

## 2.1 Materials

### 2.1.1 Chemicals Used

The sources of the chemicals used in this study are shown in table 2.1

**Table 2.1** Chemicals and its sources used throughout the methods.

<b>Chemical</b>	<b>Source</b>
<i>P</i> _ Toluene sulfonic acid	Aldrich, USA
Xylene	Aldrich, USA
Methanol	Aldrich, USA
Propylene oxide	Merk, Germany
Ethylene oxide	Merk, Germany
Sodium Metal	Fluka, UK
Hydrochloric acid	Adwic, Egypt
Isopropanol	Bio.Chem, Egypt.
Colophony acid (Rosin)	Fluka, UK
Oleic acid	Fluka, UK
Potassium hydroxide	Fluka, UK
Sodium Chloride	Fluka, UK

### 2.1.2 Crude Oil Sample

The physicochemical properties of waxy crude oil (provided by Qarun petroleum Company, Egypt) were determined according to standard methods. The results obtained are listed in table 2.2.

**Table 2.2** Physicochemical properties of the waxy crude oil sample.

<b>Specification</b>	<b>Methods</b>	<b>Results</b>
API gravity at 60°F	ASTMD-1298	32.1
Kinematic viscosity at 40°C, (cSt)	ASTMD-445	2.5
Wax contents, wt. %	IP 143/57	16.3
Asphaltenes and resins (Wt. %)	IP 143/57	1.0
Pour Point, °C	ASTMD-79	21
Water content, % Vol.	ASTMD 95-99	20
BS&W, % Vol.	ASTMD-4007	20

### 2.1.3 Crude Jatropha Oil Sample

The physicochemical properties of Jatropha oil (provided by African City of Technology, Sudan) were determined according to standard methods. The results obtained are listed in table 2. 3.

**Table 2.3** Physicochemical properties of Jatropha crude oil sample.

<b>Parameter</b>	<b>Unit</b>	<b>Value</b>	<b>Test method</b>
Density	kg/m <sup>3</sup>	870.1	ASTMD 287
Viscosity at 40°C	mm <sup>2</sup> /s	151.4	ASTMD 445
Neutralization No	mg KOH/g	0.93	AOCS 1a-64
Free fatty acid	mg KOH/g	16.1	AOCS (Ca5a-40)
Moisture content	%	7.3	Oven Method
Diglyceride	Wt (%)	2.50	ASTMD6584
Triglyceride	Wt (%)	95.16	ASTMD6584
Iodine value	mg Iodine/g	94.1	AOCS (16-87)

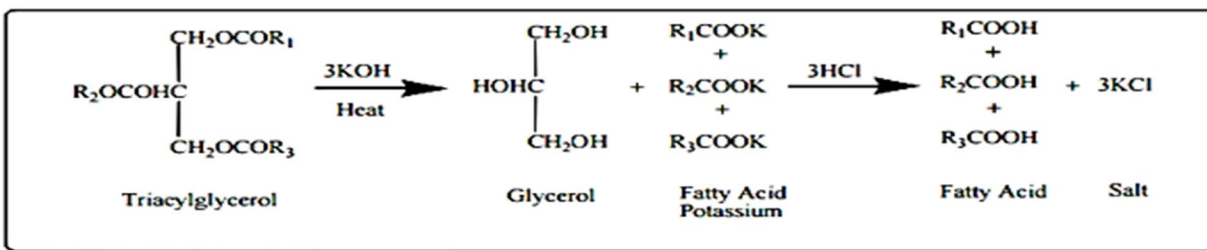
## 2.2 Preparation of Surfactant (De-emulsifiers)

### 2.2.1 Hydrolysis of Jatropha Oil

In a typical procedure, 100 g of Jatropha oil was reacted with potassium hydroxide solution (250 mL of 10 % by weight) and the reaction mixture was heated in a water bath at 45°C for 2 hrs. Then double distilled water (400 mL) was added while stirring for 90 min until the mixture became almost clear. After cooling, 300 mL of HCl solution (30 % by weight) was added portion wise (five portions each one of 60 mL) under stirring for 3 h. The reaction mixture was allowed to cool to room temperature, and then transferred into a 1 L separating funnel to separate the aqueous layer. The oil phase was then separated, washed three times with double distilled water (3, 9, 200 mL) 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 using GC and showed the following compositions:

**Table 2.4** GC analysis of hydrolyzed Jatropha fatty acids.

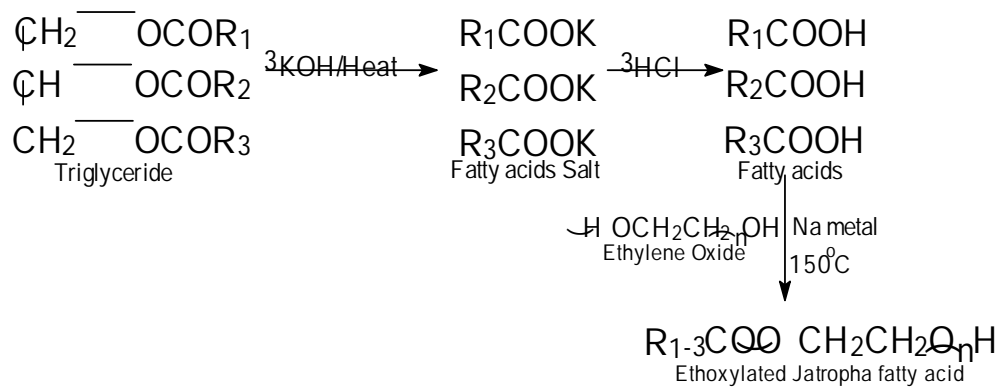
	Saturated					Unsaturated				
<b>Fatty acids of Jatropha oil</b>	C <sub>14</sub> Myristic acid	C <sub>16</sub> Palmitic acid	C <sub>20</sub> Arqchidic acid	C <sub>22</sub> Behenic acid	<b>Total</b>	C <sub>18:1</sub> Palmitoleic acid	C <sub>18:1</sub> Oleic acid	C <sub>18:2</sub> Linoleic acid	C <sub>18:3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



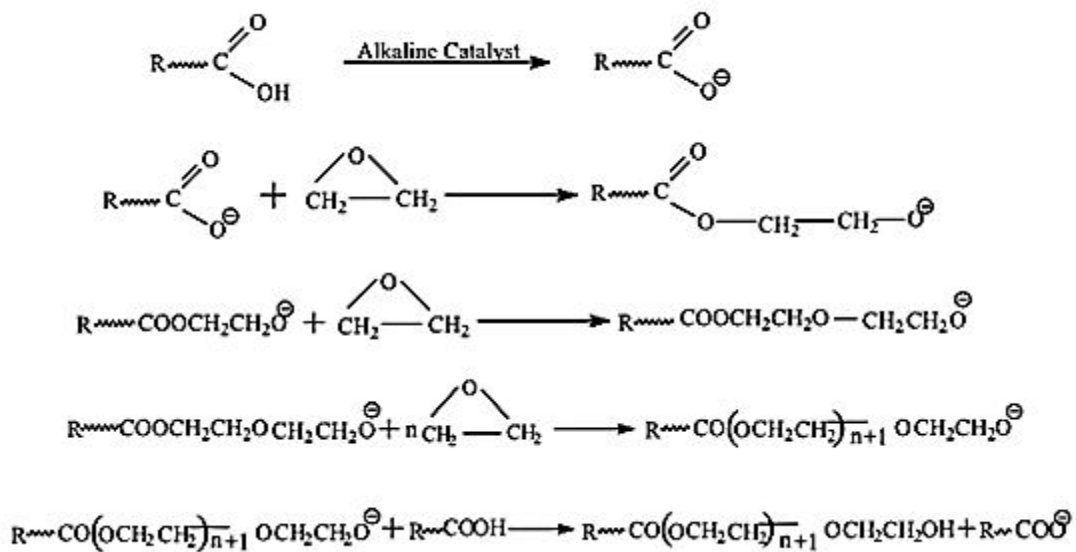
Hydrolysis reaction of Jatropha crude oil (Salimon *et al.*2011)

### **2.2.2 Ethoxylation and Propoxylation of Hydrolyzed Jatropha Oil (Jatropha Fatty Acids)**

A high-pressure stainless steel autoclave (Parr model 4848, USA) of 1L 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 or propylene oxide (10, 20, 30 unit). Generally, as a result of the introduction of ethylene oxide or propylene oxide, the pressure was substantially increased as indicated by the pressure gauge, until it reached a maximum value. The pressure drop indicates ethylene oxide or propylene oxide consumption. 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 super saturated NaCl solution. The organic layer was then separated, and the isopropanol was distilled off.



