



## Preparation of Oleic Ester of Ethoxylated Hydrolyzed Jatropha Oil as a De-emulsifier for Treating Water in Crude Oil Emulsion.

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### ABSTRACT

Non-conventional homologous de-emulsifiers derived from natural non-edible oil such as Jatropha oil were synthesized to replace the conventional de-emulsifiers. These de-emulsifiers are characterized by their high tendency toward de-emulsification. The aim of this study is to synthesize and characterize three environment friendly nonionic ester de-emulsifiers derived from Jatropha non-edible oil and to evaluate their de-emulsification efficiency in the petroleum industry, for treating water in crude oil emulsion.

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

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### المستخلص:

تم في هذا العمل تكوين عدد من كاسرات الإستحلاب غير التقليدية و المتشابهة المشتقة من زيت غير صالح للأكل و ذلك لتحل محل كاسرات الإستحلاب التقليدية. و تمتاز هذه المركبات بميولها العالي تجاه كسر الإستحلاب. الهدف من هذه الدراسة تخليق ثلاث كاسرات إستحلاب غير أيونية و صديقه للبيئة و مشتقة من زيت الجاتروفا غير صالح للأكل و تقييم كفاءتها في مجال صناعة البترول لكسر مستحلب الماء في الزيت الخام.

### INTRODUCTION

An emulsion is a mixture in which one liquid is uniformly distributed (usually as tiny globules) in another liquid<sup>(1)</sup>. In the oil industry, oil is produced from reservoirs in association with natural formation water. This mixture is in the form of oil and water emulsion<sup>(2)</sup>. Emulsions of crude oil and water can be encountered at many stages during drilling, producing, transporting and processing of crude oils and in many locations such as in hydrocarbon reservoirs, well bores, surface facilities, transportation systems and refineries<sup>(3)</sup>.

Breaking of water in crude oil emulsions involves chemical, thermal, electrical, or a combination of these processes depending on the characteristics and properties of the emulsion. The addition of chemical de-

emulsifiers in small quantities can greatly facilitate oil-water separation. The main advantages of using emulsion breakers are:

- Rapidity and effective cost.
- Reduction in the viscosity of crude oil emulsions
- Improvement of pump-ability.
- Reduction of oil waste handling.
- Reduction of the final disposal cost by a factor of 10<sup>(4)</sup> This study aims to produce chemical de-emulsifiers using locally sourced materials that are environment friendly<sup>(5)</sup>.

Nowadays, Jatropha tree has been successfully cultivated as it can grow well in the desert, 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>.

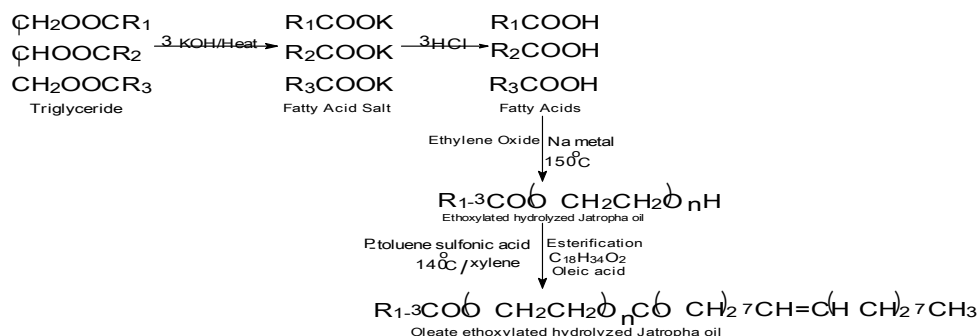
### MATERIALS and METHODS

- Crude oil used obtained from Qarun Petroleum Company, Egypt.
- All solvents and chemical used were of highly pure grade purchased from Merck.
- FTIR Nicolet IS-10.

