the electrode surfaces.

2.11.3.1- *High Voltage DC Field with AC (HVDC/AC)*

The HVDC/AC is about 15 years old with composite electrodes. The HVDC/AC ED has a different electrode configuration and transformer system than the AC systems.

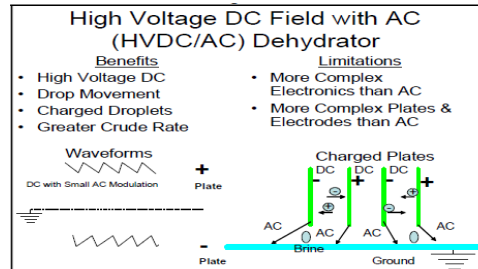


Figure 2 - High Voltage DC Field With AC [27]

2.11.3.2- *Modulated High Voltage DC Field with AC (MHVDC/AC)*

Modulated HVDC/AC (MHVDC/AC) is a modern ED technology that provides greater separation than HVDC/AC. In field applications, it is still not commonly used.

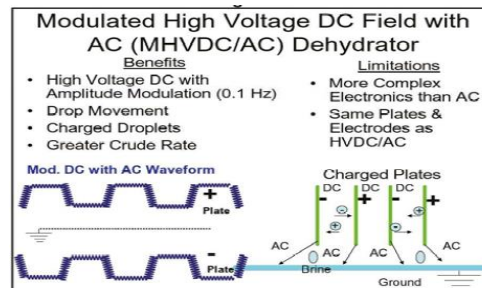


Figure 3 - Modulated high voltage DC field with AC [27]

2.11.3.3- *Bimodal Field Modulation (BFM)*

Bimodal field modulation (BFM) is a modern ED technology that has yet to be used in the field but appears to be very promising in trials. The electrode configuration used by BFM is the same as that used by HVDC/AC ED technology.

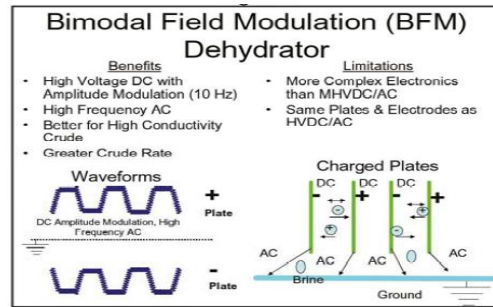


Figure 4 -Bimodal Field Modulation [27]

2.12- Dual Frequency technology

To overcome low interfacial stress, the droplet surface must be sufficiently energized. This can be achieved by modulating the power at a frequency lower than the resonant frequency of the Stokes water droplets. Dual Frequency refers to the modulation of the bimodal frequency.

2.13- Composite Electrodes

In an AC/DC treater, the standard material for the electrodes is steel. In the electrode field, to have better tolerance for higher water cuts; Composite electrodes were developed, particularly for use in electrodynamic desalters (ED).

2.14- Results of advanced ED technologies

The various conventional model and advance desalter technologies for certain crude have tested in the literature review. The crudes characteristics have included as following table 2.

Property	Heavy Crude			
	Crude A	Crude B	Crude C	Crude D
API (Neat)	21	20	8	8-10
API (Test Blend)	21	20	17	16.4
Diluent Addition	None	None	~ 35 v%	~50 v%
TAN	4	0.7	2	1
Blend Conductivity	78,000 pS/m @ 80°C	63,000 pS/m @ 80°C	112,000 pS/m @ 135°C	146,000 pS/m @ 135°C
Brine Conductivity	19.2 mS/m @ 23°C	17.6 mS/m @ 23°C	6 mS/m @ 23°C	7.6 mS/m @ 23°C

Table 2 -Characteristics of Crudes and Brines

The test results performance on applying different desalters technology has shown in figure 4.

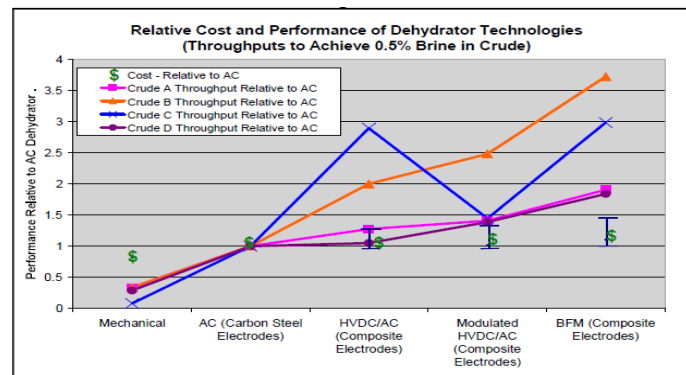


Figure 5 - Dehydrator Technologies Versus Cost And Performance [27]

- ✓ Crudes A and Crude B with APIs between 20 -21: the water dehydration efficiency will be increase 2 to 4 times with advanced ED technology relative to conventional AC ED technology for emulsions.
- ✓ Crudes C and Crude D that have APIs less than 10: The water dehydration efficiency will be increase 2 to 3 times with advanced ED technology relative to conventional AC ED technology for emulsions. These two crudes had a greater dehydration challenge
- ✓ The advanced ED technologies have been proposed in designing dehydration systems for heavy oils.

Therefore, advanced technology desalter can be an efficient method for the water/oil demulsification of heavy oil.

Chapter 3

Mathematical Modeling and Optimization of Heavy Oil Demulsification Process (Case study)

3- Mathematical Modeling and optimization of heavy oil demulsification process

Significant amounts of water often accompany oil production. Water is available in the reservoirs and cause pressure on the oil accumulations. Because of following factors such as corrosion, fouling problem and poisoning catalyst in facilities, it is essential to decrease the crude salt content before export and process the crude in the refineries. Therefore, in this regard, desalting and dehydration is necessary to separate emulsion water from the oil before the oil export.

3.1- Analyzing of Temperature Effect on Heavy Oil Physical Properties

The detailed understanding of crude oil properties has used to determine the optimum condition required for desalting this crude type.