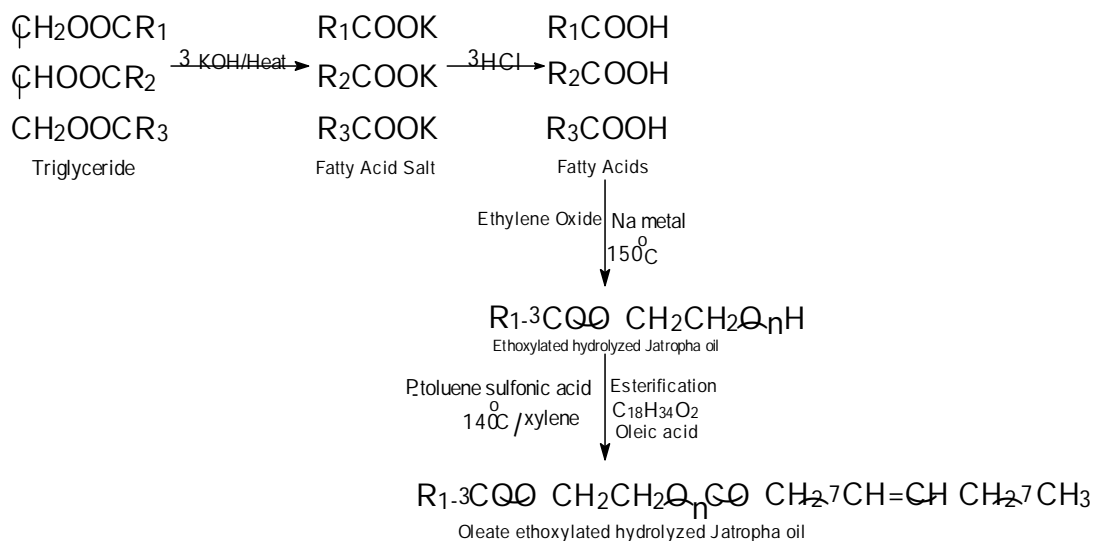
Mechanism of ethylene oxide reaction with fatty acids using alkaline catalyst



### 2.2.3 Esterification of the Ethoxylated hydrolyzed Jatropha oil

Esterification of the Ethoxylated hydrolyzed Jatropha oil in a (1L) flat-bottomed flask fitted with a Dean-Stark trap and a condenser, 1mol of ethoxylated hydrolyzed jatropha oil was esterified with 1mol of oleic acid. The reaction ingredients were refluxed in xylene in presence of *p*-toluene sulfonic acid (0.1wt. %) as a catalyst and 100ml 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.

The following equations show the preparation of mono oleic ester of ethoxylated Jatropha fatty acid as representative example:



The same reaction steps also were repeated by using rosin acid to obtain rosin (colophony) ester of ethoxylated Jatropha fatty acid. The following equations represent the mechanism of the reaction:



### 2.3.3 Effectiveness $\pi_{\text{CMC}}$ :

The effectiveness of adsorption or surface pressure  $\pi_{\text{CMC}}$  of the surfactants was also calculated from the equation:

$$\pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}}$$

Where:  $\gamma_0$  is the surface tension of water at 25 °C

$\gamma_{\text{CMC}}$  is the surface tension value of the measured solution at CMC.

### 2.3.4 Surface Excess Concentration ( $\Gamma_{\text{max}}$ )

The  $\Gamma_{\text{max}}$  is a useful measure of the adsorption effectiveness at the liquid / air or liquid/ liquid interface (Rosen, 1978).  $\Gamma_{\text{max}}$  can be calculated from Gibbs equation:

$$\Gamma_{\text{max}} = -(1/RT) \cdot (\delta \gamma / \delta \ln C)$$

Where;  $\Gamma_{\text{max}}$  is surface excess concentration,

T is absolute temperature (°C+273)

R is universal gas constant (R=8.314 Jmol<sup>-1</sup> deg<sup>-1</sup>)

$\delta \gamma / \delta \ln C$  is the surface activity ( slope of  $\gamma - \ln C$  curves) (Alsabagh *et al.*, 2000).

