



## Preparation and Evaluation of Ethoxylated Jatropha Oil Fatty Acids as De-emulsifier for Crude Oil Emulsion

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### ABSTRACT

Oil is produced from reservoirs in association with natural formation water or mixed formation during water injection. Removal of water is an essential step in petroleum refining for many technical reasons. Nonconventional homologous de-emulsifiers derived from natural oil such as Jatropha oil were synthesized to replace the commercial de-emulsifiers. They are relatively cheap, non-ionizable and environmental friend. The synthesis comprises two steps: first hydrolysis of the Jatropha oil followed by ethoxylation. The prepared ethoxylated Jatropha oil fatty acids exhibit high tendency toward de-emulsification of water in oil emulsion.

**KEYWORDS:** Surfactant, Hydrolysis, Jatropha Fatty Acids, Crude Oil, Emulsion, De-emulsifier.

### المستخلص

عادة ما يوجد خام النفط مصحوبا بالماء والماء المضخوخ أثناء الإستكشاف، وعملية إزالة الماء ذات أهميه في صناعة البترول من الناحية التقنية. الهدف من هذه الدراسة تحضير و تشخيص مادة سطوحية غير تقليديه من زيت الجاتروفا تكون غير مكلفة، غير متأينة و صديقة للبيئة ومن ثم تقييم كفاءتها في كسر الإستحلاب. تتم عملية التحضير في خطوتين، الأولى التحلل المائي (حلمأة) لزيت الجاتروفا والثانية إيثوأكسلة. أظهرت المركبات المحضرة ميول عالي تجاه كسر مستحلب الماء و البترول الخام.

### INTRODUCTION

Crude oil is a naturally occurring, flammable liquid consisting of a complex mixture of hydrocarbons of various molecular weights and other liquid organic compounds. Petroleum is a mixture of very large number of different hydrocarbons; the most commonly found molecules are alkanes (linear or branched), cycloalkanes, aromatic hydrocarbons, or more complicated chemicals like asphaltenes. Each petroleum variety

has a unique mix of molecules which define its physical and chemical properties<sup>(1)</sup>.

Crude oil is a mixture of many different substances, often difficult to separate, from which various petroleum products are derived. Water causes problems downstream of the production. Petroleum is most often produced as a water-in-oil emulsion and the water must be removed (down to a level of <1%), in a process that is

usually called de-emulsification or dehydration, which consists of forcing the coalescence of water droplets and producing their separation by settling<sup>(2)</sup>.

De-emulsifiers are typically based on the following chemistry: acid catalyzed phenol-formaldehyde resins, base-catalyzed phenol-formaldehyde resins, polyamines, di-epoxides, and polyols. De-emulsification is an essential industrial process, mainly used for removing water from crude oil. The first de-emulsifiers were based on sulfonated castor oil and the like; present day de-emulsifiers are a blend of highly sophisticated organic compounds with surface active characteristics. De-emulsifier formulations are prepared from non-ionic, cationic or anionic surfactants of various hydrophobic / lyophobic balance (HLB) values and various molecular weights<sup>(3)</sup>.

Failure to separate the oil / water mixture efficiently can result in a number of problems, including

- Overloading of surface separation equipment.
- Increased cost of pumping crude which contains significant water.
- Significant flow line or tubing pressure resulting from highly viscous emulsion.
- Increased vessel heating costs.
- Risk of corrosion in export lined, including subsea pipelines and at refinery,
- Stock tank bottoms form thick sludge, difficult to remove.
- Refinery can only accept oil of low basic sediment, water and salt content. Typical maximum acceptable salt content at a

refinery is 25 pounds salt per thousand barrels crude.

- Risk of catalyst poisoning at refinery.

The action of a de-emulsifier is to destabilize the emulsion. In order to do this the ordered structure of the natural surfactant/emulsion system must be disrupted allowing the disperse droplets to approach each other. Apart from the active component in a formulation, which contains various combinations of flocculate's emulsion breakers (droppers), wetting agents and the solvent can play a significant role.