3.1.1- Crude Oil Property Analysis

The crude physical properties result of samples oil field wells (N5 and N18) has shown as following table 3:

<i>Item</i>	<i>Crude sample N5</i>	<i>Crude sample N18</i>	<i>Applicable standards</i>
Original water cut, %	2.37~2.45	0.11~0.23	ASTM D4006
Pour point, C°	-24	-27	ASTM D97
Relative density (25C°)	0.9430	0.9380	ASTM D1298
Viscosity (20C°), mPa·s	604.67	403.11	SY/T 7549
Sulphur content, %	4.35	4.39	ASTM D1552
Acid number, mgKOH/g	0.37	0.40	ASTM D664
Wax content, %	1.84	1.93	SY/T 7550
Asphaltene content, %	12.79	12.93	SY/T 7550
Resin content, %	36.55	32.72	SY/T 7550
Ash content, %	0.416	0.106	ASTM D482
Initial boiling point, C°	100	97	ASTM D86
Wax precipitation point, C°	19.1	29.9	ASTM D 4419
BS&W, %(v/v)	3.0(BS is 1%)	0.27(BS is 0)	ASTM D4007-2

Table 3 - Crude Physical Properties Sample N5, N18

3.1.2- Crude Oil Viscosity-Temperature Curves

The laboratory viscosity tests have been done on crude oil as follows:

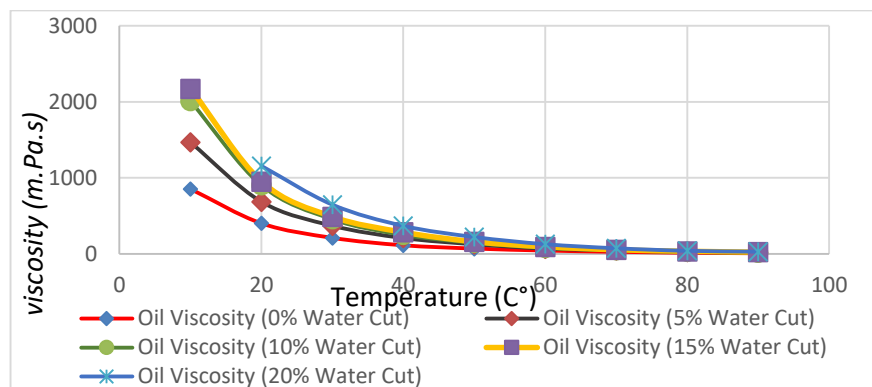


Figure 6- oil viscosity versus temperature

3.2- Demulsification Performance Evaluation and Selection

The different kinds of demulsifiers (oil base and water base) with the different dosage have evaluated in the laboratory on crude oil. In this regard, the optimum demulsifier dosage has selected.

3.2.1- Demulsifiers

The laboratory test for identifying oil demulsification efficiency has been done on the sample of crude oil. The 8 kinds of oil base and 9 kinds of water base demulsifiers have been tested. Each kind of demulsifier is evaluated with the dosage of 50ppm, 100ppm, 150ppm and 200ppm in different water cut (2%, 7.8%, 20% and 40%) in different residence time.

- *Oil Base Demulsifiers*
- *Water Base Demulsifiers*

3.3- Demulsifiers Specification

The specification of applied demulsifier in a laboratory test has demonstrated in table 4.

Sample	pH	Viscosity mPa.s	Density g/cm ³	Flash Point °C	Solidifying Point °C
<i>Water base demulsifier</i>					
Dw-1	7.76	65.90	0.985	28.1	<-15
Dw-2	3.22	2.40	1.011	58.0	-1
Dw-3	6.28	270.30	1.018	80.1	<-5
Dw-4	6.36	184.60	1.018	36.1	<-5
Dw-5	8.10	61.20	0.984	22.2	<-5
Dw-6	10.38	147.60	0.999	55.1	<-5
Dw-7	10.91	14.80	0.995	57.6	<-5
Dw-8	5.44	34.10	1.042	>85	<-5
Dw-9	7.78	10300	1.011	50.2	<-5
<i>Oil base demulsifier</i>					
Do-1	4.05	66.61	0.914	53.1	<-5
Do-2	7.59	42.95	0.948	65.2	<-5
Do-3	7.17	102.21	1.002	22.2	<-8
Do-4	7.35	112.43	0.988	>85	<-5
Do-5	8.90	247.83	1.012	57.1	-4.5
Do-6	6.70	25.46	0.938	32.1	<-5
Do-7	7.88	13.20	0.997	>80	<-5
Do-8	7.10	225.69	0.985	71.2	<-8

Table 4 - Specification of Applied Demulsifier

3.4- Evaluation of Oil Base Demulsifier Efficiency

The demulsifier test of each demulsifier has been done on crude oil in laboratory based on different dosage, water cut and residence time. In this regard only two typical test result on oil base has been shown as following:

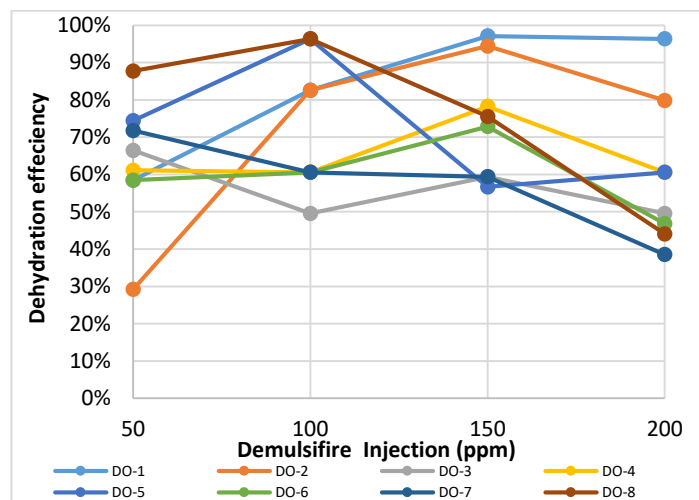


Figure 8 - Dehydration efficiency versus demulsifier injection
Water cut = 7.8% and time 6 hour

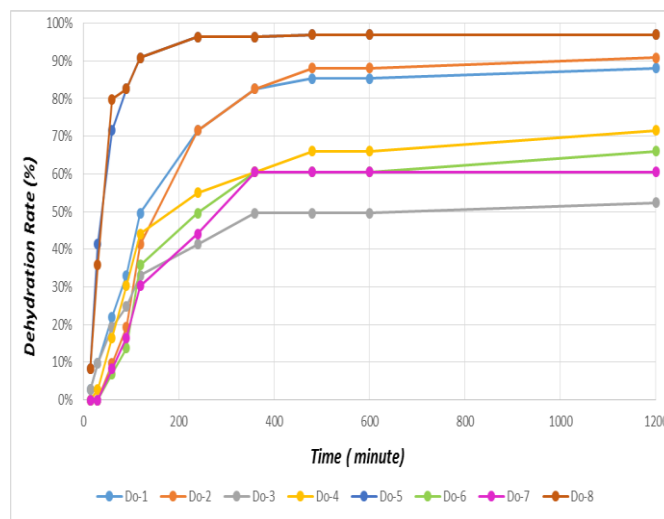


Figure 7 - Dehydration efficiency versus residence time
Water cut = 7.8% and demulsifier dosage=100ppm

