Improving the Oxidation Stability and Biodegradability of Environmentally Friendly Lubricants

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The paper discusses the possibilities to employ vegetable oil to formulate environmentally friendly lubricants. Our approach is aimed at taking advantage of the good bio-degradability of vegetable oils while testing strategies to improving their oxidation stability. The experimental results showed a two-fold strategy consisting of using a mixture between vegetable and mineral oil, coupled with the right dosage of an appropriate anti-oxidation additive may provide encouraging results with respect to the oxidation stability and biodegradability of the resulting lubricant. Furthermore, mixtures with more stable base oils such as poly-alpha-olefins, that have a better oxidation resistance and better biodegradability than the mineral oils, may further improve the lubricating properties of the resulting environmentally friendly base oil.

Keywords: lubricants and additives, vegetable oils, biodegradability

The world market demand for lubricants is approximately 38 million tons per year [1, 2] and consists of a wide range of lube oils such as engine oils, gear oils, hydraulic oils, compressor oils, turbine oils, chainsaw oils etc. Most of these lubricants are based exclusively on mineral oils (almost 94 %), while a small fraction are formulated using synthetic oils (4-5%) and vegetable oils (1.5-2%) [3, 4].

An interesting statistic presented in the table 1 shows the correlation between the composition of the lubricants and their corresponding applications. As it can be observed, the lubricants based on vegetable oils are used especially in applications that require restrictive environment conditions, such as chain saw oil, demoulding oils and two-strokes engine oils, or in applications not requiring harsh working parameters, such as high temperatures and/or pressures. Lubricants of the former category include hydraulic oils, industrial gear oils, metal working fluids, etc.

The most plausible arguments that could explain the limited capitalization of vegetable oils as base oils for manufacturing lubricants include:

-the competition with the food industry, because the use of vegetable oils to formulate lubricants will limit the offer for food consumption putting pressure on prices [5];

-the higher price for vegetable oils compared with that for mineral oils obtained from petroleum;

-the low thermal and oxidative stability of vegetable oils (i.e. decompose and oxidize in presence of air and moderate temperatures);

-the lack of specially designed additives to improve the performance of vegetable oils.

On the other hand, vegetable oils have remarkable lubrication properties, high flash point, very high biodegradability and are renewable [7, 8]. These natural and intrinsic characteristics of vegetable oils represent a major advantage for all types of lubricants, and for "environmentally friendly" lubricants in particular. Therefore, the use of vegetable oils as base oils for lubricants formulation purposes is a challenging goal mainly consisting of finding suitable solutions to overcome their poor oxidation stability and thermal resistance.

The physical and chemical properties of vegetable oils are directly related to their chemical structure. Vegetable oils have a typical glycerol ester chemical structure defined by the following distinct elements: the structure of the fatty acid carbon chain, the presence of the ester group and of the glycerol group. The presence of the ester group and of the unsaturated bonds in the fatty acid carbon chains significantly increases the chemical reactivity of vegetable oils, thus these features are responsible for their weak oxidative stability [9]. Therefore, few approaches could be possible to improving the oxidation resistance of vegetable oils such as:

-modification of the chemical structure of vegetable oil by selective hydrogenation of double bonds, or by partial addition of more stable compounds that would obstruct the reactivity of the ester groups;

-addition of efficient antioxidant additives;

-modification of the chemical structure of the fatty acid chains in vegetable oils by genetic modification of the crops used for their production, etc.

Here we report our results on the assessment of the biodegradability and oxidation behaviour of vegetable oils compared to mineral oils, and on the efficiency of additives in balancing these characteristics in environmentally friendly lubricants. Based on these results we also propose potentially sustainable solutions to improving the oxidation resistance of vegetable oil based lubricants.

Experimental part

The experimental study was designed to achieve several specific objectives:

-to assess the biodegradability of vegetable oils compared to the mineral oil usually used as base oil in lubricants' formulations;

-to assess the oxidation behaviour of vegetable oils compared to mineral oil;

-to study the effect of adding antioxidant additives on the oxidation performance of vegetable and mineral oils;

-to study the effect of antioxidant additives on the biodegradability behaviour of base oils;

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Table 1
CONSUMPTION OF LUBRICANTS IN EUROPE (X 1000 TONES/YEAR) [6]

Applications	Total lubricants	Vegetable oils	Synthetic esters	Total bio-lubricants	% bio-lubricants
Engine oils	1680	0	22	22	1.3
Two-strokes engine oils	30	1	1	2	6.7
Turbine oils	10	0	10	10	100
Automotive gear oils	300	0	4	4	1.3
Industrial gear oils	100	1	2	3	3
Hydraulic oils	660	17	22	39	5.9
Compressor oils	40	0	15	15	37.5
Metal working fluids	400	5	20	25	6.3
Textile oils	15	1	2	3	20
Chain saw oils	41	17	3	20	48.8
Demoulding oils	100	12	3	15	15
Greases	132	2	3	5	3.82
Other lubricants	1242	2	7	9	0.7
Total	**4750**	**58**	**114**	**172**	**3.6**

-to establish correlations between the oxidation resistance and biodegradability of the lubricants.

