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Research title.

Computer program for heater Treater parameters optimization

برنامج واسوري لتوحيد المعاملات الأمثل للمعالج الوراري

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صدق الله العظيم

Dedication

To our parent who always inspiring, and advising us, nothing of this

Could be done without them may, Allah saves them

always for us.

To our teachers in all of our educational life who taught as the

knowledge is the strongest response…….

To our dears, all of our family members who always be there when

we need them…..

To our best friends & colleagues who are always with us step by step supporting us to go forward....

To every one who is an integral part of our support group………

We dedicate this work which honest hope to get their satisfaction.…….

Acknowledgement

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Abstract

Emulsion refers to mixture of two or more immiscible liquids. For an emulsion to form the component should be immiscible with each other. Various equipment's are available in oil and gas industry. Heater treaters are predominantly used and it provides heat to break the emulsion. There are two types of heater treater, vertical and horizontal. In this study an attempt has been made to build a computer program that gives accurate results for heater treater sizing. To size the heater treater, three equations are used, settling equation, retention time equation, and heat required equation. At the end of this study, optimum diameter, effective length, optimum height of heater treater, and heat required to break emulsion has been provided.

التجريد

ترجع نشأة المستحلبات إلى وجود سائلين غير ممتزجين أو أكثر، ليتم تكوين المستحلب البد أن يكون أحد المكونات غير ممتزج مع اآلخر، تتوفر مختلف المعدات في الصناعة النفطية ولكن يغلب استخدام المعالج الحراري حيث يقوم بتسخين الخام للتخلص من المستحلبات، وهناك نوعان منه المعالج الحراري الأفقي والرأسي. في هذه الدراسة أجريت محاولة لبناء برنامج حاسوبي يعطي نتائج دقيقة في عملية تصميم المعالج الحراري. وتسخدم ثالث معادالت لتصميم المعالج هي، معادلة االستقرارية، ومعادلة زمن البقاء باإلضافة لمعادلة كمية الحرارة _. وفي نهاية هذه الدراسة تم الحصول على القطر الأمثل والطول الفعال، والارتفاع الأمثل للمعالج الحراري وكذلك كمية الحرارة المطلوبة للتخلص من هذه المستحلبات.

Nomenclature:

- µo= oil viscosity, cp,
- $T =$ oil temperature (F), (C),
- $API = oil$ gravity,
- d = minimum vessel internal diameter, in. (mm),
- $Qo=$ oil flow rate, (bbl/day)(,m3/hr),
- Tro = retention time, min,
- Leff = length of coalescing section, ft (m) ,
- h = height of the coalescing section, in. (mm),
- ΔSG = difference in specific gravity between oil and water (relative to water),
- dm = diameter of water droplet, microns,
- q = heat input, BTU/hr (kW),
- ΔT = increase in temperature, (F), (C),
- SGo = specific gravity of oil relative to water.

Abbreviation:

- **GOSPs** gas/oil separating plants
- **W/O** water in oil emulsion
- **O/W** oil in water emulsion
- **W/O/W** water in oil-oil in water
- **O/W/O** oil in water-water in oil

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Chapter One Introduction

Chapter 1 Introduction

1.1. General Introduction:

 The main objective of Surface Petroleum Operations (SPO), is the processing of reservoir fluids in order to produce profitable products; namely crude oil and natural gas. Crude oil is seldom produced alone. It is generally commingled with water, which creates a number of problem during oil production. Water Produced in two ways: some of water may be produced as free water (i.e., water that will be settle out rapidly), and some of water may be produced in the form of emulsion. Emulsions are difficult to treat and cause a number of operational problem, such as tripping of separation equipment in gas/oil separating plants (GOSPs). Emulsion can be encountered in almost all phase of oil production and processing inside the reservoir, wellbore, wellheads, and wet crude handling facilities, transportation through pipelines and during petroleum processing.

1.2. Problem statement:

 With increase needing of more easily solution that's handling with a problems associated in the operation of processing facilities as a result of a presence of an undesirable or unwanted petroleum emulsions in the oil industry. This solution should give accurate results by meaning a reliable, flexible and practical at the same time. In the process of emulsion thermal treatment by using heater treater affected with a various number of factors from separated water size to the amount of oil extracted and optimum diameter of heater treater with its length or height. In this work we will provide a designing methodology through an arithmetic program this will be including an optimization for a heater treater in diagnosing specific factors that's mentioned previously that helps to overcome a potential operational problems during processing of heater treater, also taking into consideration the economical aspect in separating larger amount of oil using thermal treatment for emulsions.

1.3. Research Objectives:

- 1- Design computer program to calculate the effective length, diameter, and heat required of both vertical and horizontal heater treater to minimize water cut to less than 0.5 percent.
- 2- Compare different scenarios and select the optimum sizing and heat required.
- 3- Compare the results using manual calculations.
- 4- Identify the factors (flow rate, treating temperature, API, etc) affected on emulsion separation efficiency.

1.4. Methodology adopted:

 The followed methodology in this study depends primarily on designing matlab program to calculate the optimum heater treater variables (effective length, diameter, and heat required) and compare these calculations with manual calculations. After the entering of data and run the program the above heater treater variables were calculated in their optimum values.

1.5. Research outlines:

 Through this work, a study was made for emulsions in crude oil and treating method in case of thermal method with its processing facilities. The first chapter is an introduction to the study and illustration of the project problem statement, general objective of the study and a methodology that is used to deliver the objectives. The second chapter are a literature review and background of the treatment as general. The following three chapters are the main component of the study, the three phases of problem from calculation treatment to establish a program and end with the design specification of processing facilities. First one is the Chapter three with necessary calculation of treatment and use of suitable program to achieve project goals. Chapter four will connect the parts of the study as a result to create a guideline in designing Procedure, the last one is Chapter five included conclusion and recommendation for this study.

