

MODIFICATION OF THE RECOVERED LOW- GRADE FAT TO FORMULATE ECO-FRIENDLY LUBRICANT GREASE

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Abstract— This study presents utilization of the inedible by-product fat of the municipal massacres to formulate bio-based lubricant grease. Inedible animal fat of acceptable quality has been recovered through the wet rendering process. The recovered fat was sterilized and bleached using 200 ppm chlorine dioxide solutions. The acceptable saponification and iodine values of the fat emphasize that it can be used in the chemical industry as an oleochemical resource. The fat was fractionalized into two fractions; stearic and oleic. The lithium soap of the stearic fraction was employed as a thickener and the oleic fraction has been adapted for use as base oil, depending on its proportion of combination compared to the thickener. It was found that the ideal composition of the formulated bio-grease is 15-20 % thickener to 85-80 % base oil. The performance testing shows that the formulated grease has NGLI ranges between 2- 3. The grease can be utilized as a lubricant agent in machinery and gears with an acceptable lubricating performance.

Keywords— Animal fat, Byproduct, Lubricant Grease, Tanneries.

I. INTRODUCTION

Regarding cleaner production, studies have to explore methods involved in the manufacture of value-added products via side products recycling (Ajayi and Adesanwo, 2009). Slaughterhouses around the world force a huge amount of slaughtered animal by-products. Some studies estimate the solids generated from one ton of livestock to be 275 kg. Moreover, the solid waste byproducts represent more than 25% of the slaughtered livestock. According to United States Department of Agriculture, Livestock, and Poultry, about 237.3 million tons meats represent the total world meat production around the world in 2010, and forty billion pounds are the annual slaughterhouses wastes in the United States (USDA, 2011). Skin terminals, fatty tissues and other inedible meat are the main ordinary by-products in this category. Such by-products are considered a perfect environment for bacterial growth. Therefore, they cause environmental pollution, and their recycling has an economic and environmental benefits. Animal skin terminals and fatty tissues byproducts are mainly composed of proteins and fats (Irshad and Sharma, 2015). This study is concerned with the fatty tissues and fatty material recovery. Several endeavors have been made to add

value to the inedible adipose tissues. The saponification and iodine values of these rendered fats allow the possibility of being employing as a starting material or oleochemical resources. Therefore, they can be utilized in several applications such as, soap, lubricants and leather fatliquoring manufacture (Habib and Alshammari, 2014). Nowadays, researchers try to utilize agriculture by-products to prepare value- added products (Mazo and Ríos, 2010; Campanella and Baltanás, 2005; Palmeira *et al.*, 2012). Trails to formulate bio-based lubricant grease have been achieved (Sukirno *et al.*, 2009). According to the American Society of Testing and Materials, grease is defined as a semi- fluid lubricant. Reducing the friction between two solid parts is an important factor in industrial machines. Dispersing a thickener into lubricating oil at a definite temperature is the main conception of the grease formulation. Based on the grease application, several kinds of grease are well known. In addition to its facility to protract the lifetime of machinery, the grease can act as anti-corrosion, and noise reducer (Pogosian and Martirosyan, 2007; Gow, 2010). Animal fats are mainly triglycerides, have a set of the advantage of making them of great importance in the manufacture of lubricating greases. Their resistance to viscosity change at high temperature and low volatility are the most important preferred properties, in addition to their biodegradability, oxidative stability, and non-toxicity (Battersby *et al.*, 1998). Different researchers focused on using natural oils for lubricant grease formulation. Among these, the vegetable oils that have great advantages like biodegradability and their efficacious lubricating potency (Salimon *et al.*, 2012). However, the use of these oils adverse their importance as a human food and adversely affect the price. In addition, the higher iodine value of the vegetable oils makes them less oxidation stability. Therefore, their use in the manufacture of bio-lubricants is not a competitive advantage; and their use in the manufacture of bio-fuels is more effective. To beat on with this dilemma, recycling of the low-grade by-products fat is an alternative solution in term of their advantages (Sukirno *et al.*, 2009). Wool oil or lanolin was the first lubricant used; it has corrosion inhibitor characters and rusting protection. Mineral oils are the commonly base oils. Different types of thickeners are well known, among them modified clay, silica gel, and carbon black, are all considered inorganic thickeners. Soap is the well- known thickener, can be obtained from animal or vegetables fats and oils or fatty

