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Coconut-Castor Oil Blend as Sustainable Basestock for IC Engine Oils: The Low-Temperature Fluidity

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Abstract—This paper reports the depression of the pour point of coconut oil through binary mixture with castor oil, for lubricant in IC engines. The PP of the lead oil is reduced from 18°C to 12°C and further to 3°C by blending with 50%wt castor oil and treating the mixture with 8%wt of a Malaysian synthesized pour point depressant respectively. The pour point, studied using a pour point tester (ASTM D97-12 method), of the formulation presents it serviceable in the tropics as IC engine oil. The viscosity, and viscosity index, of the blended basestock are comparable to SAE 10W-30 oil.

Keyword – Binary mixture; castor oil; coconut oil; pour point; pour point depressants; IC engine oil

1 INTRODUCTION

CURRENT advances in engine oils requirements to meet; governmental emission regulations, fuel economy demands, and modern days improved engine tolerances [1] require better basestocks for formulation of engine oils. Vegetable oils (VOs) could be these better basestocks, because of their strong adherence to metal surfaces and thin-film formation, capable of lubricating very small intervening spaces. Moreover, morden trends in pursuit of energy independent and sustainable development identify vegetable oils as best options to sparse distributed, fast depleting petroleum deposit, and eco-impacting petroleum oils. vegetable oils as regenerative and costeffective resources, non-toxic and excellent biodegradable compounds, couple to their attractive lubricant properties such as high viscosity indices, high flash points, excellent lubricity [2], good miscibility among others are desirable basestocks for machinery lubricating oils. However, vegetable oils are observed to be short of crankcase oil requirements, majorly due to insufficient tribological properties under severe loading, low thermo-oxidation resistance, hydrolytic instability, and poor lower temperatures activities [3]. The latest, traceable to the structures and arrangements of the fatty acids moieties, and waxy content of the oils, will cause poor tribological performance at low temperatures.

The poor low-temperature activities of vegetable oils occur at/or close to the flow limiting temperature of the oils, customarily called the pour point (PP). That is why PP, determined to a reasonable degree, characterizes the low-temperature properties of lubricants [4]. At this stage, the oil particles lack the kinetics to indicate any visible motion. Hence, the oil is said to solidify. This oil solidification is perceived to occur when high temperature soluble solid materials get crystallized, forming interlocking networks which trap and cease the flow of liquid oil [5].

One essential requirements of today's crankcase oils

are upgraded cold weather starting, when the oils' lowest pump-able temperatures are as low as -35°C [1]. Unfortunately, vegetable oil-based lubricants exhibit cloudiness, precipitation, loss of fluidity, high resistance to pumping, and even solidify at -15°C [6], due to the tendency of their 'bend' triglycerol backbones to uniformly stack together at low temperatures, and form microcrystalline structures [7].

Most desirable pour points for specific applications are obtained by blending the processed base stocks with pour point depressants (PPDs). PPDs lower the pour points of oils through the mechanism of physical interference in which they break down the molecular clusters of the oil to prevent nucleation, or decelerate wax crystal agglomeration by coating the wax molecules, or fit themselves into the structure of the wax crystals, thereby interrupt their growth [5]. Some achievements on depressing the pour points of native vegetable oils using PPDs have been reported [3], but there is scarcity of reports on remarkable success on the lauric oils, particularly coconut oil (CN) by this approach, pour point of native CN has been reduced from 24°C to 12°C [7], from 23°C to 13°C [8], and 20°C to 10°C [9], but with as high as 10 to 15% dose of additives. These are real achievements, but short of engine oils requirements, and cost-ineffective. One common line of thought is that vegetable oils, due to their non-uniform characteristics, could complement one another to meet lubricant requirements [10]. CN possesses high value (85 to 90%) of short-chain saturated fatty acids, giving it good friction and wear control [11]. Sadly, this also gives it high pour point and poor response to PPDS.

Castor oil (CT), a lower molecular weight oil, has cis bonds in the structure of it unsaturated ricinoleic-rich hydroxyl acid [12], giving it excellent low pour point (-33°C), good friction and wear control, but exceptionally high viscosity [6], and undesirably low viscosity index.

