MODELLING OF DEMULSIFICATION PROCESS OF WATER IN CRUDE OIL EMULSION BY NEW DEMULSIFIER

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Abstract

Castor Oil is a natural raw material, used to prepare Brominated Castor Oil (BCO) and quaternary ammonium salt based castor oil (TEt-CO). The two products were tested as demulsifiers and compared with a commercial demulsifier (Chimec2439) by using bottle test method. BCO showed a high ability on water separation efficiency 90% with a dose of 150µl at 120min time settling while TEt-CO showed a low water separation efficiency reached to 10%. The effect of the demulsifier BCO was tested by varying different variables which have an obvious effect on water separation efficiency such as: dose, temperature, time of mixing emulsion, pH and salinity of aqueous phase of emulsion, and water ratio. The effect of some additives (i.e. methanol, ethanol, xylene and toluene) on the efficiency of the BCO was tested for the purpose of enhancing its effectiveness to break the crude oil emulsion. The experimental data obtained by using BCO were formulated as a model using the Artificial Neural Networks (ANNs) to evaluating the water separation efficiency. Multi-layer perceptron artificial neural network was developed based on the collected data of this study. The results showed that the training algorithm of back propagation (BP) is sufficient enough in predicting BCO efficiency under different operation conditions. It was found that the correlation coefficient values are 0.9995 and 0.9999 for the testing and training data, respectively and the mean square error (MSE) was $6.18*10^{-5}$ at 200 epochs.

عملية كسر الاستحلاب لمستحلب الماء في النفط الخام باستخدام كاسر استحلاب جديد
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الخلاصه

زيت الخروع مادة أولية محلية طبيعية استخدم لتحضير بروميد زيت الخروع (BCO)، وملح رباعي الأمونيوم (TEt-CO). تم اختبار هذه المنتجات كمواد كاسرة للاستحلاب بالمقارنة مع كاسر استحلاب تجاري (Chimec2439) بأستخدام طريقة اختبار القنينة (Bottle Test). وأظهر الـ BCO قدرة جيدة على فصل الماء من مستحلب النفط الخام وصلت إلى 90% بجرعة 150µl عند زمن ترسيب 120min في حين أن (TEt-CO) أظهر كفاءة فصل منخفضة وصلت الى 10% . تم دراسة تأثير مجموعة من المتغيرات على عملية كسر الاستحلاب باستخدام المادة الكاسرة للاستحلاب الـ BCO حيث كان لهذه المتغيرات تأثير واضح على عملية الفصل والمتغيرات المدروسة هي: الجرعة، درجة الحرارة، زمن خلط المستحلب، درجة الحموضة والملوحة للطور المائي من المستحلب و أخيرا نسبة الماء . كما اختبر تأثير بعض المضافات (وهي الميثانول, الايثانول, الزايلين والتولوين) على كفاءة الـ BCO ولغرض تعزيز فعاليته على كسر مستحلب النفط الخام. البيانات التجريبية التي تم الحصول عليها باستخدام الـ BCO صيغت بواسطة الشبكات العصبية

الاصـطناعية (ANN) لتقيـيم كفـاءة الكاسـر علـى فصـل المـاء . طـورت شـبكة عصـبية اصـطناعية متعـددة الطبقـات بالاسـتناد علـى بيانـات هـذا العمـل. أظهـرت النتـائج أن خوارزميـة تـدريب الرجـوع العكسـي(BP) هـي كافيـة للتنبـؤ بكفـاءة الــ BCO فـي ظـل ظـروف تشـغيل مختلفـة. فقـد وجـد أن قـيم معامـل الارتبـاط هـي 0.9995 و 0.9999 , لبيانـات الاختبـار والتـدريب علـى التـوالي ، وكـان مربـع متوسـط الخطـأ بـين القـيم التجريبيـة ومخرجـات البرنـامج (MSE) هـي $6.18*10^{-5}$ لـ 200 محاولة .

Keywords: demulsification, water in crude oil emulsion, brominated castor oil, ANN.

Introduction

Crude oil is rarely produced alone because it's generally mixed-up with water. Produced water may be as "free" water (i.e., water that will settle out fairly rapidly), and it may be in the form of an emulsion. A specific definition of the emulsion is dispersion (droplets) of one liquid in another immiscible liquid. The phase that is present in the form of droplets is the dispersed or internal phase, and the phase in which the droplets are suspended is called the continuous or external phase [1]. The more common emulsion in the produced oilfield is the water in oil emulsion. There are three main criteria that are necessary for formation of crude oil emulsion. Crude oil emulsions form when crude oil and water (brine) come into contact with each other. Sufficient mixing or agitating effect must be provided in order to disperse one liquid into another as droplets. 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 third factor important in emulsion formation is the presence of "Emulsifiers" [1,2,3]. The emulsifiers stabilize emulsions and include surface-active agents and finely solids. Surface-active agents (surfactants) are compounds that are partly soluble in both water and oil. Because of this molecular structure, surfactants tend to concentrate at the oil/water interface, where they form interfacial films. That film enhances the stability of an emulsion by increasing the interfacial viscosity. Highly viscous interfacial films retard the rate of oil-film drainage during the coalescence of the water droplets by providing a mechanical barrier to coalescence, which can lead to a reduction in the rate of emulsion breakdown [1,3,4,22]. Due to the complex composition of crude oils, it is common to characterize each crude oil in terms of the four fractions (SARA): Saturates (S), Asphaltenes (A), Resins (R) and Aromatics (A) based on their polarity and solubility in the solvent [2,23] Resins, Saturates, and Aromatics, most of the times they cannot alone produce stable emulsions. However, they can associate to asphaltenes and affect emulsion stability. Resins solubilize asphaltenes in oil, and remove them from the interface, therefore lowering emulsion stability [4,24]. Emulsions are undesirable because the volume of dispersed water occupies space in the processing equipment and pipelines, causes corrosion in the pipelines and increases the cost of transportation and refining. A process of breaking emulsions in order to separate water from oil is called Demulsification, which is also one of the first, steps in processing the crude oil [1,5]. Demulsification is carried out by using either four methods such as mechanical, thermal, chemical and electrical. Chemical demulsification is the most widely applied method of treating water-in-oil and oil-in-water emulsions and involves the use of chemical additives (demulsifiers) to accelerate the emulsion breaking process. Demulsifiers 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 [1,25]. The different demulsifiers are generally tested through a "Bottle Test" method, which consists of adding a given

demulsifier in small bottles containing freshly sampled emulsion and following the percentage of decanted water as a function of time.

The aim of this study is to prepare a new demulsifier from local natural sources which are in comparison with the imported demulifiers were cheap and available as raw materials. A simple reaction to produce Brominated Castor Oil (BCO) from castor oil by bromination of the double bond in castor oil with bromine liquid (Br_2) was done. And then the brominated castor oil reacts with triethylamine [$N(CH_2\text{-}CH_3)_3$] to produce quaternary ammonium salt (TEt-CO). Both products were tested as demulsifers of water in crude oil emulsion and compared with commercial demulsifier (Chimec2439). Also a mathematical model was developed by using ANN to estimate the effect of different parameters on the water separation efficiency of BCO such as: dose (50 - 150) µl, separation time (0, 15, 30, 45, 60, 75, 90, 105 and 120) min, temperature (30 - 80)^{o}C, time of mixing (10 - 60)min, salinity (0 - 1.5)M, pH of aqueous phase (2 - 12) and water ratio of the emulsion (10 - 30)% .

Artificial Neural Networks

Artificial Neural Networks (ANNs) are a branch of the field known as "Artificial Intelligence" (AI) which may also consists of Fuzzy Logic (FL) and Genetic Algorithms (GA) [7]. Artificial neural networks are non-linear mapping structures which are powerful tools for modeling, especially when the underlying data relationship is unknown. ANNs can identify and learn correlated patterns between input data sets and corresponding target values [8]. Neural networks are composed of simple elements operating in parallel. These elements are inspired by biological nervous systems. As in nature, the network function is determined largely by the connections between elements.

You can train a neural network to perform a particular function by adjusting the values of the connections (weights) between elements. The weights adjusting process is usually called learning process. Commonly neural networks are adjusted, or trained, so that a particular input leads to a specific target output [9,26].

