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Sensitivity of Bio-Sourced Oils as Lubricants Basestocks

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Abstract: In this research, four bio-sourced oil *viz.* milk bush, orange, pawpaw and water melon seed oils were selected for assessment of their tribological properties and sensitivity as prospective lubricant basestocks. The bio-basedstocks were obtained after extraction using hexane as solvent and degumming using 85% phosphoric acid. Results showed that both orange and milk bush seeds recorded both high oil yield and low gum contents. The oils were chemically modified by hydrogenation to improve their thermo-oxidative stability. An additive-free base oil commercially coded as SN and BN were used along with the bio-sourced base oil to synthesize various lubricants using the B20 formulation. The trio of water-melon, milk bush and pawpaw seed oils were adjudged to be promising candidates. A simple model based on dimensional analysis was equally presented to predict the amount of oil recoverable from the seeds.

Key words: Dimensional Analysis · Hydrogenation · Thermo-oxidative stability · Tribological properties

INTRODUCTION

The world annual consumption of fossil lubricant is 40 million tones and is projected to continue to rise 1.6% annually for at least the next 3 years, Trans world news [1]. There is therefore urgent need to supplement gradually the fast depleting fossil oil reserves with bio-sourced oil. Fossil lubricants producers should similarly be aware of great responsibility of safekeeping the environment for future generations. There are steps currently being taken toward creating an economy that prefers a bio-based lubricant through policy formulation. Lubricants are developed to perform not only lubrication but also for many other functions, such as cooling, noise and vibration reduction, cleaning and corrosion protection [2]. Bio-sourced lubricants are preferred because they are biodegradable and non-toxic, unlike conventional mineral-based oils [3,4].

Last one and half decade has witnessed a considerable increase in the understanding of various aspect of bio-lubricating oil and mechanism of lubrication. [5,6] recently found out that Jathropha have great potential as biofuel feedstock. John [7] used both bleached and unbleached palm oil for biolubricant and observed that bleached oil possesses better lubricating properties. Vegetable oils with high concentrations of Oleic acids yield stable lubricants that oxidize much more slowly as observed by Castro *et al*. [8]. In the study of Rhee *et al*. [9] and Kassfeldt *et al*. [10], they revealed that low temperature study of most vegetable oils undergo cloudiness, precipitation, poor flow and solidification at -10°C upon long term exposure to cold temperature in sharp contrast to mineral oil-based fluids. Rapeseed and castor oils are two most common base stocks for plant-oil-based lubricants as contained in the report of Rudnick [11]. El - Kinawy [12] and Jayadas [13] respectively reported Jojoba and coconut oil as good feedstock for bio-lubricant production. Thermal stability of jojoba oil provides it with possibility to be used as an additive in variable applications that require high thermal stability such as jet engine lubricants. However, it has high pour point, causing some problems in cold weather. Many studies have confirmed that plants oils containing a high concentration of monounsaturated fatty acid, oleic acid (18:1), is considered as the best candidates for lubricants and hydraulic oils due to its desirable lubrication properties Dharma [14] and [15]. There is therefore need for an exploration of the technological viability of seed oil extraction and utilization of some of the oil for lubricant formulation.

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Moreover, as part of the recent objectives of researchers in green tribology to save energy, materials and enhance the environment and the quality of life IET, [16], thus this paper focuses on the synthesis of environmentally friendly lubricants (bio base oil + additives) from pawpaw, orange, bush milk and water melon seed oils & their mixtures and to examine their quality parameters and tribological properties as potential lubricant basestocks. Details of oil from pawpaw seeds, its physico-chemical analysis and usage in biofuel production can be found in our earlier papers [17]. Our choice of oil for this research work is to ensure both energy and food security and at the same time creating values for unconsciously discarded materials which are basically inedible seeds for this case.

In the detailed report of Trans world news [, in order] to use plant-based oils as lubricants, chemical modifications and *de novo* syntheses, breeding and/or biotechnology can be applied. Of all, selective hydrogenation of the chemical modification processes was adopted in this study.

MATERIALS AND METHODS

Extraction of Oil from Seeds: Average sized and matured pawpaw, orange and water melon fruits about fifty in number each were purchased from Ketu market (a local market) in Lagos metropolis of Nigeria (Latitude 6.5833 and Longitude 3.75). Seeds of milk bush were obtained from its tree located in front of the Chemical Sciences Department of Fountain University, Osogbo (Latitude 7.7667 and Longitude 4.5667). They were prepared for use by cutting into two longitudinal halves and the seeds were removed manually, sun dried for several days and then kept in a sealed bottle under cool dry storage. The seeds were ground into fine powder with a Marlex blender, with trademark 277985 manufactured by Kanchan International Limited, Dabhel in India. A Soxhlet extractor was used for solvent extraction of the oil. The solvent (n-hexane) was removed from the extract by distillation and the residual oil component collected and used for the analytical work. A 500 ml capacity soxhlet extractor was used in the extraction of the oil from the ground seeds. Five packs of 5g each of the ground seeds (a batch) except for pawpaw seeds where 3 packs of 5g each were packed in a whatman filter paper and inserted into the soxhlet extractor while 350 ml of n-hexane was used as the extracting solvent for melon seeds, while 300 ml, 250 ml and 200 ml were used respectively for pawpaw, milk bush and orange. The period of continuous

Fig. 1: Extraction of oil.

