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Production and properties of surfactants from *Jatropha curcas* oil

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Abstract

In this study, five new surfactants derived from Sudanese Jatropha (*Jatropha curcas*) seed oil were synthesized. Three of them, namely: Surfactant-1 (SF-1), Surfactant-2 (SF-2) and Surfactant-3 (SF-3) were methyl ester sulphonate of Jatropha oil from different locations of South Kordofan, Ad-Damazin and Al Qadarif, respectively. Surfactant-4 (SF-4) and Surfactant-5 (SF-5) were ethyl ester and soap produced from South Kordofan Jatropha oil, respectively. The characterizations were studied by FT-IR spectroscopy and GC with mass spectrometry (GC-MS), and they approved an excellent formation of functional group of surfactants produced. The execution of every surfactant was considered its emulsification quality and its thermal stability. The emulsification quality of every surfactant was tried by measuring the interfacial pressure between every surfactant and unrefined oil and by measuring the stage separation time between water and unrefined oil in the absence and in the presence of a surfactant. Surfactants (1-3) showed a reduction in the measurement of interfacial tension almost similar to that of the standard surfactant used in the field (sodium methyl ester sulphonate). SF (4 and 5) also reduced the interfacial tension, but with less quality. The measurement of phase separation time for a homogenized mixture of 100 ml water and 1.0 ml of crude oil (using a homogenizer) in the presence or absence of surfactant showed that SF (1-5) gave more time for phase separation. The results of the analysis showed that these products were real surfactants and it can be used in enhanced oil recovery (EOR) application.

Keywords: Enhance oil recovery, Interfacial tension, Jatropha oil, New surfactants.

Özet

Bu çalışma kapsamında, sütleğengillerden bir tür olan *Jatropha curcas* bitkisinin tohum yağında bulunan yağ asitlerinden 5 yeni yüzey aktif madde sentezlenmiştir. Sentezlenen maddelerden üçü; yüzey aktif-1 (YA-1), yüzey aktif-2 (YA-2) ve yüzey aktif-3 (YA-3) sırasıyla; Güney Kordofan, Ad-Damazin ve El-Kadarif bölgelerinden toplanan *J. curcas* yağında bulunan yağ asitlerinin metil ester sülfonatıdır. Yüzey aktif-4 (YA-4) ve yüzey aktif-5 (YA-5) ise güney Kordofan'dan toplanan *J. curcas* yağından elde edilen etil esteri ve aynı yağlardan elde edilen sabun ürünüdür. Yüzey aktif maddelerdeki fonksiyonel gruplar FT-IR spektroskopi ve GC-MS analizleri ile karakterize edilmiş ve yapıların çok iyi bir şekilde oluştuğu belirlenmiştir. Her bir yüzey aktif maddenin işlenmesi sırasında, maddelerin emülsiyonlaşma değeri ve ısıl kararlılığı tespit edilmiştir. Sentezlenen YA maddelerin emülsiyonlaşma değeri, bu maddenin ve ham petrolün yüzey geriliminin ölçülmesi ile hesaplanmıştır. Aynı işlemler su ile de yapılmıştır. Hazırlanan yüzey aktif maddeler Petrol ve su ile karıştırılarak ayrılma süreleri ölçülmüştür. YA'ların (1 ve 3 nolu maddeler) yüzeyler arası gerilimindeki azalmalar standart olarak kullanılan sodyum metil ester sülfonat'a yakın değerlerde bulunmuştur. YA (4 ve 5 nolu maddeler) de ise yüzeyler arası gerilimde azalma daha az oranda olmuştur. YA'ların ayrılma süreleri ölçümünde, YA (1 ve 5) için daha yüksek bir faz ayrılma süresi belirlenmiştir. Sonuç olarak, bu ürünlerin iyi birer YA madde olduğu anlaşılmış ve bunların alternatif yüzey aktif kaynakları olarak kullanılabileceği görülmektedir.

Anahtar kelimeler: Alternatif yüzey aktif kaynak, yüzey gerilimi, Jatropha yağı, yeni yüzey aktif maddeler.

Introduction

A surfactant is a material that, when present at low concentration in a system, has the characteristic of adsorbing onto the surfaces or interfaces of this system and of adjusting to a checked degree the surface or interfacial free energies of those surfaces (Milton 2004). Developments of new systems are required to supply the expanded energy demand when the production with conventional method begins to decrease. Oil and service companies have put a considerable measure in expanding recovery and productivity of mature reservoirs, particularly in enhanced oil recovery (EOR) processes (Karnanda et al., 2013). To reduce the expense of surfactant production, much consideration is centered towards alternatives such as oleochemicals, renewable substrates non-edible oils, animal fat as option food stocks (Banat et al., 2014). Many surfactants have been produced from the vegetable oils to fulfill EOR needs (Gan -Zuo et al., 2000; Qiang et al., 2006). Different procedures have been utilized for preparing diverse sorts of sulfonated fatty acid esters. In this technique, the sulfonation happens in the temperature range from 50 to 85ºC utilizing sulfur trioxide as sulfonation executor.

Due to the high cost of surfactant made using petrochemical feedstocks, the respectable thought has been given to non-edible vegetable oils as an option of feedstock. This makes the study and treatment of Jatropha oil-based surfactant an engaging interest, in view of consolidating of methyl ester sulfonate. From our literature search, it is the second time to create methyl ester sulfonate based on non-edible Jatropha oil. This study aims to incorporate a sulfuric acid monoester from methyl ester by the response of methyl esters with chlorosulfonic acid in pyridine solution. The fatty acid methyl ester was produced through a two-stage transesterification took after by sulfonation. Then again, as the purity of surfactant is not a need for enhancing oil recovery; the methyl ester sulfonate was utilized without clarification. Two steps were used for the production of first three surfactants (SF-1, SF-2 and SF-3) as methyl ester sulfonate (MES), while SF-4 and SF-5 were produced by the development of ethyl ester and soap from Jatropha oil gathered from South Kordofan state Sudan. The surfactants were then analyzed for their surface tension decrease, stability, solubility and phase separation time.