The block diagram of **Fig. 1** shows the model of a neuron, which forms the basis for designing (artificial) neural network. Here we identify three basic elements of the neuronal model [10]:
1. A set of synapses or connecting links, each of which is characterized by a weight or strength of its own. Specifically, a signal (p_i) at the input of synapse (i) connected to neuron (j) is multiplied by the synaptic weight w_{ij}.
2. An adder for summing the input signals, weighted by the respective synapses of the neuron.
3. An activation (or transfer) function for limiting the amplitude of the output of a neuron.

A nonparametric technique for performing a wide variety of estimation tasks is the Multi-Layer Perceptron (MLP).
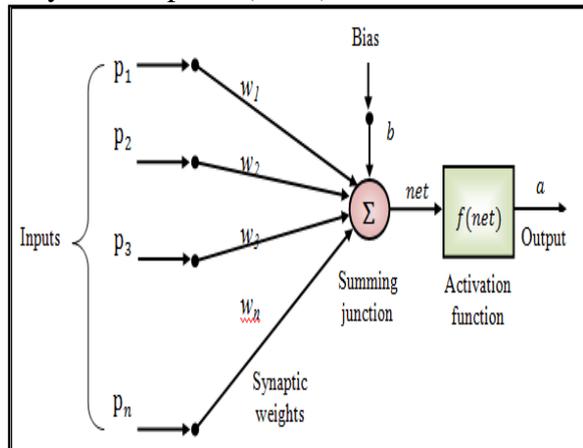

Fig. 1: Structure of a Single Artificial Neuron.

Error Back Propagation (EBP) is one of the most important and widely used algorithms for training multilayer perceptrons [11]. Training process of MLP networks continues until a certain number of iterations or a desired error rate is reached. A nonparametric technique for performing a wide variety of estimation tasks is the Multi-Layer Perceptron (MLP). The most common error approximation method used in MLP networks is mean square error (MSE) and it is defined by the following formula:

$$\text{Error} = (t - a)^2 / 2 \qquad \ldots (1)$$

where: t is the desired output for the given input and a is the output produced by the neural network.

A total MSE sums the error over all individual examples and all the output neurons in the network.

$$\text{MSE} = \left(\sum_{k=1}^{n} \sum_{j=1}^{m} (t_j^k - a_j^k)^2 \right) \Big/ s \cdot l \qquad \ldots (2)$$

Where: $a_j^{(k)}$ is the output value of the jth output of the network when k^{th} training example is presented; $t_j^{(k)}$ is the desired output for the jth output for the kth training example; s is the number of training examples in the training data; and l is the number of output neurons in the neural network [12].

MLP have been applied successfully to solve some difficult diverse problems by training them in a supervised manner with a popular algorithm known as the EBP algorithm. BP algorithm was first defined by Werbos (1974) and later improved by Rumelhart et al. (1986) [13] as a euphemism for generalized delta rule. The BP generalize delta rule is a decent method to minimize the total squared error of the output computed by the net.

The BP algorithm is used in layered feed-forward ANNs. This means that the artificial neurons are organized in layers, and send their signals "forward", and then the errors are propagated backwards [14].

The training procedure consists of two main steps: Feed-forward and back-propagation [13]. During the forward pass the synaptic weights of network are all fixed. During the backward pass, on the other hand, the synaptic weights are all adjusted in accordance with the error-correction rule. Specifically, the actual response of the network is subtracted from a desired (target) response to produce an error signal. This error signal is then propagated backward through the network, against direction of synaptic connections - hence the name "error back-propagation" [15].

The back propagation (BP) training algorithm involves three stages the feed forward of the input training pattern, the calculation and back propagation of the associated weight error and the weight adjustments. The training algorithm (for one hidden layer) is as following [16]:

Step 1: Initialize the weights.

Step 2: While squared error is greater than a tolerance, execute steps 3 to 11.

Step 3: For each training pair, do steps 4 to 11.

Step 4: Sums weighted input and bases and apply activation function to compute output of hidden layer.

$$a_j = f\left(\Sigma\, p_i\, w_{ij} + b_j \right) \qquad \ldots (3)$$

where:

a_j: actual output of hidden neuron j.

p_i : input signal of input i.

w_{ij}: weight between input i and hidden neuron j.

f : activation function.

Step 5: Sums weighted output of hidden layer and apply activation function to compute output of output layer.

$$a_k = f\left(\Sigma\, a_j\, w_{jk} + b_k \right) \qquad \ldots (4)$$

a_k : the output of neuron k.

Step 6: Compute back propagation error

$$\delta_k = (t_k - a_k) f'\left(\Sigma\, a_j\, w_{jk} + b_k \right) \qquad \ldots (5)$$

t_k: the desired output (target) of neuron k.

f' : the derivative of the activation function due to the weight.

Step 7: Calculate weight correction term

$$\Delta w_{jk}(\tau) = \eta \delta_k\, a_j + \mu \Delta w_{jk}(\tau - 1) \qquad \ldots (6)$$

Step 8: Sums delta input for each hidden unit and calculate error term

$$\delta_j = \Sigma_k \delta_k \, a_k = \Sigma_k \delta_k \left(w_{jk} \, f(\Sigma_i \, p_i \, w_{ij} + b_j) + b_k \right) \quad \dots (7)$$

Step 9: Calculate weight correction term

$$\Delta w_{ij}(\tau) = \eta \delta_j \, p_i + \mu \Delta w_{ij}(\tau - 1) \quad \dots (8)$$

Step 10: Update weights

$$w_{jk}(new) = w_{jk}(old) + \Delta w_{jk} \quad \dots (9)$$

$$w_{ij}(new) = w_{ij}(old) + \Delta w_{ij} \quad \dots (10)$$

Step 11: Compute the mean squared error.

Experimental Work

In this study, the experimental work was divided into two parts, the first one deal with the preparation of BCO and TEt-CO. The second part concerning with the using BCO as demulsifier for water in crude oil emulsion and the result will analyzed to identify the effect of operation parameters.

Materials

The materials used in the experimental work of the present study were listed below:

1. ***Castor Oil [C₃H₅ (C₁₈H₃₃O₃)₃]:*** The castor oil (CO) was obtained from local market produced by Hemani Company. The typical characteristics of CO were specified and listed in **Table 1**. CO consists mainly of esters of 12-hydroxy-9-octadecenoic a (ricinoleic acid) which comprises over 89% of the fatty acid of the oil [see **Fig. 2**]. Other fatty acids present in castor oil are linoleic 4.2%, oleic 3.0%, stearic 1%, palmitic 1%, dihydroxystearic acid 0.7%, linolenic acid 0.3%, and eicosanoic acid 0.3%. The existence of hydroxyl groups and double bonds in the structure of castor oil makes the CO suitable for many chemical reactions and modifications[17].

2. ***Bromine (Br2):*** Bromine with purity (99%) Supplied from Fluka-Garantie Company, was used to bromination CO to produce BCO.

3. ***Methanol (CH₃OH):*** Methanol with purity (99.9%) was supplied from J.T. Baker Chemicals Company.

4. ***Ethanol (CH₃CH₂OH):*** Ethanol with purity (95%) supplied from Fluka-Garantie Company.

5. ***Toluene (C₆H₅CH₃):*** Toluene with purity (99.5%) was supplied from Gainland Chemicals Company.

6. ***Xylene [C₆H₄(CH₃)₂]:*** Xylene with purity (98%) was supplied from Schar lab. S.L. Chemicals Company.

7. ***Triethylamine [N (CH₂ - CH₃)₃]:*** Triethylamine with purity 99% supplied from AVONCHEM Chemicals Company.

8. ***Crude Oil:*** Basrah crude oil with the physical properties shown in **Table 2** analyzed in South Refineries Company.

9. ***Commercial demulsifier (Chimec2439):*** Chimec2439 supplied by CHIMEC S.P.A Company, Italy. The physical properties given from the producing company, are shown in **Table 3**.

Table 1: The physical properties of castor oil.