Chapter Two

Theoretical Background and Literature Review

Chapter 2

Theoretical Background and Literature Review

2.1. Introduction:

 Removing water from crude oil often requires additional processing beyond the normal oil–water separation process, which relies on gravity separation. Crude oil treating equipment is designed to break emulsions by coalescing the water droplets and then using gravity separation to separate the oil and water. In addition, the water droplets must have sufficient time to contact each other and coalesce. The negative buoyant forces acting on the coalesced droplets must be sufficient to enable these droplets to settle to the bottom of the treating vessel. Therefore, it's important when designing a crude oil treating system to take into account temperature, time, viscosity of the oil, which may inhibit settling, and the physical dimensions of the treating vessel, which determines the velocity at which settling must occur. When selecting a treating system, several factors should be considered to determine the most desirable method of treating the crude oil to contract requirements. Some of these factors are: 1- Stability (tightness) of the emulsion,

- 2- Specific gravity of the oil and produced water,
- 3- Corrosiveness of the crude oil, produced water, and associated gas,

4- Scaling tendencies of the produced water,

- 5- Quantity of fluid to be treated and percent water in the fluid,
- 6- Paraffin-forming tendencies of the crude oil,
- 7- Desirable operating pressures for equipment,
- 8- Availability of a sales outlet and value of the associated gas produced.

 A common method for separating this "water-in-oil" emulsion is to heat the stream. Increasing the temperature of the two immiscible liquids deactivates the emulsifying agent, allowing the dispersed water droplets to collide. As the droplets collide they grow in size and begin to settle. If designed properly, the water will settle to the bottom of the treating vessel due to differences in specific gravity.

2.1.1. Emulsion Definition:

 An emulsion is a stable mixture of oil and water that does not separate by gravity alone. In the case of a crude oil or regular emulsion, it is a dispersion of water droplets in oil. Normal, or regular, oil-field emulsions consist of an oil continuous or external phase and a water dispersed or internal phase. In some cases, where there are high water cuts, such as when a water-drive field has almost "watered out," it is possible to form reverse emulsions with water as the continuous phase and oil droplets as the internal phase. Complex or "mixed" emulsions have been reported in low-gravity, viscous crude oil. A stable or "tight" emulsion occurs when the water droplets will not settle out of the oil phase due to their small size and surface tension. Stable emulsions always require some form of treatment.

2.1.2. Classification of Emulsions:

Three broad group of emulsion are now readily distinguished in principle, depending upon which kind of liquid forms the continuous phase.

- 1- Oil-in-water (O/W) for oil droplets dispersed in water
- 2- Water-in-oil (W/O) for water droplets dispersed in oil
- 3- Multiple or complex emulsions.

 The w/o emulsions consist of water droplets in a continuous oil phase, and the o/w emulsions consist of oil droplets in a continuous water phase. In the oil industry, w/o emulsions are more common, and therefore, the o/w emulsions are sometimes referred to as "reverse" emulsions. Multiple emulsions are more complex and consist of tiny droplets suspended in bigger droplets that are suspended in a continuous phase. For example, a water-in-oil-in-water (w/o/w) emulsion consist of water droplets suspended in larger oil droplets that in turn are suspended in a continuous water phase.

 This kind of classification is not always appropriate. For example, O/W/O denotes a multiple emulsion containing oil droplets dispersed in aqueous droplets that are in turn dispersed in a continuous oil phase. The type of emulsion that is formed depends upon a number of factors. If the ratio of phase volumes is very large or very small, then the phase having the smaller volume is frequently the dispersed phase. If the ratio is closer to 1, then other factors determine the outcome. Table I lists some simple examples of petroleum emulsion types. Fig. 1 shows the various types of emulsion

W/O emulsion

O/W emulsion

W/O/W emulsion

Emulsion with solids

 Fig (2-1) photomicrograph of petroleum emulsions

2.1.3. Formation of Emulsions:

Crude oil emulsions form when oil and water (brine) come into contact with each other, when there is sufficient mixing, and when an emulsifying agent or emulsifier is present. The amount of mixing and the presence of emulsifier are critical for the formation of an emulsion. During crude oil production, there are several sources of mixing, often referred to as the amount of shear, including flow through reservoir rock; bottom hole perforations/pump; flow through tubing, flow lines, and production headers; valves, fittings, and chokes; surface equipment; and gas bubbles released because of phase change. The amount of mixing depends on several factors and is difficult to avoid. In general, the greater the mixing, the smaller the droplets of water dispersed in the oil and the tighter the emulsion. Emulsion studies have shown that the water droplets can vary in size from less than 1 micron to more than 1000 micron

2.1.4. Importance of Emulsions:

Emulsion have important properties that may be desirable, for example, in a natural or formulated product, or undesirable, such as an unwanted emulsion in an industrial process. Petroleum emulsions may not be as familiar but have a similarly widespread, long-standing, and important occurrence in industry. Emulsions may be encountered at all stages in the petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions). the wide range of possible compositions, cause crude oils to exhibit a wide range of viscosities and densities, so much so that these properties are used to distinguish light, heavy, and bituminous crude oils. One set of definitions can be compiled as follow:

Table (2-1) crude oils, viscosity and density

As shown in **Table (2-2),** petroleum emulsions may be desirable or undesirable. For example, one kind of oil-well drilling fluid (or "mud") is emulsion based. Here a stable emulsion (usually oil dispersed in water) is used to lubricate the cutting bit and to carry cuttings up to the surface. This emulsion is obviously desirable, and great care goes into its proper preparation. An emulsion may be desirable in one part of the oil production process and undesirable at the next stage. For example, in the oil fields, an in situ emulsion that is purposely created in a reservoir as part of an oil recovery process may change to a different, undesirable type of emulsion (water dispersed in oil) when produced at the wellhead. This emulsion may have to be broken and reformulated as a new emulsion suitable for transportation by pipeline to a refinery. Here, the new emulsion will have to be broken and water from the emulsion removed; otherwise the water would cause processing problems in the refining process.

Occurrence	Usual Type ^a	
Undesirable Emulsions		
Well-head emulsions	W/O	
Fuel oil emulsions (marine)	W/O	
Oil sand flotation process, froth	W/O or O/W	
Oil sand flotation process, diluted froth	O/W/O	
Oil spill mousse emulsions	W/O	
Tanker bilge emulsions	O/N	
Desirable Emulsions		
Heavy oil pipeline emulsion	O/N	
Oil sand flotation process slurry	O/N	
Emulsion drilling fluid, oil-emulsion mud	O/W	
Emulsion drilling fluid, oil-base mud	W/O	
Asphalt emulsion	O/N	
Enhanced oil recovery in situ emulsions	ОW	

Table (2-2) Examples of emulsion in petroleum industry

 Emulsions may contain not just oil and water, but also solid particles and even gas. Some emulsions are made to reduce viscosity so that an oil can be made to flow. Emulsions of asphalt, a semisolid variety of bitumen dispersed in water, are formulated to be both less viscous than the original asphalt and stable so that they can be transported and handled. In application, the emulsion should shear thin and break to form a suitable water-repelling roadway coating material. Another example of emulsions that are formulated for lower viscosity with good stability are those made from heavy oils and intended for economic pipeline transportation over large distances. Here again the emulsions should be stable for transport but will need to be broken at the end of the pipeline.