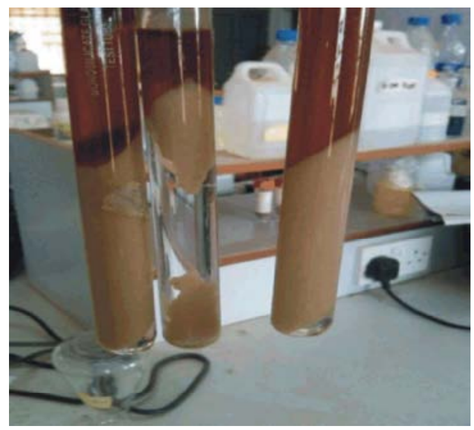

Fig. 2: Samples of degummed oil.

Fig. 3: Hydrogenation of oil samples.

extraction as shown in Fig. 1 was 2 hours. By this time, the batch of packed seeds had been de-oiled as evidenced by the continuous clear appearance of the condensed vapour from the solvent. The three packs of 5g of the ground seeds were oven dried at 65 °C ± 2 °C for 30 minutes until a constant weight was observed. The solvent was recovered by simple distillation and the res]idual oil was

Fig. 4: Degummed and hydrogenated oil sample.

Fig. 5: Blending of oil with additive.

also oven-dried at 65 °C ± 2 °C for one hour The oil was then transferred to a desiccator and allowed to cool, before being weighed. The drying, cooling and weighing was repeated until a constant dry weight was obtained, to within 0.01 g. The extracted oil sample was in a well sealed amber color glass bottle and kept for further analytical tests and subsequent chemical transformations.

Deguming of Oil: 2.5 ml of 85% H_3PO_4 diluted with 30 ml of water was added to each of the extracted oil. The mixture were placed in a water-bath for 5 minutes at 60°C before agitating the mixture in a shaker at 300rpm for 30 minutes. The resulting mixtures were placed in a centrifuge at high speed for phase separation. The gum removal is necessary to avoid its interference with further reactions of the oil samples.

Hydrogenation of Oil: 15 g of Zinc powder was weighed into a conical flask and allowed to react with 30 ml of HCl, the reaction evolves hydrogen gas and precipitation of $ZnCl_2$. The oil sample was poured into a 100 ml beaker as

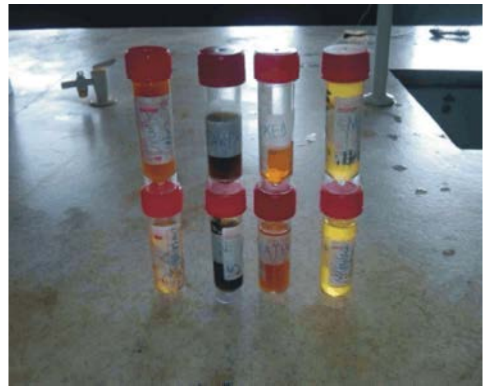

Fig. 6: Bio-based Lubricants.

shown in Fig. 3 so that the generated gas delivery tube will be in direct contact with the oil sample. Hydrogenation transforms the easily oxidisable compounds into more stable components, primarily improves the stability as well as increases the melting point of unsaturated fatty derivatives [18].

Synthesis of Biolubricant: The hydrogenated oil (Fig. 5) was measured against an additive in the ratio 4:1 industrially labeled B20 in a 100 ml beaker. The mixture was then covered with an aluminum foil as shown in the figure and agitated on a flask shaker for a period of 2 hours at a speed of 500 oscillations/hr to ensure a perfect blend. The B20 was now poured into sample bottles for further analysis to determine its lubricating properties.

RESULTS

Model Development Using Dimensional Analysis:

$$\frac{Mass\ of\ Oil\ Removed}{Volume\ of\ raw\ seed\ .Time}(E)\ f\begin{bmatrix} Mass\ of\ raw\ seeds\,(M) \\ Surface\ area\,(S) \\ Time\,(T)\ Temperature\,(\theta) \\ Solvent\ Volume\,(V) \end{bmatrix}$$

$$ML^{-3}T^{-1} = f\left[M^{a}S^{2b}T^{c}\theta^{d}V^{3e}\right]$$

$$M: 1 = a\ (1.00)$$

$$L: -3 = 2b + 3e\ (2.00)$$

$$T: -1 = c\ (3.00)$$

$$\theta: 0 = d\ (4.00)$$

$$e = \frac{-3-2b}{3} = -1 - \frac{2b}{3}(5.00)$$

$$E = f\left[MS^{2b}T^{-1}\theta^{0}V^{-1-\frac{2b}{3}}\right]$$

$$E = k\left(\frac{M}{TV}\right)\left(\frac{S}{V^{\frac{1}{3}}}\right)$$

Where k is a constant.