-to propose sustainable solutions for improvement of the oxidation resistance of vegetable oil based lubricants.

Assessment of the biodegradability of vegetable and mineral oils

"Biodegradable" means that a material has the proven capability to decompose in the most common environment where the material is disposed of within 3 years through natural biological processes into non-toxic carbonaceous soil, water, carbon dioxide or methane. The most commonly used testing methods to assess the biodegradability of materials are: the OECD 301B Modified, ASTM D-5864, and CEC L-33-A-94. In this study, for the assessment of the biodegradability of vegetable and mineral oils we have used the CEC L-33-A-94 (CEC L-33-T-82 in the past) testing method.

The CEC L-33-A-94 test applies to most organic compounds, whether soluble or insoluble in water. It determines the overall biodegradability of hydrocarbons, or similar compounds containing methylene (– CH_2 –) groups, measuring all transformations that the starting material undergoes, including oxidation and hydrolysis. The method was developed to characterize the biodegradability of outboard engine oils on the Bodensee, due to the accumulation of mineral oils that tainted fish.

The CEC test is accepted in a number of Blue Angel Environmental Labels. The German Blue Angel scheme does not intend to produce guidelines for enclosed systems. Despite being convenient and easy, the CEC test only measures the IR absorbance of lipophilic molecules extractable with chloro-alkane solvents. It should be noted that it does not measure the water-soluble metabolites, which are poorly extractable and, therefore, cannot measure the extensive degradation or mineralization. This would require a parallel test measuring oxygen consumption or carbon dioxide release. We should also mention that there is no clear structural criterion that can be adopted to compare the biodegradability of various types of structures. In our research we have followed the CEC L-33-A-94 testing procedure, using a microbial mixture prepared on spot based on bacteria, sediments and musts.

Assessment of the oxidation resistance of vegetable and mineral oils

One of the most important characteristic of lubricants is the oxidation resistance. Because it determines their stability, acidity, sediment tendency, corrosivity, etc, it is very important for the lubricants to have good oxidation stability. In our experimental study the oxidation behaviour of the lubricants was assessed by the "Rotary bomb" oxidation test method (RBOT) according to the ASTM 2272 standard. The RBOT test measures the oxidation stability of lubricants at high temperature in presence of oxygen. The sample oil is placed in a vessel that contains a polished copper coil acting as oxidation catalyst. The vessel is filled with oxygen and then placed in a bath at a constant temperature of 150°C. The oxidation stability is expressed in terms of the time required to achieve a 25.4 psig pressure drop from the maximum pressure reached during testing.

Effect of the addition of anti-oxidation additives

One of the most commonly used methods to improve the oxidation resistance of lubricating oils is the addition of anti-oxidation additives. The commercially available additives are usually very effective with mineral base oils, as these base oils are used in formulations for most commercially available lubricants. For our experimental study we have employed two types of commonly used commercial anti-oxidation additives: (a) the DTP additive, which is a mixture of di-alkyl-di-thyo-phosphate and alkyl succinic ester; and (b) the APA additive, which is a mixture of alkyl-phenol and alkyl-aryl-amine. Each of these additives was tested with vegetable sun flower oil and a mineral iso-paraffinic oil type ISO-VG 32, using different dosages of additives. The main purpose of the tests was to evaluate the influence of additive addition, of additive chemical structure, and of additive dosage on the oxidation behaviour of different base oils as determined by the RBOT method described in the previous section. At the same time, the modification of biodegradability was also assessed and correlated with the composition of different base oils. The biodegradability was determined by the CEC L-33-A-94 method described in above section.

Sustainable solutions to improve the oxidation resistance

As previously discussed, based on the reactive sites of the chemical structure of vegetable oil molecules, there are several theoretical solutions to improving the oxidation resistance of lubricants based on vegetable oils. However, the modification of the chemical structure of the vegetable oils, and the use of additives specially designed to interact with the weak sites of the vegetable oils are rather difficult alternatives at present because they require significant research effort before effective practical solutions can be proposed to this aim.

