ORIGINAL PAPER

Non-ionic Fatliquoring and Lubricating Agents Based on Ethoxylated Jojoba Fatty Acids

EL -Shahat H. A. Nashy[1] · Ghada A. Abo-ELwafa[2] · Saadia M. Aly[2] · Ragab A. Masoud[1] · Hamed Elsayed[1]

Abstract

Jojoba oil is a non-edible oil that has great importance for industrial applications. Naturally fatty acids derivatives were utilized as intermediate feed stocks in many industrial applications to replace harmful and costly petrochemicals. The aim of this work was to utilize jojoba fatty acids through an ethoxylation reaction to obtain natural fatty ethoxylates, which can be used in the preparation of non-ionic surfactants as a stable and good fat-liquoring agent with a harmless and healthy effect to replace the synthetic oil employed. The ethoxylation of fatty acids derived from jojoba oil was carried out using ethylene oxide gas in the presence of potassium carbonate, which is a cheap conventional catalyst, under different conditions to obtain an economical and valuable ethoxylated material. The obtained products were evaluated for their chemical and physical properties as well as their application as a nonionic fatliquoring agent for the chrome-tanned leather industry. The data obtained revealed that the ethoxylation reaction managed to introduce ethylene oxide moles into the fatty acids to obtain a nonionic surfactant. The number of introduced ethylene oxide moles differs depending on the reaction conditions. The ethoxylated jojoba fatty acids products were observed to be good fat-liquors with favorable hydrophile-lipophile balance values, which produce stable oil in water emulsions. Ethoxylated jojoba fatty acids improved the strength properties of fat-liquored leather. Furthermore, a significant improvement in the grain surface of the treated leather was achieved by the prepared ethoxylated fat-liquors evidenced by scanning electron microscopy images. The prepared ethoxylated products proved to be effective fat liquoring agents.

✉ EL -Shahat H. A. Nashy
    elshahatnashy@gmail.com

✉ Hamed Elsayed
    hamed_sci@yahoo.com

1   Tanning Materials and Leather Technology Department,
    Chemical Industrials Research Institute, National Research
    Centre, Dokki, Cairo, Egypt

2   Fats and Oils Department, National Research Centre, Dokki,
    Cairo, Egypt

Graphical Abstract

Chrome tanned leather

Fat-liquored leather

Ethoxylated jojoba fatty acids

Ethoxylation of fatty acids
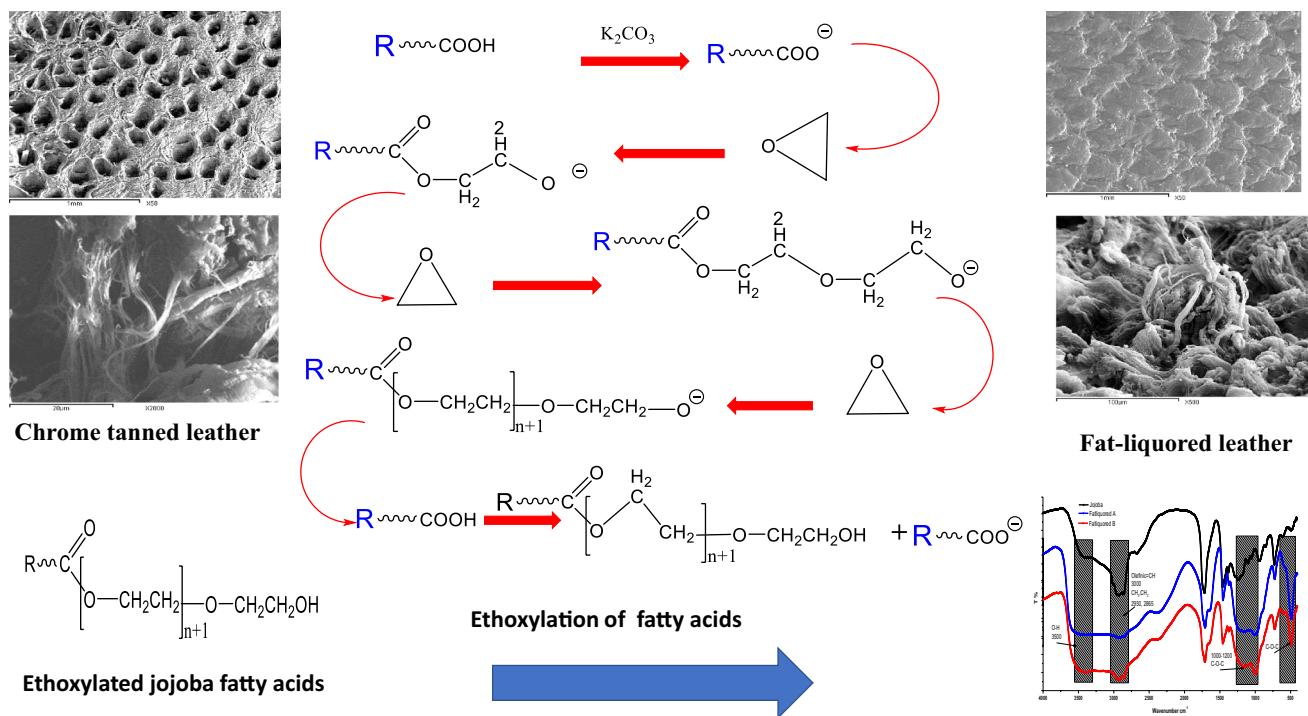
Keywords Jojoba oil · Ethoxylation reaction · Fatty acids · Fat-liquoring agent · HLB · Strength properties

Statement of Novelty

The novelty of this work was to evaluate the ethoxylation reactions of jojoba fatty acids and produced fatliquor and lubricating agents. Hence, it's the primary chance to ethoxylate the jojoba fatty and their application as fatliquoring agent in leather field. The ethoxylation method is a viable alternative for the integral use of the non-ionic fatliquoring since it is a green method that uses cheap catalyst (K2CO3) and without organic solvents. It is possible to take advantage of this available method to obtain value-added products. The prepared fatliquor was characterized by highly stable emulsion where has high HLB. the strength properties of fatliquored leather was improved and have a significant lubrication in leather fibre and grain surface of the treated leather.

