Synthesis Locally Extreme pressure additives via residual sulfur of crude oil

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Abstract: The objective of this work aimed at synthesis extreme pressure additive via residual sulfur extracted from crude oil. Residual sulfur was used in Sulforization process of plant oil (i.e.: Jatropha & Linseed oils). Sulforization process for plant oils was carried out according to certain conditions. Product obtained from Sulforization of jatropha oil, was additive A, while product obtained from Sulforization linseed oil was additive B. Comparative evaluation study between our local products A&B and two imported additives were carried out through bench and performance tests. From comparative study, it was found local additives A & B give the same efficiency at the same dose of imported once, as extreme pressure functions. Also, Additives A & B were found had antioxidant efficiency than imported once. Additive A & B by this way saving environmental from pollution of residual sulfur, beside highly economic value.
[Fathy A. El-saied, EL Sayed A S and Moustafa A. Abou Al Eneen. **Synthesis Locally Extreme pressure additives via residual sulfur of crude oil.** Life Sci J 2012;9(2):798-804] (ISSN:1097-8135). http://www.lifesciencesite.com. 119

Keywords: Synthesis; pressure; additive; sulfur; crude oil

1. Introduction

Lubricant additives are chemical compounds add to a lubricant to enhance performance and improve its operating characteristics [1- 4]. It can be defined as a material which imparts a new and desirable property not originally presented in the oil [5]. Also provide the necessary protection to oil for application at high temperature, high speed and high pressure [5, 6]. Lubricating oil additives are used to reduce the oxidative or thermal degradation of an oil, to lessen the deposition of harmful deposits on lubricated parts, to minimize rust and corrosion, to control frictional properties, to reduce wear, and to prevent destructive metal to metal contact. They are also employed to alter purely physical properties of oil such as viscosity, viscosity-temperature relationship (viscosity index or VI) and tendency to form stable foam [5, 7].

Extreme pressure additives were designed to prevent wear and reduce friction in power transmission via reducers [4]. Extreme pressure additives are organic compounds that contain one or more elements are functions such as sulfur, halogen (principally chlorine) phosphorus, carboxylate salt which can react chemically with the metal surface under condition of boundary lubrication [5].

Under high temperature and high pressure or extreme boundary condition there is severe metal to metal contact, which leads to welding followed by tearing away of large pieces of metal. Also, the additives react with the metal surfaces to form compounds that have lower shear strength than that of metal. The reaction is initiated by increased temperature caused by pressure between asperities on wearing surfaces. The reaction creates a protective coating at the specific points where protection is required. This coating works as dry lubricants and reduces friction, wear, scoring seizure, and galling of wear surfaces [3, 5-8].

The residual of these additives produce hazard materials, today the worldwide production going to produce environmental friend additives by using natural product such as plant oil or organo metallic compounds.

2. Experimental

Material specifications

Materials were used through this work are: jatropha curcas oil, linseed oil, hexyl amine, imported E.P additives (X) and (Y) and extracted sulfur from crude oil. Analysis figures of these used materials were listed in Tables (1-4).

Sulforization processes

Sulforization of jatropha and linseed oils, were carried out in a three-necked spherical flask equipped with stirrer, thermometer and a reflux condenser. Adjust conditions to obtain high concentration of non-corrosive sulfur by reaction between sulfur and double bond in fatty oil.

Sulforization steps were carried out according to the following:

- Weighed (100 gm) of jatropha or linseed oil and transfer to the three neck flask
- Increase degree of temperature up to (100°C) with stirring rate (150 rpm).
- Weighed (25gm) of extracted sulfur and dissolved in (20 gm) hexyl amine, then added drop wise to the oil.

- Increase the degree of temperature gradually up to 155 – 165 ˚C to complete reaction through 2 hrs.
- After finish the reaction, leave system to cool up to 60˚C.
- Add 10 gm isopropyl alcohol as polar solvent with stirring to prevent precipitate. Then increase temperature without condenser up to 155˚C to evaporate any excess of alcohol and amine.
- Leave system to cool at room temperature.
- Both products A (sulfurized jatropha oil) & B (sulfurized linseed oil) are dark brown colour and more viscous than original oil of jatropha or linseed oil.
- Specification of base oil blended with additives A, B, X and y was listed in table (5).