Therefore, taking into account that the commonly used additives are tailor made for hydrocarbon-based oils, the potential solution assessed in our experimental study is to mix vegetable and mineral oil with antioxidant additives. The ratio between the mineral and vegetable base oils should be selected in such a way to balance between an increased oxidation resistance and a good performance for biodegradability, therefore a 1:1 weight ratio of mineral to vegetable oil was chosen for the purpose of this study.

Different additives were added to this mixture as in the first stage of our experimental study, at the same dosages. The resulting formulations were tested to assess their oxidation resistance and biodegradability behaviour following the methods described above.

Results and discussions

There is a wide variety of vegetable and mineral oils. For our experimental investigation few of the most common vegetable oils and some representative mineral oils were chosen such that they have similar kinematic viscosities at 40°C. The representative physical characteristics of the vegetable and mineral oils used in our experiments are given in tables 2 and 3 along with their biodegradability behaviour.

The results in table 2 clearly show that the vegetable oils are characterized by very good viscosity index, high flash points and high biodegradability, these characteristics being significantly better than those observed in table 3 for mineral oils. As a disadvantage, the sun flower oil and soy bean oil show pour points slightly higher than those of the mineral oils. However, considering that the usual accepted value for the biodegradability of "environmentally friendly" lubricants is minimum 60% [10], it becomes obvious that vegetable oils have a remarkably good biodegradability, significantly higher than 60 %, while the mineral oils have a rather poor biodegradability, significantly lower than the required value.

Table 2
CHARACTERISTICS OF DIFFERENT VEGETABLE OILS

Oil type	Sun flower oil	Soy bean oil	Rapeseed oil	Castor oil
ISO - VG	32	32	32	220
Kinematic viscosity at 40°C	31,85	35,59	34,34	252
Viscosity Index	222	215	211	88
Flash Point, °C	260	300	298	284
Pour Point, °C	- 9	- 9	- 23	- 21
Biodegradability, %	93	92	86	80
Rotary bomb oxidation test, min	5	5	5	10

Table 3
CHARACTERISTICS OF DIFFERENT MINERAL OILS

Oil type	Paraffinic oil	Iso-Paraffinic oil	High refined paraffinic oil	Aromatic oil
ISO - VG	32	32	32	32
Kinematic viscosity at 40°C	29,50	32,04	31,56	33,04
Viscosity Index	95	91	98	84
Flash Point, °C	220	218	220	205
Pour Point, °C	- 12	- 15	- 10	- 18
Biodegradability, %	28	30	30	20
Rotary bomb oxidation test, min	55	50	60	45

Table 4
EFFECTS OF ANTI-OXIDATION ADDITIVES ON THE OXIDATION RESISTANCE AND BIODEGRADABILITY OF SUN FLOWER OIL

Additive and dosage	DTP.........0,6 %	DTP ....1.0 %	APA..........0.3 %	APA.........0.6 %
ISO – VG	32	32	32	32
Rotary bomb oxidation test, mn	15	15	15	20
Biodegradability	90	88	92	92

Table 5
EFFECTS OF ANTI-OXIDATION ADDITIVES ON THE OXIDATION RESISTANCE AND BIODEGRADABILITY OF THE ISO-PARAFFINIC MINERAL OIL

Additive and dosage	DTP.........0,6 %	DTP ....1.0 %	APA.........0.3 %	APA.........0.6 %
ISO – VG	32	32	32	32
Rotary bomb oxidation test, min	150	180	230	280
Biodegradability, %	24	24	29	27

With respect to the oxidation resistance, the bottom lines of tables 2 and 3 show the values determined experimentally for the same types of vegetable and mineral oils. Considering oxidation stability tested by the RBOT method, the referential value for good quality base oils is 50 to 60 min. Based on these results one can easily conclude that the oxidation resistance of vegetable oils is very poor, far from that required for lubricants for harsh conditions applications. By contrast, the mineral oils have good oxidation resistance, being recommended as base oils for formulations of oxidation resistant lubricants. From this data it becomes clear that a lubricant with good oxidation resistance is less biodegradable, thus improving biodegradability will lead to a lubricant less resistant to oxidation.

The assessment of the effects of anti-oxidation additives on the oxidation resistance and biodegradability lead to the results presented in table 4 that shows the oxidation resistance and biodegradability results obtained for sun flower oil with different dosages of each anti-oxidation additive, DTP and APA.

The results in table 4 show that the addition of antioxidant additives does not seem to influence the oxidation resistance of sun flower oil. Even more interestingly, the chemical structure of the anti-oxidation additives has no influence on the oxidation resistance of the sun flower oil, nor does the dosage. It is therefore expected that the sun flower oil with different additives and different dosages behaves similarly to the oil without any additives. Indeed, the values obtained with sun flower oil-additive mixtures are close to those observed for sun flower oil in table 2. However, the same additives at the same dosages have a significant impact on the oxidation stability of the iso-paraffinic mineral oil, as seen in table 5.

