Synthesis and Evaluation of some food grade lubricating greases from local materials

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Abstract: The objective of this research aimed to produce food grade calcium lubricating grease which is used in lubricating of bearing and gears in food processing and pharmaceutical machine using renewable sources. Jojoba oil was used as the base oil in producing two types of food grade greases. This grease was manufactured via two steps of process, saponification process and cooling & homogenization process. In normal grease we use lubricating oil and calcium hydroxide, 12-hydroxystearic acid and in complex grease we use lubricating oil, calcium hydroxide and fatty acid 12-hydroxystearic acid and acetic acid. The produced normal grease had a dropping point of 140^{o} C, good anti-wear property and consistency NLGI Grad 1, and the produced complex grease had dropping point of 335^{o}C, good anti-wear property and consistency NLGI Grade 2.
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I- Introduction

Agricultural and animal substances go through a number of processes in a manufacturing plant, such as cleansing, sterilizing, blending, mixing, cooking, freezing, cutting, packaging, canning or bottling. Large-scale food processing requires machinery such as pumps, mixers, tank, hoses and pipes, chain drives, and conveyor belts. Machinery used in food processing facilities face many of the same tribiological and lubrication challenges found in other non-food processing plant. In that sense, lubricants must offer similar protection of internal surfaces to control friction, wear, corrosion, heat and deposits. They must also offer good pumpability, oxidation stability and thermal stability where the application so requires. Many of the raw materials used to formulate lubricants that effectively address these challenges in conventional industrial applications are not permissible in food application for safety reasons.

In addition, certain applications within the food and drug manufacturing facilities demand that lubricants resist degradation and impaired performance when in contact with food products, certain process chemicals, water (including steam) and bacteria. They must also exhibit neutral behavior toward plastics and elastomers. In general, these lubricants must comply with food / health and safety regulations, as well as be physiologically inert, tasteless and internationally approved [1].

Food-grade lubricants are either compounded or uncompounded products acceptable for use in meat, poultry and other food processing equipment, application and plant. The lubricant types in food-grade applications are broken into categories based on the likelihood they will contact food. The USDA created the original food-grade designations H1, H2 and H3. The approval and registration of a new lubricant into one of these categories depends on the ingredients used in the formulation [2].

What also must be borne in mind is that these standards apply only in the US. Other countries, such as the UK, South African and those in Europe, have to date largely depended on the US for their specifications. Some, however, are in the process of developing their own standards, which in all probability will be largely based on the original USDA and FDA specifications.

The three designations are described as follows

- **H1 lubricants** are food-grade lubricants used in food processing environments where there is some possibility of incidental food contact. Lubricant formulations must be composed of one or more approved base stocks, additives and thickeners (if grease). Allowable substances, in this instance, are those listed by the FDA in accordance with the Guidelines of Security Code of Federal Regulations (CFR) title (21 CFR 178.3750). Only the minimum amount of lubricant required should be used on the equipment.
- **H2 lubricants** are used on equipment and machine parts in locations where there is no possibility that the lubricant or lubricated surface contacts food. Because there is not risk of contacting food, H2 lubricants do not have arsenic, cadmium, lead, mercury or selenium. Also, the ingredients must not include substances that are carcinogens, mutagens or mineral acids [3].
- **H3 Lubricants**, also known as soluble or edible oil, are used to clean and prevent rust on hooks, trolleys

and similar equipment applied with H3 lubricants should be cleaned by washing or wiping the surface before putting the equipment in service.

These lubricants can only consist of ingredients as shown in table (I-1).

Table: (I-1) H-3 Soluble oil Approved Lubricants [4]

Lubricant Type	Regulations They Must Meet
Edible oils (corn oils, cottonseed oils, soybean oil)	21 CFR 172,860
Certain mineral oils	21CFR 172,878
Generally Recognized as Safe(GRAS)	21CFR 182or 21 CFR 184

Deciding whether there is a possibility of contact is tough, and many have erred on the side of safety to selecting an H1 lubricant over an H2 lubricant.

II- Experimental

Materials and Methods

Base oil

Jojoba oil was investigated as the base oil part for preparing calcium lubricating greases as food grade grease.

