The Mixtures of Castor Oil and Adipic Esters with Biolubricating Characteristics

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Because the petroleum based products have a negative impact on the environment,is necessary to create and use eco-friendly lubricants. Vegetable oils are part of this category because they are a renewable natural resource, environmental safety, and show lubricating characteristics. By mixing the castor oil with two synthetic diesters (isodecyl and 2-[(p-nonyl)phenoxy]ethyl adipate respectively, isotridecyl and 2-[(p-nonyl)phenoxy]ethyl adipate) were obtained two series of new lubricants to which the physico-chemical and rheological characteristics were studied. The lubricants were also characterized using the differential scanning calorimetry (DSC) and thermal gravimetric (TG) analyses. The obtained mixtures present superior properties to mineral oils and can be used as lubricants.

Keywords: environmentally lubricants, lubricating properties, vegetable oils

Because approximately 50% of all lubricants sold worldwide end up in the environment via volatility, spills, and total loss applications, the environment must be protected against this pollution. The problem can be avoided by either preventing undesirable losses, reclaiming and recycling mineral oil lubricants or using environmentally friendly lubricants. Vegetable oils (edible or inedible) are recognized as rapidly biodegradable and are thus promising candidates as base fluids in environment friendly lubricants. Lubricants based on vegetable oils display excellent tribological properties, high flash points [1] and viscosity indices due to the double bonds and the molecule linearity [2], possibility to use additives to improve the rheological behavior [3,4], low toxicity and volatility, good lubricity (due to molecule polarity). The main disadvantage is that their thermal and hydrolytic stability is comparatively lower than that of synthetic oils and needs to be improved through a number of measures [2,5-7]. This disadvantage is eliminated by the use of additives, preferably biodegradable [8-12].

Esters, whose chemical structures are similar to natural triglycerides, are also excellent substitutes for mineral oils. Castor oil contains around 90% ricinoleic acid, and as a result, it has a higher viscosity and a lower viscosity index, compared to other vegetable oils. The high fatty acid content makes this oil relatively high in oxidative stability [13]. Lubricating properties of castor oil were studied and were reported to be similar or better than those of vegetable oils commonly used [14,15], it is used especially for engines and machines demanding.

This work was based on the production of biodegradable lubricant base fluids from castor biodiesel esters, using various chemical catalysts to yield products with interesting properties, such as high viscosity index and good oxidation stability, compared to mineral oils.

Considering the characteristics of vegetable and minerals oils, in this study we aimed to obtain and characterize lubricants based on mixtures of synthetic esters and vegetable oils. For this purpose we realized two series of new lubricants by mixing castor oil with two synthetic diesters (isodecyl and 2-[(*p*-nonyl)phenoxy]ethyl adipate, respectively, isotridecyl and 2-[(*p*-nonyl) phenoxy]ethyl adipate).

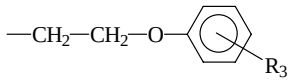
Experimental part

Materials and methods

The unsymmetrical adipic diesters are based on aliphatic alcohols like isodecyl or isotridecyl alcohol, as well as on special alcohols of a complex alkyl-aryl structure, namely 2-[(*p*-nonyl)phenoxy]ethanol. They show characteristic features of synthetic lubricating oils [16-18]. These esters are defined by the general formula (I):

$$R_1OOC\text{-}(CH_2)_4\text{-}COOR_2 \quad (I)$$

where R_1 = isodecyl or isotridecyl radical, R_2 = radical with the following structure defined by the general formula (II):



(II)

where R_3 = *p*-nonyl.

The castor oil (CO) was supplied by Fluka.

The mixtures were prepared at room temperature and contain: 25/75, 50/50 and 75/25 wt. % CO/adipic diesters.

The physico-chemical properties were determined by using standardized techniques. Density determinations were made at 20°C with a pycnometer and the refractive index was determined with an Abbé refractometer. The dynamic viscosity was measured by means of a Rheotest device, RV type (VEB Prüfgeräte-Werk, Medingen/Dresden) and kinematic viscosity with an Ubbelohde viscometer, according to ASTM D445.