2.1.5. Emulsifying Agents:

Produced oilfield water-in-oil emulsions contain oil, water, and an emulsifying agent. Emulsifiers stabilize emulsions and include surface-active agents and finely divided solids.

Surface-Active Agents: Surface-active agents (surfactants) are compounds that are partly soluble in both water and oil. They have a hydrophobic part that has an affinity for oil and a hydrophilic part that has an affinity for water. Because of this molecular structure, surfactants tend to concentrate at the oil/water interface, where they form interfacial films. This generally leads to a lowering of the interfacial tension (IFT) and promotes dispersion and emulsification of the droplets. Naturally occurring emulsifiers in the crude oil include higher boiling fractions, such as asphaltenes and

resins, organic acids, and bases. These compounds have been shown to be the main constituents of interfacial films that form around water droplets in many oilfield emulsions. Other surfactants that may be present are from the chemicals injected into the formation or wellbores (e.g., drilling fluids, stimulation chemicals, corrosion inhibitors, scale inhibitors, wax, and asphaltene control agents).

Finely Divided Solids: Fine solids can act as mechanical stabilizers. These particles, which must be much smaller than emulsion droplets (usually submicron), collect at the oil/water interface and are wetted by both oil and water. The effectiveness of these solids in stabilizing emulsions depends on factors such as particle size, interparticle interactions, and the wettability of the particles. Finely divided solids found in oil production include clay particles, sand, asphaltenes and waxes, corrosion products, mineral scales, and drilling muds.

2.1.6. Emulsion Characteristics and Physical Properties:

 Oilfield emulsions are characterized by several properties including appearance and color, BS&W, droplet size, and bulk and interfacial viscosities.

1- **Appearance and Color:** Color and appearance is an easy way to characterize an emulsion. The characterization becomes easy if the emulsion is transferred into a conical glass centrifuge tube. The color of the emulsion can vary widely depending on the oil/water content and the characteristics of the oil and water. The common colors of emulsions are dark reddish brown, gray, or blackish brown; however, any color can occur depending on the type of oil and water at a particular facility. Emulsion brightness is sometimes used to characterize an emulsion. An emulsion generally looks murky and opaque because of light scattering at the oil/water interface. When an emulsion has small diameter droplets (large surface area), it has a light color. When an emulsion has large diameter droplets (low total interfacial surface area), it generally looks dark and less bright.

2- **Basic Sediment and Water:** BS&W is the solids and aqueous portion of an emulsion. It is also referred to as BSW, bottom settlings and water, or bottom solids and water. Several methods are available to determine the amount of water and solids in emulsions. Standard methods have been proposed by several organizations including the Institute of Petroleum, American Petroleum Institute, and the American Society for Testing Materials. The most common technique for the determination of oil, water, and solids consists of adding a slight overdose of a de-emulsifier to an emulsion, centrifuging it, and allowing it to stand. The amount of solids and water separated is measured directly from specially designed centrifuge tubes. When only the water content is desired, Karl-Fischer titration can also be used. It is very accurate at low contents of water (<2%) but can also be used for determining higher content $(>10\%)$.

3- **Droplet Size and Droplet-Size Distribution:** Produced oilfield emulsions generally have droplet diameters that exceed 0.1 micron and may be larger than 100 micron. Emulsions normally have a droplet size range that can be represented by a distribution function. The droplet-size distribution in an emulsion depends on several factors including the IFT, shear, nature and amount of emulsifying agents, presence of solids, and bulk properties of oil and water. Droplet-size distribution in an emulsion determines, to a certain extent, the stability of the emulsion and should be taken into consideration in the selection of optimum treatment protocols. As a rule of thumb, the smaller the average size of the dispersed water droplets, the tighter the emulsion and, therefore, the longer the residence time required in a separator, which implies larger separating plant equipment sizes.

4- **Rheology:** Viscosity of Emulsions. Emulsion viscosity can be substantially greater than the viscosity of either the oil or the water because emulsions show non-Newtonian behavior. This behavior is a result of droplet crowding or structural viscosity. A fluid is considered non-newtonian when its viscosity is a function of shear rate. At a certain volume fraction of the water phase (water cut), oilfield emulsions behave as shear-thinning or pseudo plastic fluids (i.e., as shear rate increases, viscosity decreases). The constant values of viscosity for all shear rates, or a slope of zero, indicate that the emulsions exhibit Newtonian behavior up to a water content of 40%. At water cuts greater than 40%, the slope of the curves deviate from zero, which indicate non-Newtonian behavior. The very high viscosities achieved as the water cut increase up to 80% (compared with viscosities of oil approximately 20 cp and water <1 cp). At approximately 80% water cut, an interesting phenomenon is observed. Up to a water cut of 80%, the emulsion is a water-in-oil emulsion; at 80%, the emulsion "inverts" to an oil-in-water emulsion, and the water, which was the dispersed phase, now becomes the continuous phase. In this particular case, multiple emulsions (water-in-oil-in-water) were observed up to very high water concentrations (>95%). Temperature also has a significant effect on emulsion viscosity. Emulsion viscosity decreases with increasing temperature. The viscosity of emulsions depend on several factors: viscosities of oil and water, volume fraction of water dispersed, droplet-size distribution, temperature, shear rate, and amount of solids particles.

2.2. Stability of Emulsions:

Stability of the emulsion is determine by the degree of agitation and the nature and amount of emulsifying agent some stable emulsions may take weeks or months to separate if left alone in a tank with no treating . Other unstable emulsions may separate into relatively pure oil and water phases in just a matter of minutes. The stability of an emulsion is dependent on several factor:

1- Differential Density:The difference in density between the oil and water phases is one of the factors that determine the rate at which water droplets settle through the continuous oil phase. The greater the difference in gravity, the more quickly the water droplets will settle through the oil phase. Heavy oils (high specific gravity) tend to keep water droplets in suspension longer Light oils (low specific gravity) tend to allow water droplets to settle to the bottom of the tank. Thus, the greater the difference in density between the oil and water phases, the easier the water droplets will settle.