Al-Sabagh<sup>(4)</sup> synthesized nine types of de-emulsifiers based on bisphenol (bisphenol A (BA), bisphenol AC(BAC) and bisphenol CH(BCH) having different ethylene oxide units ( $n = 27, 34, 45$ ) namely; E ( $x + y$ ) (where E represents BA, BAC or BCH and ( $x + y$ ) represents the ethylene oxide units (27, 34, 45). The efficiency of these de-emulsifiers was tested on water-in-oil emulsion (w/o) at different concentrations (100, 200 and 300 ppm), 7.4% asphaltene content and 30%, 50% and 70% water content. From the obtained data, the best de-emulsifier was E(34)BA, which shows 100% de-emulsification after 58 min at 30% water content and 300 ppm of de-emulsifier.

Chemical method is a common method for destabilizing emulsions<sup>(5)</sup>. Thus, the major objective of this study is to produce chemical de-emulsifiers using locally sourced materials that are environmentally friendly. Nowadays, *Jatropha* tree has been successfully cultivated as it can grow well in the desert as it withstand drought and can be irrigated with treated sewage water since its oil is non-edible. *Jatropha* seeds contain about 27-40 % non-

edible viscous oil. Natural fatty derivatives have been used as intermediate materials in several industries; fatty ethoxylates are one of these fatty acids derivatives in which a fatty acid is used as the natural precursor in ethoxylates preparation<sup>(6)</sup>. The search for the appropriate de-emulsifier for water-in-crude oil emulsion is generally carried out through a well-known "bottle test" technique<sup>(7)</sup>.

The aim of this study is to synthesize and characterize relatively cheap, environmentally friendly, nonionic surfactants derived from Jatropha oil and to evaluate their de-emulsification efficiency in the petroleum industry for breaking water in crude oil emulsion.

## MATERIALS AND METHODS

### Materials:

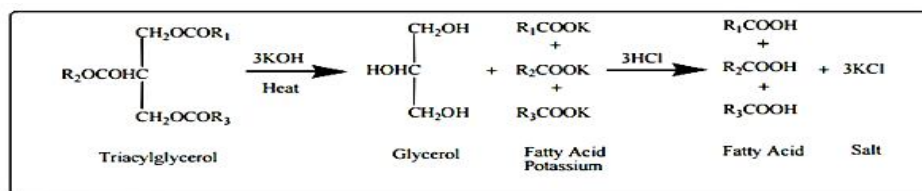
- Jatropha oil was extracted from Jatropha curcas seeds and obtained from Africa city of technology, Sudan.
- Crude oil used obtained from Qarun Petroleum Company, Egypt.
- Ethylene oxide gas cylinder, sodium metal catalyst and all solvents and chemical used were of highly pure grade purchased from Merck.

- Autoclave (Parr model 4848, USA)
- Gas chromatograph Shimadzu Model QP2010 Plus.
- FTIR Nicolet IS-10.

### Method:

#### Hydrolysis of Jatropha oil

In a typical procedure, 100 g of Jatropha oil was reacted with 250 cm<sup>3</sup> of 10 % potassium hydroxide solution (and the reaction mixture was heated in a water bath at 45°C for 2 hrs. Then doubly water (400 cm<sup>3</sup>) was added while stirring for 90 min until the mixture became almost clear. After cooling, 300 cm<sup>3</sup> of HCl solution (30 % by weight) was added portion wise (5 portions each one of 60 cm<sup>3</sup>) under stirring for 3 h. The reaction mixture was allowed to cool at room temperature, and then transferred into a 1 dm<sup>3</sup> separating funnel to separate the aqueous layer. The oil phase was then separated, washed three times with doubly water (3, 9, 200 cm<sup>3</sup>) to remove the excess acid and salts and then dried under vacuum (0.1 atm.) at 40°C for 24 h. The fatty acids obtained were analyzed by gas chromatography (GC) as shown in table 2.



