Research Article

Preparation, Characterization, and Evaluation of Fatty Amide Derivative of Soybean Oil as a Rheological and Tribological Modifier for lubricating Oils

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ABSTRACT

Since vegetable oils are rapidly biodegradable and some of their derivatives display excellent tribological properties, thus such oils or their derivatives are candidates as base fluids in environment – friendly lubricants. Depending on this basis, fatty amide was prepared by the direct reaction between soybean oil and ethanolamine. The fatty amide prepared in the present work was characterized using different analytical techniques like FT– IR and 1HNMR. The derivative of soybean oil was evaluated as the base oil by mixing different concentrations of it with lubricants and rheological and tribological properties of these oils were investigated carefully. The results indicated that fatty amide has enhanced the rheological and the tribological properties of lubricants compared with blank lube oil.

Keywords: Vegetable oils, Fatty acid amide, lubricating oil, Rheological properties, Antiwear Additives, Tribological Properties.

INTRODUCTION

Lubricants are the substances employed to reduce friction between two moving surfaces for improving the efficiency of the engines [1]. Lubricating oil may dissolve or transport foreign particles that cause corrosion or rust, and also service as sealing clearance, and dissipating heat [2].

The basic components of lubricants are base oil (90%) and additives (10%). Actually, the presence of additives enhances the oil efficiency where the best base oil without additives is lacking in some features [3]. The additives may enhance the existing properties of the base fluid or add new properties of this oil. However, the famous additives are extreme pressure, viscosity index improvers, antifoaming agents, emulsifiers, pour point depressants, and demulsifies. Most additives available at present are based upon synthetic acrylate, but, with increasing environmental constraints, the research in the field turned towards the production of multifunctional biodegradable additives [4]. In fact, the main goal of researchers in the field is to reduce the use of the compounds containing chlorine and phosphorus as lubricant additives for protecting the environment from pollution. Therefore, lubricants based upon biodegradable vegetable oils have been prepared and used as low – cost alternatives to synthetic fluids [5,6]. In this respect, sustainable monomers, polymers, and materials have been produced by transformation of the major components of vegetable oils into simple fatty derivatives. Actually, functional groups in triglycerides provide us with unique organic reactions such as hydrolysis [7,8], transesterification [9,10], and amidation for ester groups [11-14]. The transamidation reaction of long chain fatty acid ($C_{22}H_{41}$) by aliphatic amino alcohols will be produced important compounds from fatty acid alkanolamides that are suitable for a variety of applications [1]. The chemical properties of the fat amide vary according to the length of the hydrocarbon chain and the functional groups on the chain [15,16]. So, the main objective of in the present work is the synthesis of fatty amide based on soybean oil (SBO) with ethanolamine and evaluates of the compounds by FT – IR and ^{1}HNMR and adds it to lubricating oil by different concentration and studies the physicochemical properties of the formulated oils such as rheological properties, and tribological properties.

MATERIALS AND METHODS

Soybean oil (SBO) used in the current study was purchased from local market. Ethanolamine (99%) and glacial acetic acid from Aldrich Co. and lubricating oils from cooperation Co. Egypt.

SYNTHESIS OF NEW DERIVATIVE OF SBO

N-hydroxyalkyl fatty amide was prepared as follows: 100 g of SBO (almost equivalent to 0.344 mol ester group) was put on an oil bath at 100 °C and nitrogen was purged for 1 h. After cooling down to 80 °C, 1 mol of Ethanolamine (≈ 27 g) was mixed with SBO in a 500 ml round bottom flask and in the presence of sodium acetate (1% of reactants) as catalyst. The mixture was stirred at 80 °C for 4 h until conversion of the ester bond is completed. The new derivative was extracted by dichloromethane, washed several times with distilled water, and finally filtrated under reduced pressure. The yield was around 97% [3]. The synthesized fatty amide was characterized by using FTIR and ^{1}HNMR analysis.

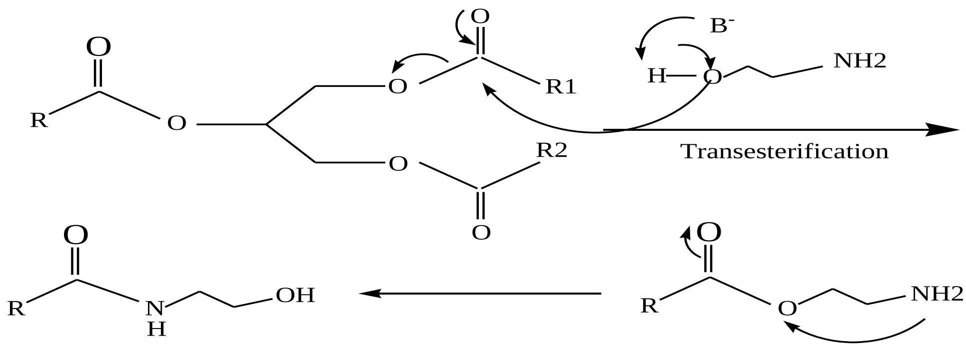


Figure 1: Reaction of ethanol amine with triglyceride (SBO)

Evaluation of the Prepared Fatty Amide as Lube Oil Additives

The fatty amide prepared in this work was added to lubricating oils at different concentrations levels e.g. 0.5 %, 1.0 %, 1.5 % and 2.0 % and rheological and tribological properties were evaluated.