2- Size of Water droplets: The size of the dispersed water droplets also affects the rate at which water droplets move through the oil phase. The larger the droplet, the faster it will settle out of the oil phase. The water droplet size in an emulsion is dependent upon the degree of agitation that the emulsion is subjected to before treating. Flow through pumps, chokes, valves, and other surface equipment will decrease water droplet sizes.

3- Viscosity*:* Viscosity plays two primary roles in the stability of an emulsion. **First**, as oil viscosity increases, the migration of emulsifying agents to the water droplet's oil–water interface is retarded this results in larger water droplets being suspended in the oil, which in turn results in less stable emulsions in terms of numbers of small water droplets suspended in the oil As oil viscosity increases, more agitation is required to shear the larger water droplets down to a smaller size in the oil phase. **Second**, as viscosity increases, the rate at which water droplets move through the oil phase decreases, resulting in less coalescence and increased difficulty in treating. As oil viscosity increases, the friction encountered by the water droplets moving through the continuous oil phase increases, which in turn impedes separation of the oil and water phases.

4- Interfacial Tension: Interfacial tension is the force that "holds together" the surfaces of water and oil phases. When an emulsifying agent is not present, the interfacial tension between oil and water is low. When interfacial tension is low, water droplets coalesce easily

upon contact. However, when emulsifying agents are present, they increase the interfacial tension and obstruct the coalescence of water droplets. Anything that lowers the interfacial tension will aid in separation.

5- Water Salinity:The salinity of the water is a measure of the total dissolved solids in the water phase. As salinity of the water increases, the density of the water increases, which in turn increases the differential density between the water and the oil. The increase in differential density aids in separation of the oil and water phases. Small amounts of salt, or other dissolved solids, in the water phase will appreciably lower the interfacial tension and thus will decrease the difficulty of separating the two phases. To some degree, this phenomenon explains the difficulty of treating water–oil emulsions formed from soft water typically found in many steam flood operations.

6- Age of the Emulsion: As emulsions age they become more stable and separation of the water droplets becomes more difficult. At such a time the emulsion has reached a state of equilibrium and is said to be aged. The older the emulsion, the more difficult it is to treat.

7- Agitation: The type and severity of agitation applied to an oil–water mixture determine the water drop size. The more turbulence and shearing action present in a production system, the smaller the water droplets and the more stable the emulsion will be.

2.3. De-emulsification:

 De-emulsification is the breaking of a crude oil emulsion into oil and water phases. From a process point of view, the oil producer is interested in three aspects of deemulsification: the rate or the speed at which this separation takes place, the amount of water left in the crude oil after separation, and the quality of separated water for disposal. A fast rate of separation, a low value of residual water in the crude oil, and a low value of oil in the disposal water are obviously desirable.

2.3.2. Mechanisms Involved in De-emulsification:

 De-emulsification, the separation of an emulsion into its component phases, is a two-step process. The first step is flocculation (aggregation, agglomeration, or coagulation). The second step is coalescence. Either of these steps can be the ratedetermining step in emulsion breaking.

1- **Flocculation or Aggregation:** The first step in de-emulsification is the flocculation of water droplets. During flocculation, the droplets clump together, forming aggregates or "floccs." The droplets are close to each other, even touching at certain points, but do not lose

their identity (i.e., they may not coalesce). Coalescence at this stage only takes place if the emulsifier film surrounding the water droplets is very weak. The rate of flocculation depends on the following factors:

A- Water content in the emulsion. The rate of flocculation is higher when the water cut is higher.

B- Temperature of the emulsion is high. Temperature increases the thermal energy of the droplets and increases their collision probability, thus leading to flocculation.

C- Viscosity of the oil is low, which reduces the settling time and increases the flocculation rate.

Density difference between oil and water is high, which increases the sedimentation rate.

D- An electrostatic field is applied. This increases the movement of droplets toward the electrodes where they aggregate.

2- Coalescence: Coalescence is the second step in de-emulsification. During coalescence, water droplets fuse or coalesce together to form a larger drop. This is an irreversible process that leads to a decrease in the number of water droplets and eventually to complete emulsifications. Coalescence is enhanced by the following factors:

- a) High rate of flocculation increases the collision frequency between droplets.
- b) The absence of mechanically strong films that stabilize emulsions.
- c) High interfacial tension. The system tries to reduce its interfacial free energy by coalescing.
- d) High water cut increases the frequency of collisions between droplets.
- e) Low interfacial viscosity enhances film drainage and drop coalescence.
- f) Chemical de-emulsifiers convert solid films to mobile soap films that are weak and can be ruptured easily, which promotes coalescence.
- g) High temperatures reduce the oil and interfacial viscosities and increase the droplet collision frequency.

3- **Sedimentation or Creaming:** Sedimentation is the process in which water droplets settle down in an emulsion because of their higher density. Its inverse process, creaming, is the rising of oil droplets in the water phase. Sedimentation and creaming are driven by the density difference between oil and water and may not result in the breaking of an emulsion. Unresolved emulsion droplets accumulate at the oil/water interface in surface equipment and form an emulsion pad or rag layer. A pad in surface equipment causes several problems including the following.

- A. Occupies space in the separation tank and effectively reduces the retention
- B. Separation time.
- C. Increases the BS&W of the treated oil.
- D. Increases the residual oil in the treated water.
- E. Increases arcing incidences or equipment upset frequency.
- F. Creates a barrier for water droplets and solids migrating down into the bulk water layer.

 Emulsion pads are caused or exacerbated by ineffective de-emulsifier (unable to resolve the emulsion); insufficient de-emulsifier (insufficient quantities to break the emulsion effectively); other chemicals that nullify the effect of the de-emulsifier; low temperatures; and the presence of accumulating solids. Because emulsion pads cause several operational problems, their cause should be determined and appropriate actions taken to eliminate them.

2.4. Methods of Emulsion Breaking or De-emulsification:

 In the oil industry, crude-oil emulsions must be separated almost completely before the oil can be transported and processed further. Emulsion separation into oil and water requires the destabilization of emulsifying films around water droplets. This process is accomplished by any, or a combination, of the following methods:

- a. Adding chemical de-emulsifiers.
- b. Increasing the temperature of the emulsion.
- c. Applying electrostatic fields that promote coalescence.
- d. Reducing the flow velocity that allows gravitational separation of oil, water, and gas.