The four-ball test was accomplished on a Seta machine according to ASTM D4172, at room temperature. The flow point was measured according to ASTM D97, and the flash point according to ASTM D92. The volatility was determined in agreement with ASTM D6184. The lubrication number was calculated on the basis of the Bötner-Rosenthal relationship [19]; the values of the minimal couple were extracted from the Brabender plastogram recorded on the Brabender plastograph, PL/3S type.

The thermogravimetric (TG), derivate thermogravimetric (DTG) and the differential scanning calorimetry (DSC) analysis were performed with a NETZSCH STA 449F1 STA449F1A-0220-M. Approximately 3÷7 mg of sample was

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heated in an Al_2O_3 crucible, with 5°C/min. in nitrogen atmosphere, within the range 20 ÷ 600°C.

Results and discussions

The physico-chemical and tribological properties of CO, C1 (isodecyl and 2-[(*p*-nonyl) phenoxy]ethyl adipate), C2 (isotridecyl and 2-[(*p*-nonyl)phenoxy]ethyl adipate) and their mixtures are presented in tables 1, 2 and 3. In tables 4 and 5 are presented the kinematic viscosity at 40°C and 100°C and viscosity indices (VI) of the studied oil mixtures.

All the obtained values are relative to bis(2-ethylhexyl) adipate (DOA) which is used as a standard.

Both the castor oil and the mixtures studied have flash points of over 150°C, which indicates a low tendency to evaporation (basic requirement in their use as lubricant). Similarly, all mixtures have pour points below -31°C proving good behavior at low temperatures, being comparable to the values obtained for the synthetic esters.

Because the values of the refractive index and density show a linear variation between corresponding values of castor oil and diesters, we can conclude that they are physical mixtures. Also, the kinematic viscosity at 40°C is between 19.46 and 103.22 $mm^2 s^{-1}$, while at 100°C it is between 3.95 and 20.72 $mm^2 s^{-1}$. The viscosity indices of the mixtures are between 96.00 and 145.44 and are better than those of synthetic base oils. The volatilities of the mixtures are lower than 1.9% being better than those of castor oil and adipic diesters.

For comparison, the physical characteristics of a commercial reference oil are presented below [20,21]:

- Kinematic viscosity , $mm^2 s^{-1}$: 31.43 (40°C), 5.29 (100°C)
- Viscosity index VI: 99
- Pour point, °C: -39
- Flash point, °C: 212
- Lubricity, wear scar diameter at 40 daN / 60 min, mm: 0.43

Property		CO	C1	C2	DOA
ρ^{20} / kg m^{-3}		960.1	971.5	959.6	920
n_D^{20}		1.4781	1.4830	1.4824	1.447
η^{20} / mPa s		1010	214-373	243-464	107
Kinematic viscosity, $mm^2 s^{-1}$	40 °C	103.22	19.46	52.00	8.11
	100 °C	20.72	3.95	7.38	2.38
Viscosity index		145.44	96.00	102.00	113.00
Pour point, °C		-31	-42	-42	-42
Flash point, °C		300	225	238	142
Volatility at 120 °C, %		0.31	1.88	1.92	1.85
Saponification index, mg KOH g^{-1}	theor.	176-187	316.38	293.23	454.90
	analyt	179	315.74	293.12	453.88
Acid value, mg KOH g^{-1}		0.33	0.24	0.23	0.22
Iodine value, g I_2 100 g^{-1}		86	-	-	-
Lubrication number c_L		-	8.11	13.39	-
Siccativity		non siccative	-	-	-

Table 1
THE MAIN PROPERTIES OF CASTOR OIL (CO) AND OF THE TWO ADIPIC ESTERS (C1, C2)