Property	Value
Specific Gravity @ 15°C	*0.9623*
Viscosity @ 40°C, cp	*59.6*
Acid value	*0.1*
Boiling point, °C	*313*
Pour point, °C	*>-22*
Appearance	*Pale Yellow Color*

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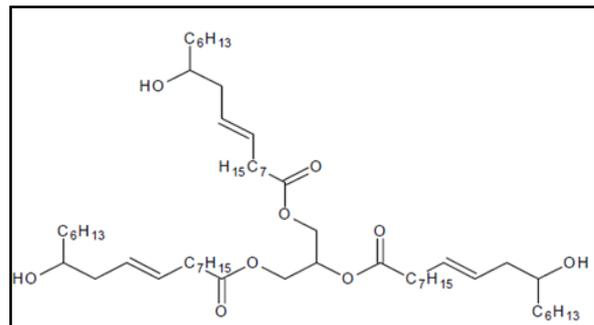**Fig. 2 The structure of ricinoleic acid molecular**

Table 2: The physical properties of crude oil sample.

Properties	Value
Specific Gravity @ 15°C	*0.9007*
API Gravity	*25.2*
Water content, vol.%	*Nil*

Water & Sediment	Nil
Salt content, 1b/1000ber ppm	8.2 26
Pour point, ^{o}C	<-30
Kinematic viscosity, cSt @ 40°C	19.65

Table 3: The physical properties of the Chimec2439 (CHIMEC S.P.A Company, Italy).

Properties	Value
Specific Gravity @ 20°C	0.94±0.02
Viscosity @40°C, cp	<50
Pour point, ^{o}C	<-30°C
Flash point, ^{o}C	>62°C
Appearance	Brown liquid

Demulsifiers Preparation

Batch reactor consists of three necks round bottom flask with (500 ml) volume used to prepared BCO and TEt-CO [see **Fig. 2-a** and **Fig. 2-b**].
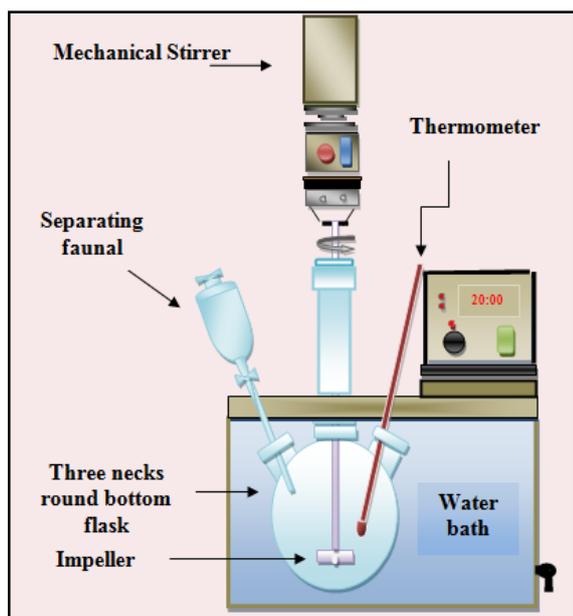
Fig. 2-a: The reaction system

Fig. 2-b: The reaction system

The flask made of Pyrex glass and connected to separating faunal to provide a drop wise adding of the bromine reactant, mechanical stirrer with mixer, and thermometer. The motor operated with different mixing speed 45 to 1000 rpm. The temperature was controlled using water bath within ±1°C and the water bath has the range 15°C to 100 °C.

Brominated Castor Oil

The reactor was charged with a solution of 46.6g (1 mole) of CO in 175 ml carbon tetrachloride (CCl_4). A solution of 28.7gm Bromine (Br_2) in 50 ml carbon tetrachloride was charged to the separator funnel and allow it to drop wise over a castor oil solution for period of half an hour. The reaction temperature was maintained at 20 ^{o}C during the whole period of the reaction, stirring was fixed at 1000 rpm and the reaction carried out avoiding the bright light. The quantity of the bromine added was in excess of the calculated theoretically. On completion of the reaction, the amount of bromine left (unreacted) in the reaction mixture was reduced by using 5% aqueous solution of sodium sulphite. The aqueous layer was then separated from organic layer, which is the desired product. Then the solvent was distilled by using rotary evaporator [18]. **Fig. 3-a** shows the structure of BCO molecular.
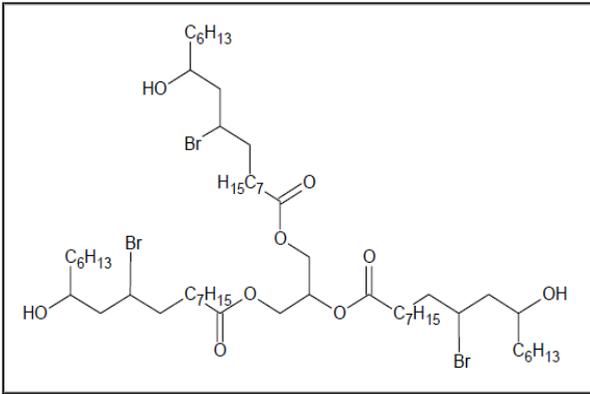
Fig. 3-a: The structure of BCO molecular.

Quaternary Ammonium Salt

The reactor was charged with a solution of 10ml Triethylamine in 30ml ethanol. 70gm of brominated castor oil was charged to the separating funnel and allow it to drop wise over Triethylamine solution for a period of 2 hr, stirring was fixed at 1000rpm. After that, the reaction was put on reflux at 79°C for 48 hr [19]. After completion of the reaction, the product was cooled and recrystallized by ethanol, and dried in a vacuum oven at 75°C for 24 hrs which gave pale yellow precipitate. Then the milting point was measured which was 249-250.5°C. **Fig. 3-b** shows the structure of TEt-CO molecule
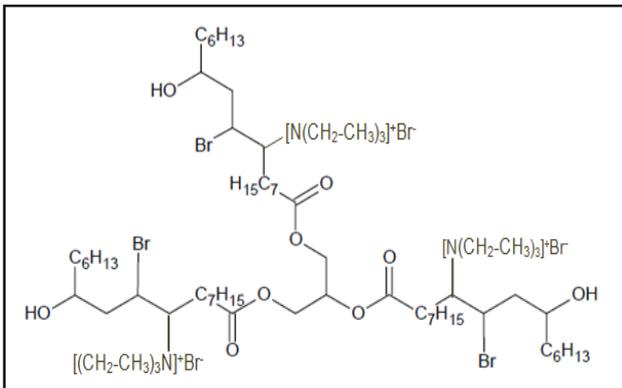
Fig. 3-b: The structure of TEt-CO molecular.

Testing Demulsifiers

The demulsifiers were tested by using bottle test method. The purpose of this process is to test the effectiveness of demulsifiers in breaking crude oil emulsion and also to evaluate the effects of the operation parameters such as temperature and demulsifer dose and the other variables on the demulsification operation. The procedure used in this study was as followed:

Beaker 300ml charged with 250ml of brine (0.5M of NaCl solution) and crude oil by ratio of 30/70 v/v% and mixed by a stirrer at 2000rpm for 60min.

After complete mixing, the emulsion directly charged to a five centrifuge tubes with 50ml volume and inserted to a constant temperature water bath set at 60°C and allowed approximately 15 min to get equilibrium.

After equilibrium, the five tubes ejected from water path, demulsifier or chemical compound was added in different doses 50, 75, 100, 125, and 150 μl to the contents of the tubes and shaked by electric shaker for 2min together and then directly return to the water bath. The volume of the separated water from crude oil emulsion for all tubes were recorded at time intervals which were 0, 15, 30, 45, 60, 75, 90, 105 and 120 min.

The efficiency of separation water (WSE) from crude oil emulsion of demulsifier in different conditions was calculated by using the following equation:

$$WSE\% = \frac{\text{volume of saperated water (ml)}}{\text{Total volume of water in the sample (ml)}} * 100\%$$
...(11)

Results and Discussion

The results are divided into two groups, the first group is experimental results and the second group is theoretical results.

Mechanism of Demulsification of Crude Oil Emulsion

Mechanism of demulsification includes diffusion the demulsifier molecules and adsorbed on the interfacial film between water and the crude oil. The main role of the demulsifiers is either to replace part of asphaltenes or combine with them, that allow to interact with emulsifier molecules and thinned the film, with the action of heat, the film will start to rupture and then the droplets will coalescence together that's lead to grow the water droplets large enough to settle out.

Effect of Demulsifiers on Water Separation Efficiency

In this investigation, the water separation efficiency (WSE) was evaluated for the products and compared with commercial demulsifier (Chimec2439) with dose 150µl and in the same condition.