Thickener

Calcium soap of normal calcium lubricating grease was obtained from the reaction between 12-hydroxystearic acid and calcium hydroxide Ca $(OH)_2$.

Calcium soap of complex calcium lubricating grease was obtained from the reaction between 12-hydroxystearic acid, acetic acid and calcium hydroxide Ca $(OH)_2$.

Preparation of normal calcium lubricating grease

Normal calcium lubricating grease under investigation was prepared from calcium soap thickener 15% and jojoba oil as the base oil 85% of total product via two steps referred as saponification process and cooling and homogenization process according to the following:

Saponification process:

A mixture of 12-hydroxystearic acid (approximately 14% of total product wt.) and about 25% of the required jojoba oil weight were uniformly mixed with a mechanical stirrer at 80°C in a 1 L autoclave, equipped with a pressure indicator, oil heater and a thermometer until all the 12-hydroxystearic acid was dissolved, then the calcium hydroxide (approximately 2.5% of total product wt.) was added slowly to the mixture. The temperature was then slowly raised to 100 – 110°C and maintained at this temperature for approximately 60 min to ensure complete saponification. After this point a sample is taken to check its alkalinity /acidity. Corrections are made by adding fatty acid or calcium hydroxide as required

Cooling & Homogenization process:

It is performed after the completion of saponification reaction. The reaction mixture is cooled gradually by stop heating while adding rest of jojoba oil to attain the required greases consistency. At first half of the rest of jojoba oil quantity was added while stirring when we reach 90^{o}C and the remained quantity of the jojoba oil was added while stirring continue when we reach 70°C. Then the final mixture was allowed to cool to room temperature to obtain normal calcium grease. The normal calcium grease product was then homogenized for structure stabilization, using high speed stirring until it was soft and thoroughly homogenous.

Preparation of complex calcium lubricating grease

Complex calcium lubricating grease under investigation were prepared product via two steps referred as saponification process and cooling and homogenization process according to the following:

Saponification process:

A mixture of acetic acid (approximately 10 % of total product wt.) and about 25% of the required jojoba oil weight were uniformly mixed with a mechanical stirrer in a 1 L autoclave, equipped with a pressure indicator, oil heater and a thermometer, then the calcium hydroxide (approximately 3% of total product wt.) was added very slowly to the mixture in about 60 minutes while keeping the temperature not exceed 60°C. After complete addition of calcium hydroxide, the temperature was then slowly raised to 100°C and start addition of 12-hydroxystearic acid (approximately 12 % of total product wt.) gradually while stirring through 15 minutes, after that the temperature was raised to 110°C for 30 minutes and then from 140 - 160°C for another 60 minutes with continue vigorous stirring to insure complete saponification. After this point a sample is taken to check its alkalinity /acidity. Corrections are made by adding acetic acid or calcium hydroxide as required.

Cooling & Homogenization process:

It is performed after the completion of saponification reaction.

The reaction mixture is cooled gradually by stop heating while adding rest of jojoba oil to attain the required greases consistency. At first half of the rest of jojoba oil quantity was added while stirring when we reach 90^{o}C and the remained quantity of the jojoba oil was added while stirring when we reach 70°C. Then the final mixture was allowed to cool to room temperature to obtain complex calcium grease. The complex calcium grease product was then homogenized for structure stabilization, using high speed stirring until it was soft and thoroughly homogenous.

Grease evaluation

In order to evaluate the prepared calcium grease the following standard routine methods were carried out.

Infrared spectra

Fourier transform (FT-IR) spectra of the prepared samples were carried out using a single beam Fourier Transform Infrared Spectrometer, AVATAR 320 FTIR. This instrument is equipped with Ever-Glo source, KBr beam splitter and DTGS- KBr detector. The FTIR spectra of the samples were obtained in the spectral range 4000 cm^{-1} to 400 cm^{-1} with resolution 4 cm^{-1}. The number of scans was set to ´´32``.

Cone penetration

The penetration is determined according to ASTM D-217 at 77°F (25°C) by releasing the cone assembly from the penetrometer and allowing the cone to drop for 5 sec. undisturbed penetrations are determined on the sample as received in its original container**.**

Un-worked penetrations are taken on samples transferred with a minimum of disturbance to container suitable for test purpose. Worked penetrations are determined immediately after working the sample for (60 strokes) in the standard grease worker. Prolonged worked penetrations are determined on samples worked more than 60 strokes.