Materials and Methods

Materials

Authentic seeds of the local *Jatropha curcas* were collected from three different locations, South Kordofan, Al Qadarif and Ad-Damazin, Sudan. All seeds were in good condition. They were cleaned using clean tap water, de-shelled manually and dried using an oven at 100 − 105ºC for 35 min.

Methods

Extraction of jatropha oil

The seed kernels were ground with a crushing mill (Petra electric, Burga, Germany). The oil was separated from the ground seed kernels with n-hexane at 50–60ºC in Soxhlet system for 6 hrs according to the AOCS method (2006). The percentage of oil in the kernels was calculated as a percentage of the obtained oil to the kernel weight (w/w). The oil obtained was stored at 4ºC for further investigations. The obtained oils were nominated as Jatropha oil from Kordofan (JOK), Jatropha oil from Qadarif (JOQ), and Jatropha oil from Damazin (JOD) according to Kordofan, Qadarif and Damazin locations, respectively. Extracted oils were utilized to synthesize surfactants after some physicochemical analysis. The analysis of samples was done in triplicate, and the mean ± SD were calculated.

Determination of free fatty acids (FFA) and acid value (AV)

Free fatty acids and acid value were determined using AOCS method (2006). In brief, 3-10 grams of the sample was dissolved in 50 ml of a mixture consisting of ethanol and diethyl ether (1:1, v/v) neutralized with 0.1 N KOH against phenolphthalein indicator. Then the solution was titrated with a 0.1 sodium hydroxide solution. Determinations were carried out in triplicate, and analysis of variance (ANOVA) was utilized to test means.

Determination of specific gravity

A specific gravity bottle was washed and rinsed with acetone and dried in the oven. Then was cooled at 25 ºC in a desiccator and the empty bottle weight of was determined using an electronic balance. The weight of bottle filled with water was recorded, then the water was poured out and the bottle rinsed with acetone and was dried in the oven. The procedure was repeated with the Jatropha oils (JOK, JOQ and JOD) and the specific gravity was calculated.

Synthesis of surfactants

Two steps were used for the production of first three surfactants (SF-1, SF-2 and SF-3) as Methyl Ester Sulfonate (MES), while SF-4 and SF-5 were produced by different methods.

Methyl ester sulfonate production

Step one: Esterification using acid catalysis

The acid catalyzed esterification aims to decrease the acid value of Jatropha oil. The initial acid value of JOK, JOQ and JOD were 2.175, 3.383 and 4.079 g, respectively, corresponding to a free fatty acid (FFA) % 1.093, 1.70 and 2.05 %, respectively (Table 1). The impact of diverse methanol/oil molar ratios (MRs) of 5:1, 6:1, 7:1 on the decreasing of acid value were examined utilizing 1% (v/w) sulfuric acid as a catalyst. In this step, the reaction was done at 60 ºC for 120 minutes utilizing 250 ml round base flask. After the reaction was finished, the blend was permitted to settle for three hours and the methanol-water phase at the top was evacuated utilizing a separating funnel. The acid value of the isolated item stayed at the base of the funnel was determined by American Oil Chemists' Society method, AOCS (2006). The item having an acid value less than 1 mg NaOH/g was hence utilized for the main transesterification reaction.

Step two: Production of fatty acid methyl ester

The transesterification reaction was carried out with methanol/oil molar ratios (MRs) (5:1, 6:1, and 7:1) using (0.275, 0.75 and 2 g) sodium hydroxide as an alkaline catalyst for samples (JOK, JOQ and JOD), respectively according to FFA%. The reaction was done at 60ºC for two hours. After the reaction was finished the obtained item was permitted to settle overnight before expelling the glycerol layer from the base in a separating funnel to recover the ester layer on the top. The top layer was washed with water to remove the residue of NaOH and methanol. At that point, the washed esters were warmed at 105ºC for 10 min to get rid of leftover water. The last obtained item was then analyzed by GC-MS to determine the fatty acid methyl ester composition of samples (JOK, JOQ and JOD) (AOCS 2006). Fatty acids determination was carried out in duplicate then averaged and means were tested using ANOVA.

Method of surfactant synthesis

Chlorosulfonic acid (2.63 g) was included gradually and with mixing to pyridine (15 ml) in an ice-cooled 250 ml round base flask. A solution of FAME (2.60 g) in 15 ml pyridine was acquainted slowly with the above blend more than 30 min. The reactor and contents were hence warmed in a steam bath until the solution turned out to be clear. The reaction was extinguished and the obtained item was changed over to the sodium salt by emptying the content into an ice-cooled aqueous sodium carbonate solution (33g in 300 ml water) and adequate solid sodium bicarbonate to keep the solution saturated with inorganic sodium salts.

A separating funnel was utilized to extract the obtained item twice with *n*-butanol (40 ml each). The *n*-butanol was removed from the product utilizing a rotary evaporator and the product was re-dissolved in water. Organic impurities were expelled from the watery solution of methyl ester sulfonate by extraction with ether. At that point, the crude obtained item was concentrated, separated, and dried under vacuum for 24 h for IR properties (Elraies et al., 2010). Synthesis of surfactants was completed in duplicate then averaged and means were tested by analysis of variance.

Synthesis of ethyl ester of jatropha oil (SF-4)

Into 240ml of the Jatropha oil, a mixture of ethanol (96ml) and KOH (4.8g) was poured dropwise while stirring for 30 minutes. Then the reaction mixture was covered and left to stir slowly (using a magnetic stirrer) for about 18hous until two layers were formed. Care was taken not to stir vigorously in order to avoid emulsification. The mixture was poured into a separating funnel and permitted to settle for 60 minutes. The lower layer was run off; which contains most of the glycerin that was realized during the reaction. About 10 ml of 50 ⁰C distilled water was added to the crude product and swirled slowly and left for some time to stand. The lower layer was then run off. This washing process was repeated until the product was clear. A small quantity of anhydrous magnesium sulfate was added and stirred for 5 minutes and the magnesium sulfate was allowed to settle. The ethyl ester was later filtered using a filter paper to separate it from the hydrated magnesium sulfate, the ethyl ester dried for IR characterization (Jibril et al., 2012).