Fig. 5 shows the comparison between adding of Chimec2439, CO, BCO and TEt-CO on WSE of the emulsion. They were tested as demulsifiers by bottle test method with sample volume 50 ml with time intervals. First of all, it is very necessary to mention that no water was separated from any tested samples for each period without adding demulsifier (the prepared emulsion was stable). From this figure, it can be observed that the WSE of BCO get near by the efficiency of Chimec2439 and gave 90% at 120min by compared with 96.7% for Chimec2439.

When CO tested as demulsifier, WSE could not reach to more than 1.7% at 120min and in compared with BCO, it's very low. From the above, it's clear that the activity of CO increased after breaking the double bond and substituting Bromine atoms (Br_2) instead of it (and produce BCO), where, adding Br_2 to CO enhanced its hydrophilic properties and increased its ability on adsorption on the interfacial surface between water and oil and displacement the naturally emulsifiers to allow the coalescence of water droplets through film drainage which lead to enhancement its ability on separating of water. After preparing BCO, triethylamine added and TEt_CO produced. When it tested as demulsifer, TEt-CO was less effective as demulsifer in comparison with BCO and also with quaternary ammonium salt based fatty alcohols which has been prepared by another workers [19,20].
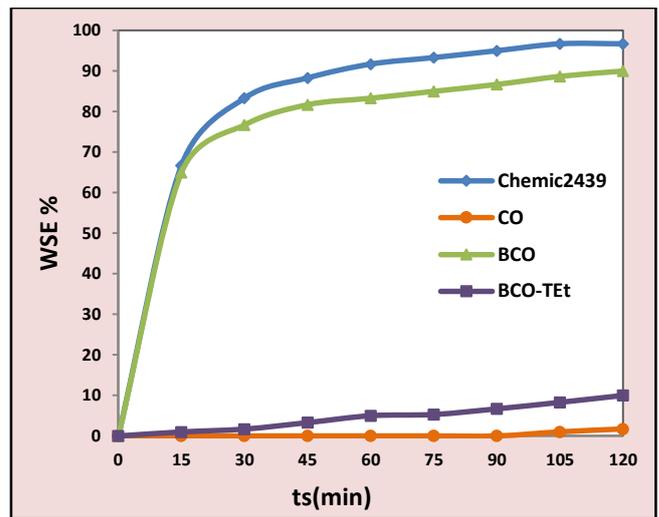

Fig. 5: Comparison between adding of Chimec2439, CO, BCO-TMt and BCO-TEt on the WSE.

Effect of Demulsifier Doses and Separation Time on WSE

From **Fig. 6**, it's clear that WSE is increased with increasing separation time(t_s) because of more time has been allowed for the phases to separate. The figure shows that WSE for BCO is increased with time until it reaches 30 min then the increasing becomes slightly, that's because of the concentration of surfactants (BCO) is large as passable as in the beginning of the operation and it consumed with time, so that WSE will became slow after about 30 min.

Also WSE increased with increasing the dose of BCO (the concentration of BCO was 50-150µl) because of the number of contacts between the demulsifier molecules and the naturally surfactants (such as asphaltenes and resins) on the interfacial film between water and crude oil in unit time will depend upon how intensively the molecules are crowded together. In case of increasing the concentration of demulsifier molecules, the amount of demulsifier molecules adsorbed to this film in unit time will increase, that will increase the rate of its rupturing which lead to increasing water volume separated at unit time.
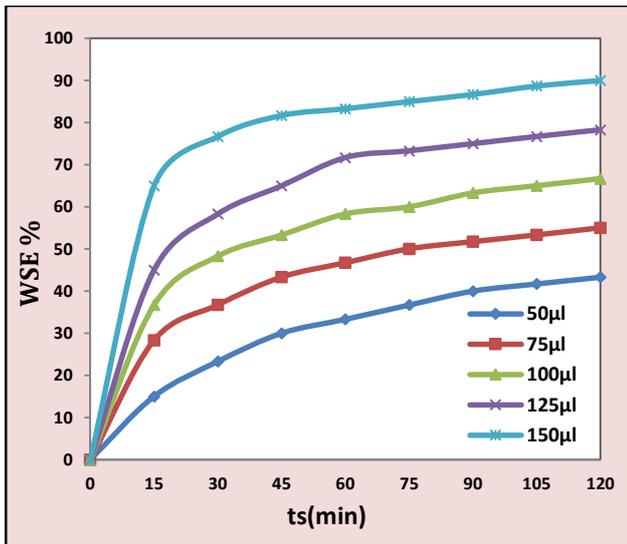
Fig. 6: WSE vs. separation time at different doses of BCO.

Effect of BCO Dose on the Density

As was discussed before dose of demulsifier has a good effect on physical and chemical properties of emulsion. **Fig. 7** shows the effect of change doses of BCO on the density of separated crude oil. It can be observed that the dose of demulsifier increases, the density of emulsion after water separation decreases. The lowest density is at dose 150µl, which equal to 0.9010 gm/ml. This is because of a good amount of water removed from emulsion, where at this dose it can reaches 90% of WSE.
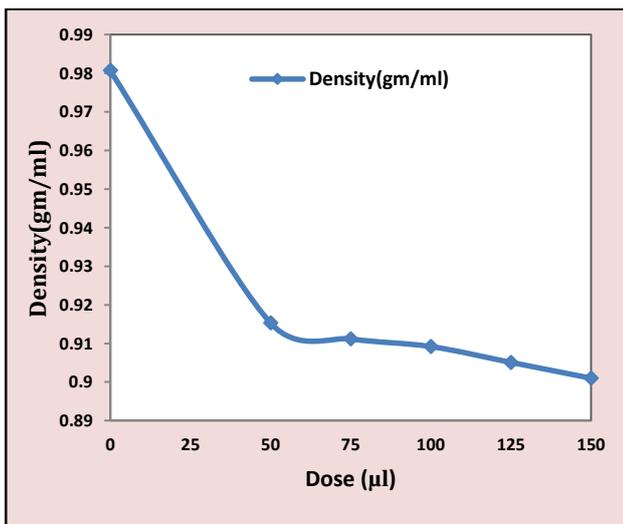
Fig. 7: Density of separated crude oil vs. different doses of BCO.

Effect of Water Ratio on WSE

The effect of changing water ratio (WR) on WSE was carried out by taking range of 10-30% v/v% water/oil ratio. Each emulsion prepared by mixing the crude oil with brine by stirrer with 2000 rpm for 60 min. **Fig. 8**, shows the difference among the three ratios at 150µl of BCO.
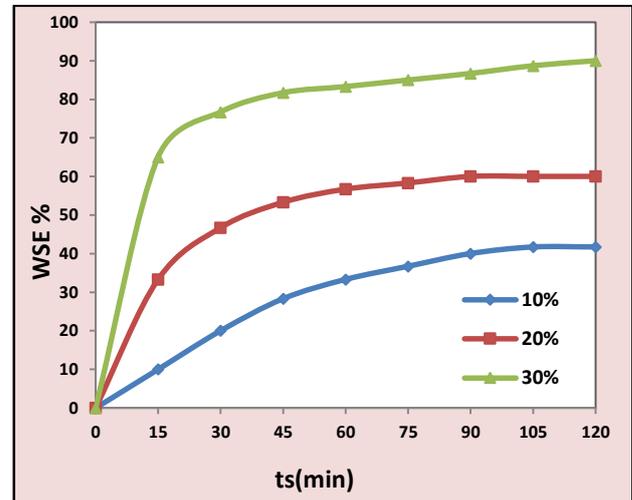

Fig. 8: WSE vs. separation time at different WR at 150µl dose of BCO.

From this Fig., it is clear that the increasing in WR leads to increase WSE. The highest separation efficiency reached 90% for 30% WR followed by 60% for 20% WR and at last the water separation efficiency was 43.3% for 10% WR at 120min. The increasing in WR of emulsion can influence the coalescence efficiency during the demulsification process also the rate of flocculation is higher when WR is higher, that's due to a reduced the distance between droplets in the sample wherever this distance can be severely narrowed with the increase of the volume of the aqueous phase in the emulsion, that's lead to raise the probability of collision between the droplets. All that makes the settled droplets increasing and leads to increase WSE.