Introduction

The whole world nowadays is suffering from severe climate change that is caused by the harmful, irresponsible practices done by humans, especially in the industrial sector, which produces many pollutants. So, environmental aspects were taken into all governments' considerations to overcome

the harmful effects of industrial applications. Therefore, to reduce the environmental contamination and health risks associated with synthetic materials, the scientists have been pointing to nature in all aspects of life. So, natural fatty derivatives (oleochemicals) were utilized in many industries to replace risky and costly petrochemicals; fatty ethoxylates are one of these oleochemicals. Natural Fatty acids or alcohols are used as precursors for the preparation of fatty ethoxylates that can be considered as non-ionic surfactants containing poly (ethylene oxide) groups as a hydrophilic terminal [1, 2]. Ethoxylated fatty acids are properly known as non-ionic surfactants of the type of ether ester and are used in many industrial applications as emulsifiers, dispersants, or oil phase controllers in cosmetics and other industries [3]. Fatty acid and alcohol ethoxylates are easily prepared by the reaction of fatty acids or alcohols containing active hydrogen with ethylene oxide gas in the presence of a basic catalyst (as NaOH) or an acidic catalyst (as $SbCl_5$) [4–7].

The Jojoba tree is successfully cultivated in Ismailia Governorate, Egypt, where it grows very well in the desert, naturally adapts to hot summers and mild winters, bears the lack of water, salinity, and is well suited to the sandy soil with good drainage. It doesn't need care, and therefore the crop is often stored or left on the tree until the gathering at any time [8]. The tree could be irrigated with treated wastewater; thus,

jojoba oil is inedible. Jojoba seeds contain about 30–45% viscid oil with a very long waxy ester (C36–C46) structure and not triglycerides. It is able to be utilized in the production of biodiesel, the manufacture of candles and soaps, the manufacture of cosmetics, paraffin alternatives, and further industrial applications. Therefore, this research explores another use of fatty acids non-edible jojoba as a fat-liquoring agent in the leather industry to provide edible fats and oils for nutritional purposes.

Tanned animals hide and/or skin were proven to be as leather [9–11]. The leather industry removes a large portions of leather materials such as hair, soluble proteins, and fats by chemical and mechanical operations [12–15]. The tanning step is a permanent protection of natural biological materials; therefore, the target of tanning is to achieve permanent stability for native proteins from decay and to enhance chemical and enzymatic degradation [16–20]. Chrome tan is the greatest and most important tanning agent, that is utilized to produce all different types of leather [21–23]. Wet blue leather means that, chrome tanned leather in its wetting state is relatively more elastic than vegetable-tanned leather [24–27]. When water is removed during the drying process, it creates solidity in the fibers, resulting in tough, persistent leather that is hard to re-moisturize [28].This means that leather tanned by chrome when dried, became skeletal, hard and thus not suitable for most purposes; moreover, the color shade became darker and less attractive [7, 29, 30].

Therefore, the process of converting fats into liquid is an essential process by which an oily substance is introduced into the skin fibers [31]. Incorporation of fatty liquors into the skin decreases the deleterious air oxidation effect and controls the shrinkage of the grain versus the skin corium during the drying step [32–34]. So, incorporation of a lubricant inside the leather fibers saves the separating of fibers throughout drying and decreases the frictional forces inside the weave, allowing the fibers to move sideways over each other [35, 36].The incorporation of fatty substances inside the leather reduces the harmful effect of air oxidation [37, 38]. Furthermore, it acquires the specific properties of leather grain, making it suitable for the most effective use [39–41]. Also, fatliquor prevents hide granules from loosening and aims to lubricate the fibers of tanned leather to get smooth, full grain, and abrasion resistance, in addition to improve the mechanical properties [29, 42–44].

In our previous work, the phosphoration, sulfation, sulfonation and ethoxylation of fatty materials have already been studied [45–47]. Oleum, sulfur trioxide (under PTC), and chlorosulfonic acid, besides sodium bisulfite have been suggested as sulfating agents [46]. The evaluation of fatliquored leather has focused mostly on its strength attributes as a proxy for fibre lubricity. According to our cited study, [46] the treated leather's tensile strength and elongation at break percentage were noticeably greater when using jojoba fatliquor than when using commercial fatliquor (TRUPONOL@SF, oxidised sulfited fatty acid ester). Because the fibres are well lubricated, treated leather has improved mechanical qualities. While the emulsified oil is mostly found between the leather fibres, the sulfited oil is chemically attached to the leather fibres during the fatliquoring of chrome-tanned leather. This happens because the sulfited oil interacts with active centres in the collagen molecules of the leather fibres. Also, the ethoxylation of jatropha fatty acids encourage to the ethoxylation the johoba fatty acids [48].

The present work aimed at using nonedible vegetable oils cultivated in Egypt, such as jojoba oil, in the preparation of ethoxylated fatty acids for using as non-ionic surfactants. On this basis, derived jojoba fatty acids were ethoxylated under different conditions, to prepare a non-ionic surfactant. The obtained products were used as leather fatty-liquor agents to substitute the imported materials, and at the same time, an environmentally safe, effective, and healthy product will be obtained. The ethoxylated derivatives were evaluated for use as non-ionic fatty liquors in addition to its application in the lubrication of leather fibers. Also, the examination of fat-liquored chrome tanned leather was investigated.