3.5- Evaluation of Water Base Demulsifier Efficiency

The demulsifier test of each demulsifier has been done on crude oil in laboratory based on different dosage, water cut and residence time. In this regard only two typical test result on water base has been shown as following:

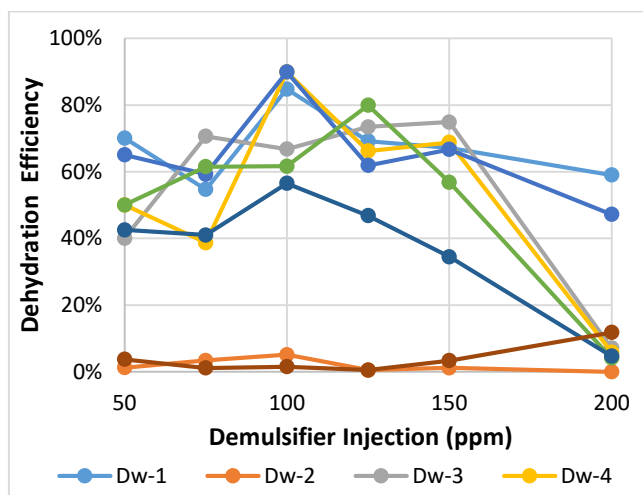


Figure 10 - Dehydration efficiency versus demulsifier injection
Water cut = 7.8% and time 6 hour

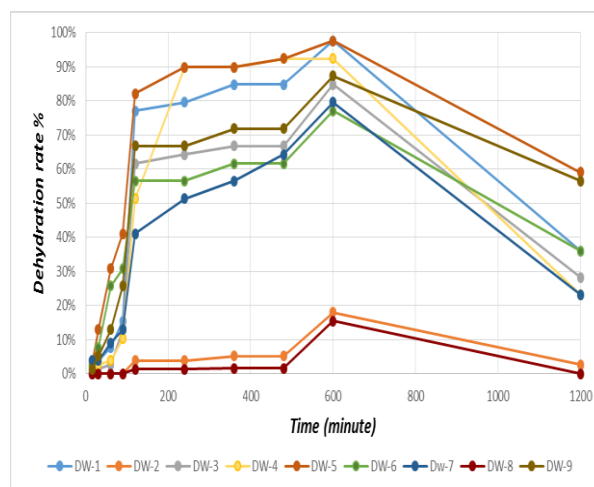


Figure 9 - Dehydration efficiency versus residence time
Water cut = 7.8% and demulsifier dosage=100ppm

3.6- Demulsifier Dehydration Efficiency

The selection principle to select oil-base/water-base demulsifier for the best performances as following: (1) Demulsification, as fast as it can, should be combined with oil field production.

(2) Each kind of demulsifier has its suitable dosage to crude oil emulsion. If the demulsifier concentration is too high, there will be a negative influence on demulsification. Demulsifier Efficiency will fall. Therefore, at the same demulsifier efficiency, demulsifier with lower dosage has better performance.

3.6.1- Oil Base Demulsifier Dehydration Efficiency

To choose the most effective demulsifiers, a screening process has used. For selecting the dehydration efficiency and each demulsifier's price has considered. Experimental data show the oil base demulsifiers have better dehydration efficiency of about 96%. Using this type of demulsifiers, cover crude oil with wide water cut range (2%-40%). So the demulsifiers Do-5, Do-8 and Do-1 have chosen as three of the best oil base demulsifiers. Also, optimal dosages are 100ppm, 100ppm and 200ppm, respectively.

3.6.2- Water Base Demulsifier Dehydration Efficiency

For a demulsification long period, it has seen that performances are approximately the same except Dw-2, Dw-7, and Dw-8. For a demulsification short period, it has seen that performances are different. Dw-4, Dw-7, and Dw-8 have abandoned, but Dw-5 and Dw-1 in dosage 75-150 ppm have excellent performance efficiency curve of 2h &4h, especially in 2h.

3.6.3- Parameters Investigation on Dehydration Efficiency (By Qualitec-4 Software)

The Qualitec-4 Software is windows operating software for the Taguchi experimental design method. It can automatically design based on experiments data and user specified parameters and levels. It provides design experiments, analyzes results and many more.

Because of the water base demulsifiers had less efficiency, the Qualitec-4 Software has used. This software has used for pH effect investigation for selecting the best efficiency for water base demulsifiers. The water separation percentage using water and oil base demulsifiers is different. The difference in separation depends on dosage, residence time and demulsifier properties such as PH.

Table 5 shows the three independent variables' range and levels for the water base demulsifiers investigated in this study.

Parameters	Dw-1 (level 1)	Dw-2 (level 2)	Dw-3 (level 3)	Dw-6 (level 4)
PH	7.76	3.22	6.28	10.38
Dosage (PPM)	50	75	100	200
Time (Min)	360	480	600	600

Table 5- Selected Water Base Demulsifiers' Independent Variables

The experimental results of each level based on variables for water base demulsifier (dehydration efficiency) have mentioned in table 5. In this regard, sixteen different runs have performed for water base demulsifiers to investigate each parameter effect, as shown in Table 6.

Water Base Demulsifier	
Levels	Efficiency
Dw-1	70.10%
Dw-2	4.56%
Dw-3	84.78%
Dw-6	4.13%

Table 6 - Experimental Level Dehydration efficiency for selected water base demulsifiers

Run	Variables			Dehydration Efficiency (%)
	PH	Dosage	Time	
1	7.76	50	360	70.1
2	7.76	75	480	61.53
3	7.76	100	600	97.62
4	7.76	200	600	60.21
5	3.22	50	480	1.25
6	3.22	75	360	3.42
7	3.22	100	600	17.98
8	3.22	200	600	0
9	6.28	50	600	65.09
10	6.28	75	600	77.48
11	6.28	100	360	66.08
12	6.28	200	480	7.08
13	10.38	50	600	60.09
14	10.38	75	360	70.64
15	10.38	100	480	61.66
16	10.38	200	360	4.13

Table 7 - Runs by Qualitec-4 Software for Choosing Water Base Demulsifiers

According to Table 7, the best separation for water base demulsifiers occurred in run 3 about 97 % dehydration efficiency, however run 8, with separation of around 0%, consider as the end of the list. The mid separation was almost 45.3% in these runs. Table 8 shows that pH is the most influential factor in separating water (56.08%), while the time had the lowest effect on separation around 9.8%. The total error is 10.1%.