Hydrolysis reaction of Jatropha crude oil<sup>(8)</sup>

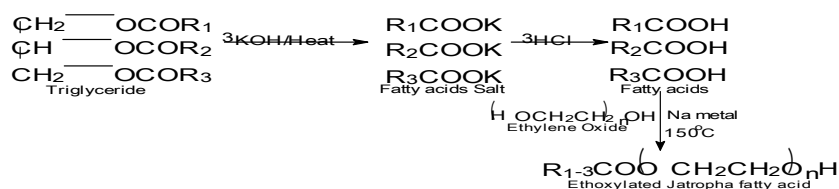
### Ethoxylation of Jatropha Fatty Acids

A high-pressure stainless steel autoclave (Parr model 4848, USA) of 1dm<sup>3</sup> capacity, 1900 psi maximum pressure, and 500°C maximum temperatures was utilized through ethoxylation reaction. The autoclave is equipped with a magnetic drive stirrer, an electric heating mantle with a

thermocouple inserted in the reactor body, a cooling coil, a pressure gauge, and a drain valve. Hydrolyzed Jatropha oil was charged into the reaction vessel individually with sodium metal as a catalyst (0.3 wt. %). The reaction mixture was heated to 150°C with continuous stirring while passing a stream of nitrogen gas through the system for 10 minutes to flush out air. The nitrogen stream was then replaced

by ethylene oxide (10, 20, 30 unit). The addition of ethylene oxide is to increase water solubility. Generally, as a result of the introduction of ethylene oxide, the pressure was substantially increased as indicated by the pressure gauge, until it reached a maximum value. The pressure drop indicates ethylene oxide consumption<sup>(9)</sup>. The reaction completion was established when the pressure reached its minimum value. At this stage, heating

was stopped and the contents were cooled gradually to ambient temperature by means of the cooling coil connected to the reactor carrying cold water. After cooling, the product obtained was discharged, weighed and neutralized with HCl solution, dissolved in the isopropanol, and then salted out with supersaturated NaCl solution. The organic layer was then separated, and the isopropanol was distilled off.



Ethoxylation reaction of Jatropa oil fatty acids

## RESULTS and DISCUSSION

Table 1: Chemical structure and abbreviation of the prepared compounds

Chemical Structure	Name	Abbreviation
$\text{R}_{1-3}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$	Ethoxylated Jatropa Oil Fatty Acids (10 Unit)	HJ.E10
$\text{R}_{1-3}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$	Ethoxylated Jatropa Oil Fatty Acids (20 Unit)	HJ.E20
$\text{R}_{1-3}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_{30}\text{H}$	Ethoxylated Jatropa Oil Fatty Acids (30 Unit)	HJ.E30

Table 2: GC analysis of Jatropa oil fatty acids

Fatty acids of Jatropa oil	Saturated				Total	Unsaturated				Total
	C <sub>14</sub> Myristic acid	C <sub>16</sub> Palmitic acid	C <sub>20</sub> Arqchidic acid	C <sub>22</sub> Behenic acid		C <sub>18:1</sub> Palmitoleic acid	C <sub>18:1</sub> Oleic acid	C <sub>18:2</sub> Linoleic acid	C <sub>18:3</sub> Linolenic acid	
Percents %	0.93	15.93	1.41	0.91	19.18	1.21	50.20	28.18	1.62	81.21

### FTIR Analysis

In order to prove the Jatropa oil hydrolysis, FTIR spectroscopy supported the FFA% by showing the main peaks and their functional groups. The comparison between

Jatropa oil and its hydrolysis are shown in figures 1 and 2.

For carboxylic acid carbonyl functional groups (C=O), FTIR spectrum showed absorption bands of hydrolyzed oil at  $1711\text{cm}^{-1}$  for stretching vibration,  $1283-1285\text{cm}^{-1}$

for stretching asymmetric while at 1413 and 940  $\text{cm}^{-1}$  for bending vibration of carboxylic acid. The hydrolyzed Jatropha oil IR showed ester carbonyl group absorption band at 1747  $\text{cm}^{-1}$  and 1166  $\text{cm}^{-1}$  indicates low hydrolysis of Jatropha oil (figure 2).