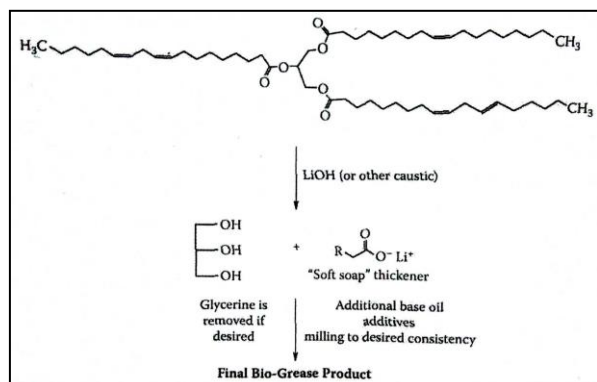


Fig. 1: bio-based lithium grease formation via one pot reaction (Sharma *et al.*, 2008).

acids. Regarding the great advantage of lithium soap over other soap kinds (softness, good temperature bearing, and metal adhering) researchers focused on developing lithium soap thickener. It is the lithium derivative of stearate and 12 - hydroxyl stearate those are widely used in lithium soap formulating. This study, aimed to offer thickener and base oil using animal fat by-product depending on the inedible by-product fat. The stearic fraction was utilized to formulate lithium soap based on the splitting of triglycerides of the stearic fraction via in situ reaction with lithium hydroxide as shown in Fig. 1 (Sharma *et al.*, 2008).

II. METHODS

A. Materials

Animal adipose tissues and skin terminals by-products were brought from a local medium municipal slaughterhouses and tanneries. Chlorine dioxide solution (200 ppm) was used as sterilizing agent. Lithium hydroxide monohydrate Li OH OH (98 %) was used as a base to prepare lithium soap thickeners. Normal hexane was used as an organic solvent. The chemicals used for analysis are high-grade chemical were brought from international companies (Merck, Germany, BHL, and England).

B. Experimental set-up

A proper amount (about 2kg) of animal skin terminals and adipose tissues by-products were classified according to their size and cut into small portions of 3-5 cm² using hand meat mixers. The tissues were skillfully impregnated in excess amounts of fresh water and strongly agitated for 30 min to remove salts and solid impurities. The washing water was siphoned out and the process was repeated for several times.

III. METHODOLOGY

A. Animal fat recovery

The clean adipose tissues were charged into stainless steel autoclave fitted with mechanical stirrer and thermometer, a twice quantity of water, based on the weight of adipose tissues, was added. The contents were heated to 90° C for 3 hours under continuous agitation (at 10 rpm). After that, the temperature was turned off and the mixture was allowed to setting down for 30 min .The

fatty layer was then floated up and the aqueous protein layer fell to the bottom and siphoned out. The upper fatty layer was disunited by scraping and re-extracted with *n*-hexane 1.0:2.0 w/v, fat: *n*- hexane, at ambient temperature. The solvent was distilled off under vacuum and the fat was stored in sealed containers for further applications.

B. Sterilization and bleaching of the recovered fat

The fat has been sterilized and bleached under the effect of a vigorous oxidizing agent, chlorine dioxide was utilized to achieve this goal (Block, 2001). The fat was melted in a stainless steel container. After 20 minutes of agitation, 200 ppm chlorine dioxide solution was added with a constant ratio of 10 % v/w, based on the weight of fat. The fat was further stirred for 20 minutes. After that, the mixture was allowed to stand for an ample time, and then the fat was re-melted and washed with water for several times to remove the colored substances and impurities.

C. Chemical evaluation of the bleached fat

The bleached fat was chemically characterized according to the American Oil Chemists Society. The iodine value, saponification value, acid value, free fatty acids, and unsaponified matters were quantified (AOCS, 1997). The recovered fat was identified by FT-IR spectroscopic analysis; it was performed by using FT-IR (Mattson500, USA spectrophotometer).

D. Fragmentation of the fat

The fat was cooled to a temperature lower than - 10 °C until double phase pellucid accumulation has been composed. The upper unsaturated oleic layer was separated leaving the lower saturated stearic layer. The saturated palmitic layer has a melting point lower than the melting point of stearic layer. Therefore, palmitic layer interfered with the stearic layer. While the unsaturated palmitoleic layer stays in the oleic layer (Santos and Gutierrez, 2007; Habib and Alshammari, 2014). The fractions were carefully stored in preserving containers for investigation and further application.

E. Lubricant grease formulation

The main objective of this work is to formulate lubricating grease which can be applied to different mechanical systems requiring grease lubrication such as, wheel bearing and gears. Basically, the lubricant has to reach the spaces where the continuous and equitable distribution of the oil onto the bearing or the open gears can be recognized. The lubricant grease is formulated through dispersing a thickener into base oil. The consistency or rigidity is the aiming factor in the grease formulation process. Hard grease may not extend and load into the spaces, and the too fluidity one may not be at home. So the lubricating power depends on the rigidity which is measured by penetration test. The National Lubricating Grease Institute NLGI put standard consistency grade numbers, ranged from 000 to 6 depending on the penetration power as shown in Table 1.