Factors	DOF	Sum Of Sqrs.	variance	F Ratio	Pure Sum	Percent (%)
PH	3	9571.326	3190.442	28.767	9238.613	56.079
Dosage	3	4290.921	1430.307	12.896	3958.209	24.026
Time	3	1946.519	648.839	5.85	1613.807	9.795
Total	15	665.423				10.1

Table 8 - Analysis of variances for selected water base demulsifiers

Table 9 contains details about the maximum and efficiency of each factor. This table shows the optimal quantity for each parameter as well as its level.

No.	Factors	Level Description	Level	Contribution
1	PH	7.76	1	27.092
2	Dosage	100	3	15.562
3	Time	600	3	13.065

Table 9 - The optimum levels for all selected water base demulsifiers

The result shows that the pH of demulsifier can affect about 56% on dehydration efficiency, and other conditions such as dosage and residence time have less impact. In this regard, selecting the water base demulsifier with PH=7.76, Dosage=100, Time=600, has the best performance (approximately 100% dehydration efficiency considering 10% error).

3.7- Overview on Process Schematic of Existing Oil Field Production Unit (Case Study)

3.7.1- Introduction

The oil field has located in the south-west of Iran in the marsh area. The plateau rate of oil production is 75000 BBL/D. Seven Oil Gathering Systems (OGM), one Central Processing Facilities (CPF) and oil gas exporting system have installed to have an oil production rate of 75,000BOPD, water cut 20%, and associated gas production rate is 39 MMSCF/d.

3.7.2- Oil gathering manifolds (OGMS)

The OGMS have designed to:

- Gather crude oil from the wells;
- Meter crude oil output of each well;
- Inject chemical into production trunk line;

3.7.3- Central Processing Facilities (CPF)

The CPF includes receiving oil facilities, separation, desalination, stabilization, storage and export. Also gas dehydration and compression exist in unit production.

3.8- Heavy Oil Desalting Mathematical Modeling

3.8.1- Introduction

Mathematical modelling of crude oil's desalination process has been done based on *population balancing method*. The population balance model is used to study water-oil emulsion separation.

3.8.2- Analysis of Effect of Temperature on Oil Properties

3.8.2.1- Oil Density versus Temperature

The density test data analyzed and the density versus temperature of oil has considered for desalting modelling. Based on data, the relation of viscosity versus temperature derived as the equation below:

$$\rho_{oil} = -0.0001T^2 - 0.6294T + 950.69 \quad \text{Equation 1}$$

3.8.2.2- Oil Viscosity as a Function of Temperature

The relation of viscosity versus temperature derived as the equation based on viscosity test data analyzed in laboratory as following equation

$$\mu_{oil} = 0.0002T^4 - 0.0441T^3 + 4.0504T^2 - 167.23T + 2769.2 \quad \text{Equation 2}$$

3.8.2.3- Oil Permittivity as a Function of Temperature

The permittivity indicates how easily a material have polarized by the imposition of an electric field. The relative permittivity is the ratio of oil to the permittivity of space or vacuum. Because of a small change of parameter versus temperature, the oil permittivity is considered 2.1 in modelling.

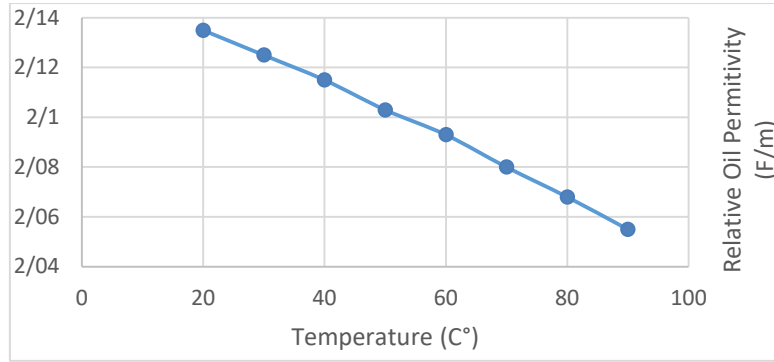


Figure 11 - Relative Oil Permittivity versus Temperature

3.8.3- Population Balance

The population balance equation has simplified as follows:

$$\begin{aligned} u \frac{\partial n(v, z)}{\partial z} = & -g(v)n(v, z) + \frac{1}{2} \int_{w=0}^v \beta(v, w)n(w, z)n(v-w, z) dw \\ & + \int_{w=v}^{\infty} m(w) f(v, w) g(w)n(w, z) dw - n(v, z) \int_{w=0}^{\infty} \beta(v, w)n(w, z) dw \end{aligned} \quad \text{Equation 3}$$

3.8.4- Mathematical Modelling of Electrostatic Desalter Electric Fields

In this case, we do not consider the term breakdown-population equation for modelling the desalting plant and using the equation because the desalter electrostatic electrical field is less than critical field intensity as is shown in equation 4.

$$\begin{aligned} u \frac{\partial n(v, z)}{\partial z} = & \frac{1}{2} \int_{w=0}^v \beta(v, v-w)n(w, z)n(v-w, z) dw \\ & - n(v, z) \int_{w=0}^{\infty} \beta(v, w)n(w, z) dw \end{aligned} \quad \text{Equation 4}$$

The critical field intensity has obtained from the following equation:

$$E_c = 0.64 \sqrt{\frac{\sigma}{\epsilon_{el} d}} \quad \text{Equation 5}$$

Throughout the electrostatic device, heavy droplets are always settling downward, and droplets that cannot settle are moving the desalter upward along the crude oil stream. To influence the droplets' movement in the desalter's modelling and investigate the number of droplets in each section of the device, the whole desalter has divided into several elements in a field's presence.