Experimental

Materials

Jojoba seeds were purchased from Ismailia governorate, Egypt, where they were cultivated. Jojoba seeds were crushed, and the oil was extracted using commercial n-hexane. Fatty acids were derived from jojoba oil through saponification using potassium hydroxide (KOH). Free fatty acids were obtained by precipitating the salt using HCL and extracting it using light petroleum ether. Ethylene oxide gas cylinder was purchased from Etico Gas Company for gases (EL-Sharqia for gases, 10th of Ramadan Industrial City). Potassium carbonate catalyst, all solvents and chemicals used were of highly pure grade and purchased from Merck. Local commercial full grain chrome tanned leather was used for the present investigation and obtained from El Shashar Tannery, Cairo, Egypt.

Methods

Determination of Fatty acid Composition

Jojoba fatty acids composition was determined using gas liquid chromatography (GLC). The methyl esters of the separated fatty acids were prepared according to Ludde

et al. [49]. Fatty acids methyl esters were separated and identified using a Hewlett Packard Model 6890 gas liquid chromatograph on an INNO wax (polyethylene glycol) Model No. 19095 N-123, 240 °C maximum, capillary column (30.0 m × 530 μm × 1.0 μm), nominal flow rate of 15 ml/min, average velocity 89 cm/sec, and pressure 8.2 psi. The maximum column temperature was 240 °C with adjusted temperature programming as follows: The initial temperature was 100 °C rising up to 240 °C maximum with 10 °C rising/minute and then holding at 240 °C for ten minutes. The back-inlet injection temperature was 280 °C, back inlet, split ratio 8:1, split flow 120 ml/min. The gas saver was adjusted 20 ml/min. Nitrogen was the carrier gas, with a flow rate of 15 ml/min. The temperature of the flame ionization detector was 280 °C. The hydrogen flow rate was 30 ml/min, and the air flow rate was 300 ml/min.

Ethoxylation Reaction

Jojoba fatty acids were reacted with ethylene oxide gas in a closed system, where 5 gm of jojoba fatty acids and (1 or 2%) potassium carbonate catalyst were mixed well using a magnetic stirrer and heated under gentle flow of nitrogen to the desired reaction temperature (120 and/or 145 °C). The nitrogen was replaced by ethylene oxide, which was kept in harmony with the reaction rate, initiating vigorous agitation at the same time. After the required period of time (5, 8, 12 h), the flow of ethylene oxide was halted and replaced by nitrogen to cool the reaction mixture. The weight difference of the whole system, before and after reaction, was recorded, and the weight difference was calculated [50].

Evaluation of The Ethoxylated Jojoba Fatty Acids

The prepared ethoxylated fatty acids were evaluated by the following analysis:

Chemical Characteristics *Determination of Iodine (I.V.), Acid (A.V.) and Saponification Values (S.V.)*: The values were carried out according to AOCS Official Methods Cd 3d-63, Cc 18–80 and Tl 1a-64 [51] respectively. Ester value (EV) was calculated from the values of saponification (SV) and acid (AV) values as follows: EV = SV − AV.

Physical Characteristics *Determination of the Solubility in Different Solvents*: The solubility of ethoxylated samples was determined in water, oil, ethanol, n- hexane and diethyl ether at room temperature, and at 75 °C or at the boiling point of the solvent.

Melting Point Determination: The melting point of the ethoxylated samples was recorded using electro thermal IA 9100 digital melting point apparatus.

Determination of the Emulsifying Properties of the Ethoxylated Samples: A stoppered 500 ml Erlenmyer flask containing 40 ml of light petroleum ether and 40 ml. of an aqueous solution containing 0.1% with respect to the emulsifying agent was manually shaken in 5 cycles. The emulsion was then poured into a 100 ml graduated cylinder, and the time required for 10 ml of the aqueous phase to separate was recorded [50].

FT-IR Analysis The FTIR spectroscopic analysis was used to investigate the change in the functional groups of fatty acids before and after ethoxylation. All ethoxylated samples compared with the control were subjected to FT-IR analysis on a Nexus 670 Fourier Transform Infra-Red Spectrometer, Thermo Nicolet, USA. The FT-IR spectra were analyzed using "Omnic 5.2a" software. A fixed sample volume (5 μl) of each sample was carefully and homogeneously spread between two KBr disks of fixed weights. The samples were referenced to their own blank KBr disks. For the collection of the data, a DTGS detector and KBr beam–splitter were used.

Quantitative Determination The ethoxylated products were quantitatively determined through:

Molecular Weight Determination Using GPC: The average molecular weight of jojoba fatty acids before and after ethoxylation was determined using a gel permeation chromatograph (GPC) coupled with refractive index (RI) detector. Samples were dissolved in tetrahydrofuran, and the GPC instrument used in the measurements was a modified HPLC with a Waters 600 system controller, 717 plus autosampler. Two columns were used: phenomenex phenogel 10 μm; 500 A, 250 × 8 mm, and phenomenex phenogel 5 μm; 50 A, 300 × 7.8 mm. The detector was Waters model 2410 refractive index, ATTN = 16x. The eluent was dimethylformamide DMF (100% by volume) with flow rate of 0.7 ml/min. The temperature was adjusted at 50 °C with injection volume of 25 μm.

Degree of Ethoxylation: Ethoxylation degree was calculated depending on the determination of the introduced number of ethylene oxide as follows:

(1) The number of ethylene oxide (n) moles introduced in the fatty acids was estimated depending on the molecular weight difference of the sample before and after ethoxylation

(2) The degree of ethoxylation (%) was calculated according to Eq. 1.

$$EO\% = \frac{(n \times 44)}{R + (n \times 44)} \times 100 \tag{1}$$

where n—number of ethylene oxide moles, 44—total molecular weight of one mole ethylene oxide, R—molecular weight of fatty acid fraction.

Hydrophile-Lipophile Balance (HLB) Hydrophile-lipophile balance of the nonionic fat-liquors was calculated based on Eq. 2 [52].

$$HLB = \frac{EO\%}{5} \tag{2}$$

where EO%—is the percent of introduced ethylene oxide.