Investigation of Rheological Properties of Lube Oil

The exam of rheological properties of lube oil before and after adding fatty amide was carried out by a Brookfild programmable Rheometer (HV DV-III UITRA) in conjunction with Brookfild software (RHEOCALC V.2). The aim of software use is to record the corresponding shear stress, shear rate, dynamic viscosity, mathematical model and confidence of fit consistence index. The influence of temperature (at 40°C and 100°C) on the rheological properties of the lubricating oil and in the presence of prepared additives was also investigated in details.

Tribological properties (Friction Co-efficient Measurement by Pin on Disc Method)

The tribological properties of the prepared fatty amide were evaluated using pin on disc apparatus at room temperature which is fabricated as shown in Fig. (1). In this respect, the test specimens (Pin) were AISI1023 steel with diameter of 10mm and HRC about20.5. However, the Disc was manufactured from wear resistant steel (Hardox 600) with diameter of 10 Cm with HRC about 59.5. Pin-on-disc experiments were carried out at different load, speed 100 rpm, and time30 min, using the formulated oil samples. The weight losses in pin were calculated.

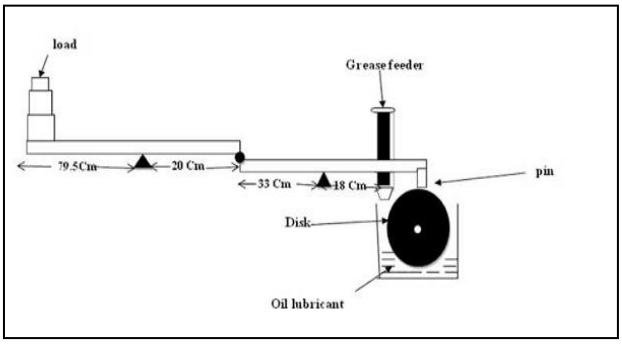


Figure 1: The schematic view of the pin on disc apparatus

Antiwar properties of the lubricating oil determined using pin on disk apparatus as shown in Fig.1.

The morphology study of metal surfaces treated by lubricants used in the present work.

The morphology of metal surfaces was investigated by scanning electron microscope (SEM) model JEOL JSM – 6510 supplied with anenergy dispersive X – ray spectrometer (EDX) as elemental analysis system (EAS).

The statistical processing and optimization of results.

The study result of the rheological and tribological properties of lubricating oil was treated statistically by Design expert – 7.

RESULTS AND DISCUSSION

The Preliminary Studies of SBO and Lube Oil

Before preparation of fatty amide derivative of SBO, some physicochemical and chemical properties of SBO should be investigated. The physicochemical characteristics of SBO were measured according to ASTM/IP standard test methods and the values are listed in Table 1. However, the quality of the SBO was evaluated by parameters like acid value, peroxide, iodine, smoke point, saponification, fire point, ester values, specific gravity, and flash point [17]. The peroxide value and total acid number are used as an index of the degree of oxidative rancidity of the vegetable oils. The experimental data in Table 1, showed that the soybean oil had lower values for both peroxide value and total acid number, this is because of the chemical structures of oil and its contain of natural antioxidants. Thus, such oils are suitable to produce lubricants. On the other hand, a fatty acid present in SBO was determined using gas chromatography – flame ionization detector system (GC – FID) model Shimadzu GC-2010. The operational conditions of fatty acids analysis by GC – FID are demonstrated in Table.2. Before injecting SBO sample, all fatty acids were converted into methyl esters according to the international standard method (ISO 5509:2000). The results demonstrated in Table. 3 show that the main components of SBO are linoleic and oleic acids with percentage of 22.85, and 51.70% respectively. On the other hand, some physicochemical properties of lube oil used in this study were investigated and the values are recorded in Table.4.

Table 1: Some physicochemical characteristics of SBO

Parameters	SBO	Test Method
Peroxide value (meq O_2/kg)	0.07	AOCS Cd 8b-90
Acid value (mg/g)	0.096	AOCS Cd 3d-63.
Saponification value (mg/g)	186.59	ASTM D 5558
Iodine value (g/g)	146.44	ASTM D 5554
Ester value (mg/g)	185.47	JIS K 0070
Specific gravity	0.97	ASTM D 1298
Smoke point (°C)	224	AOCS Cc 9a-48
Fire point (°C)	286.2	AOCS Cc 9a-48
Flash point (°C)	272.6	AOCS Cc 9a-48

Table 2: The operational conditions of gas chromatography – flame ionization detector system employed for determining fatty acids in SBO

Condition	The description or value
column	Forte GC, 30 m length, 0.25 mm inner diameter, and film thickness 0.25 μm
Sample volume, μL	2
The inlet temperature	495 K
The detector temperature	550 K
Carrier gas	He
The flow rate of carrier gas	0.5 mL / min
Temperature program	The initial oven temperature was 423 K and held for 6 min, then increased to 513 K at a rate of 281 K/min and held for 1 min, finally increased to 523 K. The last temperature has been established until the analysis is completed
Total analysis time	20 min