Dropping point Test

This method covers determination of the dropping point of lubricating grease according to **ASTM D-566**, this point being the temperature at which the first drop of material falls from the cup. In general,the dropping point is the temperature at which the grease passes from a semisolid to a liquid state under the condition of test.

The method is useful to assist in identifying the grease as to type and /or establishing and maintaining bench marks for quality control**.**

Oil Separation Test

This method covers determination of the tendency of lubricating grease to separate oil during storage in conventional and created containers According **to IP121** and **ASTM D-1724**. Place the strainer, screen side up, in the funnel and tare the assembly to the nearest 0.05 by means of a spatula, fill the space between the screen and the top of the funnel with grease. Bring the apparatus and the sample to 25± 1°C before starting the test, regulate

The air pressure to 1.72 KPS (0.25 ± 0.01 PSI) and continue the best for 24 h at this pressure and temperature, then determine the collected oil**.**

Total Acidity and Alkalinity

This method describes the procedure for determination of acidic or basic constituents in petroleum products and lubricants according to **ASTM D-664.** The method resolves these constituents into groups having weak-acid, strong acid, weak base and strong base. The sample was dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide or hydrochloric acid solution, using a glass indicating electrode and calomel reference electrode. The meter readings were plotted manually or automatically against the respective volumes of titrating solution. The end point was taken only at well-defined inflections in the resulting curve. When no definite inflections were obtained, end point was taken at meter readings corresponding to those found for freshly prepared non-aqueous acidic and basic buffer solution.

Total Acid Number

Total acid number defines as the quantity of base, expressed in milligrams of potassium hydroxide that is required to neutralize all acidic constituents present in one gram of sample.Total acid number calculated from the following equation:

T.A.N. mg KOH/G sample = (A-B) x 56.1 x N/w

Where:

A: The volume of KOH used for sample.

B: The volume of KOH used for the blank.

N: The normality of alcoholic KOH solution.

W: Grams of the sample.

The cell of potentiometric titration consists of meter, glass electrode, calomel electrode, stirrer, burette, beaker, and stand.

Detection of copper corrosion test

This method is intended for the detection of corrosive substances in lubricating grease. The detection of copper corrosion of lubricating greases through copper strip Tarnish test was detected according to **ASTM D-4048 and IP112.** A prepared copper strip is totally immersed in a sample of grease and heated in an oven for 3 hours at 100°C, and then the strip is removed, washed, and compared with ASTM copper strip corrosion standard.

Four –Ball Weld test

The test was conducted on a four-Ball machine by the following standard procedure, **ASTM D-2596.** Three 0.5 inch diameter steel balls are clamped together and then a fourth identical ball (referred to as the top ball)is pressed downward into the cavity formed by the three clamed, stationary balls. This arrangement forms a three-point contact. The top ball is rotated at 1800 rpm, and a series of test of 10 seconds duration are made at increasing loads until welding of the balls occurs. The welding point (Kg) is reported.

III- Result and Discussion

Identification and Characterization of Raw Materials

The basic raw materials required for the preparation of the most lubricating greases are saponifiable fat of 12-hydroxystearic acid, saponifying agent, and fluid lubricants, which was jojoba oil, some of these raw materials will be investigated in this study as following:

Base oil

The physicochemical properties of jojoba oil was shown in **Table (III-1**)

FTIR spectra of jojoba oil and of 12-hydroxy stearic acid was shown in **Fig.(III-1)** and **fig.(III-2)** respectively and according to the most important absorbance bands for vegetable oils in the mid-infrared spectra and their characteristic functional **groups** as shown in **Table (III-2).** [5]

In **Fig.(III-1)** for jojoba oil we can see characteristic absorption peak at ~ 3004 cm^{-1} due to C—H stretching vibration of the cis-double bond (= CH), at ~ 2925 cm^{-1} due to C–H stretching (asymmetry), at ~ 2853 cm^{-1} due to C–H stretching (symmetry)), at ~ 1739 cm^{-1} due to C= O stretching, at ~ 1655 cm^{-1} due to stretching of -C-C-(cis), at ~ 1465 cm^{-1} due to Bending vibrations of the CH2 and CH3 aliphatic groups, at ~ 1352 cm^{-1} due to Bending vibrations of CH2 groups, at ~ 1171 cm−1 due to C–O stretching and C–H bending), and at ~ 722 cm^{-1} due to C–H bending (rocking).