Figure 1 showed the main difference between Jatropha oil and its hydrolysis with completely disappearance of carboxylic acid

carbonyl group, in the same time strong ester carbonyl group absorption band at 1746  $\text{cm}^{-1}$  and 1164  $\text{cm}^{-1}$  for stretching and bending vibrations respectively.

Peaks at 2925 and 2855  $\text{cm}^{-1}$  indicated the  $\text{CH}_2$  and  $\text{CH}_3$  stretching vibrations of both Jatropha oil and hydrolyzed oil. FTIR spectrum also showed absorption bands at 723  $\text{cm}^{-1}$  for C-H group bending vibration. These results run in harmony with others <sup>(8)</sup>.

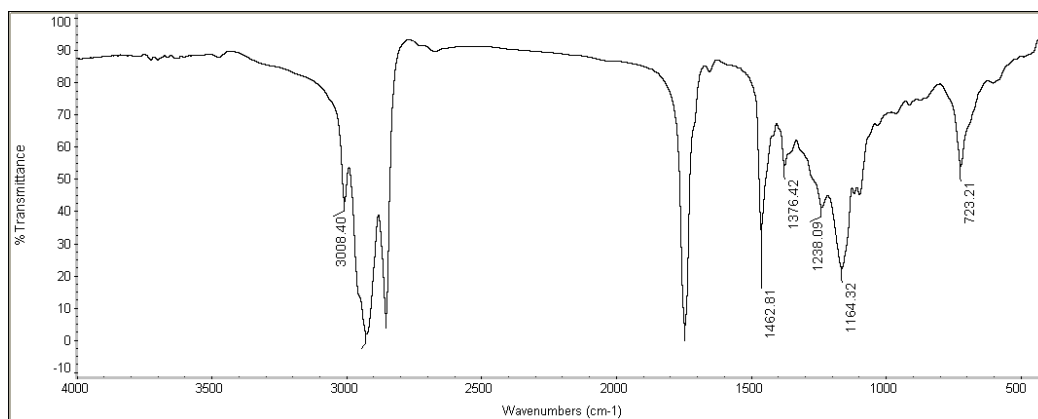


Figure 1 FTIR chart of Jatropha oil

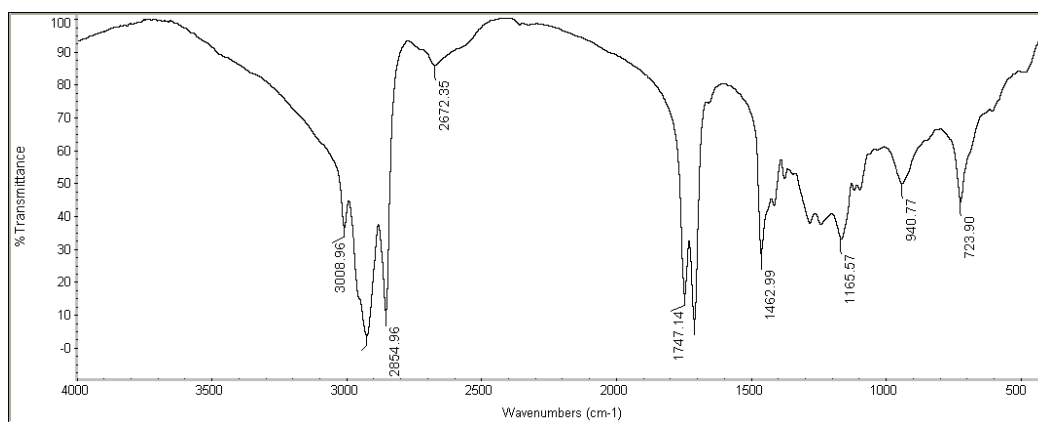
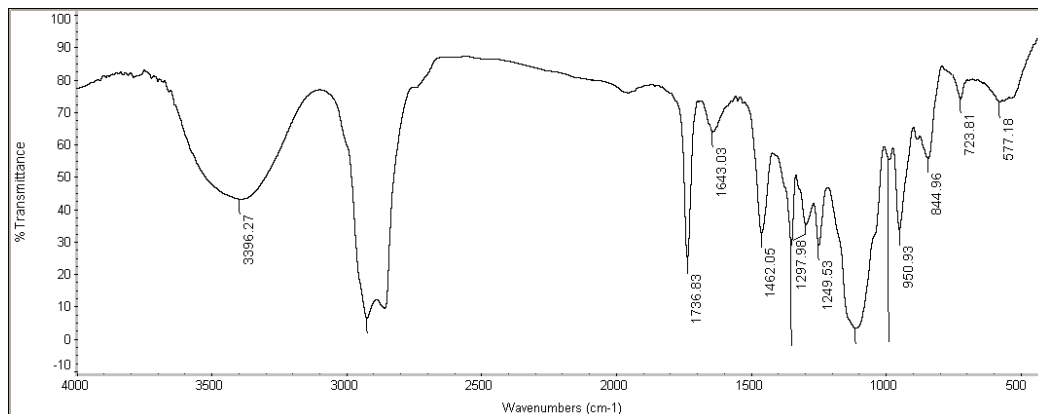