Table (1). Physical and chemical properties of Jatropha curcas and Linseed oils.

Specifications	Method	Jatropha curcas Value	Linseed oil Value
Density @ 15/4 C˚	IP 235/82	0.9182	0.920
Colour	ASTM D1500/82	2.5	3.0
Kinematic Viscosity @ C˚,CSt	IP 71/84	46.8	41.2
Flash point, C˚	IP 35/86	188	218
Pour point, C˚	IP 15/81	6+	- 9
Conradson carbon, wt %	IP 13/82	0. 60	0.037
Acid value, mg KoH/g	IP 1/81	2.87	1.42
Saponification number, mg KoH/g	ASTM D 94	193.8	193.8
Iodine value	IP 84/81	107.83	170
Sulfur, %wt	ASTM D 6443	0.15	Nill

Table (2). Specifications of imported extreme pressure additives X and Y

Specifications	Method	additive X	Additive Y
Flash point, C˚, PMCC	IP 35/86	80	82
Pour point, C˚	IP 15/81	- 18	- 40
Kinematic viscosity @ 100, C˚,CSt	IP 71/84	5	2.5
Kinematic viscosity @ 40, C˚,CSt	IP 71/84	8.5	8.5
Nitrogen, %wt	ASTM D 5291	1.17	0.76
Phosphorus, %wt	ASTM D 4951	1.93	1.32
Sulfur, %wt	ASTM D 6443	19.1	30.10

Table (3). Specifications of extracted sulfur from crude oil.

Specifications	Value
M.Wt	32.06
Melting range, C˚	111 – 119
Ignition temperature, C˚	235
Free acid, mg KoH/g	> 0.25%(H_2SO_4)
Sulphated ash, wt %	> 0.1

Table (4). Specifications of cyclo hexyl amine

Specifications	Value
Physical appearance	Clear to yellow liquid with fishy odour
Assay %	99.18
Specific gravity	0.865
Chemical formula	$C_6H_{11}NH_2$
Flash point, C˚	28.4
Refractive index at 20, C˚	1.4565

Table (5) Specification of paraffin base oil SAE 90 blended with additives A, B, X &Y.

Specifications	Method	Value
Density at, 15/4 C°	IP 235/82	0.9021
Appearance	-----------------	Clear
Colour	ASTM D1500/82	3.5
K.V at 100 C° , cSt	IP 71/84	16.7
K.V at 40 C° , cSt	IP 71/84	121
VI	IP 266/84	92
Flash point (PMCC), C°	IP 35/86	210
Pour point, C°	IP 15/81	- 3
Total acidity, mg KoH/g	IP 1/81	0.037
Conradson carbon, %wt.	IP 13/82	0.76

To evaluate active and non active sulfur several trials were carried out by blending base oil with products A and B. Blend percentages were listed in table (6). Products A & B were blended up to 10%. Standard method to detect active sulfur was applied as cupper strip ASTM D – 130.

Table (6): Ten formulation of products A & B with paraffin base oil SAE 90

Formula No.	paraffin base oil SAE90	Product A	Product B
1	99 %	1 %	……
2	97 %	3 %	……
3	95 %	5 %	……
4	93 %	7 %	……
5	90 %	10 %	……
6	99 %	……	1 %
7	97 %	……	3 %
8	95 %	……	5 %
9	93 %	……	7 %
10	90 %	……	10 %

To evaluate the efficiency of synthesis products as extreme pressure additives another four blends were carried out between base oil and products A, B and additive X by percentage (1.75%) respectively (recommended dose), to produce gear oil SAE 90 – GL3, while additive y blended with base oil by 2.4% wt (recommended dose), to give gear oil SAE90 – GL5 were listed in table (7).

Table (7) formulations of blends from synthesized products (products A&B) and two imported additives with paraffin base oil SAE 90.