In **Fig.(III-2)** for 12-hydroxystearic acid we can see a very broad band at ~ 3200 cm^{-1} due to -COOH group of the acid molecule, at ~ 2915 cm^{-1} due to C–H stretching (asymmetry), at ~ 2849 cm^{-1} due to C–H stretching (symmetry), at ~ 1697 cm^{-1} due to C= O stretching, at ~ 1470 cm^{-1} due to Bending vibrations of the CH2 and CH3 aliphatic groups, at ~ 1242, 1440, and 919 cm^{-1} due to in-plane and out-of-plane O–H bending bands and at ~ 719 cm^{-1} due to C–H bending (rocking).

Evaluation of the produced grease

Normal grease:

Normal calcium lubricating grease was prepared through saponifying 12-hydroxystearic acid by calcium hydroxide.

The infrared absorption spectra of normal calcium jojoba grease was shown in **Fig.(III-3)**. We can see the same characteristic absorption bands as in case of jojoba oil and 12-hydroxystearic acid except the appearance of new double strong absorption bands at 1575 and 1540 cm^{-1} which are corresponds to carboxylate stretching of calcium stearate, and the disappearance of the band at 1697 cm^{-1} which is corresponds to C=O stretching of stearic acid which is an evidence of the complete neutralization of 12 hydroxy stearic acid by calcium hydroxide.

The physical and chemical properties of the produced normal calcium grease was sh*own* in **table (III-3).**

Complex Calcium Lubricating Grease

Calcium soap of complex calcium lubricating greases was prepared through saponifying 12-hydroxystearic acid and acetic acid by calcium hydroxide.

Table (III-1): Physical and chemical properties of jojoba oil.

Property	**Kinematic viscosity at 40°C (cSt)**	**Kinematic viscosity at 100°C (cSt)**	**Acid value (mg/g)**	**Sap. Value (mg KOH/g)**	**Iodine value (mgI_2/g)**	**Acetyl value**	**Unsapon--ifiable matter (%)**
values	**24.060**	**6.300**	**< 2.5**	**90 – 100**	**80 – 85**	**< 2.5**	**51**

Table (III-2) FTIR most important absorbance bands of fatty materials [5]

No.	**Wave number (cm^{-1})**	**Characteristic group and mode of vibration**
1	3470	Overtone of –C=O (ester)
2	3006	Stretching of =C–H (cis)
3	2925	Asymmetric stretching of –CH (CH2)
4	2854	Symmetric stretching of –CH (CH2)
5	1746	Stretching of –C=O (ester)
6	1655	Stretching of -C-C-(cis)
7	1464	Bending (scissoring) of –C–H (CH2 and CH3)
8	1377	Symmetric bending of –C–H (CH3)
9	1237	Stretching, bending of –C–O, –CH2 –
10	1163	Stretching, bending of –C–O, –CH2 –
11	1099	Stretching of – C–O
12	723	Bending (rocking) of –(CH2) n–, HC=CH– (cis)