Effect of Time of Mixing of Emulsion on WSE

The effect of changing time of mixing (t_m) to prepare the emulsion on WSE was investigated. **Fig. 9** shows the results of different t_m 10, 20, 30, 40, 50 and 60min on WSE with time intervals at dose 150µl of BCO. The emulsions aqueous phase brine with 0.5 mol/l of NaCl mixed with 70% of crude oil

by stirrer in speed 2000rpm. The mixer with four impellers with 2cm diameter was used in preparing the emulsions. First of all, it is very necessary to mention that no water was separated from any tested samples for each period without adding demulsifier.
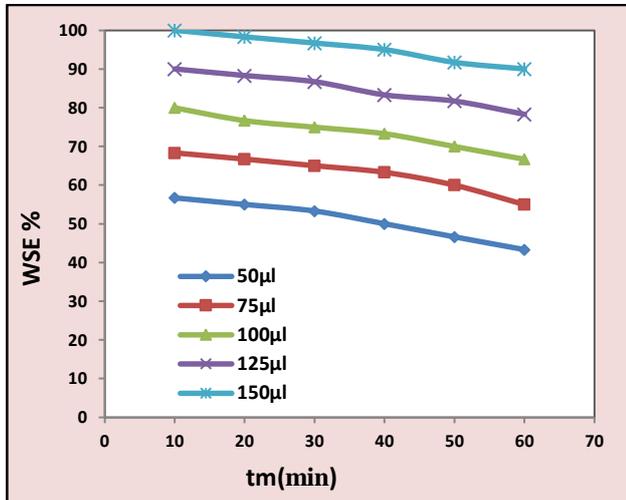

Fig. 9: WSE vs. separation time for different mixing time of emulsion at dose 150µl of BCO

From this Fig., it is clear that the increasing in t_m of emulsion lead to decreasing in WSE for different doses. Mechanical mixing is one of the well-known methods to form w/o emulsions from two immiscible phases. The interface between the dispersed and continuous phases is deformed to form droplets. At the beginning of the emulsification process, the droplets are mostly too large. During the mixing process, these large droplets are broken down into smaller ones due to the disruption process of the large droplets. Therefore, for the same mixing speed, the more mixing time supplied the more stable the emulsion will be. Smaller droplets are relatively more stable than larger droplets that's consequently enhances the emulsion stability that lead to decrease or delay droplets settling.

Effect of Temperature on WSE

A series of experiments were conducted at different temperature set points, which as 30, 40, 50, 60, 70 and 80ºC. Temperature affects the physical properties of oil, water, interfacial films, and surfactant solubility in the oil and water phases also temperature increases the

thermal energy of the droplets and, therefore, increases the frequency of drop collisions and perhaps the most important effect of temperature is on the viscosity of emulsions because viscosity decreases with increasing temperatures. For all the above reasons, it is necessary to study the effect of temperature on the W/O emulsion stability. **Fig. 10** shows that the effect of temperature for different doses of BCO at time separation 120min.
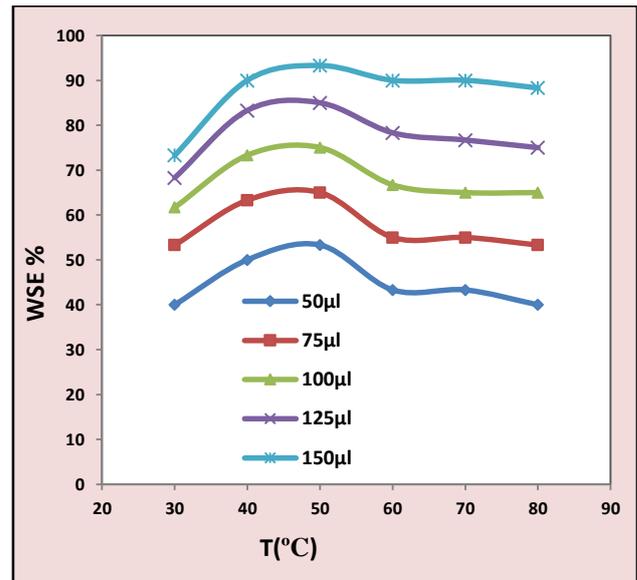

Fig. 10: WSE vs. separation time for different doses of BCO in different temperature after 120min.

From this Fig., it's clear that WSE was increasing with increasing temperature for different demulsifier doses. WSE for BCO with 150µl dose at time 120min was in minimum at 30ºC with 73.3% WSE and increased with increasing temperature to 90% water separated at 40ºC and reached to the maximum at 50ºC with 93.3% WSE. At 60ºC and 70ºC, maximum WSE reaches to 90% and at 80ºC reaches to 88.3% at 120min. An increase in temperature has two opposite effects on emulsion. The first effect of increasing oil temperature is decreasing both oil density and viscosity, which yields a significant improvement in the settling rate of water droplets. On the opposite side, as crude oil temperature increases resulting in a higher rate of power consumption lead to evaporate the low hydrocarbon molecules which

decrease diffusivity of demulsifier molecules and decrease its efficiency.

Effect of Salt Concentration of Aqueous Phase on WSE

The effect of changing salt concentration SC of emulsion's aqueous phase on WSE was carried out by using emulsion contains 70% of crude oil and 30% of brine with different concentration of NaCl 0, 0.25, 0.5, 0.75, 1, 1.25 and 1.5mol/l mixed by a stirrer at a speed of 2000 rpm for 60min. **Fig. 11** shows the effect of changing salt concentration of the aqueous at time settling 120min for different doses of BCO WSE reach to 80% for brine with 1.5mol/l of NaCl. The highest WSE reached to 93.3% for fresh water at 150µl BCO dose while. Specific ions present in the brine can influence interfacial film behavior. At the interface, these ions may react chemically with the hydrophilic groups to demulsifier to separate water.
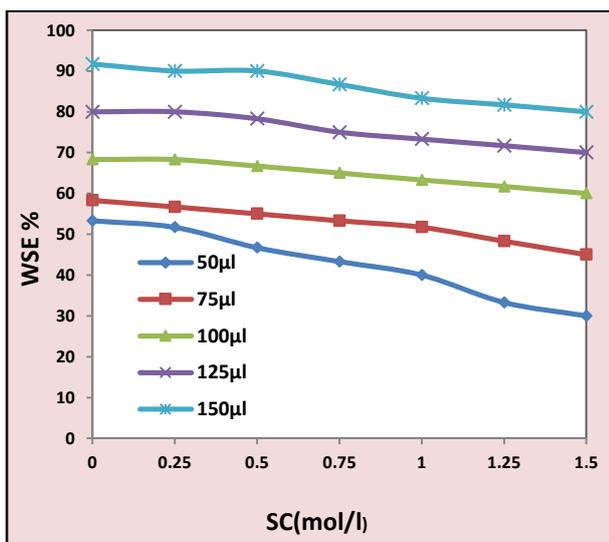

Fig. 11: WSE vs. different salt concentrations for different doses of BCO.