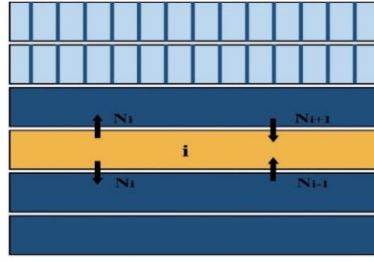


Figure 12- Mass Balance Schematic in Desalter [24]

The coefficient of adhesion of the two droplets is β coefficient.

$$\beta(d_i, d_j) = K \pi (d_i + d_j)^2 V_{ij}^{(0)} e_{ij} \quad \text{Equation 6}$$

The efficiency of horizontal alternating electrical field has considered as follows:

$$e_{ij} = 0.45 \left(\frac{2\lambda \Delta\rho (1-\lambda) g d_i}{3\varepsilon (1+\lambda)^2 E_0^2} \right)^{-0.55} \quad \text{Equation 7}$$

$$V_{ij}^{(0)} = \frac{2(\tilde{Y} + 1)(\rho_d - \rho_c) d_i^2 (1 - \lambda^2) g}{3(3\tilde{Y} + 2)\mu_c} \quad \text{Equation 8}$$

$$\tilde{Y} = \frac{\mu_d}{\mu_c} \quad \text{Equation 9}$$

$$\lambda = \frac{d_j}{d_i} \quad \text{Equation 10} \quad (\text{That is the ratio of small to big droplet})$$

u is the ratio velocity of the droplet motion to the wall of the electrostatic desalting device.

$$u_c = \frac{Q_{oil}}{A} \quad \text{Equation 11}$$

$$u = u_c - \frac{2(\rho_d - \rho_c) g d^2}{9\mu_c} \quad \text{Equation 12}$$

The critical droplet diameter has calculated the below equation 17. The bigger droplet diameter the critical diameter will be sediment and is the output of classes in each layer.

In this model, the diameter of the droplet is assumed 50 to 1300 micron.

$$u_c - \frac{(\rho_d - \rho_c) d_{crit}^2 g}{18\mu_d} - \frac{\varepsilon_0 \varepsilon_w \varepsilon_{oil} E^2 d_{crit} X^{4/3}}{3\pi\mu_d} = 0 \quad \text{Equation 13}$$

$X = \text{volumetric fraction of water}$

3.8.5- Mathematical Solving Methods

The population balance (equation 4) has applied to simulate the electrostatic coalescer unit. The summary of the desalter mathematical model has reflected in the following flowchart.

3.8.5.1- Case-Study Mathematical Solving

In this case-study, the resulting problem consists of about number classes and several integration steps, leading to a system with equations an equal number of classes multiple numbers of integration. Considering 1000 integrations and drop diameter in 20 classes, 20,000 equations should have solved. The integration step is equal to the amount of high desalter step length (dz). The distance between horizontal electrostatic electrodes is considered H. Assuming that $dz = 2.5 \text{ mm}$ is reasonable. :

Equation14

$$dt = \frac{H}{dz}$$

3.8.6- Population Balance Equation Solving Method

The Class method has widely used in the calculation of multiphase fluid mechanics due to its ease of use and acceptable accuracy; therefore, the numerical method of class solving has used in this study.

3.9- Analysis of Mathematical Modeling Result (Case Study)

The oil flow rate is for each unit production unit train. The initial distribution of droplets in the desalter's oil input is 50-1300 μm

Oil flow	37800 (bbl/day)
Water flow	2.9%
Fresh water	5.5%
Oil temperature	110 (C°)
Oil API	19.5

Table 10 - Oil Specification and Information

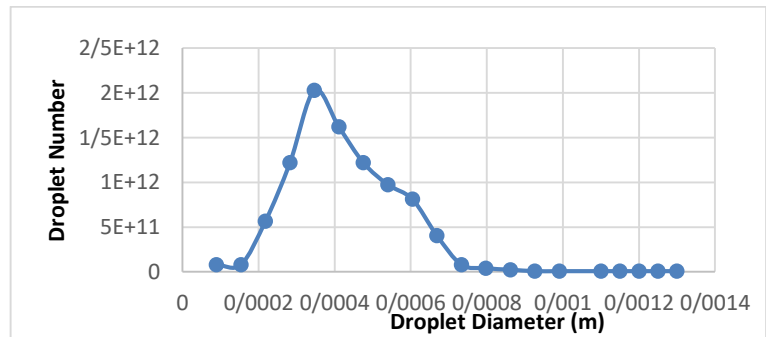


Figure 13 - Droplets Distribution in the Oil Input to Desalter

3.9.1- Electrostatic Desalter (Horizontal field)

The desalter characteristic has reflected in table 11.

<i>Electrostatic Desalter Specification</i>	<i>value</i>
Electrostatic Length (m)	27.5
Electrostatic diameter (m)	4.6
Distance electrodes (m)	2.5
Electric field intensity (kv/cm)	0.75

Table 11 - Electrostatic Desalter Specification

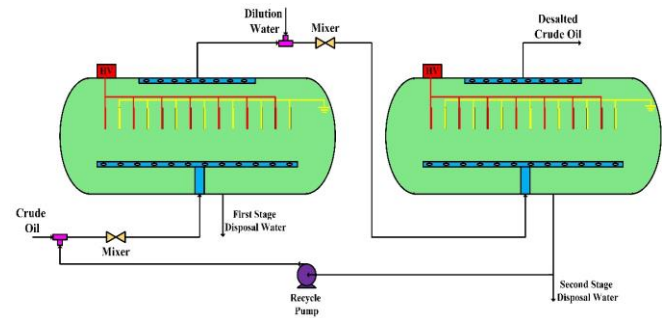


Figure 14 -Electrostatic Desalter Schematic

Figure 13 shows the distribution of water droplets at different levels of the existing desalter based on mathematical modeling. Due to small droplets' collision and producing larger droplets during the desalter, the droplet bigger of critical diameter settle down towards the floor (distributor).