The nature of respective dominant fatty acids and the potential lubricant profiles of CN and CT take positions at either extremes, particularly the low temperature fluidity.

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This reasonably suggest that, a blend wedlock between the two oils could result in considerable depression of the pour point of CN to fit into lubricants base stock standards. However, mixing the two oils in several proportions yielded no impressive results [7]. 50:50 proportion by weight of CN to CT (Indian cultivars) only reduced the pour point of the former from 24°C to 21°C. Poor understanding of crystallization mechanisms of mixed triacylglycerols acids has made bleak the prospect of achieving desirable low-temperature characteristics through the blending of vegetable oils. This may only be established through several experiments [6]. The conclusion [7] that mixing CN with CT is not effective in reducing the poor point of CN is, somewhat too early, since the resultant mix was not treated with PPD(s). This argument by the authors of the present work is based on a reported work in which the influence of a 20% polyalphaolefin on pour points of several vegetable oils [13] was not so significant, until after additivation.

CT is anticipated to exhibit better response to PPD than CN, owing to its rich unsaturated fatty acid (ricinoeic) which is of the oleic series. The postulation by the author of this current work is that the mixture of this two oils, if treated with PPD could reasonably lower the pour point. This is possible because the presence of CT molecules which are readily penetrable by copolymer chains can encourage easy co-crystallisation activities of PPDs. Several mixtures in different proportions of these two oils were made to achieve a viscosity at 100°C equivalent to SAE10W-30 engine oil, for IC engine use, considering other advantages. The resultant mix was treated with three different PPDs, separately and in several proportions, and the pour point tested in each case. The appropriate proportion of the PPD which offered the best performance in the selected mixture was tested on pure coconut oil and reported. This is to ascertain whether the blend with castor oil altered the response of coconut oil to PPD significantly as postulated. The pour point of an SAE 10W-30 premium engine oil was also tested for benchmarking.

2 MATERIALS AND METHODS

THE materials used in this work include coconut oil and castor oil obtained from local producers in Nigeria. Three PPDs, branded HB-EX-PPD-A1 (proprietary blend), HB-EX-PPD-AS1 (oil-soluble acrylate polymer copolymerized with vinyl pyridine), and HB-EX-PPD-L1 (maleic anhydride-styrene polymer), and a commercial SAE10W-30 engine oil obtained from Malaysia.

Blends of CN to CT (wt/wt %) made to arrived at a suitable viscosity and VI for IC engine oil (SAE 10W-30) were: M20% = 80:20, M30% = 70:30, M40% = 60:40, M50% = 50:50, and M60% = 40:60, similar to proportions of bio base oil blends in other literatures [7, 10]. Kinematics viscosities of the oils were determined using rotary viscometer according to ASTM D445, and the VIs as per ASTM D2270 methods. Based on arguments from literatures [7, 14], sample M50% was blended with 0, 2, 4, 6, and 8%wt of each of the PPDs separately and the PP tested in each case using a pour point tester (ASTM D97-12 method) [6, 15].

RESULTS AND DISCUSSION

FROM the viscosities at 100°C of all the tested oils (Table 1), SAE viscosities rating will classify CN and M20% as SAE 20. M30%, M40%, M50%, M60%, and the commercial engine oil (CM) will be classified as SAE 30, while CT will fall under SAE 40. Apart from CT which has very low viscosity index, each of the studied candidate oils has multi-grade viscosity index. Increase of CT in the mixture, increase the viscosity at 40°C of the mixture, but reduces the VI. The viscosity at 100°C increased until CT reached 50 %wt, after which a reduction in this viscosity is noticed. The VI of M20%, M30%, M40% and M50% are higher than that of CM. This implies that they will have sufficient viscosities to provide adequate films between rubbing surfaces at high temperatures than the commercial engine oil

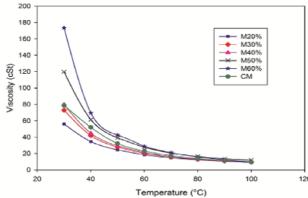
Table 1: Kinematic viscosity/VI of the oils and their blends