Effect of pH value of Aqueous Phase on Water Separation Efficiency

The effect of pH of the emulsion's aqueous phase was studied at six different pH values, namely 2, 4, 6, 8, 10 and 12. The emulsions aqueous phase with 0.5 mol/l of NaCl mixed with 70%of crude oil by stirrer with 2000 rpm for 60 min. From **Fig. 12**, it's clear that the WSE was in minimum value at pH=2 and increased with increasing pH until became in maximum at pH=10 and then decreased at pH=12. It's found that the maximum demulsification efficiency is attained at pH =10. It is clear that the minimal percentage of water separation was obtained at very acidic or very alkaline medium. This amphoteric nature of asphaltenes, which is runs in harmony with previous findings, and may be explained on the basis of the highly affected by pH change. The water droplets will get a negative charge in basic medium and a positive charge in acidic medium due to the ionization equilibrium of asphaltenes. It is a well-known fact that electrical charges on the surface of dispersed water droplets cause electrostatic repulsion. Therefore, acidic or basic pH values result in enhanced emulsion stability by offering an electrostatic barrier to coalescence in addition to the already existing steric barrier. Adding inorganic acids and bases strongly influences their ionization in the interfacial films and radically changes the physical properties of the films. The pH of water affects the rigidity of the interfacial films. It was reported that interfacial films formed by asphaltenes are strongest in acids low pH and become progressively weaker as the pH is increased. In alkaline medium, the films become very weak or are converted to mobile films. The films formed by resins are strongest in base and weakest in acid medium. Solids in the emulsions can be made oil-wet by asphaltenes, an effect that is stronger in an acidic than in a basic medium. These partially oil-wet solids tend to stabilize water-in-oil emulsions. pH also influences the type of emulsion formed. Acid or low pH generally produces water in oil emulsions corresponding to oil-wetting solid films, whereas basic or high pH produces oil in water emulsions corresponding to water-wetting mobile soap films.
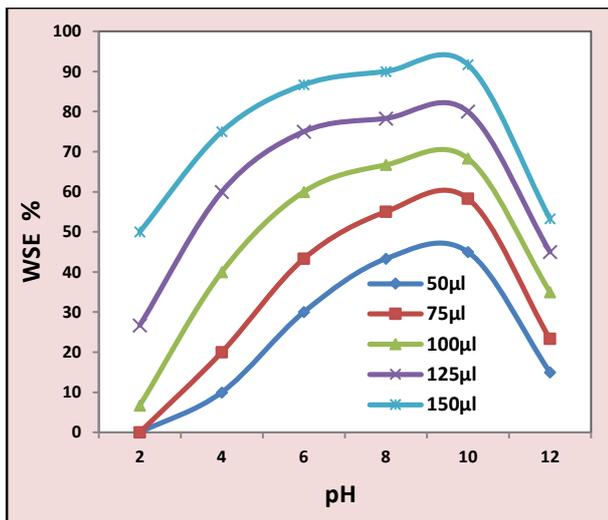
Fig. 12: WSE vs. separation time at different pH for different doses of BCO.

Effect of Adding Solvents on WSE

Solvents can be used because they are commonly employed in commercial formulations. Alcohol like methanol and ethanol are commonly used and xylene and toluene are very familiar in use also because they enhance the efficiency of demulsifer. The effect of adding alcohols on WSE was carried out by using emulsion contains 30% of brine with concentration 0.5molary of NaCl mixed by a stirrer at a speed of 2000 rpm for 60min. The concentrations were 1:0, 1:1/2, 1:1, 1:3/2, 1/2 v/v of BCO to solvents with 100μl dose for each. **Fig. 13** and **Fig14** show the effect of adding different concentrations of alcohols methanol and ethanol on water separation efficiency with time intervals.

Fig. 13 shows that the WSE increasing with decreasing methanol concentration, where maximum separation efficiency 75% was obtained at concentration 1:1/2 methanol to BCO at 120min.

Fig. 14 shows that the of WSE decreasing with ethanol concentrations increasing with time interval. Maximum separation efficiency reaches 66.7% at concentration 1:0 just BCO at 120 min after that came the concentration 1:1/2 of BCO to ethanol which reaches to 60% at 120 min. Methanol has a good ability in promoting water separation for the emulsion system compared to ethanol. This is because

short chain alcohols are very soluble in water and also the activity of methanol is greet than ethanol.
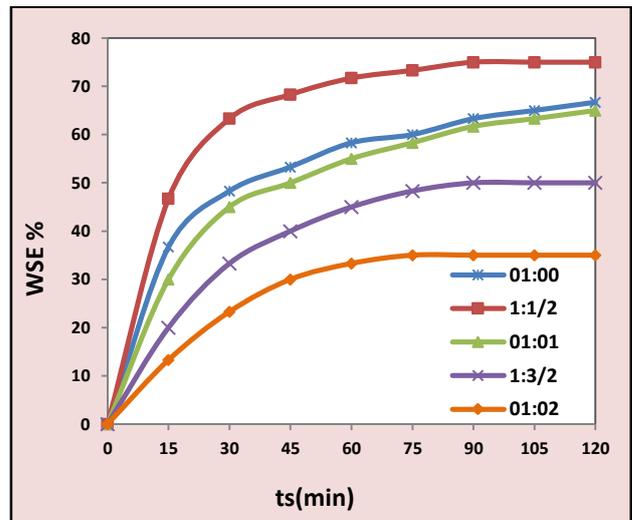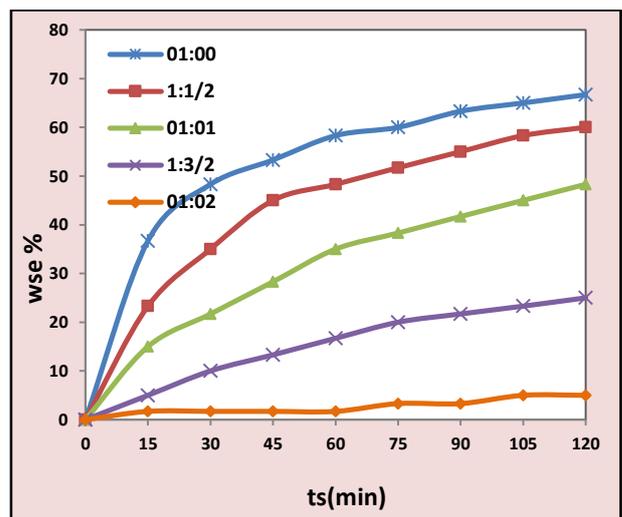

Fig. 13: Effect of adding methanol to BCO on WSE.

Fig. 14: Effect of adding ethanol to BCO on WSE.

Fig. 15 and **Fig. 16** show the effect of adding different concentrations of xylene and toluene on WSE with time intervals. **Fig. 15** shows that the WSE decreasing with increasing xylene concentration, where maximum separation efficiency 50% was obtained at concentration 1:1/2 of BCO to xylene at 120 min.

Fig. 16 shows that the WSE decreasing with increasing Toluene concentration, where maximum separation efficiency 73% was obtained at concentration 1:1/2 of BCO to

toluene at 120 min. It is clear that toluene showed more affectivity in WSE than xylene.

Fig. 17 shows the comparative between adding each solvents in ratio 1:1/2 with BCO in 100µl dose. From this Fig., it is clear that the methanol was the more effective solvent than the others followed by toluene and ethanol and at last came xylene.
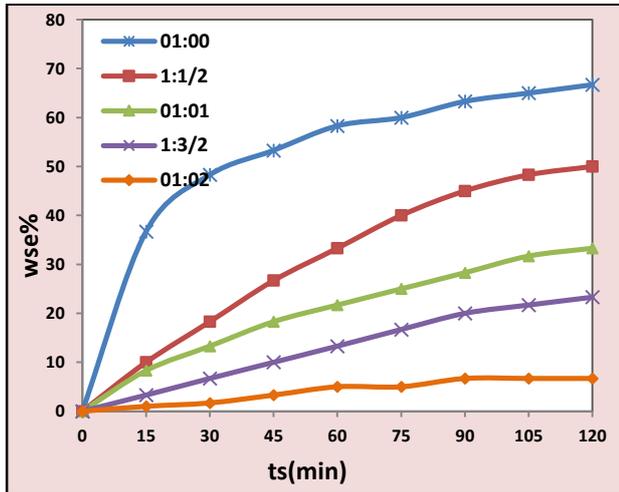

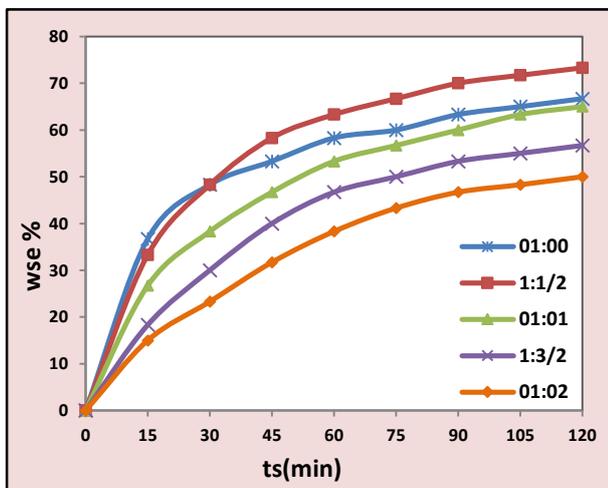**Fig. 15: Effect of adding xylene to BCO on WSE.**

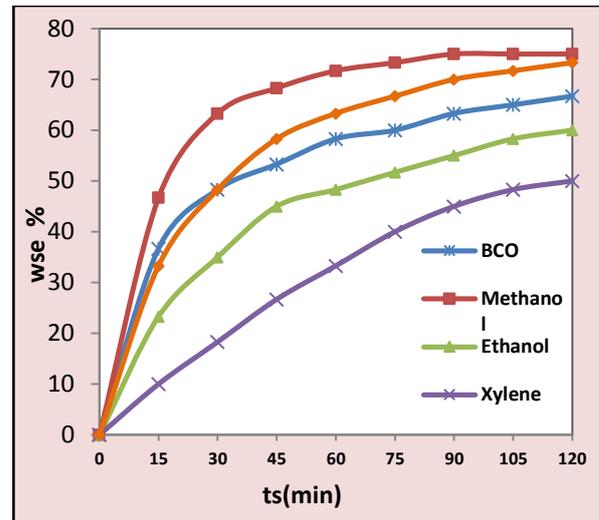**Fig. 16: Effect of adding toluene to BCO on WSE.**

Fig. 17: Comparative between adding the use solvents to BCO on WSE.