Table 3: The fatty acids present in purified SBO according to GC – FID analysis

The acids	Concentration, (%)
Saturated fatty acids	
Lauric acid (12:0)	7.24
Myristic acid (14:0)	0.11
Palmitic acid (16:0)	10.31
Stearic acid (18:0)	3.82
Monounsaturated fatty acids	
Oleic acid (18:1)	22.85
Polyunsaturated fatty acids	
Linoleic acid (18:2)	51.70
α-Linolenic acid (18:3)	6.86

Table 4: Physicochemical properties of lube oil

Test	Lube oil	ASTM methods
Viscosity at 40˚C	61.5	D 644
Viscosity at 100˚C	21.5	D644
Viscosity at index	370	D2270
Flash point,˚C	315	D 93 D94
Pour point,˚C	0.0	D97
Apparent viscosity, cP at 40˚C	66.5	

Characterization and Confirm of Syntheses Fatty Amide

The chemical structure of the fatty amide prepared in the present study was confirmed by some specific spectral measurements e.g. FT – IR and ^{1}HNMR. The spectrum of ^{1}HNMR shown in Figure. 2 demonstrate peaks at 3.3 and 3.5 ppm corresponding to methylene protons in (-N–CH_2-) group and (–O–CH_2–) group, respectively. Nitrogen proton of (–NH–) group gave peak at 5.3 ppm, whereas, the peak of methyl group protons in (–N–CH_3–) appeared at 3.1 ppm. The hydroxyl group (–OH–) gave weak peak at 7.7 ppm.

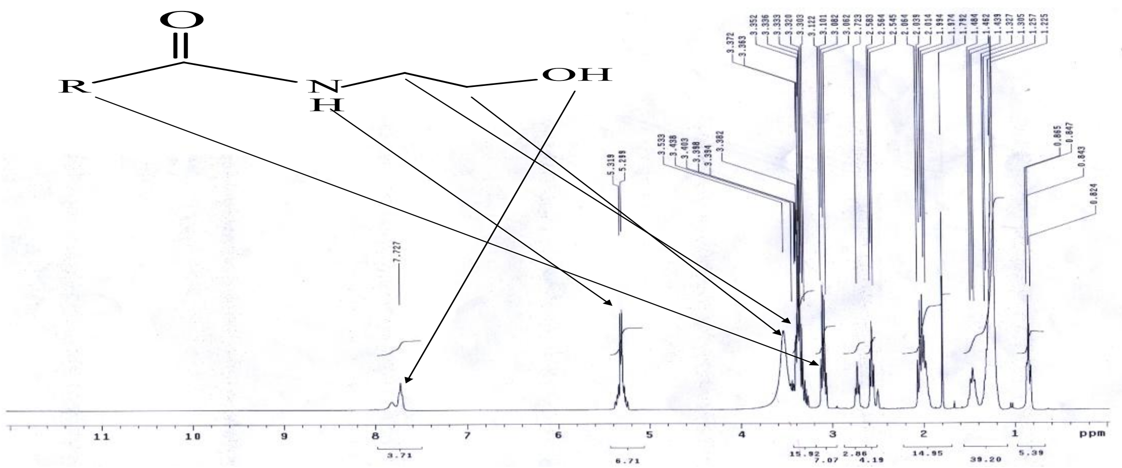


Figure 2: HNMR spectra for prepared fatty amide.

The FT – IR spectrum demonstrated in Fig. 3 provides a valuable indication of amidation process where the complete disappearance of the ester group peak (-O-C=O) at 1435 cm $^{-1}$ and appearance of two peaks at 3297 and 1566 cm $^{-1}$ corresponding to stretching and bending frequencies of (-NH) amide group, respectively indicates quantitative conversion of ester group to amide group. Another indication of amidation process is the increase of peak intensity at1642 cm $^{-1}$ corresponding to amide carbonyl group (-N-C=O). Also, FT – IR spectrum of N-hydroxyalkyl fatty amide contains peak at1454 cm $^{-1}$ for (-C-N) amide group, peaks at 2852 and 2921 cm $^{-1}$ for symmetric and asymmetric vibrations of (-CH_2), respectively.

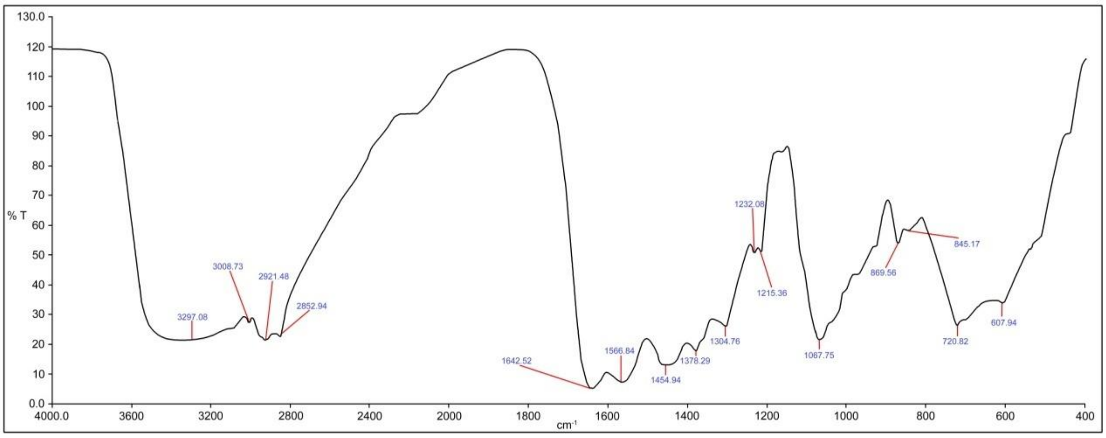


Figure 3: FT – IR spectrum of the prepared fatty amide.

