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Experimental study of desalting crude oil

Hanoon Hasan[1], Ali Nooruldeen[2], Huwaidah Ibrahim Ahmed[3], Maryam Jebur Jaafer[4]
[1,2,4] Department of Petroleum Engineering, University of Misan, Iraq
[3] Department of Production Engineering and Metallurgy, University of Technology, Baghdad, Iraq

Abstract

The project was done on AL-NOOR crude oil the process desalting was difficult for these reasons. The variance amongst the oil density & water density is small and oil's viscosity is relatively large so that the rate of droplet setting of water is few in the desalter. Heavier oils as well tend to include additional amounts of naturally occurred emulsifiers in comparison to the lighter crude oil this behave coalescence of a water droplet and allow the formation of stable emulsions in the desalter.

The aims of the current study are: Find a new method to extract water from crude oil emulsions, which involves: Determine conductivity of water in crude oil which in turn help to determine the salt amount in the emulsion and determine the volume of extracted water from crude oil.

The importance of this research comes from the fact that it addresses the removal of reservoirs water from crude oil in order to reduce the wear and tear of equipment for storing and transporting crude oil, which contributes to reducing costs and maintaining environmental integrity.

Keywords: desalting, crude oil, conductivity, ethanol, and conductivity

Corresponding Author:

Ali Nooruldeen
Department of Petroleum Engineering, University of Misan
Misan, Iraq
Email: **ali.nooruldeen@uomisan.edu.iq**

1. Introduction

Crude oil dehydration and desalting processes are based on the removal of water droplets from the crude oil. In the case of crude oil desalting, the dehydration process is preceded by wash water dosage and upstream of the desalter, which reduces the remnant water's salinity in crude. Thus, the water for wash does not essentially have to be fresh rather it should have less salinity in comparison to the water produced [1]. A great variance is observed in the crude oil's salt content relying essentially on the source or perhaps the category of generating wells and oil zones in the field. Thus, mineral salts alter along with geology formation possibly up to the 200,000 ppm. Additionally, the water of slat inoculated by tanker during shipment might subsidize to the total of content of salt at the refinery. In most of the circumstances, the crude oil's salt content comprises the dissolved salt in tiny water droplets which are distributed in crude oil. The processing unit in the oil refinery is utilized for the removal of salt from the crude is termed as a desalter [1-3]. The primary procedure is desalting in the refining of crude oil. Thus, the crude does not contain salt rather it is dissolved in water. After the desalter, the content of salt is normally measured in salt's pounds per thousands of crude oil barrels (PTB).

The desalted expression might refer to the water's desalination facility which is utilized to treat the agricultural runoff's brackish water. This might be completed to decrease the river water's salinity afore it's passing the international border normally to submit the treaty's terms or to synthesize the drinkable water for the consumption of animal and human. Deserters are also utilized to treat the groundwater reservoirs in the cattle dairies & feedlots' affected region. Moreover, the chemical composition of such salts vary, but then again almost every time sodium chloride (NaCl) having a smaller amount of magnesium and calcium chlorides. Thus, the salts which are recurrently existent in crude are calcium chloride, sodium and magnesium. When such components are not detached from oil, several issues appear in the process of the refinery. Thus, the crude oil is commonly exposed to the processing closer to the oil field's sites to eradicate the brine from oil afore the transportation of the crude to the petroleum refinery via tanker trucks, pipe-lines, sea-going crude tankers and railway [3-6].

Commonly, the oil field facilities struggle to remove the adequate sediments, salts and water that the transferred crude oil involves with a percentage of less than 1-2% by the water & sediment volume (BS and W) as well as for the pure less than 10 to 20 pounds salts/ 1000 barrels (PTB) and petroleum-free of water which is equal to the content of salt 34 to 68 part/ million by weight. However, crude oils are still offered to the petroleum refineries having a content of salt that ranges from 34-1020 part/ million by weight rendering to the spot samples of numerous distinctive crude oils as transmitted to the refineries. Further, crude oil comprises extremely tiny elements for instance, arsenic (As), cadmium (Cd), nickel (Ni), copper (Cu), vanadium (V) and lead (Pb). All of these could cause several issues in several processing units in petroleum refineries. This might be present in the form of salts that are water-soluble or in form of organo-metallic or oil soluble compounds. Regarding the water content's measurements, numerous processes are being considered in literature comprising laboratory tests and online control devices processes such as depending on the facilities obtainable, methods of standard laboratory [7-9].