Formulation No	Product A Wt %	Product B Wt %	Imported additive x Wt %	Imported additive y Wt %	Base oil SAE 90 Wt %	Performance level
Blank	……	……	………..	………..	100	………..
11	1.75	……	………..	………..	98.25	GL – 3
12	……	1.75	………..	………..	98.25	GL – 3
13	……	……	1.75	………..	98.25	GL – 3
14	……	………..	………..	2.4	97.6	GL – 5

Four ball wear standard test (IP 239) were carried out on the four samples listed in table (7).

Also standard oxidation stability tests (IP 229) were applied on the four blends beside base oil as blank as listed in table (7).

3. Results and Discussion

Product A is produced by reaction between jatropha oil and extracted sulfur.

Reaction was carried out by destroy double bonds of fatty oil and enter sulfur atoms in molecules of fatty oil [9]. Physical properties of products A & B were listed in table (8).

Table (8): Analysis figures of products A & B.

Test	Standard test method	Product A	Product B
Density at ,15/4 C°	IP 235/82	0.9437	0.9241
Appearance	----------------	Clear	Clear
Color	ASTM D1500/82	Dark – Reddish – Brown	Dark – Reddish – Brown
K.V at 100 C° ,cSt	IP 71/84	11.7	9.3
K.V at 40 C° , cSt	IP 71/84	135	94
Flash point (PMCC), C°	IP 35/86	187 C°	180 C°
Sulfur, %wt	X – ray	20.39	22.18
Pour point, C°	IP 15/81	+ 6 C°	- 3 C°
Conradson carbon, %wt	IP 13/82	0.038	0.0.041
Ash, %wt	IP 3/81	Nil	nil

FTIR spectrums of jatropha oil before and after Sulforization were illustrated in figs (1, 2) while linseed oil before and after Sulforization were illustrated in figs (3, 4).