 This is generally accomplished in large-volume separators and de-salters. Deemulsification methods are application specific because of the wide variety of crude oils, brines, separation equipment, chemical de-emulsifiers, and product specifications. Furthermore, emulsions and conditions change over time, which adds to the complexity of the treatment. The most common method of emulsion treatment is the application of heat and an appropriate chemical de-emulsifier to promote destabilization, followed by a settling time with electrostatic grids to promote gravitational separation.

2.4.1. Mechanical Methods:

 Settling time is required to promote gravity settling of the coalescing water droplets. The time necessary for free water to settle is affected by differential density of the oil and water, viscosity of the oil, size of the water droplets, and relative stability of the emulsion. There is a wide variety of mechanical equipment available for breaking oilfield emulsions including free-water knockout drums, two- and three-phase separators (low- and highpressure traps), desalters, settling tanks, etc.

Electrical Methods:

 Electrostatic grids are sometimes used for emulsion treatment**.** High voltage electricity (electrostatic grids) is often an effective means of breaking emulsions. It is generally theorized that water droplets have an associated net charge, and when an electric field is applied, the droplets move about rapidly and collide with each other and coalesce. The electric field also disturbs the interfacial film by rearranging the polar molecules, thereby weakening. The electrical system consists of a transformer and electrodes that provide high-voltage alternating current. The electrodes are placed to provide an electric field that is perpendicular to the direction of flow. The distance between the electrodes is often adjustable so that the voltage can be varied to meet the requirement of the emulsion being treated.

Chemical Methods:

The most common method of emulsion treatment is adding de-emulsifiers. These chemicals are designed to neutralize the stabilizing effect of emulsifying agents. Deemulsifiers are surface-active compounds that, when added to the emulsion, migrate to the oil/water interface, rupture or weaken the rigid film, and enhance water droplet coalescence. Optimum emulsion breaking with a de-emulsifier requires a properly selected chemical for the given emulsion; adequate quantity of this chemical; adequate mixing of the chemical in the emulsion; and sufficient retention time in separators to settle water droplets. It may also require the addition of heat, electric grids, and coalescers to facilitate or completely resolve the emulsion.

2.4.4. Thermal Methods:

Heating reduces the oil viscosity and increases the water-settling rates. Increased temperatures also result in the destabilization of the rigid films because of reduced interfacial viscosity. Furthermore, the coalescence frequency of water dropl is increased because of the higher thermal energy of the droplets. In other words, heat accelerates emulsion breaking; such as paraffin's and asphaltenes, the addition of heat deactivates, or dissolves the emulsifier and thus increases its solubility in the oil phase. Treating temperatures normally range from (100–160) F (38–70) C. In treating of heavy crudes the temperature may be as high as (300) F (150) C. Adding heat can cause a significant loss of the lower-boiling-point hydrocarbons (light ends). This results in "shrinkage" of the oil, or loss of volume. However it very rarely resolves the emulsion problem alone. Increasing the temperature has some negative effects. First, it costs money to heat the emulsion stream. Second, heating can result in the loss of light ends from the crude oil, reducing its API gravity and the treated oil volume. Finally, increasing the temperature leads to an increased tendency toward some forms of scale deposition and an increased potential for corrosion in treating vessels. The application of heat for emulsion breaking should be based on an overall economic analysis of the treatment facility. The cost-effectiveness of adding heat should be balanced against longer treatment time (larger separator), loss of light ends and a resultant lower oil-product price, chemical costs, and the costs of electrostatic grid installation or retrofitting.

2.5. Thermal treating Equipment:

 Conditioning of oil-field crude oils for pipeline quality has been complicated by water produced with the oil. Separating water out of produced oil has been performed by various schemes with various degrees of success. The problem of removing emulsified water has grown more widespread and often times more difficult as production schemes lift more water with oil from water-drive formations, waterflooded zones, and wells stimulated by thermal and chemical recovery techniques. The area of concern to this research is to study of thermal method that applied in emulsion breaking and their treating equipment which handling with a thermal method as a basic for theory of its operation and discussed their sequence as the following:

2.5.1. Heaters:

 Heaters are vessels used to raise the temperature of the liquid before it enters a gun-barrel, wash tank, or horizontal flow treater. They are used to treat crude oil emulsions. The two types of heaters commonly used in upstream operations are indirect fired heaters and direct fired heaters.

 Both types have a shell and a fire tube. The fire tube contains within it a flame caused by the mixture of air and natural gas ignited by a pilot light and the hot exhaust gases which result from this combustion. The hot external surface of the fire tube heats a bath of liquid in which it is immersed. Indirect heaters have a third element, which is the process flow coil. Heaters have standard accessories such as burners, regulators, relief valves, thermometers, temperature controllers, etc.

2.5.1.1. Indirect Fired Heaters:

 Oil flows through tubes that are immersed in water, which in turn is heated by a fire tube. Alternatively, heat may be supplied to the water bath by a heating fluid medium, steam, or electric immersed heaters instead of a fire tube. Indirect heaters maintain a constant temperature over a long period of time and are safer than direct heaters. Hot spots are not as likely to occur on the fire tube if the calcium content of the heating water is controlled. The primary disadvantage is that these heaters require several hours to reach the desired temperature after they have been out of service.

2.5.1.2. Direct Fired Heaters:

 Oil flows through an inlet distributor and is heated directly by a fire box. Alternatively, heat may be supplied to the water bath by a heating fluid medium, steam, or an electric immersed heater instead of the fire tube. Direct fired heaters are quick to reach the desired temperature, are efficient (75 to 90%), and offer a reasonable initial cost. Direct fired heaters are typically used where fuel gas is available and high volume oil treating is required. On the other hand, they are hazardous and require special safety equipment. Scale may form on the oil side of the fire tube, which prevents the transfer of heat from the fire box to the oil emulsion. Heat collects in the steel walls under the scale, which causes the metal to soften and buckle. The metal eventually ruptures and allows oil to flow into the fire box, which results in a fire. The resultant blaze, if not extinguished, will be fed by the incoming oil stream.

2.5.2. Heater treater:

2.5.2.1. Horizontal Heater-Treaters:

 For most multi-well flow streams, horizontal heater-treaters are normally required heater treater. Design details vary from manufacturer to manufacturer, but the principles are the same. The horizontal heater-treater consists of three major sections: front (heating and water-wash), oil surge chamber, and coalescing sections (see fig. 2).