Bartley (1982) designated how heavy crudes comprise of exclusive complications that demand extra design necessities. Anon (1983): recorded that could develop the efficiency of desalting. Baranov et al. (1986) suggested vessels of hydro-cyclone for usage in the initial or complete separation of non-homogeneous systems of liquid-liquid category, for instance, emulsions of water-oil. Chawla (1987) examined the wet crude problem in Kuwait & requirement for plants of desalting. Schramm (1992): explored the major principals of the emulsions of petroleum, thus, author elaborate the parameters which impact the stability of emulsion are: emulsifying agent's control, agitation control, water percentage, emulsion age, viscosity and differences in density. Moreover, the author also stated that the accomplishments of techniques of chemical treatment depend upon on the degree of heating, chemical and adequate settling resident time. Schramm also characterized techniques of sampling and testing that help in describing the composition of the stream and thus in estimating how effective a special separation process [10].

Taylor (1996) concentrated on the electrically boosted parting level of the emulsions of water-in-oil. He also utilized DC, AC pulsed DC and collection of them in the isolation of oil-water emulsions as well. Further, Al-Kandari (1997) identified several issues synthesized from the streams of wet crude oil while decreasing the efficiency of corrosion and catalysts. There are numerous current researches that elaborate the improvement of a complete grade development. An overall framework for stripping water from the crude oil require more treating after the gravitational isolation. The exist of salts in crude is one of the most significant problems facing the oil refinery [11]. These salts may contribute to:

1) The equipment corrosion by the hydrolysis of salt resulting hydrogen chloride,
2) The mechanical plugging of furnace tubes condensers and lines by deposition,
3) Still residue high ash content,
4) The deactivation of catalysts employed at the refinery.
5) Transporting ''water-in-oil'' high viscosity liquids and emulsions that need additional energy of pumping.

In addition, water and salts are stripping in day-to-day processes for threes three reasons: scale formation, corrosion, & catalysts activity lowering. As show in figure (1). The Aims of study involve Determine conductivity of water in crude oil, and Determine volume of extracted water.

Figure 1. Corrosion in pipes due to high viscosity liquid flow

The aims of the current study are: Find a new method to extract water from crude oil emulsions, which involves: Determine conductivity of water in crude oil which in turn help to determine the salt amount in the emulsion and determine the volume of extracted water from crude oil.

The importance of this research comes from the fact that it addresses the removal of reservoirs water from crude to reduce the wear and tear of equipment for storing and transporting crude oil, which contributes to reducing costs and maintaining environmental integrity.

2. Theory

The quantity of salts, sediment and water in the petroleum as received at crude oil refineries differs exceedingly with the petroleum' source, the earlier processing of petroleum at locations of source along with the transporting procedures from its origin to refineries. Essentially, production of raw oil through wells and drilling into the reservoirs of petroleum consists of brine (e.g. inorganic chloride salts consisting of water). The observed quantity of the salts of chloride among brine might be up to 20% by its weight. As water emulsifies the some of the crude oil. Moreover, the presence of salts in petroleum might comprise some of the ionized dissolved salts in brine whereas, the crystal forms distributed in oil. Thus, the occurrences of salts in petroleum are chlorides with the estimated breakdown as follows: 10% per weight Calcium chloride (CaCl2), 15% by weight Magnesium chloride (MgCl2) and sodium chloride 75% by weight (NaCl) [3, 5, 8]. The petroleum crude consists of sediment including asphaltenes, rust, iron sulfide (FeS), clay and several other water-insoluble particles.

The crude oil distillation unit (CDU) is the initial processing unit in nearly all petroleum refineries. The received crude oil is distilled by CDU to the several fractions of numerous boiling ranges which is then administered to other units of the refinery for processing. The electrostatic desalters ae used to produce the dehydrated and desalted crude containing less content of sediments. Almost, all refineries now utilize the electrostatic desalters. However, there might be a few numbers of refineries which utilize the older and less appropriate method to provide the chemical & settling tanks, to remove the water and salts. Moreover, sediment is essential to prevent the extra entangling of the equipment and corrosion from all the produced HCl or hydrochloric acid through the hydrolysis of the chloride salts existing in the obtained crude oil, more specifically, magnesium chloride (MgCl2) and calcium chloride (CaCl2). Any sort of unstripped salts indicates a purpose of minerals which can poison the expensive catalysts utilized in several operations of petroleum refinery [7].