Synthesis of soap from jatropha oil (SF-5)

10 g of NaOH was dissolved in 20 ml of deionized water, and then 20 ml of 95% ethanol was added to a 250 ml beaker. The prepared solution was added to 10 grams of Jatropha oil. The mixture was heated carefully on a hot plate for about thirty minutes. During heating the solution begins to foam, a small amount of the ethanol/water mixture was added to stop the foaming. In another 400 ml, beaker containing 50 grams of sodium chloride and 150 ml of water, the saponification mixture (Jatropha oil and alcohol) was quickly poured into this solution. Stirred and cooled to room temperature. The end product was filtered and used for IR characterization. The synthesis was carried out in duplicate then averaged and means were used.

Fourier transform infra-red (FT-IR) spectrophotometer characterization

FT-IR was used to identify the functional groups in the produced Surfactants of JOK, JOQ and JOD. The samples (JOK, JOQ and JOD) were loaded directly in the KBr introduced into the FT-IR (Nicolet iS10). A film of surfactant was put on the attenuated total reflectance (ATR) device, which was equipped with a ZnSe crystal (Van de Voort et al. 1994). The spectra were acquired utilizing 128 scans and appraised against the spectrum of the clean crystal. The reach from 4000 to 400 cm $^{-1}$ with a determination of 4 cm) was utilized to get spectral data. After every estimation, the ATR plate was carefully cleaned wiping it with acetone and dried with a delicate tissue before it was filled with the following sample. Three spectra replicates were obtained for each sample.

Analysis of fatty acids using GC/MS

The fatty acid composition was analyzed on a Shimadzu Gas Chromatograph, GC-17A linked to a QP 5000 Mass Spectrometry detector. The gas chromatograph contained a Restek Rxi-5 ms column of length and the inner diameter of 30 m and 0.25 mm, respectively, with the stationary phase being 5% phenyl. The carrier gas was helium, with a 1 ml/min continuous flow rate. A “Class-5000 application software controlled the instrumentation system on the computer. The column oven starting temperature was set at 40 ºC with a hold time of 4 minutes, then increased to 220 ºC at a heating rate of 4 ºC/min, with a hold time of 10 minutes. Lastly, the oven temperature was brought to 320 ºC at a rate of 5 ºC/min with a final hold of 5 minutes. The NIST 107 and 21 libraries were used to identify the compounds. A split ratio of 30:1 was used. This split ratio is explained as follows: 30 parts of the sample are thrown out while 1 part is allowed to enter the system from the total quantity injected. The purpose is to avoid overloading the capacity of the column. Twenty milligrams of each sample of methyl ester (JOK, JOQ and JOD) were mixed with one ml of dichloromethane (DCM) solvent. One µL of the solution was brought to the GC/MS after the column in the machine was automatically cleaned with dichloromethane (Soares et al., 2015). The analysis was carried out in duplicate then averaged and means were tested by analysis of variance.

The interfacial tension (IFT) analysis

The interfacial tension between different surfactants solutions and unrefined oil were measured utilizing Capillary Rise procedure to determine the surface activity at 30ºC. The capillary tubes and beakers first thoroughly clean of dirt and grease by washing successively in caustic soda and nitric acid and finally with distilled water. After cleaning the inside of the beaker, and those parts of the capillary tubes to be immersed in the1000ml petroleum crude oil, must not be touched by hand, to avoid further contamination by grease. The beaker is now filled to overflowing with petroleum crude oil (to facilitate reading of the rise by the traveling microscope), and one of the capillary tubes was thrust well down in the crude oil to wet freely the inside of the tube. It was then raised slightly and clamped in a vertical position when the rise (h) was measured by the traveling microscope, by first focusing on the crude oil level in the beaker and water, and then on the lower portion of the meniscus. The tube was removed from the crude oil and clamped in a horizontal position. Two readings of the diameter in directions mutually at right angles were taken with the microscope, from which the mean radius of the tube was found. The experiment was repeated, using capillary tubes of different diameters, and an average of T was obtained. The temperature of the crude oil was noted (Tyler, 1977). After that, about 2 ml of SF-1 was added to crude oil and was mixed well and the high steps were repeated and the surface tension was calculated and recorded, this method was repeated by adding 4, 6, 8 and 10 ml for SF-1 and was repeated to SF-(2, 3, 4 and 5). The results were recorded in tables 3. The same method repeated for water. The weight of the column of liquid (of density ρg per cm) the meniscus is supported by the upward forces of surface tension acting around the circumference of the circle of contact;

$2tr\pi = r2hg\rho\pi$ (3.5) Where:
T: Surface tension.
h: Rise in the tube per cm.
ρ: Density per g/cm. g: Gravity.
r: Radius of capillary tube per (cm).

Phase separation time

About 99 ml of water was added to one ml of crude petroleum oil from GNPOC (Greater Nile petroleum Operation Company, Khartoum, Sudan) in beaker (250 ml) and mixed by using homogenizer for 5 minutes and speed 24000 L/min, when it became a homogenized solution, the separation time was registered, in another beaker about 1 ml of produced SF-1 was added to 99ml of water and l ml of the same crude oil and mixed by using homogenizer Diax 900 for 5 minutes and speed 24000 rpm, when it became homogenized solution, the separation time was registered. This method was repeated to all produced surfactants and the phase separation time was recorded (Gupta et al., 1999).

Solubility measurements

The solubility of a substance is the amount of substance that will dissolve in a given amount of solvent. 1 ml of each SF- (1, 2, 3, 4 and 5) was taken in 5 large measure tube and added a 10 ml of distilled water by the cylindrical gauge to each tube and a requested good solubility was observed and the results were recorded. The process was repeated several times by adding the amount of change surfactant (2, 4, 6 and 8 ml) of distilled water and recorded; the result was shown in table 4.