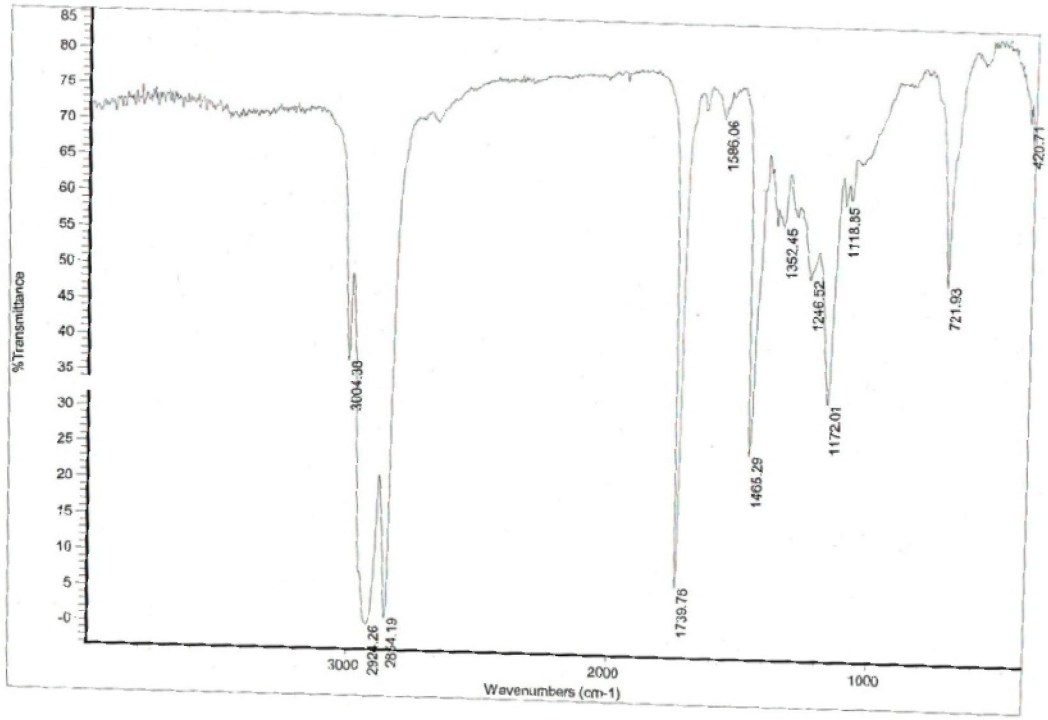
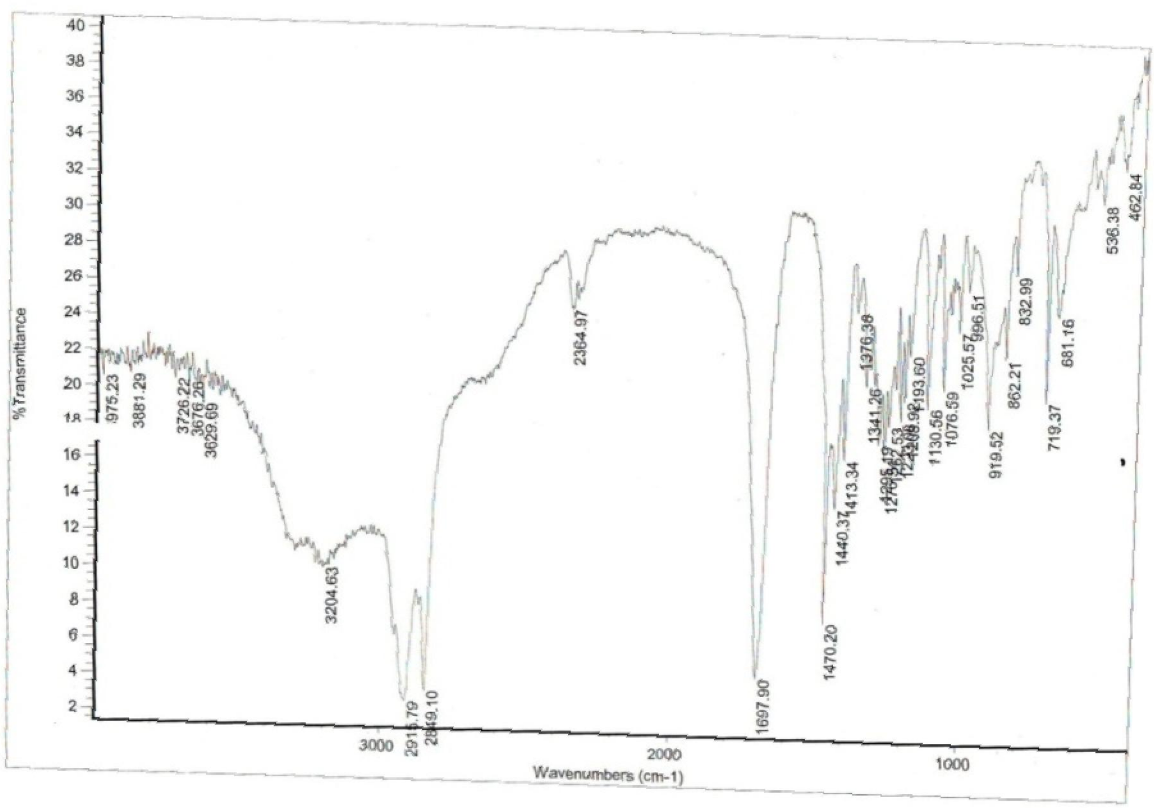