Numerous meters have been created on the literature of petroleum and water content for the estimation of crude oil specimen's electrical characteristics which are under the influence of water content. Consequently, the blend of upright homogeneous conditions must be achieved. Hence, as a key parameter of magnitudes, homogeneity depends on the electrical properties as well as is serious for the optimal sampling to attain the demonstrative samples [2]. Test systems of three standard lab-scale have been utilized to find the content of salt in petroleum [4,8,9]:

1. Titration and extraction by traditional Mohr's technique that comprises the content of salt which is determined by extraction method and volumetric titration.
2. Potentiometric practices include the services of an extraction device which is electrically heated extraction device and with a further addition of a weighed aliquot of petroleum previously dissolved in xylene. Thus, the fixed water, alcohol and acetone volumes are also added as an extraction fluid in the device.
3. The electrometric technique is established on the valuation of crude oil's solution conductivity in the blended solvent of alcohol through the utilization of the electrode's set and beaker. The content of salt (chloride) is acquired by the chloride calibration curve vs. recognized mixtures' concentration of conductivity.
4. Microwave irradiation: provides an uncontaminated, lower cost and adequate heating process which sometimes offer higher yields and shorter times for reactions. The liquid heating utilizing the microwaves could be revealed through the interaction of matter with incident irradiation's electric field resulting in movement of ions and stimulating the continuous dipole molecules as well. Summarizing this, the usage of microwave to separate the oil & water phases showed higher rates that are being mentioned for the following mechanisms:

(i) The fast heat emulsions of microwaves reduce oil's viscosity (continuous phase), hence, supporting the contact of water droplets.

(ii) The escalation of temperature could cause a decrease in the rigid viscosity. However, the natural species that are surface active for instance, waxes, oil-soluble organic acids, asphaltenes, resins & solids inside the interface of oil and water makes the adhesion easier amongst the water's dispersed droplets.

(iii) The molecular rotation is excited by the microwave which further balances the zeta potential's dispersed droplets. Hence, reducing the stabilization of active species' ionic surface.

(iv)The ideal microwaves' absorption through the droplets of water in the emulsions of oil in water causing a huge pressure in all those droplets, which further instigates the extension of dispersed phase as well as a decrease in interfacial width. Contrarily, the chemical breakage of the bonds cannot be encouraged through absorption of simple microwaves in lower photon's energy in comparison to the energies related to the chemical bonds. The utmost substantial aspects affecting the performance of desalting which have been observed and considered comprise:

1) Settling time: The maximum desalting and dehydration devices rely upon the effect of gravity to isolate the droplets of water from a continuous phase of oil. The variation in gravity is a dynamic factor in such practice; production of the water droplets is denser as compared to the displaced oil's volumes. The produced water recurrently transfers some thin film of oil-coated salts and solids or spontaneously.

2) Injection of chemical demulsifier: The chemical destabilizers are used to further treat the emulsions. Such surface-active chemicals are adsorbed to an interface of water and oil, break the film around the water drops & dislodge the agents of emulsification agents back into oil. Thus, film breakage permits the drops of water to collide through a natural molecular attraction force. The demulsifier' propagation occurs with the assistance of time & turbulence through the oil to an interface.

3) Heating: Heat causes a reduction in the thickness, cohesion & viscosity of the film around the drops of water. It also decreases the oil viscosity of the continuous phase while assisting the water drops to pass quickly and freely for assimilation. The control of temperature during procedures is a peculiar job. Any extra heat might cause evaporation that leads to the not just loss in oil volume rather a decline in the price because of the drop in the API gravity.

4) Dilution through freshwater: salts infrequently come in crystal line's solid form in the emulsion. Therefore, there is a requirement to dissolves these crystal salts by freshwater which has become an essential factor in procedures of desalting and dehydration. Hence, the freshwater is commonly inoculated before the rise of mixing efficiency through exchangers to inhibit the scaling inside the pipes and scaling tubes.

5) Mixing: actions of high shear from the emulsions. Likewise, the addition of diluted freshwater to the freshwater requires mixing to dissolve the salt's crystalline as well as to assist the assimilated distributed droplets. Mixing is carried out in three steps: it helps the combining of smaller droplets, mixes the chemical demulsifier with the emulsion, and breakdown of free inoculated wash water's volume into the drops of emulsion size while distributing it equally.