DISCUSSION

In this research, the SN and BN lube are set as standards. The two are industrial codes for fossil fuel basestocks for synthetic lubricant. They were used for lubricant synthesis and were all subjected equally to the laboratory analysis. The ability of the bio-lubricants to mix with other liquid especially water is dictated by their various densities. All the samples have density less than one which will help in case of contamination with water as it will settle below the oil and therefore allowing easy drainage. Pawpaw and water melon bio-lubricant are very close to the two synthetic lubricants in terms of density. Viscosities are extremely important in classifying lubricants. It determines the fluidity of the lubricant at certain temperatures. It determines the formation of a film between a moving and a stationary part. The synthetic lubricants exhibited relatively high viscosity followed by water melon, milk bush and pawpaw oil lubricant. The pour points show the reverse with melon and bushmilk in that order. The relatively low viscosity value recorded for some of the bio-lubricants make them suitable to withstand use during humid period but still the viscosity can be improved for better performance.

Similarly, the pour points of the melon seed oil followed by orange seed oil were next to the two synthetic lubricants, implying that the samples could be used both in humid and temperate regions of the world. The pour point is minimum temperature of a liquid, particularly a lubricant after which on decreasing the temperature the samples cease to flow. It is therefore important to note that the samples under consideration have pour points that satisfy their use as engine lubricating oils.

The flash points which for all are expectedly high is the minimum temperature at which the vapour from oil sample will give a momentary flash on application of a standard flame under specific test conditions. This is used to predict the possible fire hazard during transportation, storage and handling.

Table 1-4 are summarized in Table 5 which consists of the percentage oil obtained from each of the seed oil. Table 6 further presents the final percentage oil recovery after the gum removal with pawpaw seed oil having the highest level of gum.

Table 1: Pawpaw seed oil extraction results.

Batch	$I.W_1$	$I.W_2$	$I.W_3$	T.I.W	$F.W_1$	$F.W_2$	$F.W_3$	T.F.W	T.I.W-T.F.W
1.	6.19	6.24	6.34	18.77	4.79	4.82	4.94	14.55	4.22
2.	6.17	6.17	6.24	18.58	4.87	4.89	5.13	14.89	3.69
3.	6.35	6.18	6.21	18.74	4.99	4.86	4.92	14.77	3.97
4.	6.24	6.19	6.41	18.84	5.08	4.88	5.18	15.14	3.70
5.	6.26	6.18	6.18	18.62	4.94	4.98	4.90	14.82	3.80
6.	6.12	6.35	6.38	18.85	4.75	5.19	5.00	14.94	3.91
7.	6.11	6.11	6.24	18.46	4.79	4.88	4.91	14.58	3.88
8.	6.32	6.37	6.12	18.81	4.98	4.97	5.04	14.99	3.82
9.	6.21	6.36	6.26	18.83	4.86	5.18	4.95	14.99	3.84
10.	6.16	6.28	6.43	18.87	4.77	4.90	5.00	14.67	4.20
				187.37				148.34	39.03

Table 2: Milk bush seed oil extraction results.

Batch	$I.W_1$	$I.W_2$	$I.W_3$	$I.W_4$	$I.W_5$	T.I.W	$F.W_1$	$F.W_2$	$F.W_3$	$F.W_4$	$F.W_5$	T.F.W	T.I.W-T.F.W
1.	6.37	6.31	6.32	6.38	6.31	31.69	4.08	3.83	4.46	4.34	4.04	20.75	10.94
2.	6.29	6.33	6.30	6.28	6.36	31.56	4.37	4.65	4.95	3.77	4.29	22.03	9.53
3.	6.35	6.35	6.33	6.42	6.29	31.74	3.94	3.65	3.81	3.80	3.56	18.76	12.98
4.	6.32	6.37	6.37	6.32	----	25.38	3.83	4.18	3.74	4.06	-----	15.81	9.57
						120.37						77.35	43.02

Table 3: Water melon seed oil extraction results.