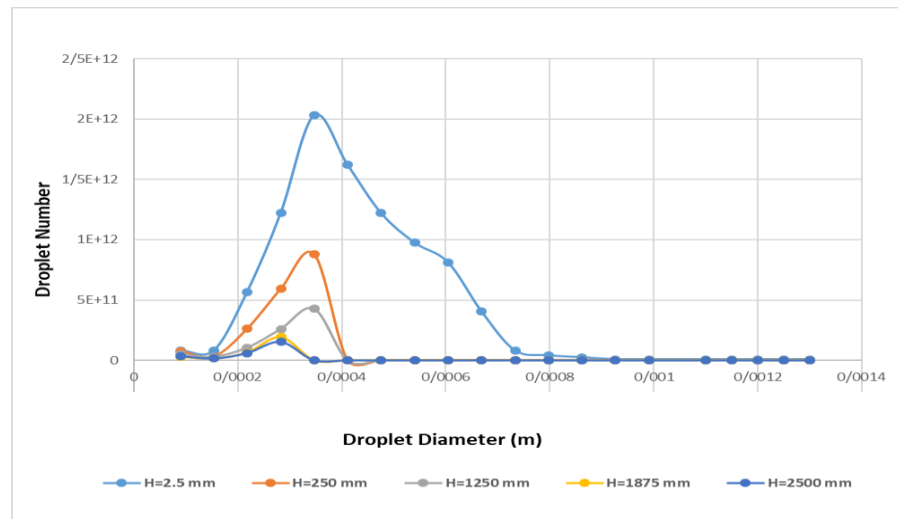
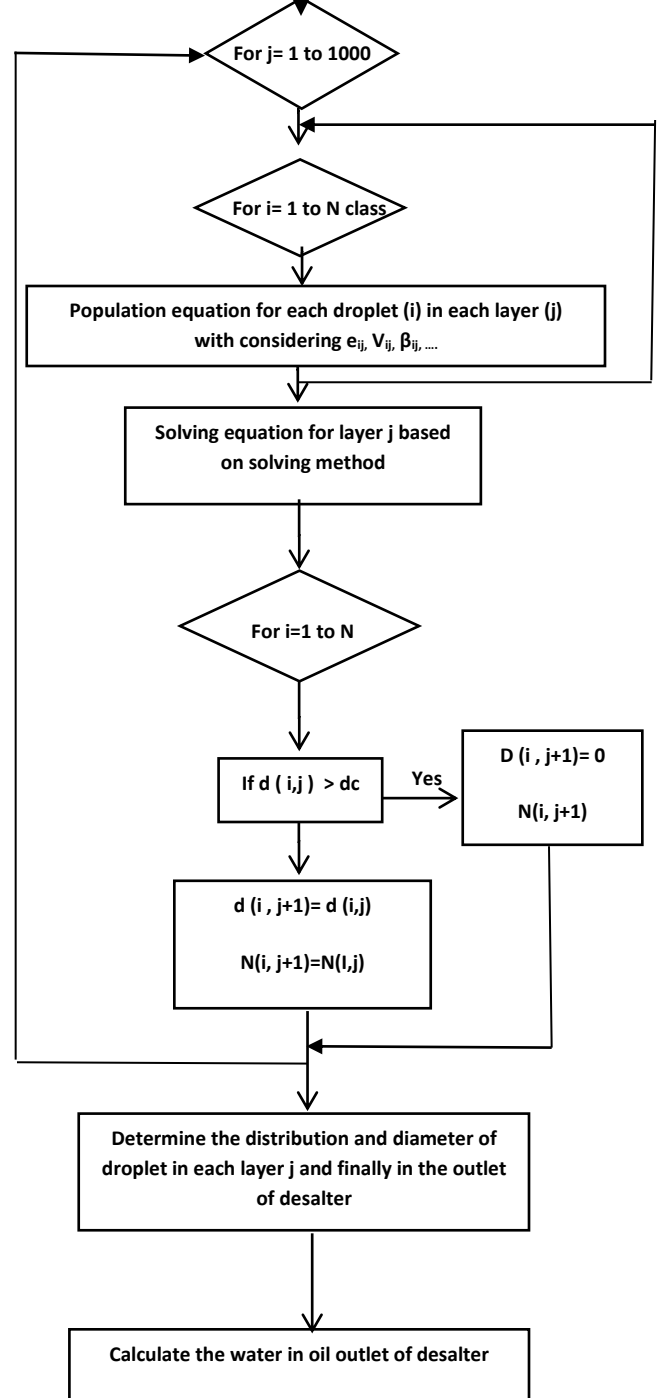
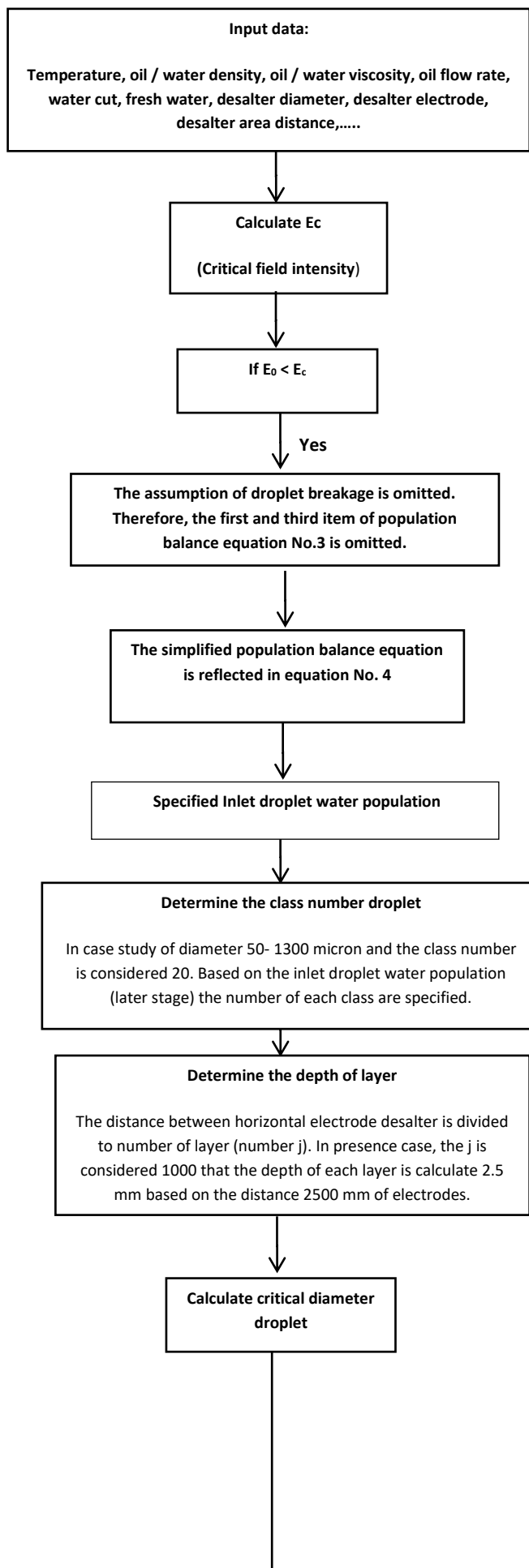


Figure 15 -Distribution of water droplets during electrostatic desalter ($T=110\text{ }^{\circ}\text{C}$, $E_0=0.75$, fresh water=5.5%)



3.9.2- Electric Field Effect

By increasing the electric field intensity (the smaller fields of the critical field), the gravity of the power between the droplets increases. So the number of droplets in the crude oil output of electrostatic is reduced, and the efficiency has increased.