Fatliquoring Process

The fatliquoring process was worked up as usual in the wet-finishing process, where chrome tanned leather pieces were first washed with water for about 15 min and, then drained off. Then the neutralization process was carried out using 1% sodium format for 15 min, and thereafter, 0.5% sodium bicarbonate was added and the drum was run for an additional 10 min. The leather pieces had a greenish blue color with bromo cresol green throughout the whole thickness (pH 5.0–5.5). The neutralized leather pieces were retanned and dyed (5% acid dye) for 30 min. Then, the fat-emulsion was added to the dye bath at room temperature, and the drum was run for 40 min at 30 °C. The leather pieces were washed with water for about 10 min, removed from the drum, sammed, and left to dry in the air by hanging up at room temperature. The dried leather pieces were used for the various physical properties' investigations.

Mechanical Measurements

Determination of mechanical properties by dumbbell shaped specimens were used for the measurement of the tensile strength and elongation at break (%), these tests were carried out using a Zwick/Roell (Z010) according to ASTM D

412. The results were confirmed based on the average values for three samples of each test. The cross-head speed was controlled at 50 mm/min, and the tests were done at room temperature (25 °C) [53].

Scanning Electron Microscope

Specimens for experimental and control experiments were prepared as circular samples (10 mm) and then subjected to sputter coating of gold ions to prepare a conducting medium (sputter coater, Edwards Model S-150 A, Eng). A Jeol scanning microscope (Japan) JSM-T20 was used for the microscopic study.

Results and Discussion

Oil Characterization

Table 1 displays the chemical and physical characteristics of the locally sourced jojoba oil. Its calculated ester value was 92 mg KOH/g oil, its saponification value was 93 mg KOH/g oil, and its iodine content (IV) was 90.0 mg I_2/g oil, all of which were of a greater value than the average for imported jojoba oil. Other properties, such as unsaponifiables, AV, and acetyl number, were below average. The data shows that the oil has relatively more unsaturated moieties and ester groups and fewer free fatty acids than other oils. The findings are in line with those of prior research [46].

Table 1 Physical and chemical properties of jojoba oil

Property	Value
Refractive index at 25 °C	1.472 ± 0.03
Specific gravity at 25 °C	0.901 ± 0.05
Saponification value (mg KOH / g oil)	93.0 ± 3
Acid value (mg KOH/g oil)	0.61 ± 0.4
Acetyl number (mg/g acetyl oil)	1.00 ± 0.5
Ester value (mg KOH)/g oil	92.0 ± 2
Iodine value (mg I_2/g oil)	90.0 ± 4
Unsaponifiable matter (%)	50.1 ± 2
Peroxide value meq.O_2/Kg	2.89 ± 0.2

Table 2 Fatty acids composition of jojoba oil

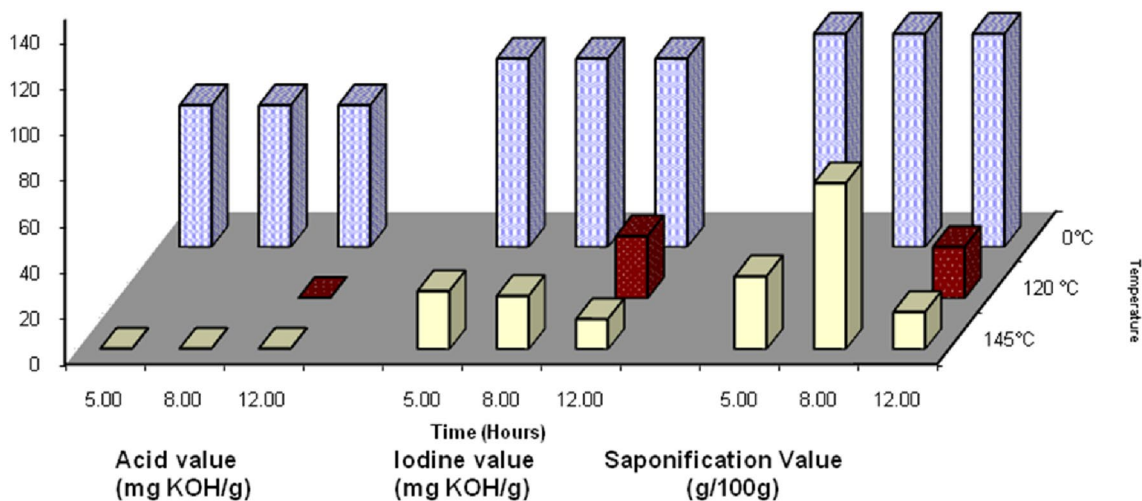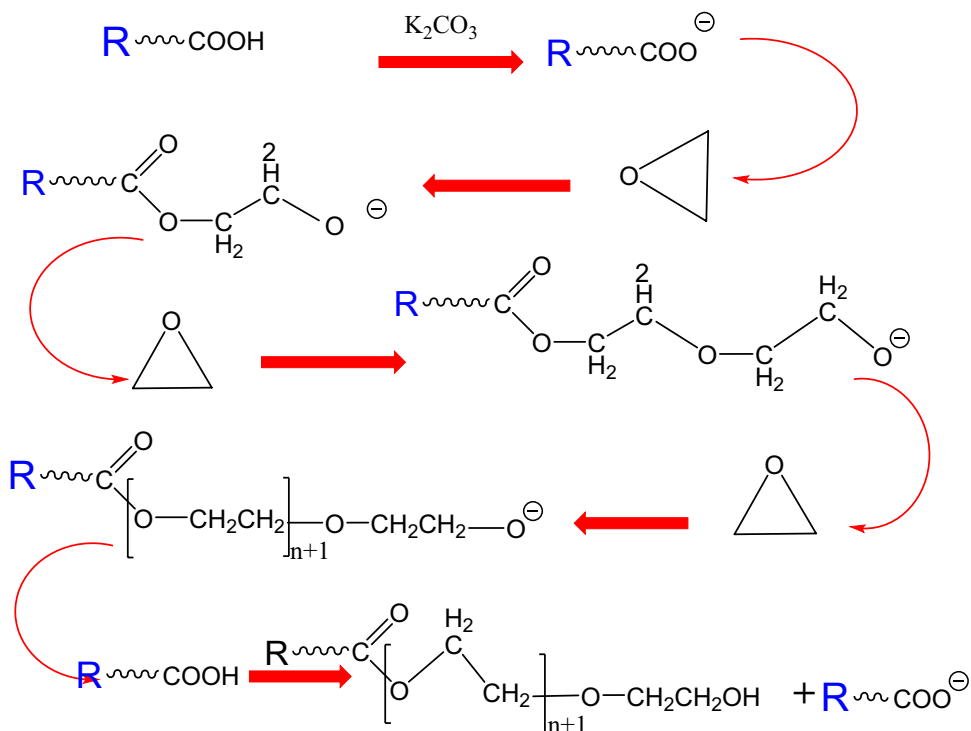| Fatty acids	Percent (%)
Saturated	
Palmitic (C16:0)	1.60
Stearic (C18:0)	0.14
Arachidic (C20:0)	0.20
Behenic (C22:0)	0.20
Lignoceric (C24:0)	0.02
Total	2.16
Unsaturated	
Palmitoleic (C16:1)	0.10
Oleic (C18:1)	11.2
Eicos-11-enoic (C20:1)	70.7
Erucic (C22:1)	14.1
Nervonic (C24:1)	1.64
Total	97.74