Electric mixing was proposed as a highly efficient substitute for the conventional valves in mixing the dilution water and the crude oil in the crude oil desalting plant, Hosseinpour, 2017.
ZhenjunWang et al., 2018 the static experiment of super heavy crude oil demulsification and dehydration using ultrasonic irradiation at high temperatures.

3. Experimental work

The experimental work was achieved in Misan oil company (MOC) laboratory as in the following steps.

3.1 Several experimental tools were used in this work these are:

1. A thermometer is a device that measures temperature;
2. pipette used to pull up water extracted;
3. The centrifuge is a laboratory piece device, motor-driven, which help in liquid samples spins at high velocity. There are different centrifuges types, rely on the size and capacity of the sample. Similar to all other centrifuges, centrifuges of laboratory work by the principle of sedimentation, where the acceleration of centripetal is used to separate higher and lower density substances;
4. Graduated cylinder, is a laboratory device piece used to determine the liquid volume. Graduated cylinders are usually more precise and accurate than laboratory beakers and flasks.
5. Flask: it is help extensions that could be added to application properties as if they were applied in Flask itself. Extensions exist for the map of object-relational, upload handling, form validation, different open technologies of authentication and many mutual framework related devices.
6. Tubes are laboratory equipment pieces used to hold a small number of substances subject to testing or experimentation. They are generally made of glass and differ in purpose and size.

7. Magnetic mixer or magnetic stirrer is a laboratory tool that utilizes a rotating magnetic field to raise a stir bar liquid immersed to spin with high speed, so stirring it. The rotation field can be created either by a rotation magnet or a stationary electromagnet set, placed below the container that contains liquid.

3.2 Material used in experiment

1. Crude oil: the crude oil in this project is from NOOR oil field in **Misan** city. The properties of crude as in the Table 1.

TABLE 1. NOOR crude oil properties

Sample	T °C	Density at T 24 ° C	Density at 15° C	API
NOOR-1	24	0.904	0.9097	23.9

2. Distilled water: in this water, it had been used a distilled water in order not to affect the conductivity which causes error in the experiment

3. NaCl: it is used in order to draw a calibration chart for the conductivity as shown in the next section.

4. Ethanol: Ethanol including gran alcohol and ethyl alcohol is clear, having a tolerable odor in hydrous dilute solution. Moreover, this is lightler in flavour, however, in more rigorous circumstances, this has a burning like the taste. Thus, Ethanol (CH3CH2OH) is an alcoholic group of chemical compounds, whose molecules comprise a carbon atom with which a hydroxyl group –OH is attached. Therefore, the Ethanol was selected in this research due to its no. of properties which assist the solvent according to its principles and crude oil's reduced viscosity Figure (2). The density of Ethanol is 0.789g/ml at 20 ° C while melting point is – 114.1 ° C as well as the boiling point is 78.5 ° C. However, the low freezing point of ethanol has prepared it to be useful as the fluid of thermometers for temperatures underneath the freezing point of mercury (–40°C), and for purposes of lower temperature, for instance, for the anti-freeze radiators of automobiles.

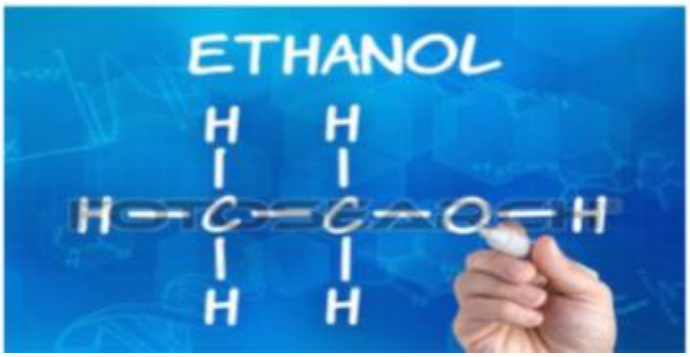

Figure 2. Ethanol

5.demolsphire: to break the bounds between oil and water in order to easily extracted water.

3.3 Experimental parameters

Four main parameters were tested in details: freshwater addition as per cent, chemical dosage (part per million, ppm), settling time and temperature. It is famed how settling time and temperature influence viscosity of oil and the downward settling rate respectively. The experimental designing that was a count in this study actually, settling time is observed in the primary level of designing & manufacture of dehydration or desalting plants, which is implemented by the designer depending on customer's inclinations. Though, rate of flow is the main factor which subsidizes the time setting & thus, could vary on a daily basis. However, the current experiment would focus on the three parameters designated over the operations of desalting and dehydration.