Batch	$I.W_1$	$I.W_2$	$I.W_3$	$I.W_4$	$I.W_5$	T.I.W	$F.W_1$	$F.W_2$	$F.W_3$	$F.W_4$	$F.W_5$	T.F.W	T.I.W-T.F.W
1.	6.26	6.27	6.32	6.26	6.41	31.52	4.90	4.96	5.03	4.97	5.12	24.98	6.54
2.	6.42	6.42	6.42	6.23	6.22	31.71	5.20	5.12	5.13	4.97	4.89	25.31	6.40
3.	6.35	6.27	6.45	6.19	6.22	31.48	5.09	4.92	5.09	4.87	4.94	24.91	6.57
4.	6.19	6.17	6.36	6.30	6.26	31.28	4.93	4.96	5.14	5.33	4.95	25.31	5.97
5.	6.38	6.33	6.46	6.33	6.31	31.80	5.12	5.03	5.36	5.22	5.02	25.75	6.05
6.	6.11	6.37	6.35	6.22	6.21	31.26	4.84	5.13	5.11	4.88	4.90	24.86	6.40
						189.05						151.12	37.93

Table 4: Orange seed oil extraction results.

Batch	$I.W_1$	$I.W_2$	$I.W_3$	$I.W_4$	$I.W_5$	T.I.W	$F.W_1$	$F.W_2$	$F.W_3$	$F.W_4$	$F.W_5$	T.F.W	T.I.W-T.F.W
1.	6.43	6.40	6.43	6.30	6.45	32.01	4.19	3.79	4.08	4.04	3.85	19.95	12.06
2.	6.45	6.35	6.48	6.45	6.42	32.15	4.66	3.76	4.34	3.81	4.02	20.59	11.56
3.	6.43	6.75	6.41	6.34	6.42	32.35	4.04	3.95	3.86	3.72	3.80	19.37	12.98
4.	6.45	6.38	6.47	6.44	6.33	32.07	3.96	3.97	3.81	3.79	3.68	19.21	12.86
5.	6.40	6.39	6.36	6.36	6.41	31.92	3.74	3.73	3.94	3.81	3.87	19.09	12.83
						160.5						98.21	62.29

Table 5: Summary of oil extraction results.

Seeds	T.I.W	T.F.W	T.I.W-T.F.W	Actual mass of Oil Obtained	% Oil Yield
Pawpaw	187.37	148.34	39.03	29.41	15.70
Milk Bush	120.37	77.35	43.02	33.81	28.09
Water Melon	189.05	151.12	37.93	28.91	15.29
Orange	160.50	98.21	62.29	47.45	29.56

Table 6: Results obtained from the deguming process.

Seeds	Actual mass of Oil Obtained Before Deguming	Mass of Oil Obtained After Deguming	Mass of Gum Obtained	% Oil Recovery
Pawpaw	29.41	18.25	16.11	62.05
Milk Bush	33.81	30.08	3.73	88.97
Water Melon	28.91	21.23	7.68	73.43
Orange	47.45	43.55	3.90	91.78

N.B:

I.W: Initial weight of seed + filter paper + thread

T.I.W: Total Initial weight of the four samples (i.e. A Batch)

T.F.W: Total final weight of the four samples (i.e. A Batch)

F.W: Final weight of seed + filter paper + thread

T.I.W ¯ T.F.W: Indicates the mass of oil obtained per batch.(Theoretical mass)

All Values are in gramme except otherwise stated.

ASTM: American Standard and Testing Method

Table 7: Lubricating properties of oil samples.

Properties and Test Method/Oil	Water-Melon	Orange	Jatropha	Mixed oil	SN-Lube	Milk- Bush	Pawpaw	BN-Lube
Density,g/cm^3 (ASTM D289)	0.891	0.881	0.964	0.88	0.903	0.951	0.892	0.902
Viscosity mpa.s(@25 °C) (ASTM D2393)	28.59	18.51	14.91	17.1	208.75	25.76	22.94	74.4
P^H	2.75	3.64	4.44	3.66	5.69	4.63	4.1	5.64
Colour (ASTM D1500)	5	4	2	3.5	8	2.5	5.5	3.5
Cloud Point,°C (ASTM D2500)	12	10	8	8	21	11	13	18
Pour Point °C (ASTM D97)	8	6	-7	0	18	4	3	10
Flash Point °C ASTM D93	>200	>200	>200	>200	>200	>200	>200	>200

CONCLUSIONS

The quality parameters of the synthesized lubricants from bio-sourced oil and that from fossil based oil using B20 formulation were compared. All the bio-lubricants demonstrated high degree of acidity which may further aid attack on metallic components; however they can be subjected to further treatment to reduce the acidic level. The trio of water melon, milk bush and pawpaw seed oil mostly seem to be more sensitive as good candidate for lubricant feedstock. A cocktail of the trio is recommended for further research work. The edibility of water melon oil however, may pose future problem as a basestock for lubricant. The high gum contents of pawpaw seed oil may require another process unit for gum removal which are always capital intensive. The low gum contents coupled with the high oil content of the milk bush of the selected seed oil is considered a likely candidate for bio-lubricant basestock.

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