Fatty Acids Composition

Table 2 shows the fatty acids composition of jojoba oil, where the unsaturated fatty acids predominate by about 97.74% of the total fatty acids, while saturated fatty acids constitute only 2.16%. The ratio of saturated to unsaturated fatty acids was 1: 45.25. Eicos-11-enoic acid (C20: 1) is the most abundant unsaturated fatty acid, making up more than 70% of the total fatty acids, followed by erucic acid (14%)

and oleic acid (11%). While palmitic acid was the highest saturated fatty acid with a very low percentage (1.6%). These results indicate that the nature of this oil is promising for the preparation of different useful derivatives.

Ethoxylation Reaction

When the ethoxylation reaction was attempted directly on jojoba oil at a wide range of temperatures (80–180 °C)

Scheme 1 The reaction of ethylene oxide with fatty acids using alkaline catalyst

Fig. 1 Acid, Iodine and Saponification values of Jojoba fatty acids before and after ethoxylation at 120 and 145 °C using 1 or 2% K$_2$CO$_3$ for different periods of time

and by using different percentages of K_2CO_3 catalyst, the reaction failed and no products were obtained. This was explained by the absence of active hydrogen necessary to initiate the ethoxylation reaction with K_2CO_3 basic catalysts because of the structure of jojoba oil, which is mainly a wax ester. This problem was solved by separating free fatty acids from the oil to make the active hydrogen available. As illustrated in Scheme 1, active hydrogen was required to activate the reaction with basic K_2CO_3 in order to enhance the reaction after free fatty acids were extracted from the oil.

Due to the formation of monoesters, it appears that the ethylene oxide reaction will be preferred over the esterification reaction. In this case, it is significant that no product was obtained when the reaction was carried out at 80–130 °C using 1% K_2CO_3. However, the ethoxylated products were obtained at 145 °C with 1% K_2CO_3 and at 120 °C with 2% K_2CO_3.

Evaluation of the Ethoxylated Jojoba Fatty Acids

Chemical Characteristics The chemical properties of jojoba fatty acids ethoxylated at 145 °C with 1% K_2CO_3 and at 120 °C with 2% K_2CO_3 for different periods of time are shown in Fig. 1. The ethoxylation led to a drastic reduction in acid, iodine, and saponification values, as shown in Fig. 1.

In the first place, the ethoxylation reaction with free carboxylic groups greatly depletes fatty acids, reducing the acid value. Second, the iodine value drastically dropped, indicating that the ratio of unsaturated centers to the final product's molecular weight had decreased as a result of the ethoxylation reaction. As a third point, the ethoxylation reaction significantly diminished the saponification value by blocking the saponifiable carboxylic groups of fatty acids. Acid, iodine, and saponification values were found to decrease as the reaction temperature and time increased.

Figure 1 also shows that there was no product obtained after 5 h, but the reaction started 8 h later. This may be because during the initial phase of fatty acid ethoxylation, only minute quantities of the final product are generated. The reaction started five hours after it was carried out at 145 °C and continued for another eight hours at 120 °C. In addition, it was discovered that throughout the process at 120 °C, the acid, iodine, and saponification values all decreased [47, 48].

Physical Characteristics *Melting Point*: The samples appearance was found to be different before and after the ethoxylation reaction. In practice, it has been seen that with increasing temperature and reaction time, the liquid fatty acid transforms after ethoxylation, at ambient temperature to become solid. Table 3 illustrates that the melting point of the ethoxylated fatty acids was found to increase as the reaction time and temperature increased. This could be attributed to the reduction in the unsaturation fraction throughout the reaction.

Solubility in Different Solvents: It was observed from Table 3 that, ethoxylated jojoba fatty acids prepared at 120 °C for 12 h sparingly dissolved in all solvents and water except for hot (oil and ethanol). While at 145 °C and after 12 h of reaction, ethoxylated jojoba fatty acid samples were soluble in water either at room temperature or in hot water. All prepared samples were soluble in warm vegetable oil and hot ethanol. With an increase in the time and temperature of the ethoxylation reaction, the dissolvability of the samples sharply diminished in either n-hexane or ethyl ether.