Table 1: NLGI standard consistency grade numbers of the grease (Rudnick, 2005)

NLGI Grade	Penetration ranges, at 25 °C	Deformability
000	445-475	Very soft
00	400-430	Very soft
0	355-385	Soft
1	310-340	Creamy
2	265-295	Almost solid
3	220-250	Hard
4	175-205	Hard
5	130-160	Very hard
6	85-115	Very hard

Table 2: The different ratios of thickener to base oil of formulated grease samples

Formulation	Sample 1	Sample 2	Sample 3	Sample 4
Thickener (Lithium soap %)	10	15	20	25
Base oil (Oleic fraction %)	90	85	80	75

The grease to be used in the wheel bearing and gear lubrication should be almost solid or hard with the NLGI value from 2 to 3. The soap is the more favorite thickener used in the grease formulation. Different kinds of soap may be used; lithium and sodium bases are the favorites. Grease of lithium soap base has desired attributes that make it more favorable to others. It is characterized by its good mechanical stability and good water and heat resistance, in addition to its high dropping point (Sukirno *et al.*, 2009). Lithium soap of 12-hydroxystearate is the common fatty acid that has been utilized for this task after saponification with lithium hydroxide monohydrate LiOH. OH, 98%. In this study, the stearic fraction was utilized as a thickener after it was saponified with lithium hydroxide monohydrate. The methyl ester of the oleic fraction was used as base oil. Effect of the proportion of the thickener to the base oil on the properties of the formulated grease was evaluated. Different samples of lubricant grease were formulated; the samples were varied according to the proportion of the thickener (Table 2).

The performance of the different formulated samples was evaluated. The ratio of thickener was controlled via adjusting the amount of stearic fraction during the reaction with lithium hydroxide monohydrate. Regarding its reasonable degree of unsaturation and lower viscosity compared with stearic fraction, the methyl ester of the unsaturated oleic fraction was used as base oil. It was subjected to limited transesterification to enhance liquidity. However, the oleic fraction was pre-treated to reduce the acid value and avoid the reaction between the

mineral base catalyst and the free fatty acids that form soap. Therefore, soap formation reverses the transesterification reaction. The pre-treatment was achieved via esterification with methanol at 65 °C in the presence of sulfuric acid as a catalyst until the phase separation takes place and the acid value was reduced to the acceptable extent (< 3 mg KOH/g). The transesterification process was obtained at optimal condition (molar ratio of oil / commercial methyl alcohol: 1/4; 50 °C reaction temperature; catalyst weight percentage of Na OH: 0.75 and 15 min reaction time) (İşler *et al.*, 2010). The grease was formulated according to the following procedures; a mixture of 10 % stearic fraction (taken as 1:1 of lithium hydroxide monohydrate) and 80 % methyl ester oleic - fraction was mixed in a grease kettle equipped with a mechanical stirrer (10 rpm) and a thermometer. The mixture was vigorously stirred at 100 °C until complete mixing. The lithium hydroxide was slowly added as a saturated aqueous solution under continuous stirring. After the soap solution was formed, the temperature of the mixture was gradually raised to 170°C with a continuous stirring for 3 hours. Then, the temperature was raised to 200°C until the soap was completely melted. After that, the mixture was allowed to cool to 120°C and the complementary amount of oleic fraction (10% of total mass) was added. The final product was homogenized and stabilized under double intense stirring at room temperature. The formulated grease has a smooth paste like texture. The grease samples made with other compositions of thickener to base oil were formulated according to the same procedures.

F. Evaluation of the formulated lubricating grease

Rigidity, penetration and water washout are the main three factors which mainly determine the grease properties. All of them were quantified according to the American Standard Test Methods. The rigidity was measured with the penetrometer according to ASTM D 217. The water washout and the dropping point were measured according to ASTM D 1264 & ASTM D 566 respectively.

IV. RESULTS AND DISCUSSION

A. Chemical evaluation of the fatty materials

The chemical properties of the reclaimed fat are illustrated in Table 3.

From the data, the overall rudimental observation is that the fat has considerable iodine value, a very low ratio of unsaponified matter and an expected high saponification value. Such data indicate that, the fat can be run into industrial applications as an oleochemical

Table 3: The chemical properties of fatty materials.