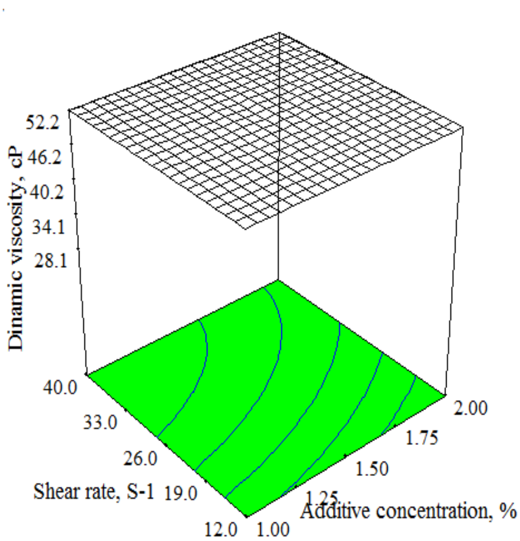
Rheological Properties of Formulated Oil

The fatty amide of SBO prepared in this work was tested as improver of rheological properties of lube oils. The new derivative was mixable with lubricating oils at different concentrations levels. Series of experiments was carried out by using the Brookfield Rheometer to test the flow characteristics of the used oil samples. These samples were prepared by adding different concentrations (0.5% up to 2.0 % wt by wt) of fatty amid as additives to lubricating oil and measuring rheological properties at temperatures (40 ^{0}C to 100 ^{0}C).

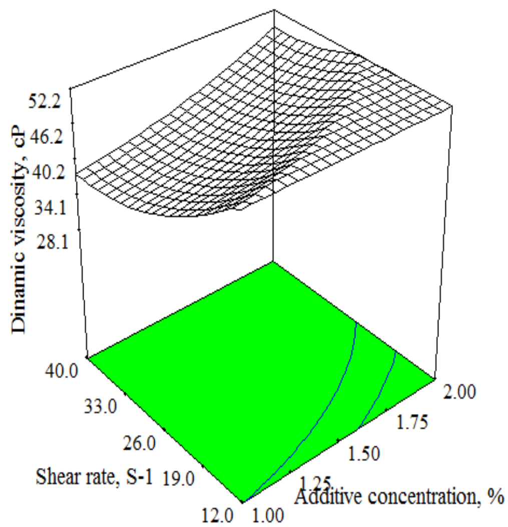
Viscosity – Shear Rate Dependence

Fatty amide prepared in the present study was evaluated as viscosity improver for the selected lubricating oil by performing a series of rheological measurements at concentration from 0.5 to 2.0% (wt/wt) of fatty amide and at different temperatures in the range of 40 – 100 ^{0}C. Figs. (4,5) show that the viscosity of lubricating oil initially decreases with increase of shear rate and temperatures denoting shear thinning behavior while after that it is almost constantly and showing Newtonian behavior. On the other hand, Figs. (4,5) indicate that the viscosity the selected lubricating oil has increased with increments of concentrations of the fatty amide, therefore, the fatty amide prepared from SBO can be considered as an efficient viscosity improver of lubricating oils.

40^{o}C



60^{o}C



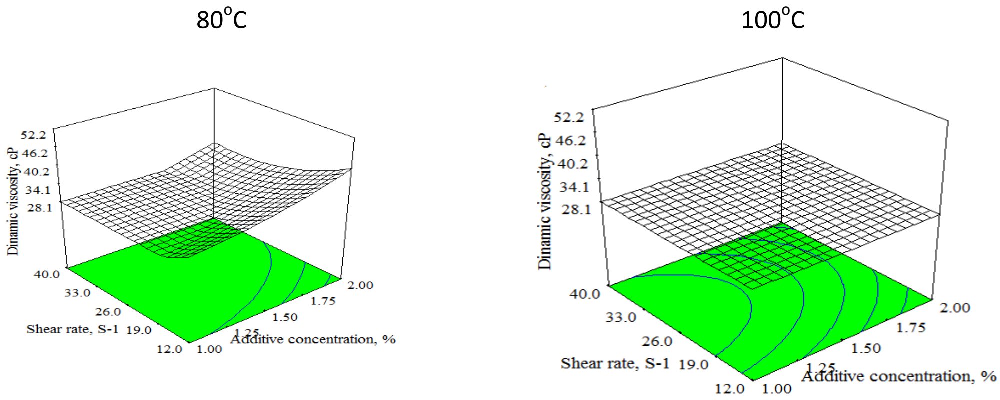


Figure 4: The curves of viscosity – shear rate of lubricating oil after adding different concentrations of fatty amide at different temperatures.