Statistical analysis

The analyses were performed with three replicates. The mean values were calculated and tested using the Student-t-test ($p<0.05$). A statistical analysis of variance (ANOVA) was performed on all values using the statistical program Statgrafics® (Statistical Graphics System version 4.0 1985–1989).

Results and Discussions

Physicochemical analysis of Jatropha oil

Table 1 shows, physicochemical analyses of Jatropha oil collected from three Sudanese locations. Values of oil content of JOK, JOQ and JOD were 34.19%, 29.62% and 31.87%, respectively; these values were high enough for non-edible oil to be suitable as a feedstock in oleochemical industries. The oil content was found to be significantly different ($p \leq 0.05$) in seeds collected from three Sudanese localities. The oil content of Jatropha from South Kordofan was found to be the highest of all. The outcomes are in great concurrence with past result of Azam et al., (2005) who reported 28-35% oil content of *Jatropha curcas*. Jatropha oil content fluctuates relying upon the sorts of species and climatic conditions, however for the most part of the altitude where it is planted (Pant et al., 2006). Nayak and Patel (2010) reported high oil content of 46.31% for Malaysian samples. The density at 20ºC (g/ml) of the oil from the three locations was 0.913, 0.890 and 0.940 for JOK, JOQ and JOD, respectively, which was found to be a little bit less than that of water. Ntaganda, et al. (2014) reported less density 0.9004 (g/ml) for Rwandan Jatropha. For the most part, the density of oil reduces with molecular weight, and increments with the unsaturation level (Gunstone, 2004). The higher percentage of the FFA more than 1% (w/w) will improve soap formation and subsequently the partition of obtained items will be exceedingly troublesome and therefore, it has a low yield of ester product. The acid catalyzed esterification of the oil is an option (Crabbe et al, 2001), however, it is much slower than the base-catalyzed transesterification reaction. In this way, an option process, for example, a two stages procedure was examined for feedstock with high FFA content (Veljkovic et al., 2006). The FFA% content of JOK, JOQ and JOD were 1.093, 1.70, and 2.05%, respectively, showing that the oil of South Kordofan is more stable and cannot easily degrade when it is properly stored hence it can be utilized in formulating storage chemicals demanding low fatty acid content. From Table 1, the acid values from the three states were significantly different ($p \leq 0.05$). These values were 1.97, 3.38 and 4.07, for Jatropha oil from South Kordofan, Al Qadarif and Ad-Damazin, respectively. The acid value gives a measure of the extent to which the constituent glyceride has been decomposed by lipase action.

Table 1: Physicochemical analysis of the Jatropha seeds oil from three Sudanese locations South Kordofan, Al Qadarif and Ad-Damazin.

Parameter	JOK	JOQ	JOD
Oil content (%)	34.19±0.3^{a}	29.20±0.2^{b}	31.70±0.3^{c}
Density at 20º C (g/ml)	0.913±0.1^{a}	0.890±0.2^{b}	0.940±0.3 ^{c}
Specific gravity (g)	0.316±0.3^{a}	0.300±0.3^{b}	0.290±0.2 ^{c}
FFA (%) as oleic acid	1.093±0.1^{a}	01.70±0.3 ^{b}	2.050±0.3^{c}
Acid value (g)	02.18±0.2^{a}	03.33±0.3^{b}	4.090±0.4^{c}

**Values are means ± SD of three (n = 3) measurements. Values with different superscript letters within a row indicate significant differences at p ≤ 0.05. JOK: Jatropha oil from Kordofan, JOQ: Jatropha oil from Qadarif and JOD: Jatropha oil from Ad-Damazin*

Production of fatty acid methyl esters

In the first step, the acid value (AV) of the unrefined Jatropha oil was significantly impacted by the methanol-oil molar ratio (MR) over the 120 minutes reaction time. The pretreatment of the Jatropha oil with a MR of 5:1 diminished the AV from 2.1761, 3.383, and 4.079 for oil from South Kordofan, Al Qadarif and Ad-Damazin individually to 0.221 mg NaOH g-1 oil; with MRs of 6:1 and 7:1 the AV diminished to 0.156 and 0.056 mg NaOH g-1 oil separately. Subsequently the least MR of 5:1 was chosen for this study to diminish the AV, despite the fact that it was much lower than the suggested value of 2.0 mg KOH/g oil (Canakci and Van Gerpen, 2001). Along these lines, the methanol/oil molar ratio and reaction time can be lessened to bring down the expense of the pretreatment process on a business scale. In light of the weight of oil utilized as a part of this step, a normal yield of around 100% could be calculated. This is like the yield acquired by (El-Mashad et al., 2008) who carried out the pre-treatment of salmon oil that contained 12.05 mg KOH/g oil−1 utilizing % H_2SO_4 and MR of 9.1:1. In the second step, the pre-treated oil at a MR of 5:1 was utilized as feedstock for the alkali-catalyzed transesterification at three distinctive MRs of 5:1, 6:1, and 7:1. As an aftereffect of the 120 minutes reaction time, the methyl ester yield of 99.3, 96.34, and 99.8 were obtained individually, there were no critical contrasts in the methyl ester yield between MR, therefore, the ideal value to yield 99.3% of the methyl ester. As indicated by (Liu et al., 2008) a most extreme yield of 95% was obtained with MRs 12:1 and 3 hours reaction time from soybean oil, this makes Jatropha oil a promising source for methyl ester production.

Surfactant characterization

GC/MS for methyl esters

The main methyl esters of the fatty acids of Jatropha oil from South Kordofan, Al Qadarif and Ad-Damazin were linoleic, palmitic, stearic and oleic acids methyl esters (Table 2). The three oils showed significant differences ($P \leq 0.05$) in their fatty acid methyl esters.