First, the use of both additives significantly improves the oxidation resistance of the iso-paraffinic oil as measured by the RBOT from 50 min to over 150 min , while the same additives had only a minor effect with the sun flower oil. Second, the chemical structure of the antioxidant additive influences the efficiency of the additive; at the same dosage the APA additive is almost twice more effective than the DTP additive. The efficiency of the additive also increases with the dosage, with the APA effect influenced stronger by the dosage compared to DTP.

On the other hand, the effect of the additive on the biodegradability is similar to that observed for the vegetable oil, that it is the addition of additives does not significantly influence the biodegradability of the mineral oil. The poor improvement of the oxidation resistance of the vegetable oil following additive addition is most likely due to the fact that the known additives are designed to prevent oxidation in hydrocarbon based lubricating oils and not for vegetable oils. Therefore the oxidation mechanism of the vegetable oil is likely significantly different than that of mineral oils, so that anti-oxidation additives effective for vegetable oils should be specially designed to block that particular oxidation mechanism.

It becomes clear from the data presented and discussed above that the mineral oils have good anti-oxidation properties, while the vegetable oils have appropriate biodegradability. It is therefore intuitive that a mixture of the two types of base oils may reconcile in resulting base oils with good oxidation resistance and satisfactory biodegradability. The oxidation resistance and biodegradability data obtained with a 1 to 1 (by weight) mixture of sun flower oil and iso-paraffinic mineral oil with and without anti-oxidation additives are given in table 6.

The values obtained for oxidation resistance and biodegradability characteristics emphasize the following aspects:

-the mix between mineral and vegetable oil, without additives has a poor oxidation stability, almost similar to that of vegetable oils; the influence of mineral oil addition is insignificant;

-the biodegradability of the mixture is good enough, balanced between the specific values of vegetable and mineral oils, but closer to that of the vegetable oil;

-mixing the vegetable oil with mineral oil and antioxidant additives has proven to be a promising solution for a formula with improved oxidation resistance; however, these test results are not comfortable enough for all formulations, but are close to those required (RBOT, min.50-60 min);

Table 6
EFFECTS OF ANTI-OXIDATION ADDITIVES ON THE OXIDATION RESISTANCE AND BIODEGRADABILITY OF A 1 TO 1 MIXTURE OF SUN FLOWER OIL AND ISO-PARAFFINIC MINERAL OIL

Additive and dosage	0%	DTP......0,6%	DTP 1.0%	APA......0.3%	APA......0.6%
ISO – VG	32	32	32	32	32
Rotary bomb oxidation test, min	10	40	45	50	65
Biodegradability, %	72	64	61	70	65

-the biodegradability of the mixtures decreased compared to the vegetable oils, but the values are still better than those required (min.60% according to CEC L-33-A-94).

Conclusions

Reviewing all results, there are several concluding remarks that may be summarized as follows:

-vegetable oils have a very good biodegradability behaviour, which recommend them as "environmentally friendly lubricants"; they have also very good lubricity, high flash point and high rate of renewability that represent important advantages over traditional lubricants;

-however, vegetable oils have a poor oxidation resistance which limits their use to specially environmentally regulated applications, or in applications with easy work condition;

-addition of antioxidant additives have a positive effects on the behavior of mineral oils, but it does not increase significantly the oxidation stability of vegetable oils, most likely because the traditional additives are usually tailor made for mineral or synthetic base oils, and the oxidation mechanisms of vegetable oils is significantly different than that for mineral oils; also, the significantly higher instability of vegetable oils may also contribute to the poor effect of the anti-oxidation additive efficiency in their case;

-with respect to the biodegradability, addition of additives actually does not influence this characteristic for vegetable oils, nor for mineral oils;

-because mineral oils have appropriate oxidation stability and vegetable oils have remarkable biodegradability, the idea of mixing the two types of base oils may actually reconcile in resulting base oils with good oxidation resistance and satisfactory biodegradability;

-the mixture between mineral and vegetable oil, with no additives, has a poor oxidation stability, almost similar to that of the vegetable oil, but the biodegradability of the mixture is sufficiently high, up to the required value (min.60% in conformity with CEC L-33-A-94); however, adding anti-oxidation additives provide encouraging results with respect to the oxidation stability preserving good biodegradability behaviour;

-other possible solutions to improve the oxidation stability of lubricants based on vegetable oils, could be the modification of their chemical structure, addition of specially designed anti-oxidation additives, use of mixtures with more stable base oils such as poly-alpha-olefins that have a better oxidation resistance and better biodegradability than the mineral oils.

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