Theoretical Results

Theoretical work which is represented by ANN modeling. The neural network is implemented using neural network toolbox that is available in MATLAB program version 7.10.0 R2010a. A well trained neural network utilized here to develop to be able to predict WSE of BCO. The configuration and training of neural networks is a trial-and-error process due to such undetermined parameters as the number of hidden layers, the number of nodes in the hidden layers, the learning parameter, and the number of training patterns.

Selection of The Training and Testing Patterns

The total experimental data are divided in to two sets: a training set and a testing set. The training set is used for computing the gradient and updating the network weights and biases to reduce the training error, and find the relationship between the input and output parameters. Hence, the learning process is a essential phase in NN modeling. The testing set is used to evaluate the generalization ability of the learning process.

In this study the testing set contains 20% of total database. The parameters used in this study are shown in **Table 4.** The experimental values used to train the neural network as training data are those measured using Bottle test method. The total number of 1080 reading

cases were utilized, the training set contains 864 readings and the testing set comprises of 216 readings.

In this investigation, the parameters which may be introduced as the components of the input vector consist of the settling time(p_1), demulsifier dose (p_2), time of emulsion mixing (p_3), temperature (p_4), salt content (p_5), pH of aqueous phase (p_6) and water ratio (p_7). The output data is one parameter represented the efficiency of BCO (WSE). Therefore, the nodes in the input layer and output layer are 7 and 1, respectively.

Normalization of input and output data sets within a uniform range before they are applied to neural network are essential to prevent large number from overriding smaller ones, and to prevent parameter saturation of hidden

Table 4: Input and Output Parameters

nodes, which impedes the learning process. The limitation of input and output values within a specified range are due to large difference in the values of data provided to the network. Besides, the activation function used in the back-propagation neural network is hyperbolic tangent function, the lower and upper limits of this function are -1 and +1, respectively. The used function for normalization is [21]:

$$pn_i = 2\left[\frac{p_i - p_{min}}{p_{max} - p_{min}}\right] - 1 \qquad ....13$$

Where: p_i is the value of i-th variable, p_{min} is the minimum value of p_i and p_{max} is the maximum value of p_i.

The selection of the numbers of hidden layer is critical for the network to predict the network output with less error. Usually the optimum number of hidden layers is decided through trial and error procedure and the lowest number of hidden layers with satisfactory generated error is selected. The reason for such selection is that as the number of hidden layers kept at an optimum low, the less time required for training the network. The majority of optimization problems can be solved with acceptable calculated error with

one or two hidden layers. Studies shows that only 1-2% of neural networks require three or more hidden layers to find accurate solution. It is usually to start with a relatively small number of hidden units and increase it until we are satisfied with the approximation quality of the network. The number of nodes in a hidden layers significantly affects the outcome of the network training. Therefore, trial-and-error approach is carried out to choose an sufficient number of hidden layers and number of nodes in each hidden layer for different types of training functions.

The number of nodes in the hidden layer is selected according to the following rules:

1. The maximum error of the output network parameters should be as small as possible for both training patterns and testing patterns.
2. The correlation coefficient should be as

No. of Hidden layers	No. of Nodes	Activation functions	Training Function	R test	MSE
1	25	logsig, tansig	trainlm	0.99937	0.000157
2	17-9	tansig,tansig,tansig	trainlm	0.9995	0.0000618
2	17-9	logsig,tansig,tansig	trainlm	0.99936	0.000101
2	17-9	tansig,logsig,tansig	trainlm	0.99917	0.000152
2	17-9	tansig,tansig,tansig	traincgp	0.99721	0.001557

high as possible especially [is that means approaching 1]. It is a measure of how well the variation in the output is explained by the targets. If this number is equal to 1, then there is perfect correlation between targets and outputs.

The choice of the training function depends on the network application. Three types of training function are used in the neural networks modeling of the present study. Although, using trainlm algorithm might be sufficient in solving many functional approximation problems, some other problems may be easier to be solved with traincgb or trainrp training function.

In this study the network is tested with one and two hidden layer configurations with an increasing number of nodes in each hidden

layers. Different activation function arrangements are investigated which are tansig, logsig and pureline activation function. The optimal topology is determined first by using one hidden layer with activation function as hyperbolic tangent (togsig) function for hidden layer and tansig function for output layer. Different numbers of nodes from 5 to 30 nodes are investigated. The network with 25 nodes in the hidden layer gives best performance and correlation coefficient than other.

Then two hidden layers are used with different activation functions for both first hidden layer, second hidden layer and output layer. Different numbers of nodes in each hidden layer from 5 to 20 nodes are used. The network with 17-9 nodes [17 nodes in the first hidden layer and 9 nodes in the second hidden layer] gives best performance and regression for both training and testing than other. The results show that a network with two hidden layers is significantly better than that with one hidden layer. **Table 5** shows the compare between the best different algorithms for network models.

Table 5: MSE and Regression of the different algorithms for network model.

From the above analysis, for different arrangements of neural networks it can be seen that trainlm training function with tansig activation functions for the two hidden layers and output layer gives the best MSE and correlation coefficient for both training and testing than other. Therefore, this network can be selected as a proposed network for the present study. **Fig. 18** shows training performance of the proposed neural network.
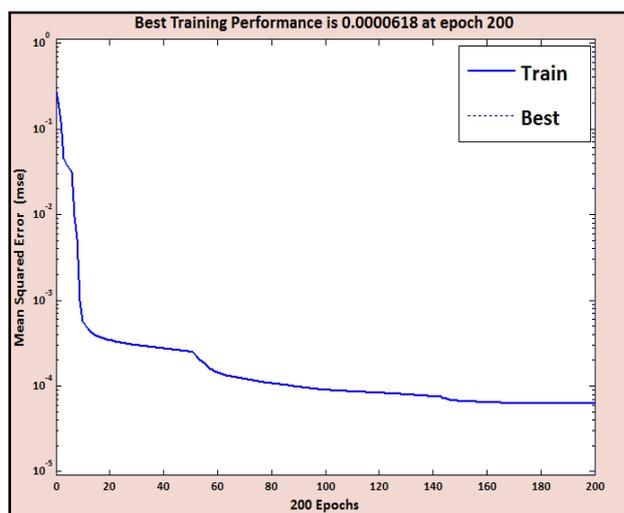

Fig. 18: Training performance MSE of the proposed neural network.