IR spectra

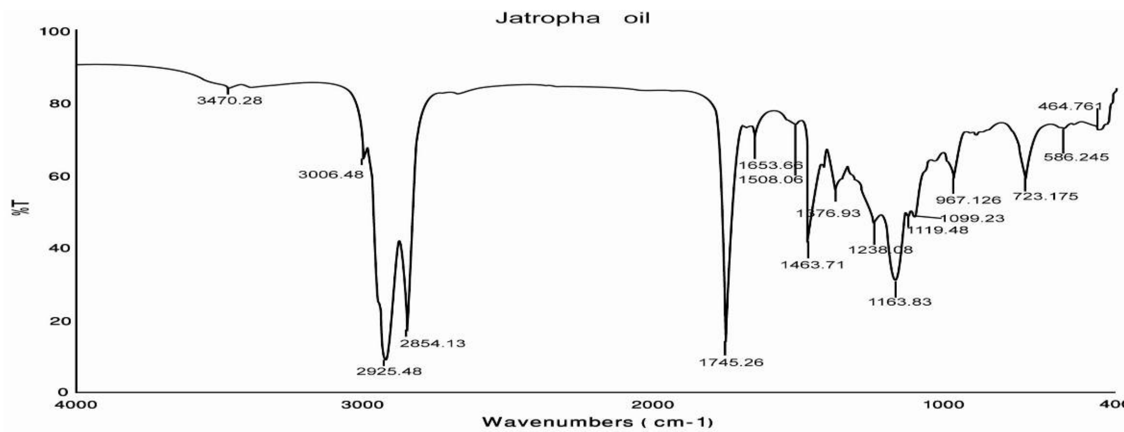

Fig. (1) IR Spectrum of jatropha oil

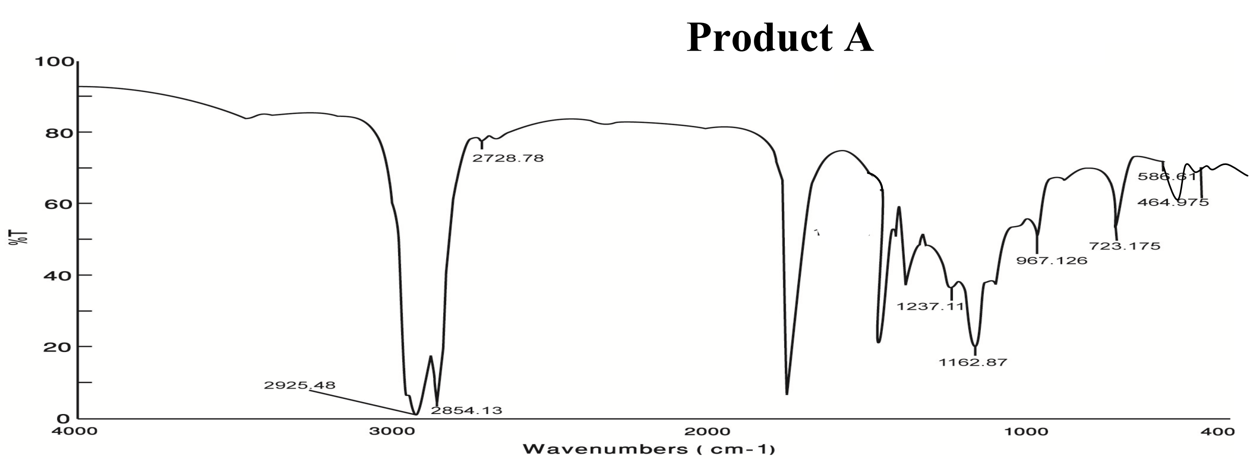

Fig. (2) IR Spectrum of product A (sulfurized jatropha oil)

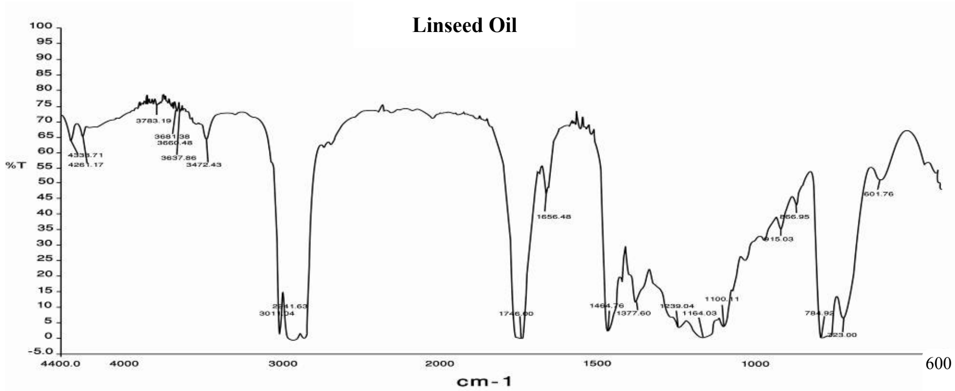

Fig. (3) IR Spectrum of Linseed oil

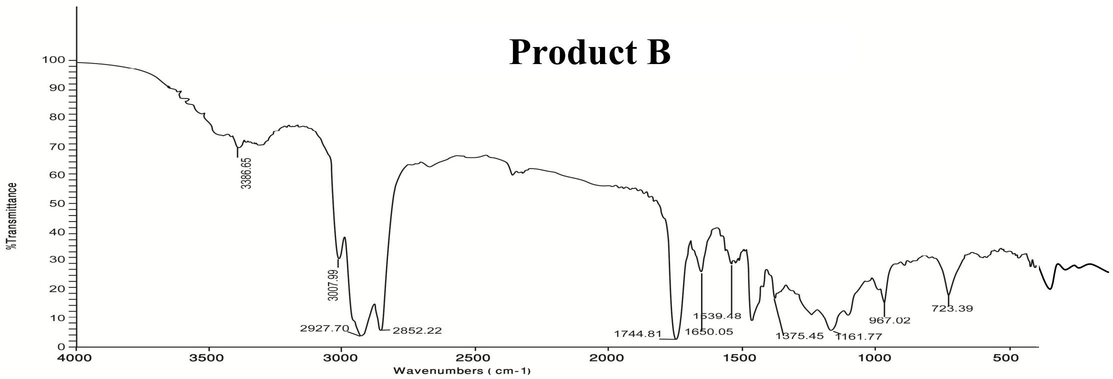

Fig. (4) IR Spectrum of product B (sulfurized linseed oil)

Evaluation study of analysis figure for product A are listed in table (8), while figs (1, 2) show FTIR spectrums before and after Sulforization.