Figure 2 FTIR chart of Jatropha oil fatty acids

Ethoxylated Jatropha fatty acids IR spectrum showed ester carbonyl group stretching vibration absorption band at 1736  $\text{cm}^{-1}$  and bending vibration at 1125  $\text{cm}^{-1}$  while at 2925 and 2855  $\text{cm}^{-1}$  for  $\text{CH}_2$  and  $\text{CH}_3$  stretching vibration,

C-H bending vibration showed absorption band at 723  $\text{cm}^{-1}$ , and the absorption band at 1297  $\text{cm}^{-1}$  for C-O stretching vibration (figure 3).

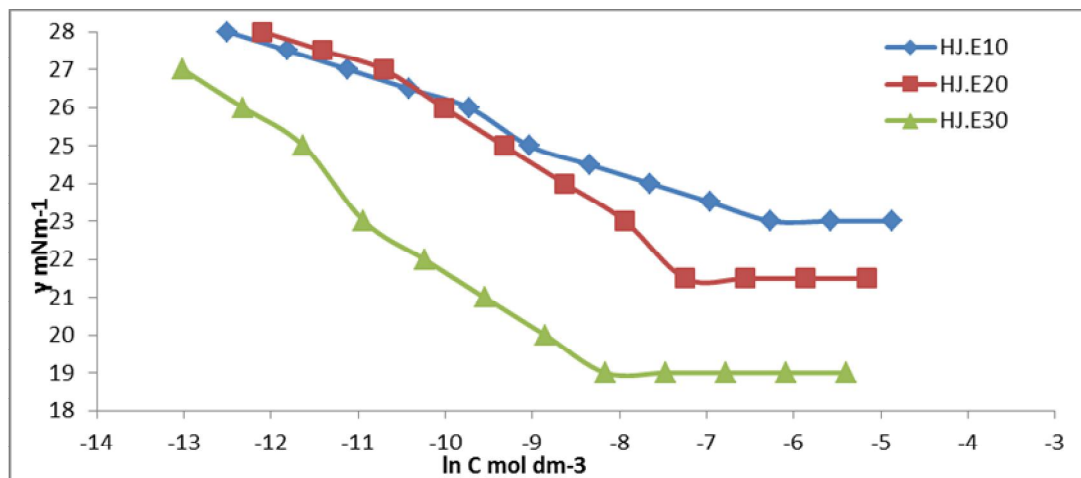


**Figure 3** FTIR chart of ethoxylated Jatropha oil fatty acids

### Surface Tension Parameters

Micelles of de-emulsifiers are formed in bulk aqueous solution above a given concentration for each de-emulsifier and this concentration known as the critical micelle concentration (CMC).