3.4 Experimental procedure

1- (10) ml from freshwater was added to (50) ml of crude oil
2- Mixture was mixed used magnetic stirrer for (10) minute
3- Then added 5 drops of demolsphire and 50 ml from xylene and shake the mixture.
4- Putting the mixture in an electric oven for 15 min.
5- Put the mixture in the centrifugal is rotated at 500 rpm at a specific time.
6- Read amount the separated water in a tube of the centrifugal and pull up by pipette.
7- The last step is to determine the conductivity of the extracted water and by use of the chart, and salt's quantity in the crude oil was quantity observed.

Figure 3. Pull extracted water by pipette

Figure (3) pull the extracted water from the centrifugal tube by pipette the same technique was done to determine salt quantity in crude oil but with settling time of 24 minutes to rely on the effect of increasing the settling time. Thus, to study the change the quantity of distilled water impact that had been added to wash the crude oil to show if its impact on the extracted salt from the crude oil and to discover the heating effect the sample crude oil with water that was heated to 50º c while stirring it with the magnetic stirrer then put it into the centrifugal and rotate at 500 RPM then separate the water and measure the conductivity to determine the salinity. The same procedure was done to determine the salinity with increasing the temperature to 70ºc.
To find the impact of Ethanol dosage (CH3CH2OH) petroleum was mixed with 10 ml of water and 5ml of Ethanol and it had been mixed at the magnetic stirrer for 10 min and put in the centrifugal for 10 min at 500 RPM then the conductivity was measured and by the use of the salinity chart the salinity was determined but after the conductivity of the distilled water & the Ethanol was minus from the value of the conductivity of the mixture the same procedure was done for the amount of 10 ml of Ethylamine.

3.5 The conductivity chart

To determine the quantity of the salt in the crude from the conductivity that we had measured we should make the conductivity chart by adding an amount of salt to distilled water (known conductivity) for a different amount of salt amount and from the conductivity that we measure for the extracted water for each experiment we can determine the amount of salt in each time. amount of conductivity increases with the amount of NaCl as see in figure (4) and table (2). Figure (5) to figure (8) experimental results.

Table 2. NaCl & conductivity

NaCl (ppm)	**0**	**20**	**30**	**40**	**50**	**150**	**200**	**300**	**400**
Conductivity (µsec/cm)	200	341	462	612	776	1352	1414	1572	1672