Table 3 also recorded that with increasing the reaction time in the preparation of ethoxylated jojoba fatty acids at

Table 3 Melting point, emulsifying properties and solubility of the ethoxylated Jojoba fatty acids in different solvents at different temperatures

Solvent	Temp.	Solubility in different solvents at different temperatures			
		Ethoxylated jojoba fatty acids			
		at 120 °C	at 145 °C		
		12 h	5 h	8 h	12 h
Water	Room Temp.	SS	SS	PS	S
	75℃	SS	SS	S	S
Oil	Room Temp.	PS	PS	PS	PS
	75℃	S	S	S	S
Ethanol	Room Temp.	PS	PS	SS	PS
	75℃	S	S	S	S
Diethyl	Room Temp.	SS	SS	SS	SS
Ether	Boiling point	SS	SS	SS	SS
n – hexane	Room Temp.	SS	SS	SS	SS
	Boiling point	SS	SS	PS	PS
Melting point (°C)		–	55.2	54.5	56.8	57.0
Emulsifying properties, seconds (s)		–	–	–	–	1200

Where: no product was obtained at 120 °C after 5 or 8 h

S soluble, *PS* Partially soluble, *SS* Sparingly soluble, *I* Insoluble

Table 4 Weight difference of ethoxylated jojoba fatty acids at 120 and 145 °C for different periods of time

Fatty acid	Reaction temperature (°C)	Time of reaction (hrs)	Increase in weight (gm)
Jojoba fatty acids	120	12	11.2
	145	5	11.45
		8	14.80
		12	9.65

Molecular weight of ethylene oxide = 44.00

Table 5 Mn, Mw and PDI of ethoxylated jojoba fatty acids

Samples	Mn (gm/mol)	Mw, (gm/mol)	PDI (M$_w$/ M$_n$)
Jojoba fatty acids	1.4061×10^3	1.5997×10^3	1.1376
Ethoxylated Jojoba fatty acids at 120 °C for 12 h using 2% K$_2$CO$_3$ catalyst	2.1742×10^3	3.1879×10^3	1.4662
Ethoxylated Jojoba fatty acids at 145 °C for 8 h using 1% K$_2$CO$_3$ catalyst	2.4893×10^3	4.799×10^3	1.9278

Where: *Mn* number average of molecular weight, *Mw* weight average of molecular weight, *PDI* polydispersity

145 °C, the emulsifying strength increased, reaching to the maximum in the prepared sample for 12 h, while no emulsifying strength was recorded for the samples prepared from jojoba fatty acids at 120 °C.

Quantitative Analysis of Ethoxylated Products

Determining the Number of the Introduced Ethylene Oxide Moles The moles number (n) were determined depending on the increase in sample weight after ethoxylation as follows:

GPC Molecular Weight and Quantitative Determination (Determination of Weight Difference) The weight gains obtained from the prepared ethoxylated sample are shown in Table 4. Depending on the highest weight gain, two ethoxylated samples (prepared at 120 °C for 12 h and at 145 °C for 8 h) were selected to be analyzed for their molecular weight determination.

The weight and number of the average molecular weights (Mws, Mns) of jojoba fatty acids are displayed in Table 5. This table compares the weight and number of these values before and after the reaction. Because of the presence of a high number of ethylene oxide moieties in the fatty acids, the molecular weight of the product of ethoxylation was

significantly increased by more than three times compared to that of the original fatty acids, as shown in Table 5. It could be noticed that an increase in the temperature of preparation led to an increase in the average molecular weight (Mws) of ethoxylated jojoba fatty acids, which means that more ethylene oxide moles were introduced.

Ethoxylation Percent (EO%) and Hydrophile–lipophile Balance (HLB) Differences in molecular weight were used to calculate the ethylene oxide percentage (EO%) of ethoxylated Jojoba fatty acids in addition to the hydrophile-lipophile balance (HLB). Table 6 displays the results of the correlation between the specified ethoxylation parameters and the rise in EO%. One of the most important considerations when evaluating a fatty liquor emulsion is the idea of hydrophile-lipophile balance (HLB). What sort of emulsion is produced depends on the surfactant's HLB, which is a reflection of the simultaneous relative affinity of water and oil (or two phases) [54, 55]. It was known that a low estimation value of HLB would enhance or stabilize W/O emulsions [56], intermediate values would stabilize O/W emulsions, and high values would act as a solubilizer [57].

Due to the fat separation from the emulsion before adhering to the leather fibre, an unstable fat-liquor is unable to exert its full fat-liquoring impact. In this way, the HLB value may be used to identify the fatliquor type and evaluate the emulsion stability when it is created as a non-ionic fatty fluid. The HLB value of an ethoxylated product manufactured at 120 °C for 12 h with a 2% K$_2$CO$_3$ catalyst was determined to be 9.97, whereas the HLB value of a sample ethoxylated at 145 °C for 8 h with a 1% K$_2$CO$_3$ catalyst was found to be 13.33 (Table 6). This means that it is completely dispersed in water and forms an O/W emulsion. However, since both the ethoxylated and non-ethoxylated portions of the ester are emulsifiable, a pure emulsion can be created. The obtained HLB demonstrated that the ethoxylated Jojoba fatty acids synthesized for use were capable of forming a stable emulsion, diffusing out of the aqueous medium, and penetrating leather fibres. This suggests that they may be used as a suitable non-ionic fatliquor [48, 58].