The CMC of the investigated individual de-emulsifiers at 60°C was determined by plotting the surface tension ( $\gamma$ ) versus logarithm de-emulsifier concentration ( $-\ln C$ ), as shown in figure 4.



**Figure 4** Relationship between surface tension and  $\ln C$  for ethoxylated Jatropha oil fatty acids at different units (10, 20, 30) at 60°C

**Table 3: The surface tension parameters of the prepared de-emulsifiers**

De-emulsifier	Temp	CMC mole/dm <sup>3</sup>	$\gamma_{\text{cmc}}$ mN/m
HJ.E10	60°C	$1.91 \times 10^{-3}$	23
HJ.E20	60°C	$7.17 \times 10^{-4}$	21.5
HJ.E30	60°C	$2.86 \times 10^{-4}$	19

It is obvious that, the CMC values decrease at temperature of 60°C for all undertaken de-emulsifiers. This may be explained by the fact that, increasing the temperature leads to an increase of the mobility of the de-emulsifier that might be adsorbed on the W/O interface. It was also observed that decrease of the CMC values when the molecular weight increases this means that the number of molecules required for micelle formation decreases as a result of the size and coiling of surfactant molecule. This finding runs in harmony with others<sup>(10)</sup>.

**De-emulsification Efficiency:**

The de-emulsification efficiency was carried out using bottle test technique, at five different concentrations for each prepared de-emulsifier at 60°C, the de-emulsification efficiency data for the prepared de-emulsifiers with different molecular weights in this work are shown in the tables 4, 5 and 6. The de-emulsification efficiency % was calculated using the following equation:

$$\text{The de-emulsification efficiency \%} = \frac{\text{(volume of water separated after a given time/total volume of water)} \times 100}{100}$$

It was found that the de-emulsification efficiency increase by increasing of the number of ethylene oxide units (increasing the molecular weight), increasing the ethylene oxide units leads to increase in de-emulsifier surface area, the de-emulsifiers molecules were adsorbed gradually on oil-water interfacial film and replaced the emulsifiers. That replacement decreased both the strength and the life of oil film and film thickness until it collapsed<sup>(11)</sup> leading the water droplets to merge and separate.

HJ.E10, 20, and 30 at concentration 100 ppm are representative example, also HJ.E30 showed excellent water separation compared with both HJ.E10 and HJ.E20 at all concentrations after 24 hours. But it was found that, this observation in not applicable in other concentrations, for example, HJ.E10 exhibit good water separation at concentrations 200, 300 and 500 ppm at different time while HJ.E20 which is higher molecular weight is not.

Water separations of HJ.E10, HJ.E20 and HJ.E30 at five different concentrations at 60°C after 24 hours are shown in figures 5, 6 and 7 respectively.

The Blank sample exhibits no water separation at any time.

**Table 4: De-emulsification efficiency of HJ.E10 at five different concentrations with time at 60°C**

De-emulsifier (Effective conc. ppm)	Time / De-emulsification efficiency %				M.W.
	60 min.	120 min.	180 min.	24 hrs.	
HJ.E10 <sub>(100)</sub>	0	0	0	0	1310
HJ.E10 <sub>(200)</sub>	25	45	45	55	
HJ.E10 <sub>(300)</sub>	45	50	55	65	
HJ.E10 <sub>(400)</sub>	0	0	0	0	
HJ.E10 <sub>(500)</sub>	30	40	45	50	





**Figure 5** Water separation of HJ.E10 at five different concentrations at 60°C after 24 hours

**Table 5: De-emulsification efficiency of HJ.E20 at five different concentrations with time at 60°C**

De-emulsifier (Effective conc. ppm)	Time / De-emulsification efficiency %				M.W.
	60 min.	120 min.	180 min.	24 hrs.	
HJ.E20 <sub>(100)</sub>	5	10	25	30	1750
HJ.E20 <sub>(200)</sub>	5	5	20	20	
HJ.E20 <sub>(300)</sub>	0	0	0	10	
HJ.E20 <sub>(400)</sub>	0	0	0	10	
HJ.E20 <sub>(500)</sub>	0	0	0	20	