Electric field (kV/cm)	0.75	1.5	2.5
Water separation efficiency (%)	61.8	82.5	90.7

Table 12 - Effect of electrical field on dehydration efficiency

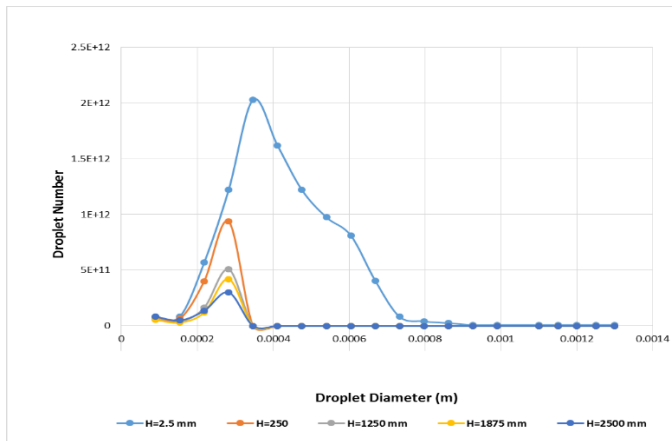


Figure 16 - Electric Field Effect on the number of droplets on Desalter ($E_0=1.5$, $T=80^\circ\text{C}$)

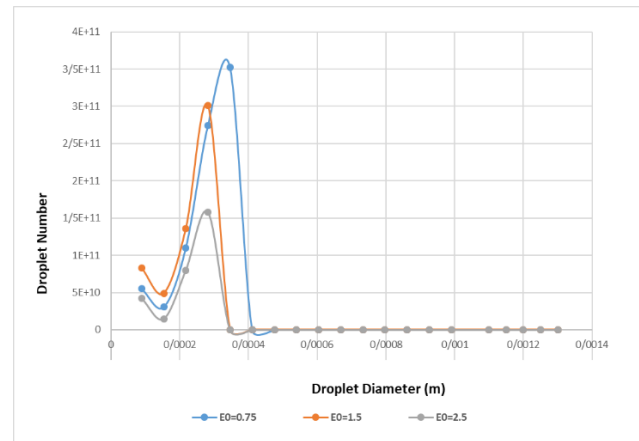


Figure 17 - Comparing Electric Field Effect on the number of droplets on Desalter outlet stream ($T=80^\circ\text{C}$, Fresh water=5.5%)

3.9.3- Fresh Water Effect

With increasing fresh water, the number of water droplets in the system increases because of the possibility that water droplets have placed in each other's path, and the number of encounters has increased. Thus, by increasing the discharge of fresh water, water separation efficiency is increased. The effect of increasing fresh water discharge is well in figure 96, so that the increase in the discharge of fresh water from 5.5% to 15% increases water separation efficiency from 91.4 to 97.4%.

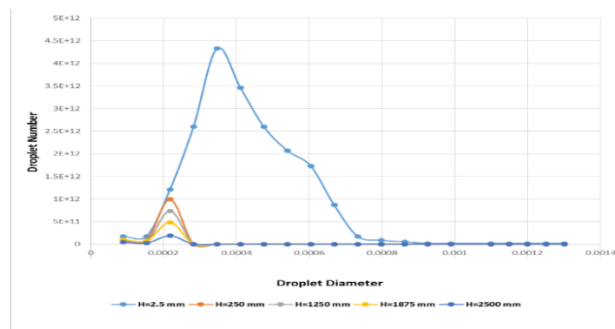


Figure 18 - Fresh water effect on the number of droplets on desalter (fresh water =15%, $E_0=2.5$, $T=80^\circ\text{C}$)

3.9.4- Temperature Effect

By increasing the continuous phase temperature, the viscosity will be decreases, and the small droplet displacement has increased, so the droplet's collision increases and the smaller droplets can be settled in desalter, quickly. The results show, increasing the temperature reduces the water in oil outlet of desalter. The modelling results show an increase of 40 °C continue phase temperature, and the dehydration efficiency has increased more than 41.6%.

Temperature (C°)	110	90	80	70
Water separation efficiency (%)	91.4	80.4	58.8	49.8

Table 13 - Effect of oil inlet temperature on water separation efficiency

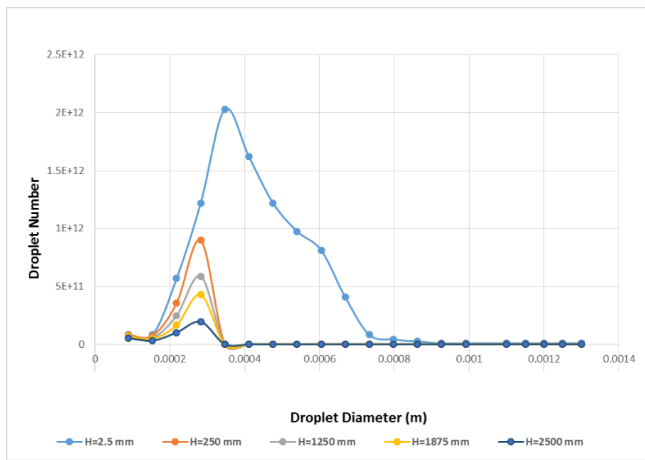


Figure 19 - Temperature Effect on the Number of droplets on Desalter (E0=0.75, T= 90C°, Fresh water =5.5%)

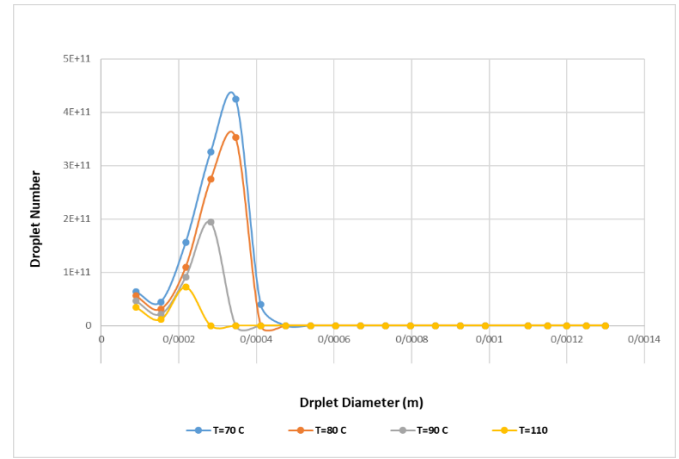


Figure 20 -Comparing Temperature Effect on the Number of droplets on Desalter outlet stream (E0=0.75, Fresh water =5.5%)

3.9.5- Modelling Analysis Accuracy

To evaluate the modelling accuracy, the obtained results include water separation efficiency of existing desalter condition (E0=0.75, T=110 C°, Fresh water=5.5%) compared with the oil field desalter results. The comparison between the effects of modelling and industrial data shows the good accuracy of the modelling. Therefore, the model has reasonable accuracy.