Table 6 Effect of ethoxylation on jojoba fatty acids and their EO% and HLB values

Sample type	Molecular weight (gm/mol)	Moles number of ethylene oxide introduced (n)	EO%*	HLB*
Jojoba fatty acids	1599.7	–	–	–
Ethoxylated jojoba fatty acids at 120 °C for 12 h using 2% K$_2$CO$_3$ catalyst	3188.9	36.12	49.84	9.97
Ethoxylated Jojoba fatty acids at 145 °C for 8 h using 2% K$_2$CO$_3$catalyst	4799.5	72.72	66.66	13.33

*EO% = (Difference in molecular weight/molecular weight of ethoxylated jojoba fatty acids) × 100

*HLB = EO%/5
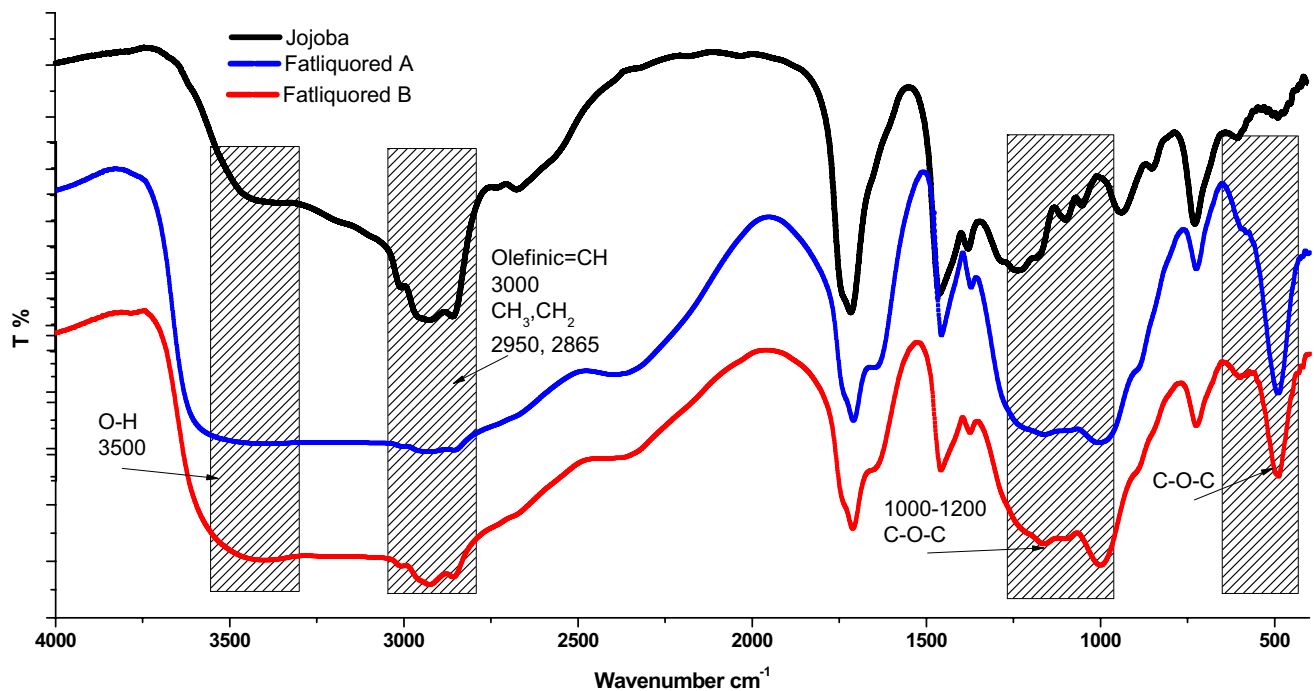
Fig. 2 FT-IR chart of Jojoba fatty acids and its ethoxylation at different conditions. **A**: at 145 °C using 1% K$_2$CO$_3$ for 8 h, **B**: at 120 °C using 2% K$_2$CO$_3$ for 12 h

Table 7 The mechanical properties of leather treated with two ethoxylated jojoba fatty acids

Samples	Tensile strength, Mpa	Elongation at break, %
Chrome tanned leather	18.5	61
Fat-liquored leather A (145 °C /8 hrs 1% K$_2$CO$_3$)	33	130
Fat-liquored leather B (120 °C /12 hrs 2% K$_2$CO$_3$)	23	121

FT-IR Spectra Analysis

Figure 2 shows the FT-IR spectra of jojoba fatty acids and the two selected ethoxylated jojoba fatty acids (prepared at 120 for 12 h and at 145 °C for 8 h). Comparison of the spectra reveals a wide absorption band at around 3500 cm^{-1} for extending vibrations in the intermolecular hydrogen O–H bond caused by the ethoxyl groups. This band was discovered to be broader and more robust for the sample ethoxylated at 145 °C for 8 h, followed by the sample prepared at 120 °C for 12 h. The absorption band at 3000 cm^{-1} representing the unsaturated fatty acid fraction, was found to vanish after the ethoxylation process and taken as an excellent proof of oxidative fatty acids development. A band exhibited at 1180 cm^{-1} after the ethoxylation that exemplifies the C–O–C group. In general, the bands were stronger and more recognizable on the prepared samples at 145 °C than those

prepared at 120 °C. Bands similar to those described above are often observed and estimated for these families, and they fit the pattern established by Nashy et al. [8].

Mechanical Characteristics of the Fatliquored Leather The surface of the leather must be activated before the fatliquoring procedure can be performed using a fatliquor concentration of 6%. Since they provide an indicator of the fibre's lubricating properties, the mechanical qualities (strength properties and elongation at break %) were calculated, and have been awarded the best reflection in evaluating lubricated leather [59, 60]. Table 7 showed that, as compared to untreated leather, the fatty leather had greater tensile strength and elongation at break. Table 7 further shows that the mechanical qualities of the leather treated with the prepared fat-liquor A, (145 °C for 8 h using 1% K$_2$CO$_3$) were higher than those of the leather treated with the prepared fatliquor B (120 °C for 12 h using 2% K$_2$CO$_3$). Scanning electron microscopy analysis confirmed the lubrication of the fibres, resulting in an increase in mechanical characteristics Fig. 3 [61, 62].