### Esterification of the Ethoxylated Hydrolyzed Jatropha oil

Jatropha oil was hydrolyzed and the hydrolyzed Jatropha oil was ethoxylated <sup>(7)</sup>. Esterification of the ethoxylated hydrolyzed

Jatropha oil was carried in a 1-dm<sup>3</sup>, flat-bottomed flask fitted with a Dean-Stark trap and a condenser, 1mol of ethoxylated hydrolyzed Jatropha oil was esterified with 1 mol of oleic acid. The reaction ingredients were refluxed in xylene in presence of *p*-toluene sulfonic acid (0.1 %) as a catalyst and 100 cm<sup>2</sup> xylene as a solvent, with continuous stirring until the theoretical amount of water was collected and the homogeneous solution was obtained. Then, the solvent was distilled off under vacuum and the product was dissolved in isopropanol and salted out by super saturated NaCl solution. The organic layer was separated and the solvent was distilled off <sup>(8)</sup>. The following equations show the preparation of oleate ethoxylated hydrolyzed Jatropha oil as representative example:



### RESULTS and DISCUSSION

Table 1: Chemical structure and abbreviation of the prepared compounds

Chemical Structure	Name	Abbreviation
$\text{R}_{1-3}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{CO}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3$	Oleate Ethoxylated Hydrolyzed Jatropha Oil (10 Unit)	OHJ.E10
$\text{R}_{1-3}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{CO}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3$	Oleate Ethoxylated Hydrolyzed Jatropha Oil (20 Unit)	OHJ.E20
$\text{R}_{1-3}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_{30}\text{CO}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3$	Oleate Ethoxylated Hydrolyzed Jatropha Oil (30 Unit)	OHJ.E30

Table 2: GC analysis of fatty acids of Jatropha oil

Fatty acids of Jatropha oil	Saturated					Total	Unsaturated				Total
	C <sub>14</sub>	C <sub>16</sub>	C <sub>20</sub>	C <sub>22</sub>			C <sub>18:1</sub>	C <sub>18:1</sub>	C <sub>18:2</sub>	C <sub>18:3</sub>	
	Myristic acid	Palmitic acid	Arqchidic acid	Behenic acid			Palmitoleic acid	Oleic acid	Linoleic acid	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

Ethoxylated Jatropha fatty acids IR spectrum shows ester carbonyl group stretching vibration absorption band at 1736

cm<sup>-1</sup> and bending vibration at 1125 cm<sup>-1</sup>, while at 2925 and 2855 cm<sup>-1</sup> for CH<sub>2</sub> and CH<sub>3</sub> stretching vibration respectively; C-H bending vibration shows absorption band at

723  $\text{cm}^{-1}$ , and the absorption band at 1297  $\text{cm}^{-1}$  for C-O stretching vibration. Hydroxyl group showed stretching vibration

absorption band at 3396  $\text{cm}^{-1}$  and bending vibration absorption band at 1249  $\text{cm}^{-1}$  (Figure 1).