 Fig (2-2) Simplified schematic of horizontal heater treater

2.5.2.2. Vertical Heater-Treaters:

 The most commonly used single-well treater is the vertical heater-treater. The vertical heater-treater consists of four major sections: gas separation, free-water knockout, heating and water wash, and coalescing-settling sections. Incoming fluid enters the top of the treater into a gas separation section, where gas separates from the liquid and leaves through the gas line. Care must be exercised to size this section so that it has adequate dimensions to separate the gas from the inlet flow. If the treater is located downstream of a separator, the gas separation section can be very small. The gas separation section should have an inlet diverter and a mist extractor (see **fig. 3).**

Fig (2-3) Simplified schematic of vertical heater treater

2.5.2.3. Electrostatic Heater-Treaters:

 Some horizontal heater-treaters add an electrostatic grid in the coalescing section. Figure 7-25 illustrates a simplified schematic of a typical horizontal electrostatic treater. The flow path in an electrostatic heater treater is basically the same as in a horizontal heater-treater, except that an electrostatic grid is included in the coalescingsettling section, which helps to promote coalescence of the water droplets.

 The electrostatic section contains two or more electrodes, one grounded to the vessel and the other suspended by insulators. An electrical system supplies an electric potential to the suspended electrode. The usual applied voltage ranges from 10,000 to 35,000 V, and the power consumption is from (0.05 to 0.0910KVA/ft2) of grid. The

intensity of the electrostatic field is controlled by the applied voltage and spacing of electrodes. In some installations the location of the ground electrode can be adjusted externally to increase or decrease its spacing to the "hot" electrode. Optimum field intensities vary with applications but generally fall within the range of 1,000 to 4,000 V/in. (39 to 157 V/mm) of separation. The use of an electric field is most effective whenever the fluid viscosity is less than 50 cp at separating temperature, the specific gravity difference between the oil and water is greater than 0.001, and the electrical conductivity of the oil phase does not exceed 10−6 mho/cm.

 The electrical control system that supplies energy to the electrodes consists of a system of step-up transformers (either single or three-phase) in which the primary side is connected to a low-voltage power source (208, 220, or 440 V) and secondary windings are designed so that the induced voltage will be of the desired magnitude.

 Oil and small water droplets enter the coalescing section and travel up into the electrostatic grid section, where the water droplets become "electrified" or "ionized" and are forced to collide.

 The electrodes have electrical charges that reverse many times a second; thus, the water droplets are placed in a rapid back-and-forth motion. The greater the motion of the droplets, the more likely the water droplets are to collide with each other, rupture the skin of the emulsifying agent, coalesce, and settle out of the emulsion. Because of the forced collisions, electrostatic heater-treaters typically operate at lower temperatures and use less fuel than horizontal heater-treaters. The time in the electronic field is controlled by electrode spacing and the vessel configuration. An electronic field exists throughout the body of the oil within the vessel, even though most coalescing takes place in the more intense fields in the vicinity of the electrodes.

Fig (2-4) Elecrostatic heater treater

2.6. Special Topics in Crude Oil Emulsions:

 Field Emulsion-Treatment Program: There is a lack of specific case studies on emulsion treatment in the open literature for the following reasons:

- a. An emulsion treatment program is very site-specific. Each producing system is unique and is reviewed individually for solutions.
- b. The scope of emulsion treatment is very broad, and it is usually difficult to address the complexities in generalized studies. Parts of the specifics have been reported extensively.
- c. Most of the operating oil companies have some sort of optimization programs for emulsion treatment. In general, this includes addition of chemicals, heat, and retrofitting.

 The design of emulsion-treating equipment and procedures for a given field or application requires experience and engineering judgment. There is no standard solution available for striking a balance between, for example, the amount of chemical and heat to resolve emulsions. The greater the treatment temperature, the lower the amount of de-emulsifier needed. In general, economic analysis dictates the type and size of equipment used and the balance between the amount of chemical used and heating requirements. In some cases, crude oil specifications may decide the system to be used for emulsion treatment.

2.7. Literature review:

 (Gidley and Hanson, 1974) present an old but very valid case history. A sophisticated and expensive oil-treating system, consisted of a wash tank, four electrostatic heater-treaters, a holding tank and a heater treater for off-spec oil. Severe upsets were experienced whenever wells were stimulated or line were pigged. When these problems were studied, the solution involved, finding a de-emulsifier that would water wet these fines, using a new corrosion inhibiter that did not contribute to emulsion formation, adding a degassing boot upstream of the wash tank, and rearranging the inlet and exit pipes in the wash tank to reduce short circulation. And recommended that, do not create emulsion problems by poor choice of chemicals, Minimize non-ideal hydraulic, and the most sophisticate treatment is not necessary.

In February 1999 (Bojan Hafskjold) and (Harald K.Celious) provide a computer program (FORTRAN code) that make it possible to analyze the different parts of separator system: pipe, inlet section, and the vessel, separately and sequence. The simulation is based on input values for droplet size distribution, flow rate, water cut, separator geometry, adjustable parameters that indirectly describe the physic-chemical properties of the fluid, and parameters that describe the physical condition in the separator system (shear energy). The main conclusion from their study can be summarized as follows, the model can be applied to analysis and improvement of existing separator process, as well as design of a new equipment, evaluation of different options for pigging and inlet design in terms of energy dissipation and coalescence, could lead to alternative design of pigging and inlet section to enhance and improve separator performance, the model gives drop size distribution and remaining concentration of dispersed phase as a function of retention time, and the combined emulsification, coalescence, and settling process of oil/water system has been modeled as a function of initial drop size distribution, energy dissipation, and fluid properties.

 In 2016, Deepankar Chadha and Pulkit Chaudhary attempt to design horizontal heater treater for de-emulsification of crude oil from water for a number of well (ten wells), and they focus on the coalescing section. At the end of their paper they give an economical solution with full validation for their calculation. And recommended, that their calculation methods are done if laboratory data is unavailable.

 These development, plus continuing experience and research, has provided the producer with the necessary tools to break any emulsion in the field and to deliver a salable product to the pipeline or other carrier.

Chapter Three

 Methodology

Chapter 3

Mathematical model and work procedures

3.1. Introduction:

 In an integrated specific methodology, a computer program was used for a thermal treatment calculation that has been done in heater treater sizing. In this study we will provide a computer program that's giving operators and processing engineers an accurate calculation with results that have been compared with manual calculation to ensure that the program provide accurate results. Also create guideline in choosing of heater treater specification, thus, result will be appeared in a better processing and high separation efficiency of heater treater.