Property	Unbleached fat	Bleached fat	Stearic fraction	Oleic fraction
Color	Dark yellow	White-yellow	White	White
Moisture %	2.20	2.30	2.90	2.50
Ash %	3.10	1.90	1.60	1.90
Acid value mg KOH/g fat	12.00%	13.40%	14.00%	13.50%
Iodine value, mg I ₂ /g fat.	55.00	53.00	30.00	59.00
Saponification value, mg KOH/g fat	188.00	195.00	196.00	197.00
Unspecified matter	2.90	1.80	1.20	1.30

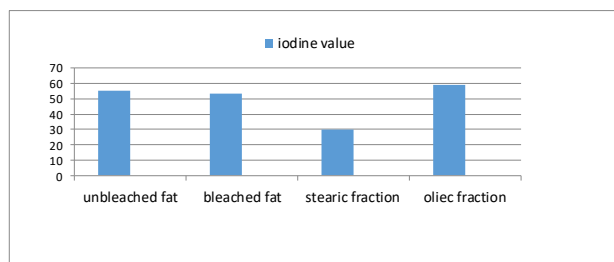


Fig. 2: Iodine value of different fatty materials.

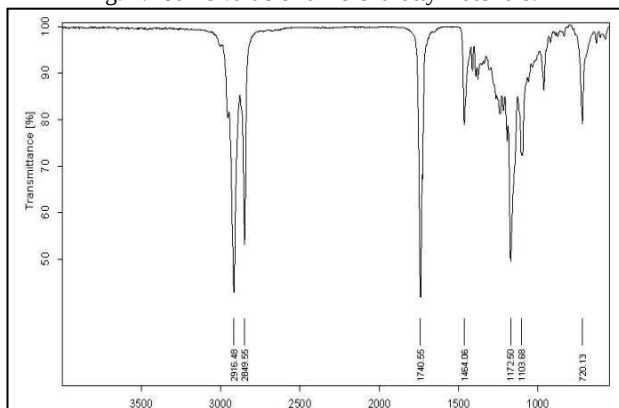


Fig. 3: FTIR of the bleached fat.

resource. The recovered fat represents about 15 - 20% of the total by-product tissues. This quantity has been completely converted into grease. Taken into account the low cost as well as the abundance of the by-product, recycling of fat is economically feasible. The high saponification value was caused by the existence of the polar groups such as hydroxide, esters and carboxylic. The increase in the acid value attributed to the splitting of some glycerides and fatty acid liberation under the effect of temperature during the extraction and bleaching processes. The obvious reduction of iodine value in the stearic fraction is evolving due to the increase the percentage of saturated stearic radicals, while an expected increase in the iodine value of the oleic radical is due to the presence of unsaturated oleic radicals (Fig. 2).

The FT-IR spectrum of the extracted fat in Fig. 3 shows that the fat was not degraded during bleaching and extraction and there was no significant fat hydrolysis. The common and characteristic absorption bands of the animal fat; the strong absorption bands at 2916 cm^{-1} & 2849 cm^{-1} characterize to the asymmetric stretching of CH_3 & CH_2 . The peaks appear around 1740 cm^{-1} & 1464 cm^{-1} represent the stretching vibration of -C=O corresponding to the ester groups in the triglycerides (carbonyl stretching) and C-H CH_2 & CH_3 bending respectively, the peaks at 720 cm^{-1} and 3004 cm^{-1} represent the bending and stretching of olefinic ($\text{cis} = \text{CH}$). The peak around 1172 cm^{-1} represents C-O stretching (Guillen and Cabo, 1997).

C. Evaluation of the formulated lubricant grease

The lubricant greases are particularly formulated according to their performance and use. Basically, the grease must possess a suitable flow rate, it may infiltrate

away from the lubricated area if it was so soft. On the other hand, the hard one would not reach the intended area. In a few words, it depends on the grease consistency or rigidity. The grease consistency is expressed as the resistance of the grease to the deformation against the applied force. The consistency is measured by the penetration test; the sinking of a given mass coin into the grease for 5 seconds at room temperature is measured as a depth in tenths of a millimeter. The relation between grease composition and penetration is illustrated in Fig. 4.