The highest percent of methyl ester in all samples was oleic acid. The oleic percentage was 64.66, 50.76, and 48.90% in JOK, JOQ, JOD, respectively. The main methyl esters of South Kordofan Jatropha oil explained in Table 2. GC/MS showed that the most dominant fatty acids were palmitic, linoleic, oleic, and stearic acids methyl esters with the percentage of 20.39, 8.677, 64.66 and 6.279, respectively. The percentage (%) of total area for unsaturated esters was 73.34 and for saturated esters was 26.67%. The main methyl esters of Al Qadarif Jatropha oil were explained in Table 2, GC/MS showed that the methyl esters of palmitic, linoleic, oleic, and stearic acids methyl esters had a percentage (%) 10.26, 35.22, 50.76 and 3.75, respectively. The amount of the unsaturated esters was 85.98% and for saturated esters was 14.013%. In Table 2 it was clear that the main methyl esters found in *Ad-Damazin* Jatropha oil were palmitic, linoleic, oleic, and stearic acids. These fatty acids had an area % of 9.24, 38.20, 48.90 and 3.67, respectively. The total area% for unsaturated esters was 87.1% and saturated esters 12.91%. The three Sudanese Jatropha oils showed higher unsaturated fatty acids when compared to Jatropha oils from Malaysia and Nigeria. JOQ and JOD showed higher oleic acid content than Malaysian Jatropha oil. JOK showed higher palmitic, and oleic percentages than oil extracted from Malaysian and Nigerian Jatropha seeds.

Table 2: Fatty acid Methyl Ester Analysis (%) by GC/MS for Jatropha Oil from different three Sudanese states.

Fatty acid methyl ester	JOQ	JOD	JOK	Malaysia*	Nigeria**
Palmitic acid	10.26±0.1	09.24±0.1	20.39±0.3	19.18	14.69
Linoleic acid	35.22±0.2	38.20±0.2	08.68±0.1	36.70	80.07
Oleic acid	50.76±0.3	48.90±0.3	64.66±1.2	43.32	ND
Stearic acid	03.75±0.1	03.67±0.1	06.28±0.1	06.36	05.23
Σ Saturated Fatty acid	14.02±0.1	12.91±0.2	26.67±0.2	25.54	19.92
Σ Unsaturated Fatty Acid	85.98±1.3	87.10±1.3	73.34±1.1	80.02	80.07

*Jatropha Oil from Al Qadarif (JOQ), Jatropha Oil from Ad-Damazin (JOD) and Jatropha Oil from South Kordofan (JOK). *Abdullah et al. (2013), ** Inekwe et al. (2012).*

FT-IR Spectroscopy analysis

An FT-IR spectrophotometer was utilized to focus on the chemical functional groups present in the surfactants. Distinctive functional groups are defenseless to absorb properties frequencies of IR radiation. Figures 1A, 1B and 1C demonstrate the FT-IR spectrum of methyl ester sulfonate, and figures 2A, and 2B spectra of ethyl ester and soap respectively. All the IR absorption bands are broke down with reference to the spectrometric distinguishing proof of organic compounds by Silver-stein et al. (2005). The wide absorbance peaks between 3300-2500 cm^{-1} represent the O−H extending of carboxylic acid. The vicinity of esters is demonstrated by the absorbance peak of C=O extending vibration between 1744-1739 cm^{-1}. The presence of the huge peak at 1450 cm^{-1} compares to the asymmetrical bending vibration band of a methyl group (C-H). Peaks between 1160 - 1120 cm^{-1} demonstrate the existence of sulfonate groups because of S=O stretching (Silverstein et al., (2005); Awang and Seng, (2008). The peaks at 1410 and 1068 cm^{-1} are another sign of the existence of sulfonate groups because of the S=O stretching vibration. These outcomes demonstrate that this compound must be methyl ester sulfonate. The surfactants delivered in light of sodium methyl ester sulfonate were additionally described by FT-IR. The IR spectrums reported of the five obtained surfactants indicated similar pattern however the percentage of transmission is distinctive because of the variety in their molecular weights. The IR spectrums show that the chemical structures of these five surfactants are the same. Figures 1A, 1B and 1C show the FT-IR spectrum for the surfactant. The methyl ester sulfonate (MES) demonstrated a decent surface activity and thermal stability. The IR spectrum of methyl ester sulfonate is demonstrated in Figures 1A, 1B and 1C.