Property	Composition CO/C1, wt. %				
	100/0	75/25	50/50	25/75	0/100
ρ^{20} / kg m^{-3}	960.1	964.2	965.5	968.7	971.5
n_D^{20}	1.4781	1.4789	1.4811	1.4815	1.4830
Iodine color scale	5	5	5	5	4
Iodine value, g I_2 100 g^{-1}	86	39.41	22.67	15.12	-
Volatility at 120 °C, %	0.31	0.18	0.67	0.94	1.88
Flash point, °C	300	274	248	231	225
Pour point, °C	-31	-33	-35	-39	-42

Table 2
THE MAIN PROPERTIES OF THE MIXTURES CO/C1

Property	Composition CO/C2, wt. %				
	100/0	75/25	50/50	25/75	0/100
ρ^{20} / kg m^{-3}	960.1	956	959.8	959.6	959.6
n_D^{20}	1.4781	1.4794	1.4808	1.4821	1.4824
Iodine color scale	5	5	5	5	4
Iodine value, g I_2 100 g^{-1}	86	50.06	41.22	20.16	-
Volatility at 120 °C, %	0.31	0.26	0.75	1.12	1.92
Flash point, °C	300	284	262	249	238
Pour point, °C	-31	-35	-35	-41	-42

Table 3
THE MAIN PROPERTIES OF THE MIXTURES CO/C2

CO/C1 wt. %	Kinematic viscosity, $mm^2 s^{-1}$		Viscosity index (VI)
	40 °C	100 °C	
100/0	103.22	20.72	145.44
75/25	96.43	15.17	125.52
50/50	60.81	8.44	104.05
25/75	38.25	6.20	103.76
0/100	19.46	3.95	96.00

Table 4
KINEMATIC VISCOSITY AND VISCOSITY INDICES OF CO/C1 MIXTURES

CO/C2 wt. %	Kinematic viscosity, $mm^2 s^{-1}$		Viscosity index (VI)
	40 °C	100 °C	
100/0	103.22	20.72	145.44
75/25	93.40	17.89	140.46
50/50	88.61	13.76	122.99
25/75	71.15	10.10	110.46
0/100	52.00	7.38	102.00

Table 5
KINEMATIC VISCOSITY AND VISCOSITY INDICES OF CO/C2 MIXTURES

Sample	Wear scar diameter, mm			Welding load, daN		
	a*	b	c	a	b	c
C1	1.12	0.40	0.90	120	160	170
C2	0.95	0.50	0.80	130	140	160
DOA	1.20	-	1.30	200	-	190

* a-non additivatted oil; b-oil with 1.5 % Zn dithiophosphate; c-oil with 1.5 % dithiocarbamate ashless

Table 6
FOUR BALL TEST [17]