Parameter	Modelling result	Industrial result
Water separation efficiency (%)	91.4	93.1

Table 14 - Comparing Modelling and Industrial Result

3.10- Modelling with HYSYS Simulation

The result of mathematical modelling shows that the desalter unit can be meet the water specification with some changes in operation, such as a decrease in oil temperature. As the inlet oil temperature to desalter is high about 110 °C, the oil recovery decreases, and the gas stream has included heavy hydrocarbon and valuable component. Therefore, for the production unit's optimisation, the HYSYS modelling of the existing system is developed based on design and tune with field operating data.

3.10.1- Oil and Gas processing simulation

The oil production unit modeled with HYSYS.

3.10.2- Equation of State

The PR and SRK state equations applied in the model.

3.10.3- Assumptions for Equipment

Based on the reference the pressure drop assumed for equipment.

3.10.4- Simulation Modeling with HYSYS

The unit production oil processing has done with HYSYS software. The field operation data have used for tuning the model. The schematic of oil processing has shown in figure 101.

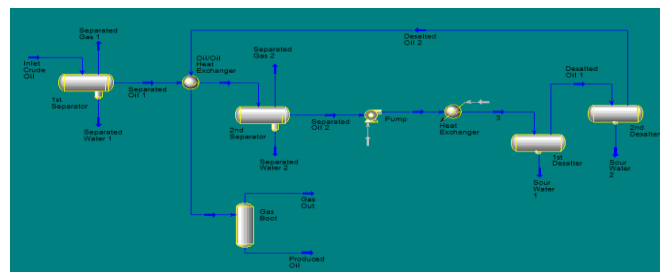


Figure 21 - Oil Processing Schematic in HYSYS Modeling

The oil recovery versus desalter inlet oil temperature as following table:

<i>Inlet oil temperature to desalter (c°)</i>	<i>Oil produced (m³/hr)</i>	<i>Oil produced (BBL / D)</i>
70	509.31	76882
80	508.03	76689
90	506.55	76467
110	504.64	76115

Table 15 - Effect of inlet oil temperature to desalter on oil recovery

The result shows that the decreasing temperature from 110 to 80, increases oil production to about 574 BBL/D and the recovery meet the better situation. Assume the oil price about

50-70 \$/BBL, the annual saving is about 11-15 MM\$, and while oil production filed age about 30 years, the total income will be about 315-434 MM\$. Also, the produced gas and heat exchanger duty will decrease.

<i>Inlet oil temperature to desalter (c°)</i>	<i>Required Duty(KW)</i>	<i>gas produced (MMSCF/D)</i>
70	5314	99.5
80	9503	100
90	13817	100.7
110	23328	102.8

Table 16 - Effect of oil desalter inlet-temperature on produced gas and required duty

As demonstrated above, reducing the oil temperature desalter cause required the energy for heating oil temperature will decrease about 1383 Kw, which could impact about 950M\$ saving in cost during investment. Part of the gas produced is using a gas lift and remained about 28 MMSCF/D is flaring. The developing of this model can decrease about 2.8 MMSCF/D of the gas flaring that equal 1 percent. Based on the mathematical modelling, when the inlet oil temperature to desalter, decreases to 80 °C, the oil recovery factor increases as above investigation. In this regards, the dehydration efficiency has increased to 90.7 % by increasing the electrical field to set equal 2.5 kv/cm. The proposed condition shows have good accuracy. Therefore, applying the results of this study, in addition to increasing oil production, revenue and reduces environmental pollution.

Cases	Temperature C°	E₀ (kv/cm)	Critical droplet diameter (micron)	Dehydration efficiency
Proposed condition	80	2.5	328	90.7%
Existing condition	110	0.75	325	91.4%

Table 17 - Comparing Proposed and Existing Condition Based On Mathematical Modeling

4-Conclusion

The destabilization of emulsifying films around water droplets is needed for emulsion separation of oil and water. Either or a combination of the following methods have been used to complete this process:

- Considering chemical demulsifiers
- Higher emulsion temperature
- Applying electrostatic fields for promotion of coalescence
- Reduce the velocity of flow which cause gravitational oil, water, and gas separation

For heavy crude, a variation of the above technique may be necessary to have effective oil/water separation. ***Therefore, the advanced-technology-desalter can be an effective method for water-oil demulsification of heavy crude.***

In the study, the experimental demulsifier result has investigated to select a better demulsifier type. The result has shown oil base demulsifier efficiency was over 96% when dosage at 200ppm of Do-1 and dosage at 100ppm of Do-5 & Do-8. The water base demulsifier has a low efficiency than oil base demulsifier.

Then in the later stage of the study, the mathematical modelling of desalter has been developed. The model solved (programming with MATLAB software) to meet the outlet oil specification of desalter. The result compares with the industrial data, which shows acceptable accuracy. The result shows that the increase in temperature, fresh water and electrical field has a good effect on water separation in desalter, but the increasing temperature has more effect and also cause of a decrease in oil recovery and loss of light hydrocarbon. In the last stage, the effect of decreasing temperature on HYSYS modelling of production unit has seen. The simulation result shows that the decrease in inlet oil temperature from 110 to 80 °C can be increased oil production to about 574 BBL/D. This will be a benefit during oil field production.

Applying the project results, in addition to the fact that due to the increase in oil about 574 BBL/D and depending on the oil price, can increasing the annual income about 11- 15 MM\$.

It is also relevant in the following cases:

- Decrease the CAPAX about 1 MM\$
- Decrease environmental pollution
- Demulsifier optimal consumption

It is obvious that the desalting system by applying the project result will meet the water-oil specification.

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