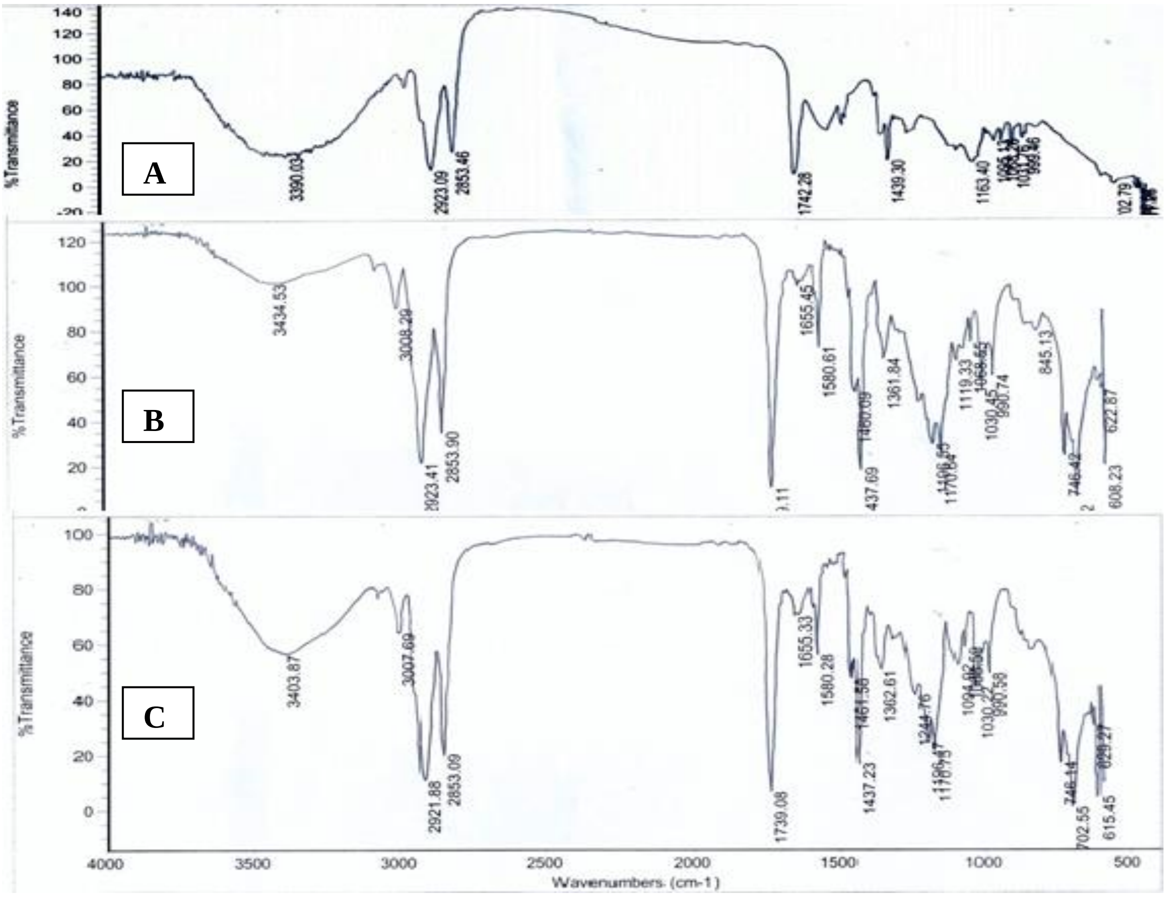

Figure 1: IR Spectrum of methyl ester sulfonates of South Kordofan (A), Al Qadarif (B), and Ad-Damazin (C) Jatropha oil.

Methyl ester sulfonate of south Kordofan (SF-1)

According to the scan, saturated (-C-H) starching peaks were found at 2923, and 2854cm^{-1} respectively (Figure 1A). Bending peaks of a methylene group (-CH_2-) at1439 cm^{-1}; bending peak of a methyl group (-CH_3) at 1163 cm^{-1}, peak (O-H) at 3390cm^{-1}, a peak of (C=O) at 1742 cm^{-1} indicates the presence of ester. Peaks around 1160 - 1120 cm^{-1} show the presence of sulfonate groups (S=O stretching vibration) (Silverstein et al., 2005; Awing and Seng, 2008) and long chain band peak at 703 cm^{-1}, which demonstrate that this compound must be methyl ester sulfonate indicated in figure 1A.

Methyl ester sulfonate of Al Qadarif (SF-2)

According to the scan, saturated (-C-H) starching peaks were found at 2923, 2854 cm^{-1} respectively. Bending peaks of a methylene group (-CH2-) at 1438 cm–^{1}; bending peak of a methyl group (-CH3) at 1361 cm^{-1}, peak (O-H) at 3435 cm–^{1}, the peak of (C=O) at 1739 cm–^{1}, and (C-O) at 1119 cm–^{1} these two indicate the presence of ester. Peaks around 1160 - 1120 cm^{-1} show the presence of sulfonate groups (S=O stretching vibration) (Awang and Seng, 2008) and long chain band peak at 703 cm^{-1}, which demonstrate that this compound must be methyl ester sulfonate shown in figure 1B.

Methyl ester sulfonate of Ad-Damazin (SF-3)

According to the scan, saturated (-C-H) starching peaks were found at 2922, 2853 cm^{-1} respectively. Bending peaks of methylene group (-CH_2-) at 1437 cm^{-1}; bending peak of methyl group (-CH_3) at 1362 cm^{-1}, peak (O-H) at 3403 cm−1, peak of (C=O) at 1739 cm^{-1} indicates the presence of ester, peaks around 1160-1120 cm^{-1} show the presence of sulfonate groups (S=O stretching vibration) (Silverstein et al., 2005) and long chain band peak at 703 cm^{-1}, which demonstrate that this compound must be methyl ester sulfonate as shown in figure 1C.

Ethyl ester of jatropha oil of south Kordofan (SF- 4)

According to the scan, saturated (-C-H) starching peaks were found at 2925, and 2854 cm^{-1} respectively. Bending peaks of methylene group (-CH_2-) at 1436 cm^{-1}; bending peak of methyl group (-CH_3) at 1363 cm^{-1}, peak (O-H) at 3466 cm^{-1}, peak of (C=O) at 1743 cm^{-1} and peak of (C-O) at 1119 these two indicate presence of ester, also long chain band peak at 723 cm^{-1} indicates that this compound must be ethyl ester (Figure 2A).

Soap of jatropha oil of south Kordofan (SF-5)

According to the scan, saturated (-C-H) starching peaks were found at 2922, and 2852 cm^{-1} respectively. The broad peak of (O-H) at 3353 cm^{-1}, the peak of (C=O) at 1744 cm^{-1} and (C-O) at 1050 cm^{-1}, also long chain band peak at 722 cm^{-1}, which indicate that this compound must be soap (Figure2 CB).