Figure (III-1) FTIR spectra of Jojoba oil



Figure(III-2) FTIR spectra of 12-hydroxystearic acid

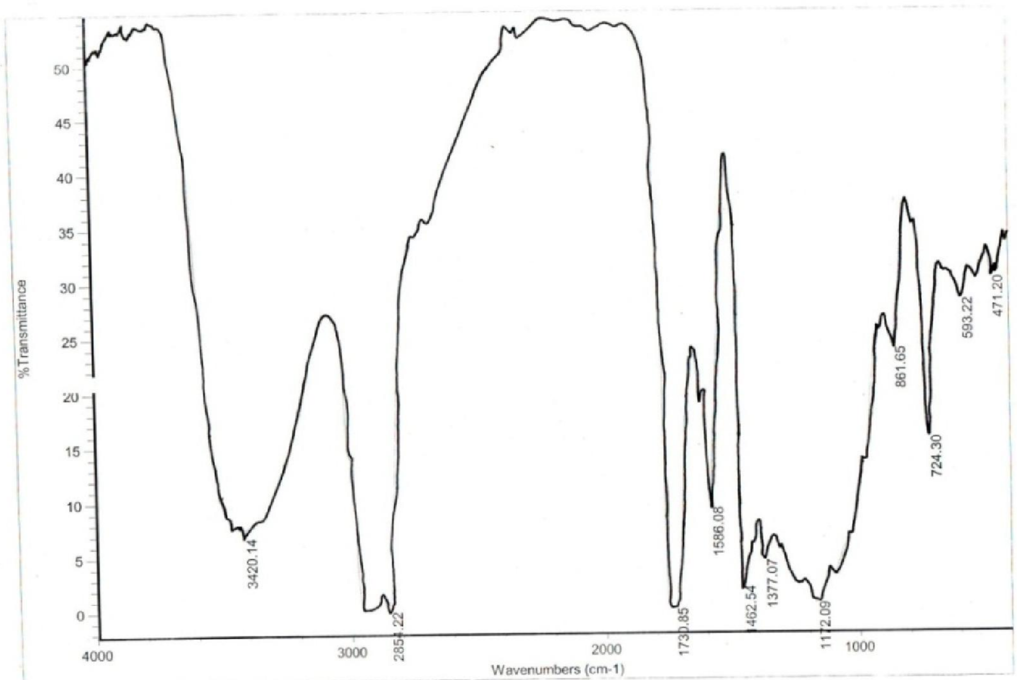


Figure (III-3) FTIR spectra of normal calcium grease

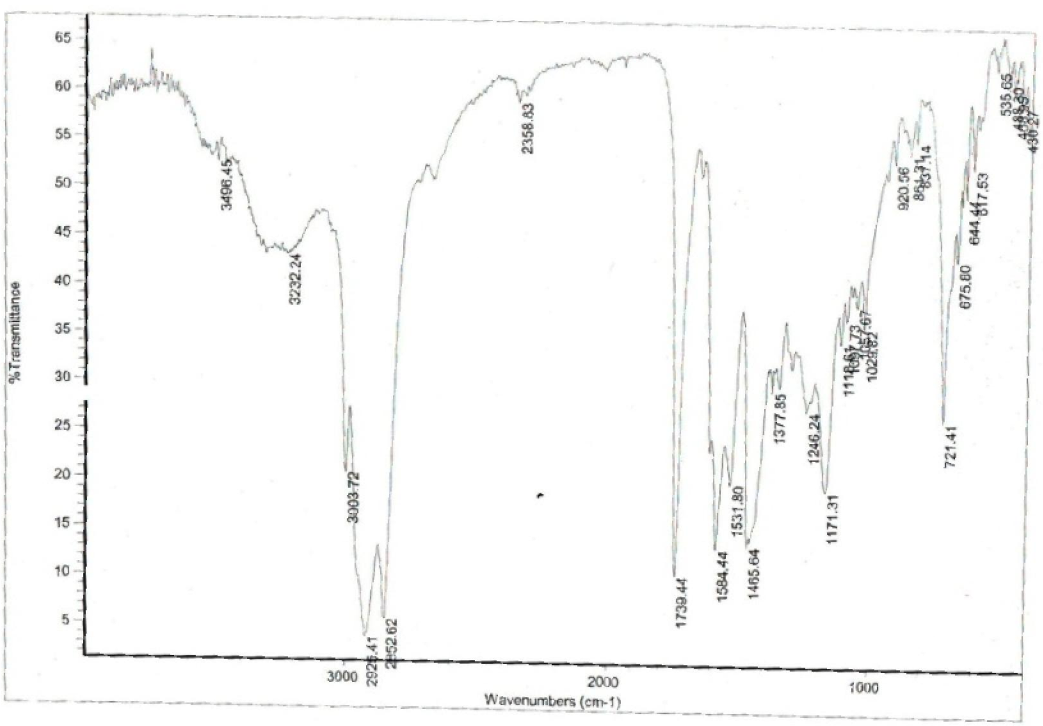


Figure (III-4) FTIR spectra of complex calcium grease

The infrared absorption spectra of the prepared complex grease was shown in **Fig.(III-4)**. We can see the same characteristic absorption bands as in case of normal grease with the appearance of the double strong absorption bands corresponds to carboxylate stretching of calcium at 1584 and 1531 cm^{-1}, and the disappearance of the band at 1697 cm^{-1} which is corresponds to C=O stretching of stearic acid which is an evidence of the complete neutralization of 12-hydroxystearic acid by calcium hydroxide.

The physical and chemical properties of the produced complex calcium grease was sh*own* in **table (III-4).**

Table (III-3) Physical and chemical properties of the produced normal grease

Test	Results	Test method
Penetration at 25°C **Un- worked** **worked**	 **325** **326**	**ASTM D-217**
Dropping point °C	**140**	**ASTM D-566**
Alkalinity, wt%	**0.7**	**ASTM D-664**
TAN, mg KOH/gm @ 72 h	**o.68**	**ASTM D-664**
Oil separation, Wt%	**1.5**	**ASTM D-1724**
Copper Corrosion 3h/100°C	**1 a**	**ASTM D-4048**
NLGI grease code	**1**	**NLGI standard**
Four ball weld load, kg **Scar Diameter**	**250** **0.4**	**ASTM D-25**

Table (III-4) Physical and chemical properties of the produced complex grease

Test	Results	Test method