Scanning Electron Microscopy (SEM)

Because it provides a detailed view of the leather fibres and shows how the fat-liquor affects the fibres and grain surface, scanning electron microscopy (SEM) is the gold standard

Fig. 3 SEM of **a** grain surface of chrome tanned leather, **b** fiber bundles of chrome tanned leather, **c** grain surface of chrome tanned leather fat-liquored (B), **d** fiber bundles of chrome tanned leather fat-liquored (B), **e** grain surface of chrome tanned fat-liquored (A), **f** fiber bundles of chrome tanned leather fat-liquored (A)
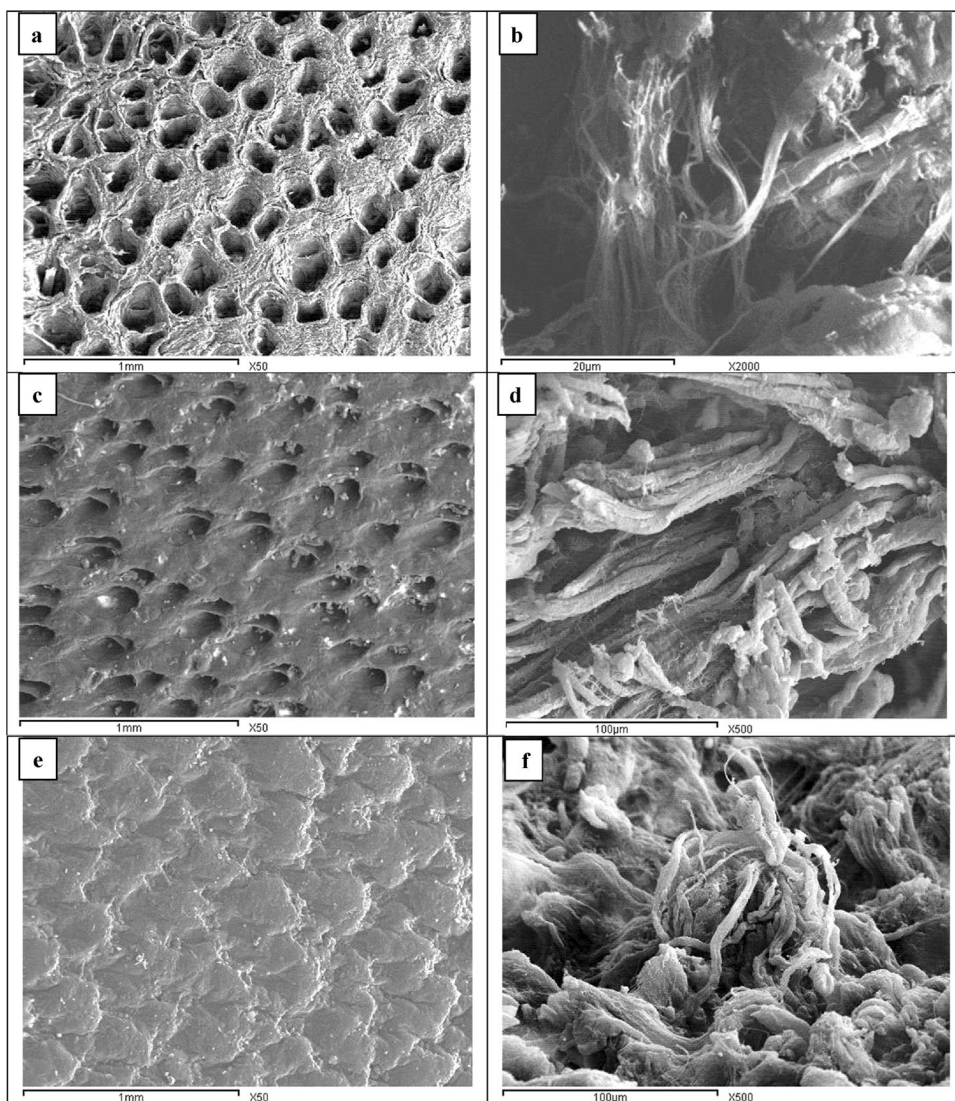
for evaluating fat-liquored leather. The prepared fat-liquors shield the fibres with a thin coating during fat-liquoring, resulting in a smooth leather, as seen in Fig. 3 from microscopic studies. Within the leather fibril cross-section, SEM analysis both before (Fig. 3a) and after fat-liquoring revealed essential lubrication of fibre bundles and grain surfaces with fine and loose texture (Fig. 3c–f).

Additionally, there are no splits or fissures in the grain surface (stable grain) and no fat-spew on the treated leather (× 50), as shown in Fig. 3 c, e. It's possible that this is because of the low concentration of free fatty acids in the final goods; large concentrations of free acids have been linked to an increase in fat during the manufacturing of split leather. Because the fat-liquored leather has a lower iodine value, it was also able to obtain the dazzling shadow, i.e., the leather treated has a similar covering of shadow. Because ultraviolet (UV) light and heat can break down the unsaturation part [62, 63], which causes the ejection of fats

(fat-spew) as a possible confusion, that leads to yellowing and the production of unpleasant odors, leathers with a high iodine value tend to turn out looking yellow when treated with fatliquor. The fading fatliquors were most noticeable against bright backgrounds.

Conclusions

Different conditions have been used to achieve ethoxylation of jojoba fatty acids, with the best results obtained at 120 °C for 12 h at 2% potassium carbonate (Fatliquored leather B) and 145 °C for 8 h at 1% potassium carbonate (Fatliquored leather A). The ethoxylated fatliquors developed from derived fatty acids have found widespread use in the production of chrome-tanned leather. In terms of HLB value, the fat-liquored leather (A) has superior characteristics of better penetration in the leather than the fatliquored

leather (B). Additionally, the texture of the leather's fibres and the leather's tensile strength and elongation at break percent have both been enhanced thanks to the effective penetration of the ethoxylated fat-liquors. Here, it's proposed that Egyptian leather tanneries may easily reach the number specified in regional standards for this type of fat-liquored leather.

Data Availability Enquiries about data availability should be directed to the authors.

Declarations

Conflict of interest The authors declare that there is no conflict of interests regarding the publication of this paper.

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