### 2.3.5 Minimum Surface Area per Molecule ( $A_{\text{min}}$ )

$A_{\text{min}}$  is the minimum area per molecule in nm<sup>2</sup> / molecule at the oil/water or air/ water interface (Bhattacharyya *et al.*, 1994). The average area occupied by each adsorbed molecule is given by:

$$A_{\text{min.}} = 10^{16} / (N_A \cdot \Gamma_{\text{max}})$$

Where;  $\Gamma_{\text{max}}$  is the surface excess in mol/cm<sup>2</sup>, and



N is “Avogadro’s number =  $6.023 \times 10^{23}$  molecules/ mole (Alsabagh *et al.*, 2000). The thermodynamic parameters of micellization expressed by the standard Gibbs-free energy,  $\Delta G_{mic}$ , (micellization) of the de-emulsifiers & inhibitors are calculated from the equation:

$$\Delta G_{mic} = R T (1 + \alpha) \text{Ln CMC}$$

Where R: the universal gas constant ( $R = 8.314 \text{ J/mol.K}$ ),

T: the absolute temperature ( $T = t + 273$ ), and

$\alpha$ : the fraction of counter ions bound by micelle in case of ionic surfactants ( $\alpha = 0$  for nonionic surfactants), and

CMC: critical micelle concentration in g/mol.

Thermodynamic free energy of adsorption  $\Delta G_{ads}$  was calculated from the following equation

$$\Delta G_{ads} = \Delta G_{mic} - [0.6022 \times \pi_{CMC} \times A_{min}]$$

## 2.4 De-emulsification performance

The graduated bottle test (Sany-glass) was used to estimate the efficiency of de-emulsifiers toward resolving water-in-oil emulsions. Each de-emulsifier was dissolved in xylene (10 % active material), and then added in different concentrations (ppm) to a 100 ml of the emulsion placed in graduated bottle test (Sany-glass) and then was shaken vigorously for 1 min. (60 times). The bottle was placed in a thermostated water bath at  $60^\circ\text{C}$ . Water separation (in ml) is observed and recorded at different time intervals depending on the efficiency of the de-emulsifier under investigation. A blank sample was considered in each set of experiments.

$$\text{Water separation} = (v/v^0) * 100$$

Where: v is the volume of the separated water and v<sup>0</sup> is the original volume of water content in the crude oil (Young, 1996).

## 2.5 Rheological Properties

Oil viscosity was measured by using "Haakviscometer model Rotovisco RV12" with a heating/cooling water bath. The crude oil used in this study was considered as non-Newtonian fluid because the viscosity of the crude oil changes while being measured with a rheometer at different speed rotation. The viscosity measurement started from low shear rates. The shear rate was then increased at constant temperature (60 °C). The rheological properties were measured over a shear range of 1-1200 s<sup>-1</sup>. The flow curve can be analyzed using the Herschel-Bulkley equation (Tahany, 2013):

$$\tau = \tau_B + k D^m$$

Where  $\tau$  is the shear stress;  $\tau_B$  is the dynamic yield stress "Bingham yield value"; k is the consistency index; m is the shear thinning index and D is the shear rate. The Bingham yield value ( $\tau_B$ ) can be obtained from the intercept of the graph relation between shear rate and shear stress. On the other hand, the linear line from the relation between shear rate and viscosity give us the dynamic "apparent" viscosity.

The rheology parameters were obtained from the following equations:

$$\text{Shear Stress, } \tau = A. S \quad (\text{Pa})$$

$$\text{Viscosity, } \eta = G. S / n \quad (\text{mPa. s})$$

$$\text{Shear Rate, } D = M .n \quad (\text{s}^{-1})$$

Where n = Number of Revolution, rpm; S = Torque;

$$M = 2.34 \text{ (min / s);}$$

$$A = 3.22 \text{ (Pa / S K t) and } G = 1347 \text{ (mPa. s / S K t. min)}$$