It can be observed that the consistency of the grease is directly proportional to the amount of the thickener. Regarding the scale in table 1, moderate consistency grease with 2 to 3 NLGI corresponding to 285 and 205 penetrations 0.1mm has been attended at 15 - 20% ratio of the lithium soap thickener. It was shown that the low thickener content soap results in smooth lubricant grease that shows better wetting properties of the metal surface. However, the grease has to contain a thickener ratio > 5 wt %. On the other hand, the thickener ratio > 25 wt % causes cracks in the grease (Sharma *et al.*, 2008). This result is in a good agreement with the results found by Abdulbari *et al.* (2011). Moreover, the prevalent grease consistency for the commercial lubricating grease lies in the range of grade 2 - 3 (Silver and Stanley, 1974). The dropping point is an important property of the grease; it is considered an indicator of the heat resistance. As a general principle, when the temperature of the grease increases, the grease gradually changes to soft, semi-fluid and finally loses its rigidity. In general, the dropping point is the maximum temperature at which the grease holds over its structure. The relation between dropping point and the grease composition or amount of thickener is illustrated in Fig. 5.

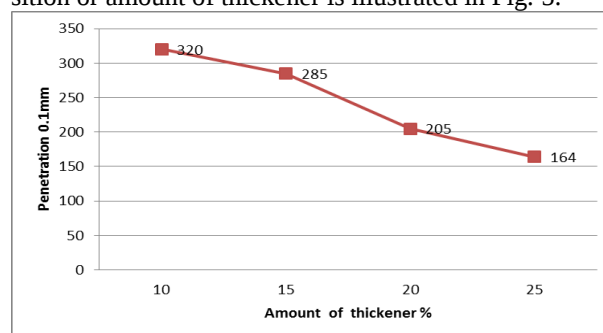


Fig. 4: The relation between the grease composition and penetration.

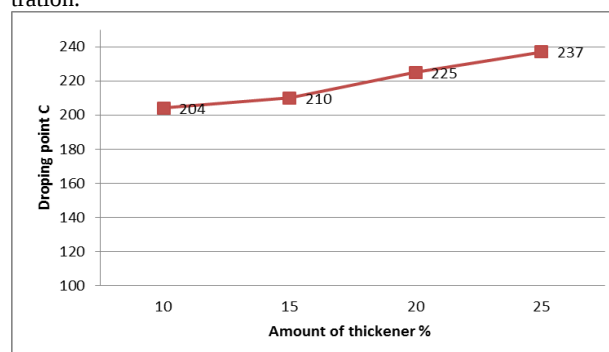


Fig. 5: The relation between the grease composition and dropping point.

Table 4: The overall results of formulated grease samples evaluation testes.

Formulated sample	1 (10%*)	2 (15%*)	3 (20 % *)	4 (25%*)
Penetration(1,mm)	320	285	225	164
NLGI number	1	2	3	5
Dropping point (°C)	204	210	225	237
Water washout (%)	< 20*	< 15*	< 15*	< 10*

(%*) the ratio of the thickener



Fig. 6: Sample of bio-based formulated lubricant grease.

It was found that the dropping point values of the formulated samples were in the acceptable range which characterizes the machinery grease. The figure shows that the dropping point is directly proportional to the amount of lithium soap thickener. The moderate value of the dropping point (210 - 255) has been reached at 15 – 20 % ratio of the thickener. Therefore, the formulated samples possess considerable heat resistance properties. These results are consistent with those reported in previous studies (Sharma *et al.*, 2008). The water washout test expresses the facility of the grease to resist the water effect without change in its lubricating potency. The oil in the grease constituents could separate and suspend in the contact water composing an emulsion, as a result, the grease consistency and texture is transmuted. The data in table 4 show that the formulated grease has a considerable water resistance without a transmutation in its lubricating puissance; these results are in a good accordance with the result reported by Sukimo *et al.* (2009). The overall results of formulating grease evaluation tests have been illustrated in Table 4.

The results show that the overall properties of the grease are depending on the grease composition. The higher ratio of lithium soap thickener, the lower penetration, lower NLGL grade takes place. In general, the grease performance is effective and acceptable if it has high resistance to initial flow; at same time, it should have very low resistance to flow under the yield stress (Sharma *et al.*, 2008). These advantages can be attained at NGLI value between 2 and 3, such grease is often appropriate for machinery and gear lubrication. Based on previous facts, the intended bio-based lubricant grease was formulated at an ideal composition of 80-85% of base oil and 20% - 15 % lithium soap thickener and it can be operated in the lubrication process with the

desired quality and efficiency. A sample of formulated bio-based lubricant grease is shown in Fig. 6.

V. CONCLUSIONS

Animal fat with a considerable industrial potential was recovered from abattoir and tanneries by-product. The fat was utilized to formulate bio-based lubricant grease based on lithium soap thickener. The formulated grease has better lubricating potency for metallic gears and machinery. The work adds value to by-product wastes via transferring them into an utilizable product. An environmental and economic return has been achieved.

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