	Oil	Specific	Kinematics Viscosity		VI
		gravity	(cSt)		
			at 40°C	at 100°C	
1	CT	0.960	243.57	16.23	56
2	CN	0.905	26.97	8.59	327
3	M20%	0.910	34.49	9.06	261
4	M30%	0.910	41.81	9.52	222
5	M40%	0.915	44.70	9.80	213
6	M50%	0.930	61.29	11.99	196
7	M60%	0.940	69.44	9.75	121
8	CM	0.860	51.98	9.43	167

Candidate oils M20%, M30% and M40% have reasonably lower viscosities at 40°C (Table 1) than the CM, implying better pumpability, hence better flow to tribocontact zones at low temperatures. Candidate blends M50% and M60% have higher viscosities at low temperatures than the CM (Figure 1), implying poorer pumpability and higher losses to viscous friction at lower temperatures. However, the moderate tribo-film possibility by M50%, due to its closer viscosity range to CM will rather offer a preferred oil film thickness capable of reducing wear and friction.

At high temperatures, candidate blend M20% may have slightly lower film supply than CM, but candidates M30%, M40%, M50% and M60% will offer better tribofilms than the CM.

Figure 1. Viscosity-temperature plots of the mixed base oils and the commercial oil



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3.1 Pour points of the experiment oils

A The pour point of the coconut oil sample in this experiment is measured to be 18°C, very close to the value (20°C) obtained in literature [9], but significantly differs from 23°C and 24°C [7, 8]. These variations may not be unconnected with the climate, soil and growing location of the oil plants, among other factors responsible for the nonuniform characteristics of vegetable oils, even those of the same cultivar. CT was used at varying proportion (20, 30, 40, 50, and 60% wts) to blend CN to see how the former can affect the pour point of the latter. 20 and 30 %wt of CT made no noticeable impact on the pour point of CN, but when diluted with 40 %wt of CT, the pour point of CN stepped down to 12°C (see Table 2). However, further diluents (at 50 %wt and 60 %wt of CT) could not make any improvement on the poor point again. This confirmed that diluents have limited effect on the pour points of vegetable oils [6]. The achieved lowest pour point by this mixture may without further treatment provide certain levels of lubrication in engines at relatively low temperatures, especially in the tropics. However, it is evident that the viscosity of the oil (mixture) at warm-up in these regions, will exhibit poor flow to intervening spaces, and greater frictional losses the conventional counterparts under the same conditions. These losses at warm-up can be so high, around 2.5 times above the frictional losses in sufficiently heated lubricants [16].

Table 2: Pour point of the studied oils

	Oil Sample	Pour point (°C)
1	CT	-18
2	CN	18
3	M20%	18
4	M30%	18
5	M40%	12
6	M50%	12
7	M60%	12
8	CM	<-30

It is not so certain how CT molecules affect the molecules and/or wax content of CN in lowering the PP. However, one can suppose that there is a co-nucleation of the CT molecules with those of the lead oil which modifies the original crystallisation matrix of the latter, as temperature lowers, such that the composite matrix delays crystal growth and may not allow early fusion of nucleated crystals that will cause solidification or hinder fluidity at the original solidification temperature of CN. Notwithstanding, at lower temperatures, a limit may be reached where the differing of solidification by the influential molecules (CT) is not possible as the bonding of the lead oil molecules gets stronger with falling temperature. Possibly, 40, 50, and 60 %wt of CT in CN formed a plateau zone (from the PP values in Table 2) after which the PP of the blended oils may fall. But the resultant viscosities (at 40°C) and viscosity indices of mixtures having higher proportions of CT may not be suitable for the intended application, since the two parameters (of the mixtures) are noted to increase and decrease respectively with rising proportion of the CT.

3.3 Response of the selected blended base oil to PPDs

M50% was selected and treated with varying proportions of PPDs to prove the postulation of the authors of this work, and to argue and/or concomitantly put up a course on the 'brickwork' laid by Ajithkumar [7]. Although the responses of M50% to PPDs failed to meet the minimum standard requirement for pour point of lubricants (Figure 2), one of them still ensures safe pour point within low temperature working limits in the tropical regions. Impressively, at 8 %wt of HB-EX-PPD-A1, the PP of the said oil was depressed to 3°C. This PPD is likely to be of the linear alkyl side-chain type, having varying length structure with most of the chain lengths closely matching that of hydrocarbon chains in the mixed base oil, giving it an optimum performance.