Results obtained shows that product A contains 20.39 %wt sulfur content. Also FTIR spectrum illustrate disappearing double bonds at 1610 cm^{-1}, 907 cm^{-1}, while forming υ C – S bond at 586, 577 cm^{-1}[8,9]

This proves forming sulfurized fatty material. High percentage of sulfur contents in fatty material work as extreme pressure additives.

Also analysis figure of product B are listed in table (8). Figs (3, 4) show FTIR spectrum, before and after Sulforization.

Results obtained shows that product B contains 22.12 %wt sulfur contents, while FTIR spectrum, illustrate disappearing double bonds at 1610 cm^{-1} & 790 cm^{-1} and forming bond of υ C – S at 500 – 400 cm^{-1}. This proves forming sulfurized fatty material. High percentage of sulfur content in fatty material work as extreme pressure additive.

Results obtained of standard test ASTM – D130 for blends of products A & B with base were listed in table (9).

Evaluation study of copper strip results for standard ASTM D130 method illustrates all blends has class (1A).

Table (9): Result of cupper corrossion test for different percentage formulation from products (A & B) (ASTM D130).

Formula No.	Results (A)	Results (B)
1	1 a	……
2	1 a	……
3	1 a	……
4	1 a	……
5	1 a	……
6	……	1 a
7	……	1 a
8	……	1 a
9	……	1 a
10	……	1 a

These excellent results prove that all sulfur reacts with double bond of fatty oil (inactive sulfur), while dissolved sulfur (active sulfur) give class B or C or D.

High percentage of inactive sulfur (non corrosive) in fatty material work as extreme pressure additive with saving the machine metal surfaces from corrosion, it was also worked as antiwear additive for metal to metal surfaces.

Results obtained of performance standard four ball wear test (IP 239) were listed in table (10).

Evaluation study of scar diameter and welding load results of standard four ball wear test (IP 239) show that local products A & B have in good results than or equal imported additives.

Fig (5) shows the comparative evaluation between blends 11, 12, 13 and 14 which containing percentage of different types of E.P additives. From the figure indicate that local products A & B have in good function as extreme pressure additive similar to imported additives.

Table (10): Four ball and oxidation stability results for formulation of 4 pilot blends from paraffin base oil SAE 90 and product (A&B) and two imported additive.

Formulation No	Results		
	Oxidation Stability / min	Scar diameter/mm	Welding load/Kg
Blank	28	0.60	150
11(A)	278	0.35	280
12 (B)	314	0.3	285
13 (X)	22	0.35	275
14 (Y)	155	0.25	290