Measurements of interfacial tension (IFT)

The term interfacial tension is often utilized instead of interfacial free energy per unit area. The tendency for accumulation at the interfaces is a fundamental property of surfactant. The degree of surfactant at a boundary depends on several factors (Ye et al., 2008): (i) chemical structure of surfactants, (ii) concentration of the surfactant, (iii) chemical structure of the nonpolar polar phase, (iv) temperature (Negm and Tawfik, 2014). Interfacial tension (IFT) measurements were carried out between 1000 ml of crude oil of GONPOC and aqueous solutions of sodium methyl ester sulfonate (SMES) (SF-1, SF-2 and SF-3) as well as methyl ester sulfonate, SF-4 and SF-5. All first measurements were conducted for pure 1000 ml of crude oil and we started adding 2 ml of surfactant till 10 ml. same interfacial tension (IFT) measurements were conducted for 1000 ml of water. All the measurements were conducted at 30 ºC using the rise in a capillary tube method, tables 3 showed the interfacial tension as a function of SMES and surfactants produced. *r* and *h* are radius and height of the capillary tube, respectively. At 2ml added of SMES and other surfactants produced (SF-1, SF-2, SF-3, SF-4 and SF-5), SMES and other surfactants reduced the interfacial tension for water and crude oil from about 471.6642 dynes/cm to 114.4366, 125.2616, 129.901, 126.8081, 159.2833, 329.3917 dynes/cm, respectively for crude oil (Table 3), and from 70 dynes/cm to 66.052, 66.640, 65.268, 68.012, 68.404, 68.796 dynes/cm respectively for water (Table 4). This demonstrates the surface adsorption and aggregative properties of the new surface-active compounds. The interfacial tension of the system crude oil-SMES solution was reduced drastically as surfactant volume (concentration) was increased; these results are in a good agreement with that of Karnanda et al (2013) who reported a sharp exponential IFT decline with the increase of surfactant concentration. For instance, when the surfactant volumes were increased from 2ml to 4ml and 6ml the IFT was reduced. These results indicate that there is no much difference in the interfacial tension reduction while the cost of the produced surfactant is very much lower than the commercial SMES, and the results indicate that what was produced is a real surfactant.

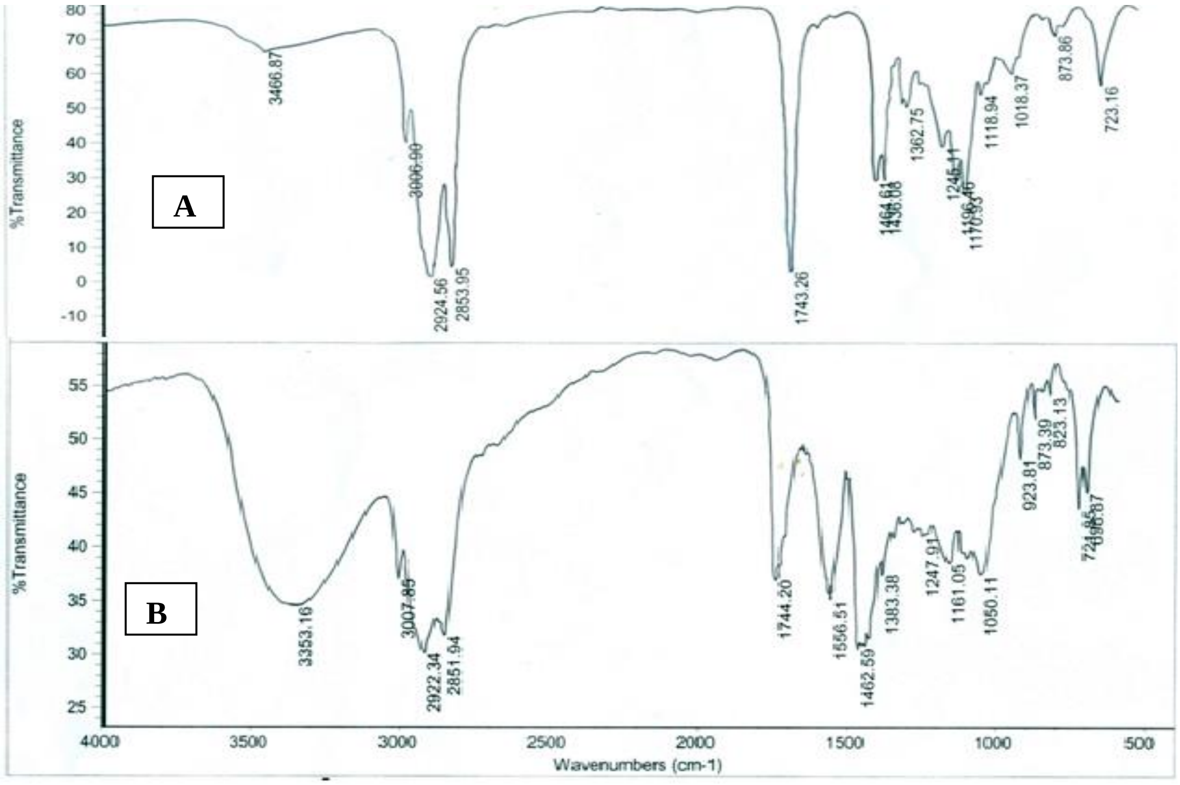

Figure 2: IR Spectrum of Ethyl ester (A) and soap (B).

Table 3: Interfacial Tension (IFT) between 1000 ml of crude petroleum oil of GONPOC, density 0.789g/ml and Surf-1-5 added.

IFT between 1000 ml of CPO of GONPOC, density 0.789g/ml and Surf-1 added				
No.	Amount of Surf-1 Added (ml)	r(cm)	h(cm)	T dynes/cm
1	0	0.4	03.May	4.716.642
2	2	0.4	0.81	1.252.616
3	4	0.4	0.63	974.257
4	6	0.4	0.41	634.041
5	8	0.4	0.22	3.402.168
6	10	0.4	0.08	1.237.152
IFT between 1000 ml of CPO of GONPOC, density 0.789g/ml and Surf-2 added				
1	0	0.4	03.May	4.716.642
2	2	0.4	0.84	1.299.010
3	4	0.4	0.60	927.864
4	6	0.4	0.39	6.031.115
5	8	0.4	0.18	2.783.590
6	10	0.4	0.06	927.864
IFT between 1000 ml of CPO of GONPOC, density 0.789g/ml and Surf-3 added				
1	0	0.4	03.May	4.716.642
2	2	0.4	0.82	1.268.081
3	4	0.4	0.69	1.067.044
4	6	0.4	0.40	6.185.760
5	8	0.4	0.27	4.175.388
6	10	0.4	0.063	974.257
IFT between 1000 ml of CPO of GONPOC, density 0.789g/ml and Surf-4 added				
1	0	0.4	03.May	4.716.642
2	2	0.4	01.Mar	1.592.833
3	4	0.4	0.97	1.500.047
4	6	0.4	0.84	1.299.010
5	8	0.4	0.71	1.097.972
6	10	0.4	0.45	695.898
IFT between 1000 ml of CPO of GONPOC, density 0.789g/ml and Surf-5 added				
1	0	0.4	03.May	4.716.642
2	2	0.4	Şub.13	3.293.917
3	4	0.4	02.Eyl	323.206
4	6	0.4	Oca.53	2.366.053
5	8	0.4	Oca.34	2.072.230
6	10	0.4	Oca.29	1.994.908
IFT between 1000 ml of CPO of GONPOC, density 0.789g/ml and SMES added				
1	0	0.4	03.May	4.716.642
2	2	0.4	0.74	1.144.366
3	4	0.4	0.67	1.036.115
4	6	0.4	0.44	6.804.335
5	8	0.4	0.15	231.966
6	10	0.4	0.07	111.343