Shear Stress- Shear Rate Dependence.

The relationship of shear stress – shear rate of lubricating oils before and after adding different concentrations of fatty amide are plotted in Figs. (5,6). The figures show that the Bingham yield stress value (the intercept with the y axis) and plastic viscosity of lubricating oils dramatically increase with increasing of concentrations of the fatty amide regardless of temperature.

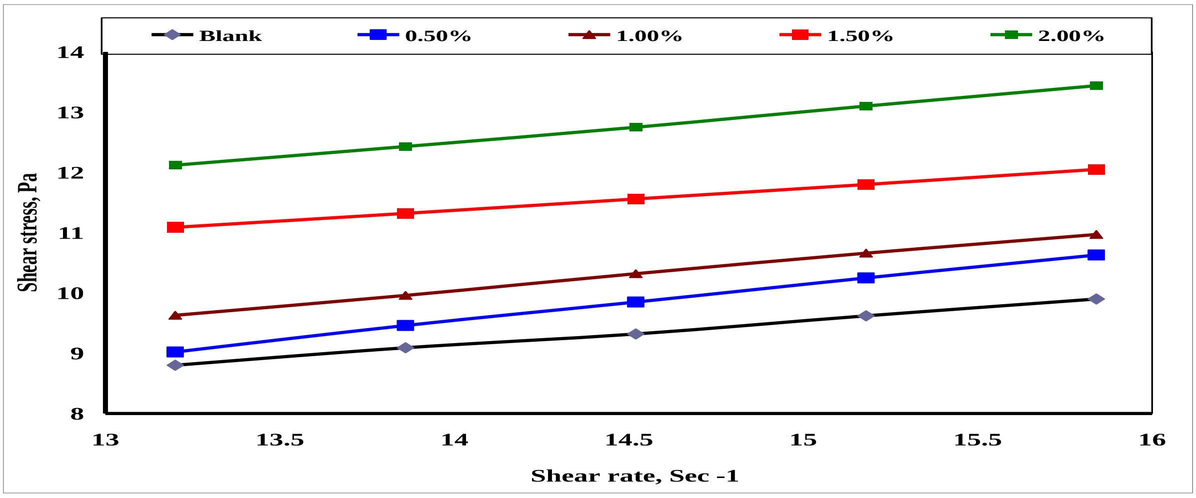


Figure 5: The relationship of shear stress – shear rate of lubricating oils at different concentrations of fatty amide, (The measurements were carried out at 40 ^{0}C).

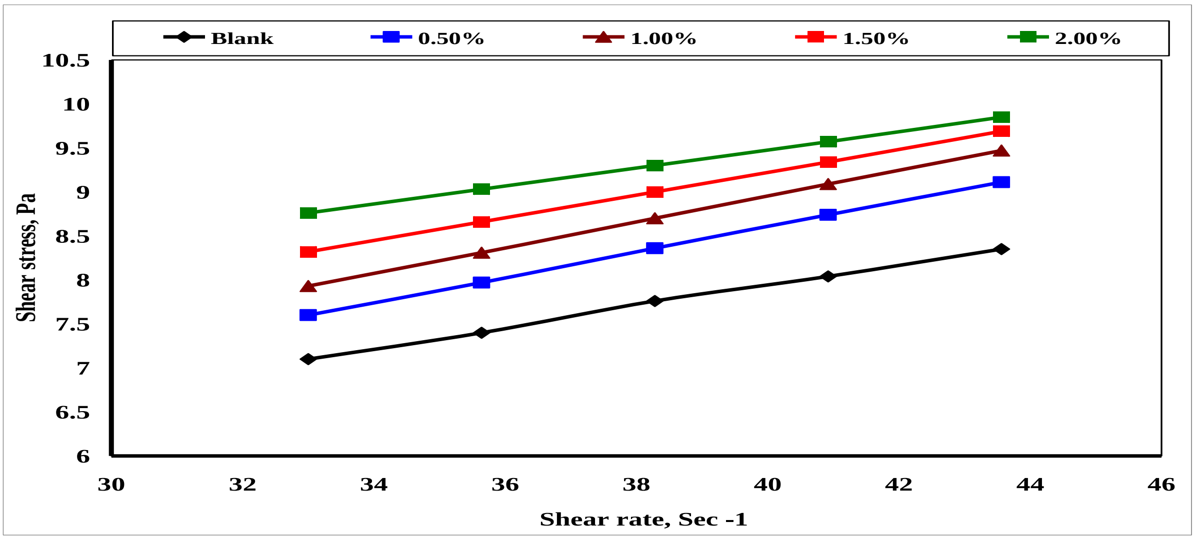


Figure 6: The shear stress – shear rate curves of lubricating oil treated with different concentrations of fatty amide at temperature 100 ^{0}C.

Rheological Models.