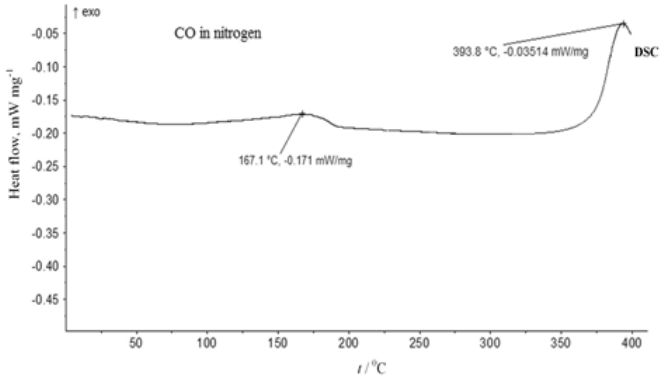

Fig. 1. DSC curve of castor oil in nitrogen atmosphere

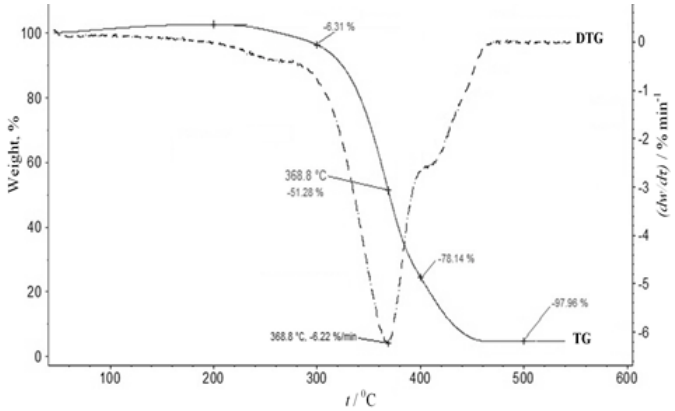

Fig. 2. TG and DTG curves of castor oil in nitrogen atmosphere

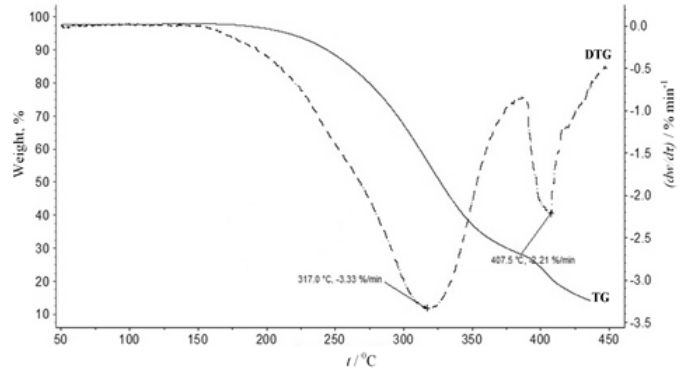

Fig. 3. TG and DTG curves of castor oil in synthetic air

As a conclusion we can say that all the properties of the analyzed mixtures and diesters have better values than those of a commercial reference oil.

The lubricant number values of C1 and C2 permit to include the tested compounds within the internal lubricants category (c_L < 20) [17].

In table 6 are presented the four-ball tests of these synthetic oils (C1 and C2). The results recorded for the additivated terms implicitly demonstrate good compatibility of these synthetic diesters with the antiwear additives and this feature represents in fact a very important quality [17].

In figure 1 and 2 are presented the DSC curve and TG/DTG curves of castor oil in nitrogen atmosphere; figure 3 shows the TG/DTG curves of castor oil in synthetic air.