3.2. General Design Procedure:

- 1- Choose a treating temperature.
- 2- Determine the heat input required from Eq. (3.5).
- 3- Determine oil viscosity at treating temperature. In the absence of laboratory data.
- 4- Select a type of treater, and size the treater using the appropriate design procedure below.
- 5- Choose the design minimum droplet size that must be separated from experimental data, analogy to other treaters in service or Eq. (3.2).
- 6- Repeat the above procedure for different treating temperatures.

3.3. Sizing a horizontal-treater:

Settling Equation:

 The specific gravity difference between the dispersed water droplets and the oil should result in the water "sinking" to the bottom of the treatment vessel.

Where:

 μ = oil viscosity, cp,

 $T = oil$ temperature, (F) ,

dm = diameter of water droplet, microns.

d Left = 438[
$$
\frac{Qo \mu o}{\Delta SG (dm^2)}
$$
] (3-6)

Where

 $d =$ minimum vessel internal diameter, in. (mm),

 $Qo = oil$ flow rate BOPD (m3/hr),

 μ = oil viscosity, cp,

Leff = length of coalescing section, ft (m) ,

 $\Delta SG =$ difference in specific gravity between oil and water (relative to water).

Retention Time Equation:

 The oil must be held at temperature for a specific period of time to enable deemulsifying the water-in-oil emulsion. This information is best determined in the laboratory but, in the absence of such data, 20 minutes is a good starting point.

Where:

 T_{TO} = retention time, (min).

Heat Input Required:

q= 16 Qo ∆T [0.5 (SG)o + 0.1] ………………………………………….. **(3-8)**

Where:

 $q =$ heat input BTU/hr (kw)

 ΔT = increase in temperature, (F),

(SG)o= specific gravity of oil.

ΔS.G = (S.G)w – (S.G)o ……………………………………………………… **(3-9)**

(S.G)o = 141.5 131.5+ ……………………………………………………. **(3-10)**

Where:

 $(S.G)w$ = specific gravity of water

Design Procedure for Horizontal Heater-Treaters:

- 1- For various standard diameters, develop a table of effective length versus standard diameters, using Eq. (3.3) for settling.
- 2- For the same diameters used in step 1, calculate the effective lengths required using Eq. (3.4). For retention time.
- 3- Select a treater, which satisfies the larger effective length requirements for the selected diameter.

3.4. Sizing a vertical-treater:

Settling Equation:

 = 81.8 [ₒₒ (∆SG)2] 1/2……………………………………………. **(3.11)**

Retention Time Equation:

 d^2 h = $\frac{Qo \, Tro}{Q$ 0.12 ………………………………………………………… **(3-12)**

Where:

 $h =$ height of coalescing section, in. (mm),

Design Procedure for Vertical Heater-Treaters:

- 1. Calculate the minimum treater diameter using Eq. (3.6).
- 2. For various diameters greater than the minimum, calculate the height required in the coalescing-settling section using Eq. (3.7).
- 3. Calculate the height required to keep the oil above its bubble-point pressure if the emulsion is heated after the gas has been separated from it.

 The above procedure allows the production facility engineer to choose the major sizing parameters of heater-treaters when little or no laboratory data are available. This procedure does not give the overall dimensions of the treater, which must include inlet gas separation and free-water knockout sections. However, it provide a method for specifying treater and a minimum size for the coalescing section (where the treating actually occurs) and provides the engineer with the tools necessary to evaluate specific vendor proposals. Final aim for Practical balance was developed by using a program to carry out these procedure for both horizontal and vertical heater treater. A brief description of the program as follows:

3.5. Introduction to Matlab:

 The name MATLAB stands for Matrix Laboratory. MATLAB is a highperformance language for technical computing. It integrates computation, visualization, and programming environment. Furthermore, MATLAB is a modern programming language environment: it has sophisticated data structures, contains built-in editing and debugging tools, and supports object-oriented programming. These factors make MATLAB an excellent tool for teaching and research. MATLAB has many advantages compared to conventional computer languages (e.g. C, FORTRAN) for solving technical problems. MATLAB is an interactive system whose basic data element is an array that does not require dimensioning. The software package has been commercially available since 1984 and is now considered as a standard tool at most universities and industries worldwide. It has powerful built-in routines that enable a very wide variety of computations. It also has easy to use graphics commands that make the visualization of results immediately available. Specific applications are collected in packages referred to as toolbox. There are toolboxes for signal processing, symbolic computation, control theory, simulation, optimization, and several other fields of applied science and engineering.

3.6. Program screens:

- 1- Main screen.
- 2- Treater type selection screen.
- 3- Vertical terater screen.
- 4- Horizontal treater screen.

3.6.1. Main screen:

Fig (3-1) Program main screen

3.6.2. Treater type selection screen:

In this screen two type will appear:

- A- Vertical button
- B- Horizontal button

When selecting one of the two buttons above, the next (input and output screen) will appear.

 Fig (3-2) Treater type selection screen

3.6.3. Horizontal treater screen:

 When the user press on horizontal button on the above screen the horizontal input and output screen will appear, so the user needs to input the following data:

- 1- Oil flow rate.
- 2- API value.
- 3- Basic water sediment percent.
- 4- Retention time value.
- 5- Diameter step.
- 6- Temperature values.

Beside the inputs screen the outputs appear as plotting function and heat required value, after that the following screen will appear.

Fig (3-3) Horizontal treater screen

3.6.4. Vertical treater screen:

Fig (3-4) Vertical treater screen

Chapter Four

Results and Discussion

Chapter 4

Results and Discussion

4.1. Introduction:

 In this chapter we present a heater treater calculations to obtain an optimum effective length, optimum diameter of heater treater, and its required heat quantity. As discussed previously, heater treater calculation depends on settling equation, retention time equation, and heat required equation for both vertical and horizontal treater.

 For designing the heater treater, the input parameters required are oil gravity (API), oil flow rate (bbl/day), inlet oil temperature (F) and Inlet BS & W (percent). After obtaining these parameters, settling equation (at various temperatures) and retention time equation are solved. After that, heat required is estimated followed by selection of adequate d and Leff was done. For solving the settling equation, difference in specific gravity of oil, viscosity of oil, diameter of water droplet in microns at different temperatures is required.