Table 4: Interfacial Tension (IFT) between 1000 of water, and Surf-1-5 added.

IFT between 1000 ml of water and Surf-1 added				
No.	Amount of Surf-1 Added (ml)	r(cm)	h(cm)	T dynes/cm
1	0	0.4	Mar.57	70.000
2	2	0.4	Mar.40	66.640
3	4	0.4	Şub.99	58.604
4	6	0.4	Şub.31	45.276
5	8	0.4	Oca.88	36.848
6	10	0.4	Oca.29	25.284
IFT between 1000 ml of water and Surf-2 added				
1	0	0.4	Mar.57	70.000
2	2	0.4	Mar.33	65.268
3	4	0.4	Şub.97	58.212
4	6	0.4	Şub.27	44.492
5	8	0.4	Oca.78	34.888
6	10	0.4	Oca.15	22.540
IFT between 1000 ml of water and Surf-3 added				
1	0	0.4	Mar.57	70.000
2	2	0.4	Mar.47	68.012
3	4	0.4	Şub.29	64.484
4	6	0.4	Şub.78	54.488
5	8	0.4	Şub.43	47.628
6	10	0.4	Oca.19	23.324
IFT between 1000 ml of water and Surf-4 added				
1	0	0.4	Mar.57	70.000
2	2	0.4	Mar.49	68.404
3	4	0.4	Mar.14	61.544
4	6	0.4	Şub.99	58.604
5	8	0.4	Şub.83	55.468
6	10	0.4	02.Ara	41.552
IFT between 1000 ml of water and Surf-5 added				
1	0	0.4	Mar.57	70.000
2	2	0.4	Mar.51	68.796
3	4	0.4	Mar.17	62.132
4	6	0.4	Şub.91	57.036
5	8	0.4	Şub.67	52.332
6	10	0.4	Şub.31	45.276
IFT between 1000 ml of water and SMES added				
1	0	0.4	Mar.57	70.00
2	2	0.4	Mar.37	66.052
3	4	0.4	Şub.98	58.408
4	6	0.4	Şub.65	51.940
5	8	0.4	Oca.96	38.416
6	10	0.4	01.May	20.580

Separation time analysis

The presence of surface-active compounds does not influence the settling time of a partially miscible liquid mixture as it phase separates. On the other hand, when the same mixture is agitated isothermally while in its two-phase state, its settling time greatly increases if surfactants are added (Gupta et al., 1999). During phase separation, the repulsive interactions were decreased and facilitate the formation of large aggregates (Mukherjee et al., 2011). Separation time measurements between one ml of crude oil and 100 ml of water after mixed well by homogenizer for 5 minutes with speed 26000 at 12.30 minutes the oil separated from water as in Table 5, but when added 1 ml of surfactant (sodium methyl ester sulfonate (SMES) time was increased up to 47.9 min and when Jatropha oil surfactants (SF-1-5) were added the separation time was increased to 45.3, 40.6, 39.1, 23.7 and 20.3 min respectively, demonstrating that phase separation is governed by the convective motion due to capillary forces, convection is induced by the coalescence among drops which, in turn, is the result of a non-equilibrium capillary force that indeed dominates both diffusion and gravity forces (Mauri et al. 2003). The first three surfactants (SF-1, SF-2 and SF-3) as methyl ester sulfonate (MES) showed good separation time near to that of SMES (commercial surfactant) and better than SF-4 and SF-5. At room temperature, all surfactants produced were found soluble (data are not shown). The newly produced Jatropha oil surfactants (SF-1-5) increased the separation time when added so it’s possible can be used to enhance oil recovery.

Table 5. Description of separation time.

Crude oil (ml)	Water (ml)	Surfactant (ml)	Separation time (min.)
1ml	100ml	-	12.30
1ml	100ml	1ml of Surf-1	45.3
1ml	100ml	1ml of Surf-2	40.6
1ml	100ml	1ml of Surf-3	39.1
1ml	100ml	1ml of Surf-4	23.7
1ml	100ml	1ml of Surf-5	20.3
1ml	100ml	1ml of SMES	47.9

Conclusions

From this study the following conclusions are summarized:

- Production of methyl ester sulfonate (MES) using Jatropha oil can fulfill EOR prerequisites, in light of the fact that it is an inexpensive, natural, and renewable raw material.
- The MES offers a strong economic incentive to substitute sodium dodecyl sulfate (SDS), SMES and other commercial surfactants for EOR applications, and the other surfactants ethyl ester and soap can be utilized in other applications in addition to EOR
- The newly produced surfactants showed excellent surface tension, solubility, separation time and thermal stability properties. The interfacial tension at various aqueous surfactants solutions and crude oil was very low.
- These results showed that non-edible Jatropha oil can conceivably be utilized as surfactant feedstock, and there were no any distinctions found in MES from different locations in Sudan, just in the ratio of free fatty acids and oil content.

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