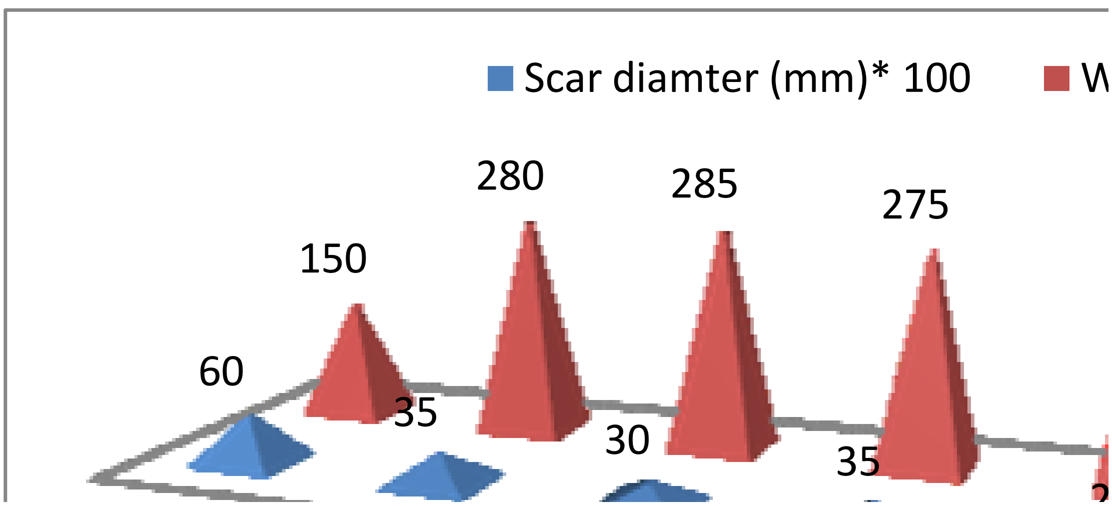

Fig (5): Shows the comparative between scar diameter and welding load of four blends and base oil.

Results obtained of oxidation stability by using standard methods IP 229 for base oil and blends 11,12,13,14 which contains 1.75%wt from product A,B and additive X with base oils as SAE 90 GL – 3 respectively, while 2.4 %wt from additive Y in blend 14 as SAE 90 GL – 5 were listed in table (10).

Evaluation study of induction periods (min) for oxidation resistance according IP (229) show blends 11 and 12 highly oxidation resistant than blends 13 & 14.

This proves that locally synthesized products A & B have in good resistant for oxidation of oils, while additives X (GL – 3 level) doesn't have any resistance and additive Y (GL – 5) have slightly resistance against oxidation.

This proves that locally products A & B have further function as antioxidants more than imported additives as shown in fig (6)

This may be due to the efficiency of natural resistant in fatty oil.

Final Conclusion

Evaluation study of this work proves that, success using extracted residual sulfur from crude oil in production useful E.P additives.

Additives produced having high efficiency as extreme pressure and antioxidant function than imported additives.

Production additives A & B by this way saving environmental from pollution of residual sulfur, beside highly economic value.

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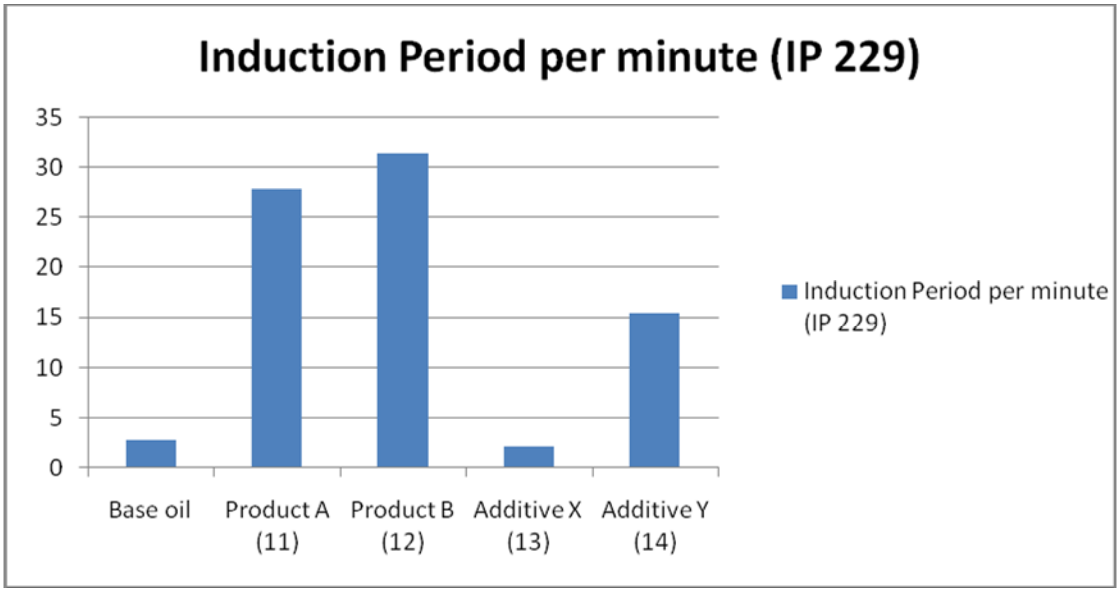

Fig (6): induction period per minute (IP 229)

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4/22/2012