The rheological models have been proposed to describe the lubricant behavior:

- Bingham model

$$\tau=\tau_o+\eta\gamma^{\bullet} \qquad (1)$$

- Herschel – Bulkley model

$$\tau=\tau_o+K\gamma n \qquad (2)$$

where τ and τ_0 are shear stress and Bingham yield stress, respectively, η is the formulated oils viscosity and K and n are parameters dependent on structure that are determined experimentally.

As mentioned in [18, 19], the model of Herschel–Bulkley represents the highest yield stress more than Bingham plastic models. However, the measured values of shear stress were compatible with equations (1, 2) and the results obtained were tabulated in Table 5. Table 5 shows that the yield stress values and plastic viscosity of formulated oil have increased with increasing concentrations of fatty amide. However, confidence of fit (%) suggests that the most appropriate model for formulated oil is Herschel-Bulkley.

Table 5: Bingham plastic model against Herschel–Bulkley model to describe rheological properties of formulated lubricating oil

Conc.	Bingham			Herschel Bulkley			
	Plastic Viscosity (cP)	Yield Stress (D/cm²)	Confidence of Fit (%)	Consistency Index (cP)	Yield Stress (D/cm²)	Confidence of Fit (%)	Flow Index
Blank	51.5	1.8	99.3	34.6	2.00	100.0	1.13
0.5	53.6	2.07	99.5	40.6	3.37	100.0	1.13
1.0	55.5	2.63	99.7	45.3	3.55	100.0	1.04
1.5	58.3	3.86	99.5	85.2	3.63	100.0	0.91
2.0	66.5	3.91	99.2	188.3	4.01	100.0	0.76

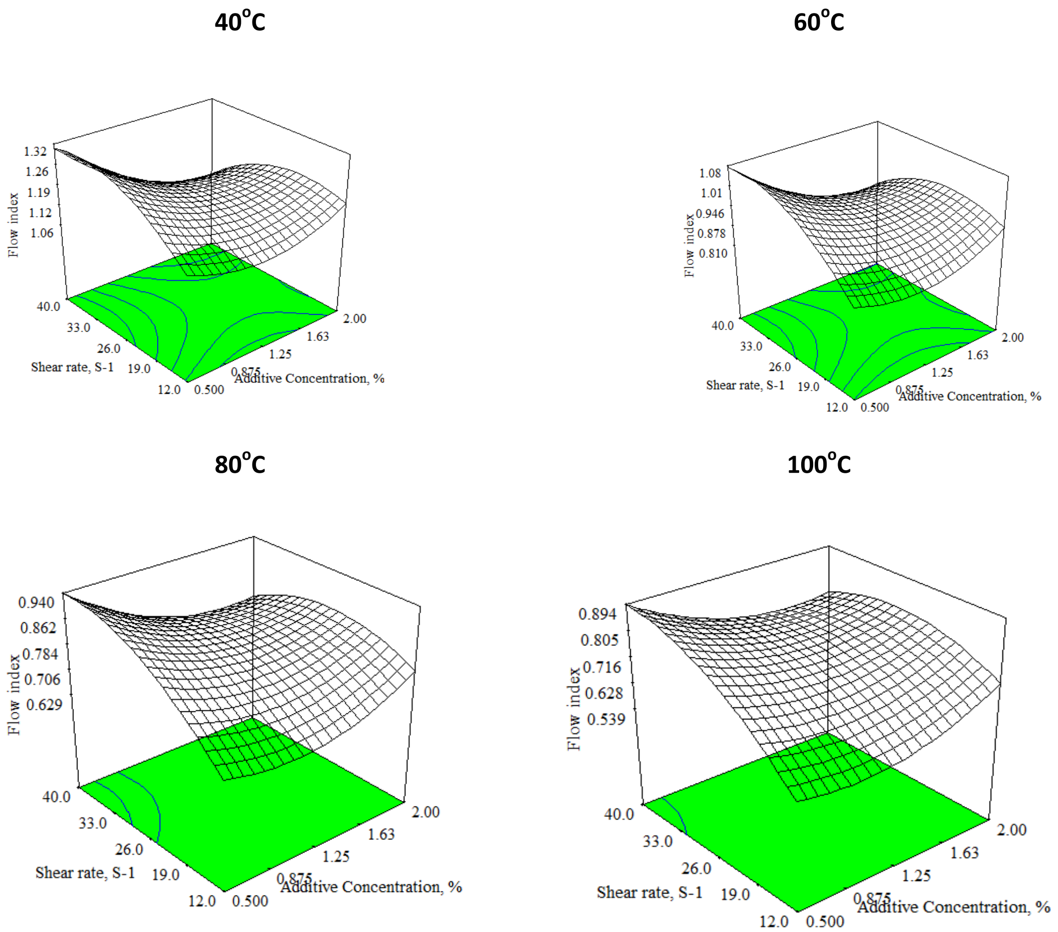


Figure 7: Flow index properties of lubricating oil using different concentration of fatty amide additives.