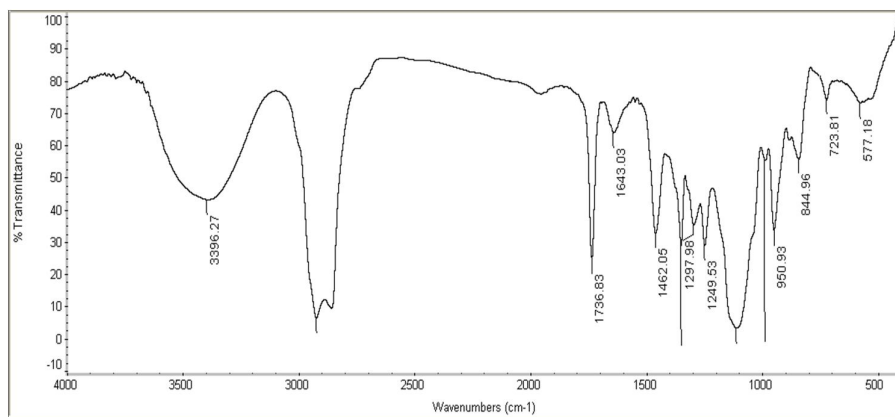


Figure 1: FTIR spectrum of ethoxylated hydrolyzed Jatropha oil

Oleate ethoxylated hydrolyzed Jatropha oil IR spectrum shows weak ester carbonyl group stretching vibration absorption band-shoulder- at 1725  $\text{cm}^{-1}$  and bending vibration at 1100  $\text{cm}^{-1}$ , while at 2925 and 2855  $\text{cm}^{-1}$  for  $\text{CH}_2$  and  $\text{CH}_3$  stretching vibration respective-ely; C-H bending

vibration shows absorption band at 725  $\text{cm}^{-1}$ , and the absorption band at 1298  $\text{cm}^{-1}$  for C-O stretching vibration; carbon carbon double bond ( $\text{C}=\text{C}$ ) shows stretching vibration absorption band at 1666  $\text{cm}^{-1}$  (Figure2).

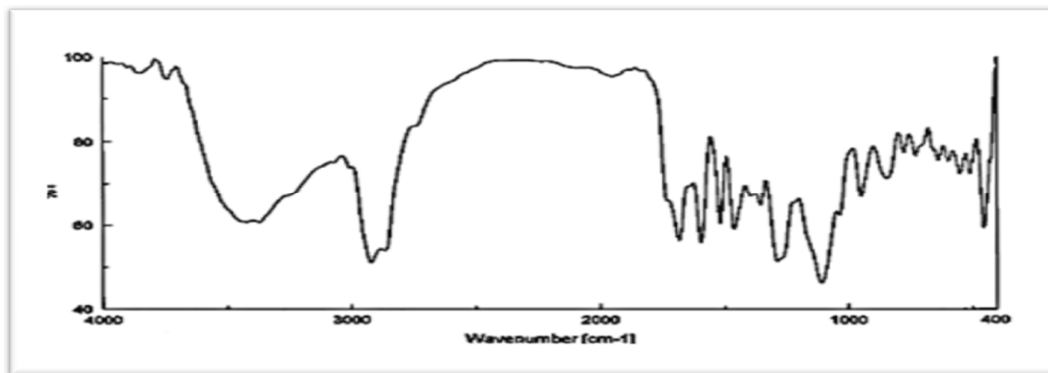


Figure 2: FTIR spectrum of oleate ethoxylated hydrolyzed Jatropha oil

### Surface Tension Parameters

Micelles of surfactants 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-emulsifier (surfactant) at 60°C was determined (Table 3), and the relation between the surface tension ( $\gamma$ ) and logarithm de-emulsifier concentration ( $-\ln C$ ) was plotted in Figure 3.

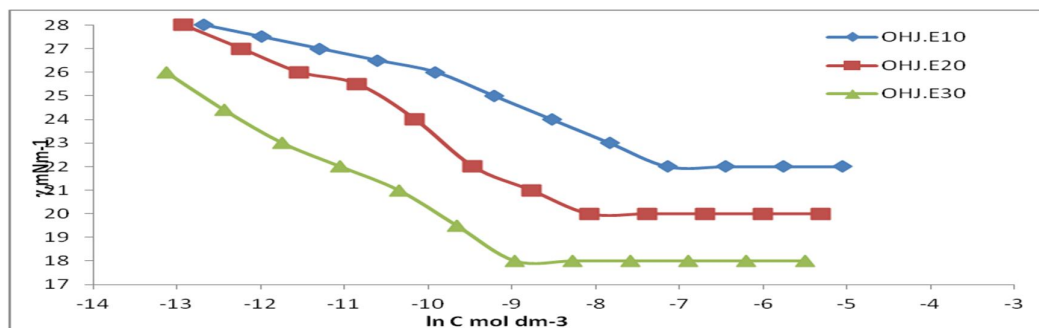
Table 3: shows the surface tension parameters of the prepared de-emulsifiers