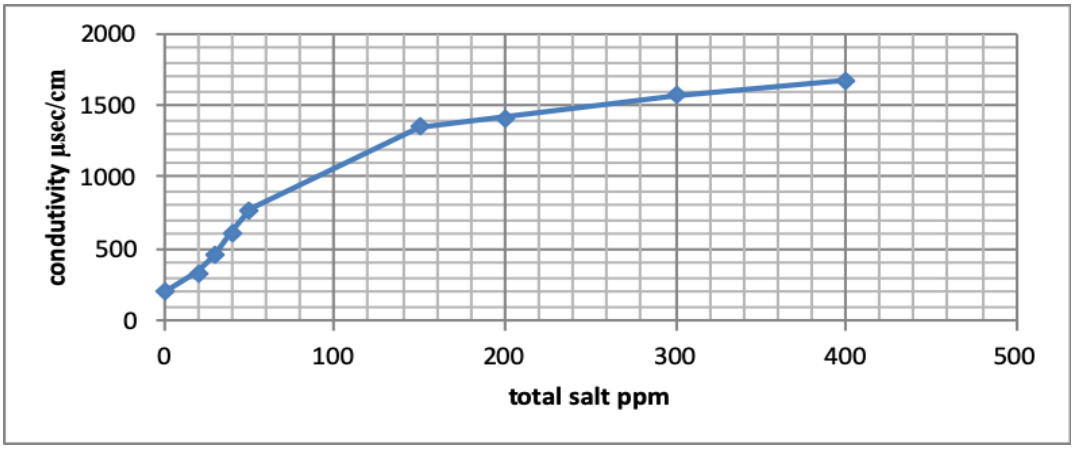

Figure 4. Conductivity Chart

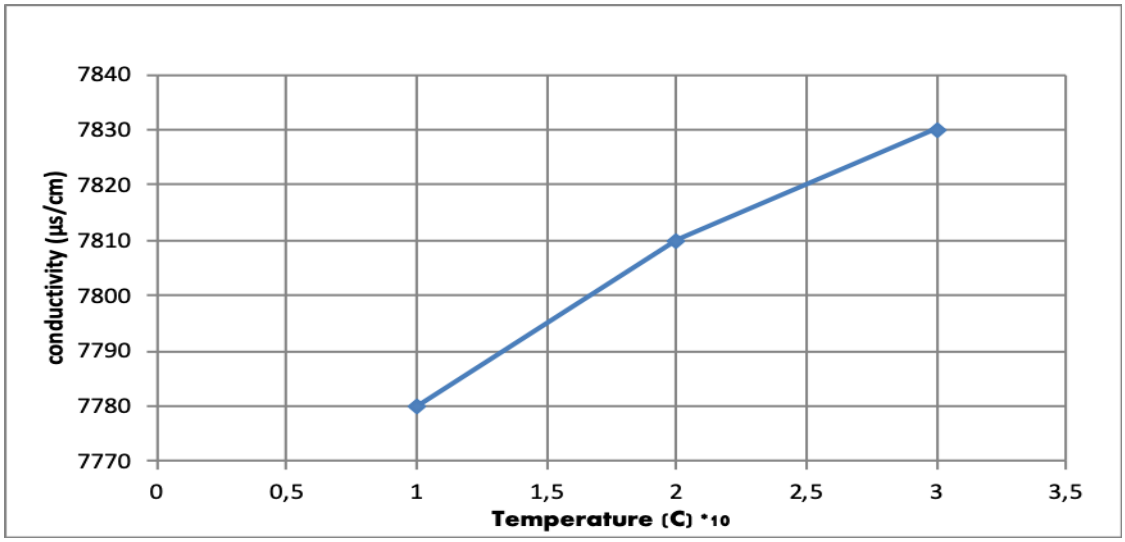

Figure 5. Relationship between temperature and conductivity

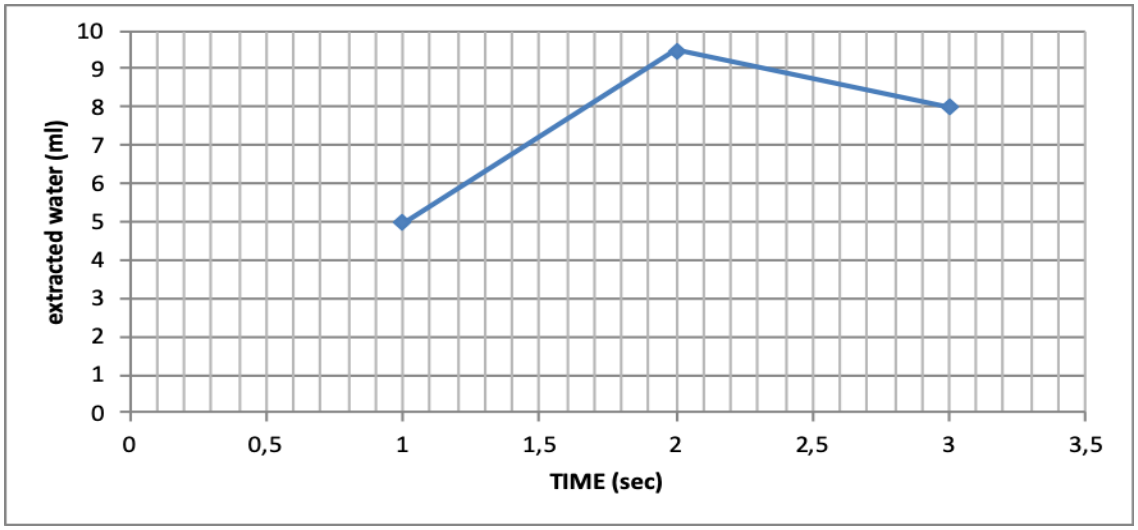

Figure 6. Relationship between settling time and extracted water

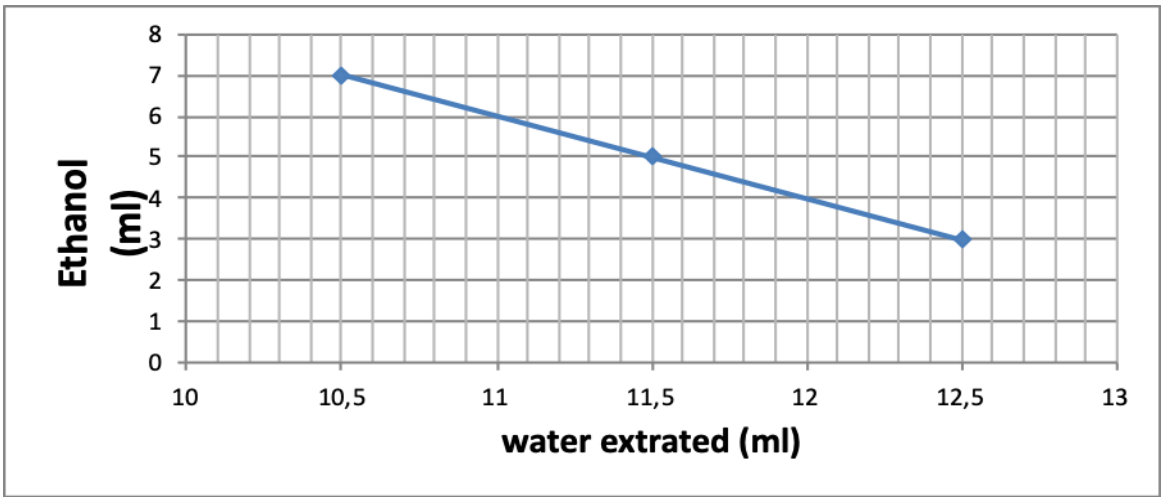

Figure 7. Chemical dosages, water separated for AL-Noor1 crude oil

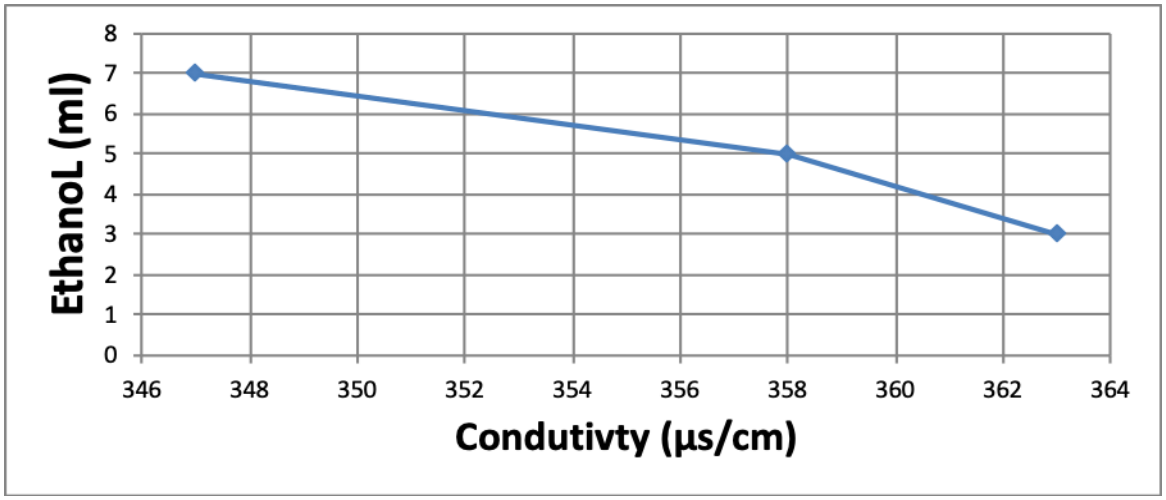

Figure 8. Relationship between chemical dosage and conductivity

5. Conclusions

The project was done on AL-NOOR crude oil the process desalting was difficult for these reasons. The density variation amongst the oil & a water is smaller while the oil's viscosity is comparatively higher. Thus, the rate of the settling of water droplet in desalters is settling is slightly low. Moreover, the heavier oils comprise of additional naturally forming emulsifiers as compared to the lighter crudes which inhibit the cohesion of water droplet while stimulating the formation of stabilized emulsions in desalter. To control all such difficulties, we follow the following: Added water (washing process) to help the separate water, where small water molecules stick with the big. Heat: heat reduces the viscosity and thus increase susceptibility the separate, and Demolsphire: to break the bounds between oil and water. In some test it is not possible to extract much water to measure the conductivity since the device does not measure for an amount less than 5 ml, so dilution was done to the extracted water by adding distilled water to increase amount water.

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