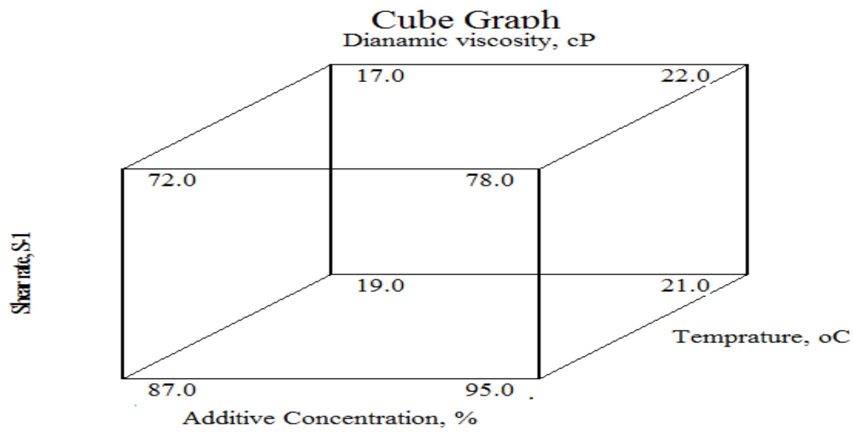


Figure 8: Optimization of the all rheological parameters of formulated lubricating oil

Tribological Properties

When a metal surface touches another metal surface during sliding motion, a significant wear and tear of the metal surfaces arise. However, the accurate analysis of worn metal's surface characteristics provides valuable information about the extent of metal protection by fatty amide as boundary lubricant. In fact, fatty amide molecules service as a stable thin film which prevents metal – metal contact [2]. However, this preventive mechanism may be absent at high load where the protective lubricant film is squeezed out between contact metals. Under the present experimental conditions, a formulated lubricating oil is allowed to flow between the metals and form a stable film. The stability and tendency of the film to adhere to the metal surface specify film ability in the protection of wear. However, the addition of fatty amide into lubricating oil has given more consistency (stability) as observed from SEM analysis of wear track surfaces [20,21]].

Weight loss measurement for fatty amide additives.

The variation of wear rate with different loads and sliding distance is shown in Fig.8. From this figure, we can observe that the wear rate loss (WRL) linearly increased with increasing load. However, the wear rate of lubricating oil in the presence of fatty amide as additive is lower than that observed in the absence of fatty amide. This is attributed to boundary lubrication which occurs when polar groups in fatty amide additives are allowed to form film by physico – chemical adsorption on the metal surfaces in contact [2].

200 N **400 N** **600 N**

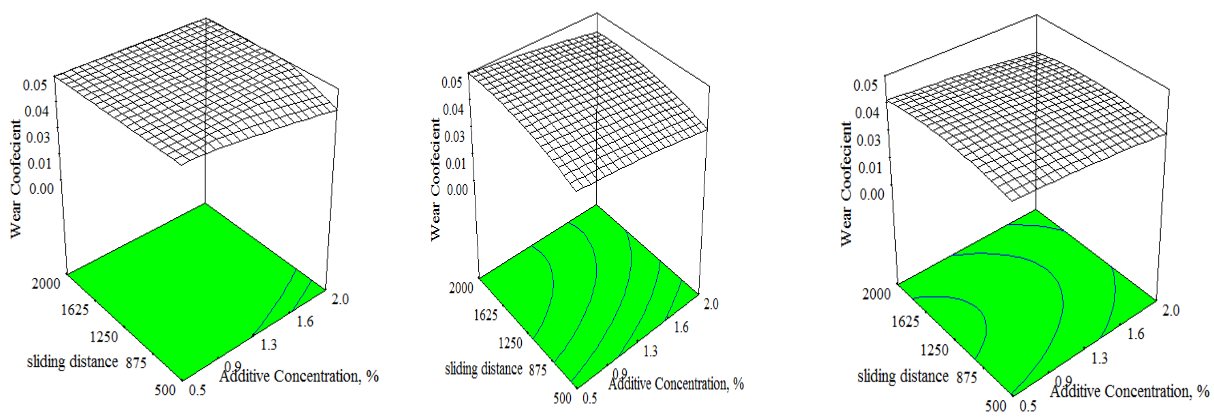


Figure 8: The variation of wear coefficient of lubricating oils with load at different concentrations of fatty amide additive.

SEM for metal without and with fatty amide additives.

Fig.9 presents the SEM images of pin in the absence of fatty amide (A), and when addition of derivative with concentration of 2% w/w (B). The presence of fatty amide makes the metallic surface very smooth and reduces the friction because polar functional groups in the chemical derivative arise strong interaction between fatty amide and metal surface, this means establishing a stable, and efficient lubricant layer. On the other hand, and in absence of fatty amide, Fig. 9 (A) shows grooving with metallic flakes dislodged from the disk surfaces. In fact that, the long hydrocarbon chain of the fatty amide plays an important role in improving lubricant efficiency where such hydrocarbon chains provide a distinctive molecular barrier while the polar groups present in fatty amide can coordinate with iron to form a protective layer on the metal surfaces [2].