4.2. Calculations:

The input parameters are shown in **table (4-1).**

Table (4-1) the input parameters

4.2.1 Matlab calculations:

After the input parameters in **table (4-1)** have been entered in the program interface the following plotting will appear for both vertical and horizontal treater.

4.2.1.1 Horizontal treater:

Fig (4-1) Matlab plotting for horizontal treater

 From above plot it is obviously that the first point come out above the retention time line (green line) is intersecting between the settling equation at $T=80$ F (red line) and the retention time equation (green line). This point represents the optimum dimension of heater terater. So the optimum diameter and effective length of heater are Leff = 9.33 ft and d = 76.36 respectively.

4.2.1.2. Vertical terater:

From the following plot it is clear that there are three points where the retention time equation (blue line) intersect with settling equation at different temperature (red, green, and black line), and the heater treater can work at the three conditions of temperature, which indicates that the economical and operational consideration have been taken to identify the optimum dimensions (diameter and height).

Fig (4-2) Matlab plotting for vertical treater

 According to above plot there are three choices for diameter and height, **first** d=103inch, h= 44inch, **second** d= 85 inch, h= 62 inch, **third** d=77 inch, h= 80 inch, and the optimum selection is made for the choice two because it provides suitable heat quantity. So the optimum diameter and height of vertical heater treater are d= 85 inch and h= 62 inch respectively.

 The required heat to break the emulsion inside the heater terater is the same for both vertical and horizontal treater and it equal to (0.8826 mm btu/hr).

4.2.2 Manual calculations:

Manual calculation was made to ensure that the matab program gives accurate results.

4.2.2.1 Horizontal heater terater:

 The primary parameters in heater treater are the temperature, specific gravity of oil which calculated from **Eq (3-10)**, difference in specific gravity between oil and water which calculated from **Eq (3-9)**, oil viscosity calculated with the help of **Eq ((3-2),(3- 3),(3-4),(3-5)),** and water droplet diameter which calculated from **Eq (3-1)**.All of this parameter and their values are summarized in **table(4-2)**.

Table (4-2) settling and retention time parameters

 The settling equation is given by **Eq (3-6)**, using this equation and retention time equation **Eq (3-7)**, a combination of d and Leff at different temperature has been calculated and shown in **table (4-3).**

Table (4-3) Combination of d and Leff at different temperature

The above values of effective length and diameter have been taken and entered in excel sheet and gives the following plot (see **Fig (4-3)**).

Fig (4-3) Excel plotting for horizontal treater

 From the above plot as discussed in matlab calculation the first point intersected with the retention time line is at leff = 9 ft. and $d= 76$ inch, and represent the optimum dimension of heater treater with heat required equal to (0.8826 mm btu/hr).

4.2.2.2 Vertical heater terater:

 As discussed above in horizontal treater manual calculation, the input parameters for the settling equation and retention time equation for vertical treater are given in **table (4-4)**.

No	$\mathsf T$ (F)	$\triangle S.G$	μ (cp)	Om (micron)	(in)
$\mathbf 1$.	80	0.19	19.42	419.85	104.23
2.	100	0.19	9.23	348.60	86.54
3.	120	0.19	5.61	307.80	76.41

Table (4-4) data required for settling and retention time equations

 By using settling equation **Eq (3-11**) and retention time equation **Eq (3-12)** the following values of diameter, height, and heat required are summarized in **table (4-5)**.

Table (4-5) Diameter, height, and heat required for vertical treater

 Fig (4-4) Excel plotting for vertical treater

 From **Fig (4-4)** and according to economical consideration, the optimum choice is made for the point where the retention time equation (blue line), intersect with the settling equation line (grey line), and the optimum values are height $h=60$ inch and diameter $d = 85.5$ inch with heat required equal to $(0.8826 \text{ mm} \cdot \text{btu/hr})$.

4.3. Results:

Horizontal treater:

 The above study reveals that the effective length should be ideally equal to 9.33 ft in case of matlab and 9.1 ft. in case of manual calculation, and the diameter should be 76.36 inches in case of matlab and 76 inches in case of manual, with the heat required equal to 0.8826 (mm btu/hr).

Vertical treater:

 Also the study reveals that the optimum diameter should be equal to 85 inches in case of matlab, 85.5 inches in case of manual calculation, and the height should be

equal to 62 inches in case of matlab, 60 inches in case of manual calculation, with heat required equal to 0.8826 (mm btu/hr).

This following tables summarize the above results:

Horizontal terater:

 Table (4-6) Optimum diameter and effective length for horizontal treater

Vertical treater:

Table (4-7) optimum diameter and height for vertical treater

Heat required for two types of treater:

No	Heat required
	0.8826

 Table (4-8) required heat

4.4. Discussion:

 From results that obtained we run a different scenarios with a different temperature values until attained the optimum variables values (effective length, diameter, height and required heat) that satisfy the two equation (settling and retention time equation) for both horizontal and vertical heater treater. Hence the importance of our calculation procedure its represent a simple and alternative method rather than manual calculation which lack of accuracy and consume time, also we consider economic aspects in our design. Water entered the treater with high ratio of water cut will leave the treater with less than 0.5 percent.

 There is a little different in the result calculated in **table (4-8)**, **table (4-10)** due to the expected error in manual calculation and handling the values from different plots

Chapter Five

Conclusion and Recommendations

Chapter 5

Conclusion and Recommendations

5.1. Conclusion:

 This research included developing a computer program to calculate the effective length, diameter, and heat required for both vertical and horizontal heater treater to minimize water cut to less than 0.5 percent.

 After the data was entered to the program input-interface, the program provides results, to ensure the accuracy of that results we compare it with manual calculations, and we found that there is a little difference between the program and manual calculations.

 After Comparing program results with results obtained from manual, we found that for horizontal treater (Leff = 9.33 ft and $d = 76.36$ in), and for vertical treater (h = 62 in and $d = 85$ in) with heat quantity equals to (0.8826 MM BTU/Hr).

5.2. Recommendations:

- 1. This program also can be applied on field site in case there is already a heater treater with known Parameters to adjust the flowing temperatures.
- 2. One of the limitations of our program is manual handling to values from plots, so we recommended to use alternative method more accurate such as provide a code to handle the values from plots automatically.
- 3. When there is more than one value for optimum diameter and corresponding height and length it's better to consider economic aspects.
- 4. The program depends primarily on the intersect between the settling equation and retention time equation. If there is no intersection, we recommended to adjust the parameters until satisfaction the requirement.

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