To verify the contribution of CT to the response of CN to the PPDs, the very proportion (8 %wt) of the best performing PPD (HB-EX-PPD-A1) in M50% was tested on pure CN. The result (Figure 2) showed that mixing CN with the CT has contributed immensely to the response of the former to the PPD. The presence of the ricinoleic fatty acid from the CT in the mixed oil (M50%) may have engineered the favourable response of CN to the said PPD. This by far justifies the postulation by the authors of the present work: that the mixture of CN with CT may not show immediate significant effect on the low-temperature fluidity of CN, but may provide a good playground for PPDs.

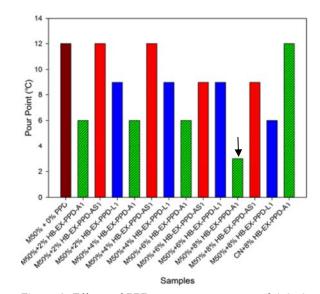


Figure 2. Effects of PPDs on coconut-castor oil (50:50 wt/wt) mixture, and on pure coconut oil

It is noticeable from the response of pure CN to 8 %wt blend of HB-EX-PPD-A1 that the presence of ricinoleic molecules of CT in blend M50% might have suppressed the resistance of the dominant lauric acids in CN against PPD. This may be achieved by making soft the clustering molecules of the composite oil for the PPD to break and defer nucleation, or creating more penetrable allowances for the inclusion of molecules of PPD into the propagating crystals, to envelop the small nucleated crystals and or co-crystallizing with them (the nucleated crystals) at slower rate. By these, the PPD may be able to

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postpone early crystallization of the M50% at higher temperatures than what had happened in pure CN. Moreover, the rincinoleic acid molecules might have brought a balance between the saturated and the unsaturated fatty acids in the mixed base oil, giving it an equivalent low-temperature characteristic suitable for the activities of PPDs.

The effect of HB-EX-PPD-A1 on the mixed base oils have not yet indicated pour point reversal. Higher proportion of HB-EX-PPD-A1 may further reduce the pour point of this mixture. However, due to economic and technical reasons, a higher proportion is not advisable. The mixed vegetable oils are in crude form, implying high waxy fluid, therefore, the performance of HB-EX-PPD-A1 point to the fact that it has high wax interaction factor (i.e. high strength of interaction or waxy side-chains).

2 and 4%wt of HB-EX-PPD-AS1 in the mixed candidate oil (M50%) produced no effect on its (oil) pour point. At 6 %wt addition, the pour point of the oil was reduced by 3°C to 9°C. Further increase of the dose made no improvement on this property. This means that the spatial stabilisation of the PPD against the crystals of the base oil became insufficient. Hence, the wax crystals built up sufficient structure(s) that halted the mobility of the oil molecules. Additional %wt of the PPD may only add extra wax to the oil molecule network leading to PPD reversal.

2%wt of HB-EX-PPD-L1 reduced the pour point of the oil to 9°C, but no reduction was recorded until at 8 %wt of the pour point. This remarkable response at 8 %wt concentration means that the base oil wax particles were responsible for non-reduction at the intermediate %wt.

CONCLUSION

ONE-TO-ONE mix ratio of coconut oil to castor oil produced adequate viscosity, equivalent to SAE 10W-30 engine oil, and with even higher viscosity index. This also lowered the pour point of the coconut oil, and more importantly, prepared a better base for pour point depressants to have reasonable impacts on the pour point of coconut oil. Employing a proprietary pour point depressant, branded HP-EX-PPD-A1, at 8 %wt in the said binary mix of the oils lowered the pour point to as low as 3°C. This result gives assurance that the treated oil can flow to the various tribological contacts (intervening spaces) of IC engine assembly at all practical temperatures conceivable in the tropical region.

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