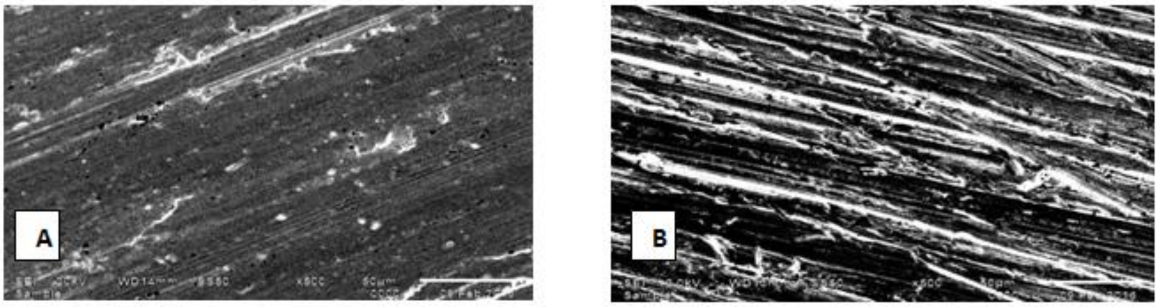


Figure 9: SEM image of the wear rate for the metal. (A) Pin as blank and (B) Pin with concentration of (2%) of prepared additive.

EDX for metal without and with fatty amide additives.

Fig. 10(A, B) shows EDX analysis result of the friction region surface samples after wear without and with additive (prepared fatty amide), respectively. The data from Fig.10(A, B) illustrates that the nitrogen element have been adsorbed and appeared on the metal surface of pin with additive of fatty amide compared to the pin without additive. The presence of nitrogen element on the surface of the metal means that there is tirbochemicale film composed from fatty amide with the surface of the metal.

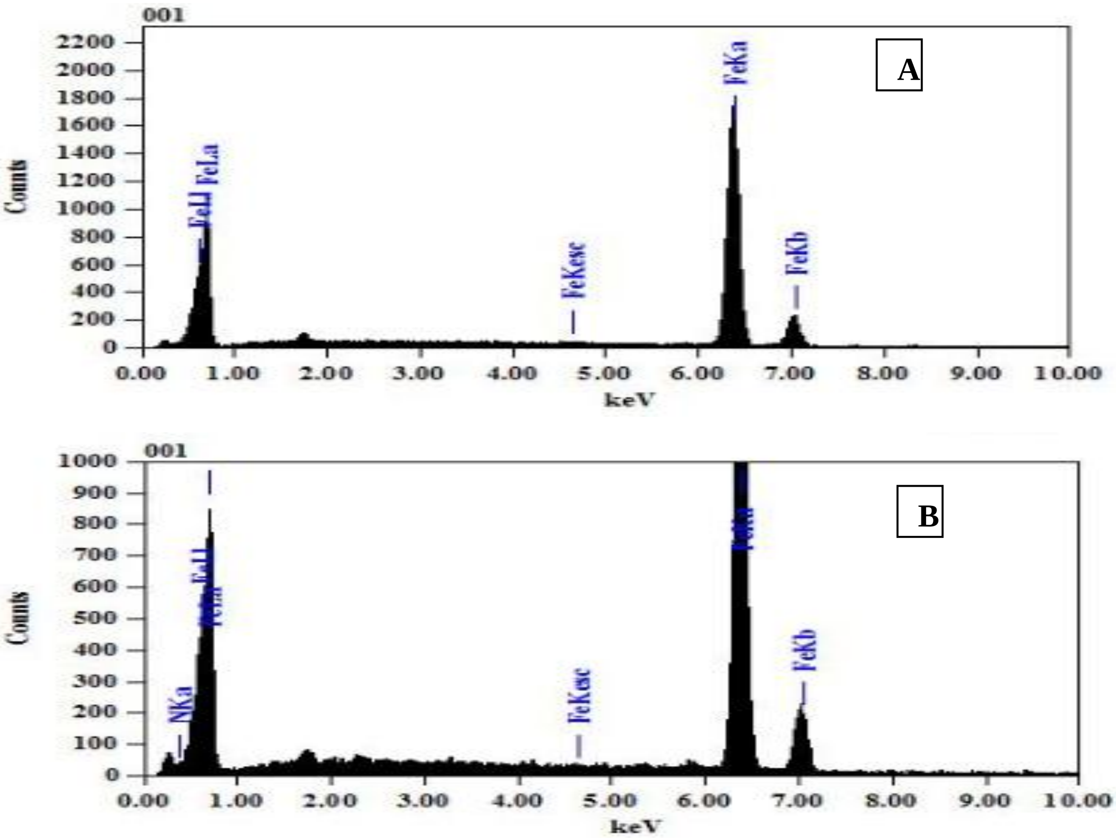


Figure 10(A , B): EDX of the wear rate for the metal A)Pin blank and B)Pin with (2%) concentration of additives

CONCLUSION

In the present study, we provided new derivative of SBO by reaction of this oil with mono- ethanolamine. This derivative namely fatty amide was characterized using different spectroscopic techniques. Then, the rheological properties of lubricating oil containing known concentrations of fatty amide were studied. It was proved using different mathematical models that the addition of new derivative of SBO to lubricating oil has improved the rheological properties dramatically. On the other hand, and because of increasing the polar functionality in fatty amide structure, the addition of this derivative provides a positive impact on wear protection resulting from stronger adsorption potential on metal surface. Therefore, the fatty amide prepared in this work can be employed as a modifier of rheological and tribological properties of lubricating oils in variety of industrial applications.

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