De-emulsifier	Temp	CMC mole/dm <sup>3</sup>
OHJ.E10	60°C	8.01x10 <sup>-4</sup>
OHJ.E20	60°C	3.13x10 <sup>-4</sup>

OHJ.E30

60°C

$1.28 \times 10^{-4}$



**Figure 3: Relationship between surface tension and  $\ln C$  for oleate ethoxylated hydrolyzed *Jatropa* oil at 60°C**

It was obvious that, the CMC had low values at 60°C for all undertaken de-emulsifiers. This may be explained by the fact that increasing the temperature led 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 increased decreases the number of molecules required for micelle formation as a result of the size and coiling of de-emulsifier molecule. This finding runs in harmony with those of previous workers who found that increasing ethylene oxide units decreases the CMC as the result of coiling the ethylene oxide chains<sup>(8)</sup>.

#### **Effect of Hydrophilic-Lypophilic Balance (HLB)**

The HLB concept is normally used as an important parameter to predict the action of de-emulsifiers on certain water-in-oil emulsion. However, this concept has not been used extensively by scientists working in the field of de-emulsifiers. In the present study, the calculated values of HLB for the de-emulsifiers under investigation were presented in the Tables 4, 5 and 6. HLB values for normal nonionic de-emulsifiers were determined by simple calculation, a commonly used formula for non ionics:

$$HLB = 20 [MH / (MH + ML)]$$

Where;

MH: molecular weight of hydrophilic portion of the molecule.

ML: molecular weight of lypophilic portion of the molecule<sup>(8)</sup>.

It can be seen that the HLB of the de-emulsifiers increased with increasing of ethylene oxide units. The data reveal that the amount of water separated after a certain time, expressed as percentage coalescence, was in accordance with the increase of HLB. This finding may be explained by the following speculation: The increasing of HLB value increased the solubility of the de-emulsifier in the aqueous phase (dispersed phase). When the de-emulsifier was initially introduced to the water-in-oil emulsion, it would be more thermodynamically stable at the interface of the water droplets. Accordingly, the concentration of the de-emulsifier in the interface increased by increasing their HLB value. As the concentration of the de-emulsifier increased at the interface, a continuous hydrophilic pathway was formed between the dispersed water droplets. This led to rupture of the interfacial oil film surrounding the water droplets<sup>(9)</sup>.

The present work dealt with a water-in-oil emulsion, and hence it is clear that the higher the HLB, the higher the de-emulsification efficiency.

#### **De-emulsification Efficiency**

The de-emulsification efficiency was carried out using bottle test technique, at

different five 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.

OHJ.E10 showed no water separation at any concentration and any time and that would be attributed to its low HLB value (5.59), which affected the solubility of the de-emulsifier in the aqueous phase (dispersed phase) leading to decreasing of the de-emulsifier concentration at the interface<sup>(9)</sup> OHJ.E20 and OHJ.E30 showed (as expected) high efficient water separation as

a result of their higher HLB values 8.73 and 10.76, respectively.

It was found that the de-emulsification efficiency increased by increasing the number of ethylene oxide units (increasing the molecular weight): OHJ.E10, OHJ.E20, and OHJ.E30 which were used as representative example at all concentrations and at all times.

Figures 4 and 5 show the water separation of OHJ.E20 and OHJ.E30 at five different concentrations (Blank, 100, 200, 300, 400 and 500 ppm, respectively).