**Figure 6** Water separation of HJ.E20 at five different concentrations at 60°C after 24 hours

**Table 6: De-emulsification efficiency of HJ.E30 at five different concentrations with time at 60°C**

De-emulsifier (Effective conc. ppm)	Time / De-emulsification efficiency %				M.W.
	60 min.	120 min.	180 min.	24 hrs.	
HJ.E30 <sub>(100)</sub>	15	45	50	55	2190
HJ.E30 <sub>(200)</sub>	40	55	75	80	
HJ.E30 <sub>(300)</sub>	40	55	75	85	
HJ.E30 <sub>(400)</sub>	15	45	50	55	
HJ.E30 <sub>(500)</sub>	5	35	50	55	





**Figure 7** Water separation of HJ.E30 at five different concentrations at 60°C after 24 hours

## CONCLUSION

Three non-conventional non-ionic demulsifiers were prepared from the Jatropha oil by the reaction of ethylene oxide with fatty acids obtained from the hydrolysis of Jatropha oil. The prepared ethoxylated Jatropha oil fatty acids exhibit high tendency toward demulsification of water in oil emulsion. It was found that, the efficiency of demulsification increased with the increase of ethylene oxide units (increase of the molecular weight) which increase the de-emulsifier surface area that playing an important role in water separation and hence demulsifier efficiency. Further work may establish a consistent pattern in ethylene oxide units to enhance the demulsification efficiency.

## REFERENCES

1. Speight J. G. (1999), “*The Chemistry and Technology of Petroleum*,” Marcel Dekker, New York.
2. Miguel R., Patrick B., and Jean L. (2006), Breaking of Water-in-Crude Oil Emulsions. 1. Physicochemical Phenomenology of Demulsifier Action. *Energy & Fuels* **20**:1600-1604.
3. Byoung-Yun Y., Jun H., Tae-Hyun S., Seung-Man Y. and Jong-Duk K. (2002). Demulsification of water in crude oil emulsion by a continuous electrostatic dehydrator. *Separation science and technology* **37**(6):1307-1320.
4. Al-Sabagh A. M., Nadia G. K., Rasha A. E. and Mahmoud R. N. (2011). Synthesis and evaluation of some new de-emulsifiers based on bisphenols for treating water-in-crude oil emulsions. *Egyptian Journal of Petroleum* **20**(2):67 -77.
5. Odisu T. and Salami D. (2010). Formulation and production of crude oil demulsifiers from locally sourced materials. *Journal of Physical Sciences and Innovation* **2**: 26-37.
6. Elshatory Y., Ghada A., Saadia M. and Elshahat H. (2012). Production of ethoxylated fatty acids derived from Jatropha non-edible oil as a nonionic fat-liquoring agent. *Journal of Oleo science* **61**(5):255-266.
7. Goldszal A. and Bourrel M. (2000). De-emulsification of Crude Oil Emulsion: Correlation to Micro-emulsion Phase Behavior. *Ind. Eng. Chem. Res.* **39**: 2746 – 2751.
8. Salimon J., Bashar M. and Nadia S. (2011). Hydrolysis optimization and

characterization study of preparing fatty acids from *Jatropha Curcas* seed oil. *Chemistry central journal* **5**: 67.

9. Sheu E. Y. and Mullins O. C. (1995). *Asphaltenes: Fundamentals and applications*. Plenum press. New York.

10. Tahany M. A. (2013). *Preparation of some novel (oxyethylene/oxypropylene) derivatives from alkylene amines as demulsifiers*

*to break water in oil emulsion in petroleum industry*, M.Sc. thesis, Benha University, Egypt.

11. Wanli Kang, Guolin Jing, Hongyan Zhang, Mingyuan Li, and Zhaoliang Wu (2006). Influence of demulsifier on interfacial film between oil and water. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **272**: 27–31.