Penetration at 25°C **Un- worked** **worked**	 **275** **277**	**ASTM D-217**
Dropping point °C	**335**	**ASTM D-566**
Oxidation stability **99±96, h, pressure drop, psi**	**4**	**ASTM D-942**
Alkalinity, wt%	**0.7**	**ASTM D-664**
TAN, mg KOH/gm @ 72 h	**0.68**	**ASTM D-664**
Oil separation, Wt%	**1.5**	**ASTM D-1724**
Copper Corrosion 3h/100°C	**1 a**	**ASTM D-4048**
NLGI grease code	**2**	**NLGI standard**
Four ball weld load, kg **Scar Diameter**	**250** **0.4**	**ASTM D-25**

Conclusion

Two types of jojoba-grease has been made normal calcium soap grease and complex soap calcium grease, based on using jojoba oil as the base oil and calcium thickener. From this study, several conclusions can be summarized as follow:

1- Additive-free normal calcium-grease can be manufactured using jojoba oil as the base oil and about 15%-20% calcium soap thickener obtained from reaction between 12-hydroxystearic acid and calcium hydroxide, to get dropping point of 140°C, and NLGI grease code 1 according to NLGI standards, with good anti-wear performance.

2- Additive-free complex calcium-grease can be manufactured using jojoba oil as the base oil and about 15%-20% calcium soap thickener obtained from reaction between 12-hydroxy stearic acid and acetic acid with calcium hydroxide, to get dropping point of 335°C, and NLGI grease code 2 according to NLGI standards with good anti-wear performance.

3- Both of the two produced greases can be used as H2 food grade lubricating greases according to USDA and FDA specifications [6].

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