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

De-emulsifier (Effective conc. ppm)	Time / De-emulsification efficiency %				HLB	M.W.
	60 min.	120 min.	180 min.	24 hrs.		
OHJ.E10 <sub>(100)</sub>	0	0	0	0	5.59	1574.46
OHJ.E10 <sub>(200)</sub>	0	0	0	0		
OHJ.E10 <sub>(300)</sub>	0	0	0	0		
OHJ.E10 <sub>(400)</sub>	0	0	0	0		
OHJ.E10 <sub>(500)</sub>	0	0	0	0		

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

De-emulsifier (Effective conc. ppm)	Time / De-emulsification efficiency %				HLB	M.W.
	60 min.	120 min.	180 min.	24 hrs.		
OHJ.E20 <sub>(100)</sub>	15	40	60	70	8.73	2014.46
OHJ.E20 <sub>(200)</sub>	40	45	50	75		
OHJ.E20 <sub>(300)</sub>	25	35	40	50		
OHJ.E20 <sub>(400)</sub>	15	25	45	55		
OHJ.E20 <sub>(500)</sub>	20	30	45	55		



Figure 4 Water separation of OHJ.E20 at five different concentrations at 60°C after 24 hours

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

De-emulsifier (Effective conc. ppm)	Time / De-emulsification efficiency %				HLB	M.W.
	60 min.	120 min.	180 min.	24 hrs.		
OHJ.E30 <sub>(100)</sub>	30	45	65	90	10.76	2454.46

OHJ.E30 <sub>(200)</sub>	45	45	50	80
OHJ.E30 <sub>(300)</sub>	45	50	55	80
OHJ.E30 <sub>(400)</sub>	25	50	55	80
OHJ.E30 <sub>(500)</sub>	25	35	45	65



**Figure 5** Water separation of OHJ.E30 at five different concentrations at 60°C after 24 hours

## CONCLUSION

The conclusion can be summarized in the following points:

- Three non-conventional, non-ionic de-emulsifiers were prepared from the Jatropha oil by the reaction of ethylene oxide with fatty acids obtained from the hydrolysis of Jatropha oil followed by esterification of ethoxylated Jatropha fatty acids.
- The prepared oleate ethoxylated hydrolyzed Jatropha oil exhibit high tendency toward de-emulsification of water in oil emulsion as a result of high degrees of water separation obtained.
- It was found that, the efficiency of de-emulsification increased by increasing the HLB value of the de-emulsifier and with the increase of ethylene oxide units (increase of the molecular weight).

## REFERENCES

1. Kate V. D. (1997). *Fundamentals of Petroleum*. 4<sup>th</sup> ed. pp. 174. University of Texas, at Austin, USA.
2. Jinxin L., Jinjun Z., Haijun Y. and Yongcheng N. (2006). Separation and characterization of alkyl phenol formaldehyde resins demulsifier by adsorption chromatography, gel permeation chromatography, infrared spectrometry and nuclear

magnetic resonance spectroscopy. *Analytica Chimica Acta*, **566**: pp. 224-237.

3. Langevin D., Poteau S., Hénaut I. and Argillier J.F. (2004). Crude Oil Emulsion Properties and their Application to Heavy Oil Transportation. *J. of Oil & Gas Science and Technology*, **59**: 511-521.
4. Shweta D. M. (2005). *Making and Breaking of Water in Crude Oil Emulsion*. Texas University Press, United States of America.
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. Haitham A. T., Alsabagh A. M. and Elmugdad A. A. (2016). Preparation and evaluation of ethoxylated Jatropha oil fatty acids as de-emulsifier for crude oil emulsion. *Journal of Natural and Medical Science* **17**(1): 26-35.
8. Tahany M. A. (2013). *Preparation of some Novel (oxyethylene/oxypropylene)*

*Derivatives from Alkyleneamines as De-emulsifiers to Break Water in Oil Emulsion in Petroleum Industry.* M.Sc. thesis, Benha University, Egypt.

9. Zaki N. N., Abdel Raouf E. and Abdel Azim A. (1996). Propylene oxide-Ethylene

oxide copolymers as de-emulsifiers for water in oil emulsion, I. effect of molecular weight and hydrophilic-lipophylic balance on the de-emulsification efficiency, *Monatshefte fur chemie* **127**: 621-629.