Fig. 19 and **Fig. 20** show the regression analysis between the output of neural network and the corresponding target for training and testing data respectively. In the figures, outputs are plotted versus the targets as open circles. The solid line indicates the best linear fit and the broken line indicates the perfect fit output equals target. The values of the slope are 1 for both, interceptions with y-axis are -0.02 and 0.0282 respectively, and correlation coefficients are 0.9995 and 0.9999

Item	Symb.	Parameter	min. value	max. value	Unit
Input Parameters	P_1	Separation time	0	120	min
	P_2	Dose	50	150	μl
	P_3	Time of mixing	10	60	min
	P_4	Temperature	30	80	${}^{o}C$
	P_5	Salinity	0	1.5	mol/l
	P_6	pH	2	12	-
	P_7	Water ratio	10	30	%
Output parameter	WSE	Water separation efficiency	0	100	%

respectively. These values indicate that the mapping of neural network for the training and testing data is very good.
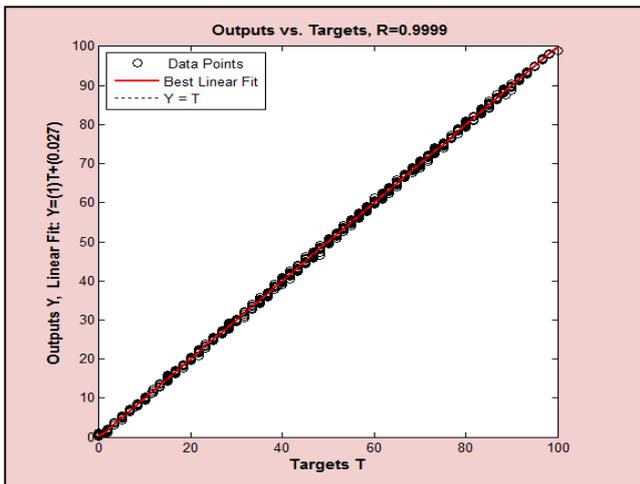
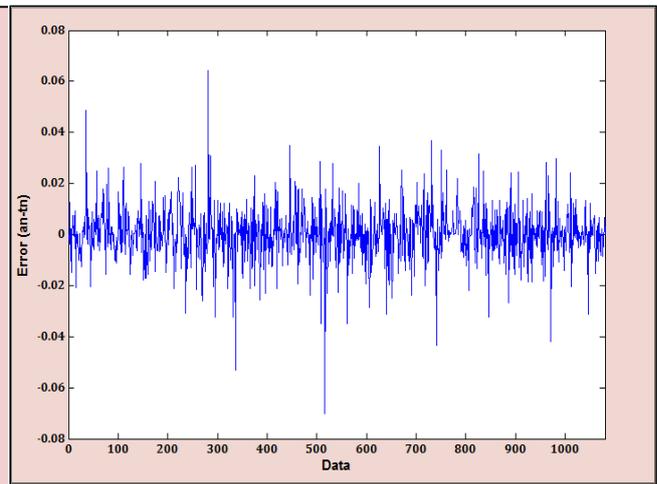**Fig. 19: Training Regression of the Proposed Neural Network.**

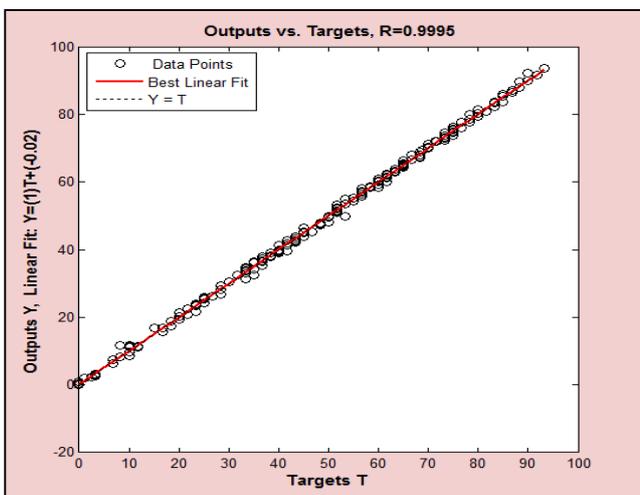**Fig. 21: Error Analysis between Output and Target for the Proposed Network.**

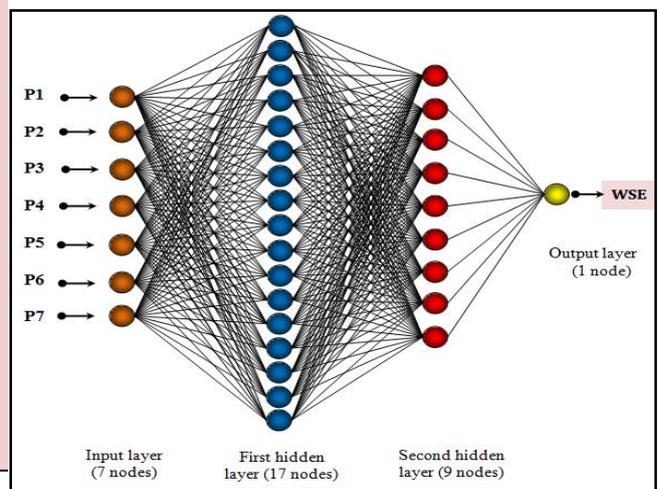**Fig. 20: Testing Regression of the Proposed Neural Network.**

Fig. 22: Configuration of Neural Network 7-17-9-1.

Fig. 21 shows error analysis between normalized targets and outputs for the proposed network. The configuration of the neural network is shown in **Fig. 22**.

Fig. 23 shows the graphical user interface operating mode for the neural network demulsification process model, it is coded using the "GUIDE" program in MATLAB 2010 [see **Fig. 23**]. **Fig. 24** shows the flowchart of the neural network program.

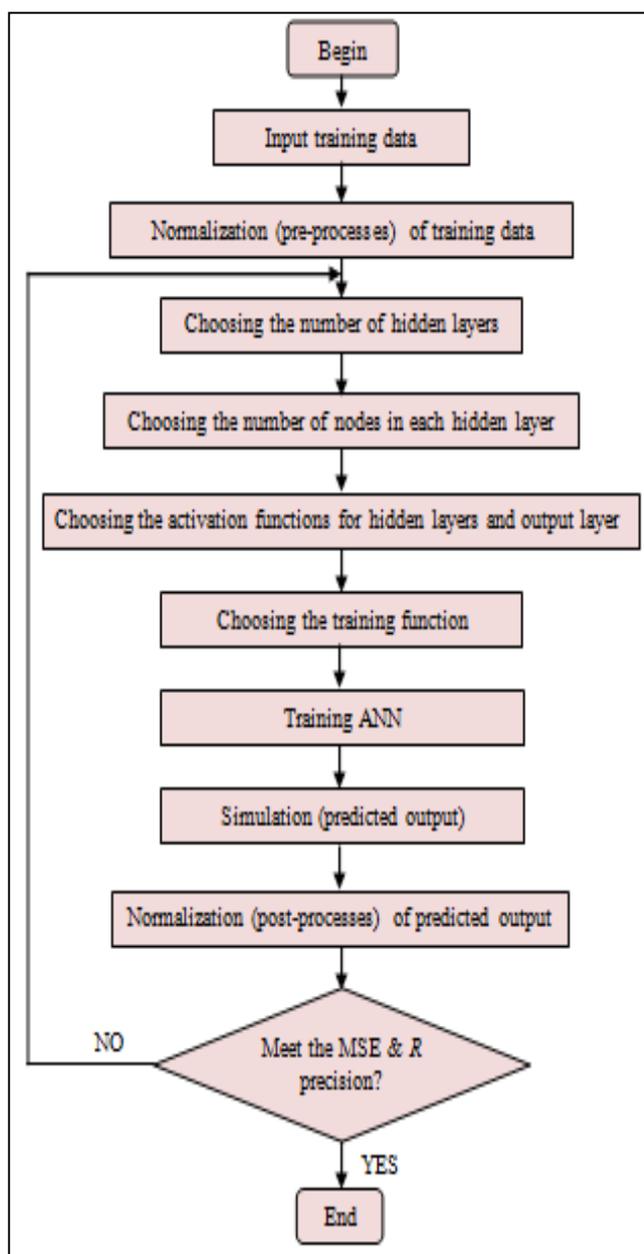**Fig. 23: Graphical User Interface Using MATLAB Program.**

Fig. 24: The Structure of the Neural Network Program

Conclusions

BCO showed good ability on separation water from w/o emulsion when compared with commercial demulsifier Chemic2439, but the TMt-CO was less effective as demulsifer. WSE of BCO increases with increasing separation time and with increasing dose of BCO. Density of emulsion after water separation has an inverse proportionality to BCO dose. Increasing time of mixing to prepare the emulsion lead to increase the dispersed of water droplets in crude oil phase and that lead to decrease WSE of BCO. As the temperature increase the WSE increases. The changes in salinity and pH of the aqueous phase of the emulsion enhance its stability and decrease the demulsification efficiency of the applied BCO. Adding methanol, ethanol, xylene and toluene as modifier agents improve the performance of demulsification process. Two hidden layers with 17-9 nodes neural network model is proved to be very efficient to predict in WSE of BCO with different conditions.

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