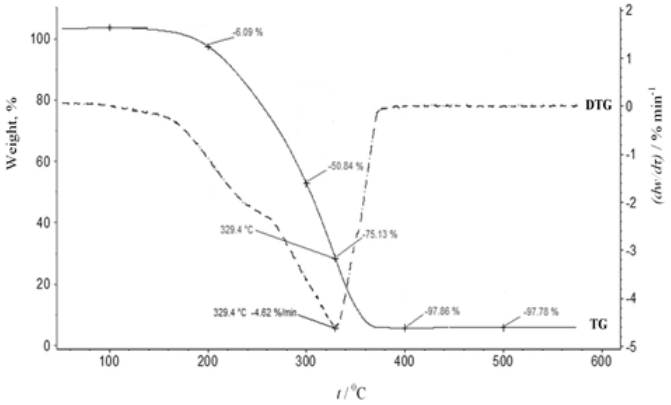

Fig. 4. TG and DTG curves of C1 in nitrogen atmosphere

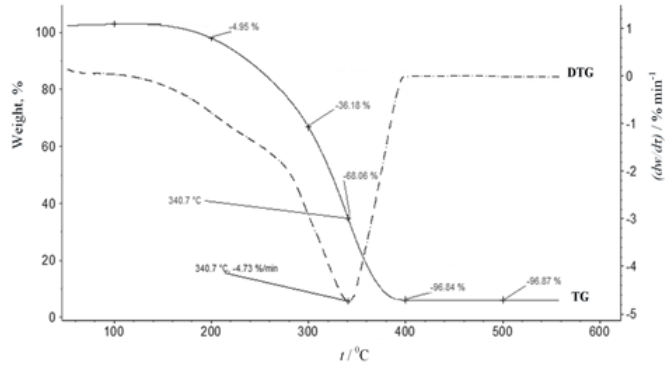

Fig. 5. TG and DTG curves of C2 in nitrogen atmosphere

In figure 1, an exothermic process at 167.1°C (probably due to the double bonds C=C involved) and a thermal decomposition process at 393.8°C are recorded. The TG/DTG curves of castor oil in nitrogen atmosphere (fig. 2) registered a 6.31% loss of mass at 300°C. The major decomposition process begins at 368.8°C with 51.28%. The higher decomposition rate is recorded at 400°C with 78.14% and the total mass loss is recorded at 600°C.

In figure 4 and 5 are presented the TG/DTG curves of C1 and C2 in nitrogen atmosphere.

In figure 4 is registered: a 6.09% loss of mass at 200°C, a major decomposition process at 329.4°C with 75.13% loss of mass, a higher decomposition rate at 400°C with 97.86% and a total mass loss at 600°C.

In figure 5 is registered: a 4.95% loss of mass at 200°C, a major decomposition process at 340.7°C with 68.06% loss of mass, a higher decomposition rate at 400°C with 96.84% and a total mass loss at 500°C. In figure 6 and figure 7 are presented the TG/DTG curves of CO (50%) - C1 (50%) in nitrogen atmosphere and in synthetic air. In figure 8 and figure 9 are presented the TG/DTG curves of CO (50%) - C2 (50%) in nitrogen atmosphere and in synthetic air.

In figure 6 a 1.35% loss of mass at 200°C is registered. The major decomposition process begins at 366.2°C with 51.23%. The higher decomposition rate is recorded at 500°C with 97.79% and the total mass loss is recorded at 600°C.

In figure 8 a 1.03% loss of mass at 200°C is registered. The major decomposition process begins at 375.5°C with 54.9%. The higher decomposition rate is recorded at 500°C with 97.76% and the total mass loss is recorded at 600°C.

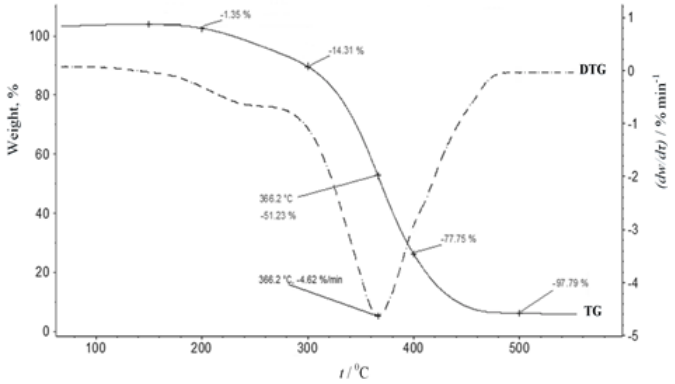

Fig. 6. TG and DTG curves of CO (50%) - C1 (50%) in nitrogen atmosphere

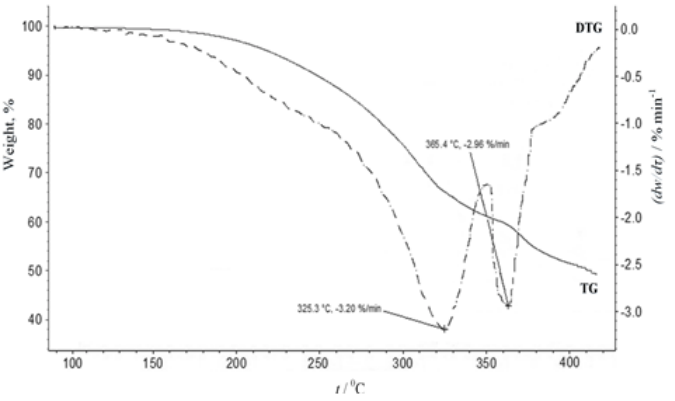

Fig. 7. TG and DTG curves of CO (50%) - C1 (50%) in synthetic air

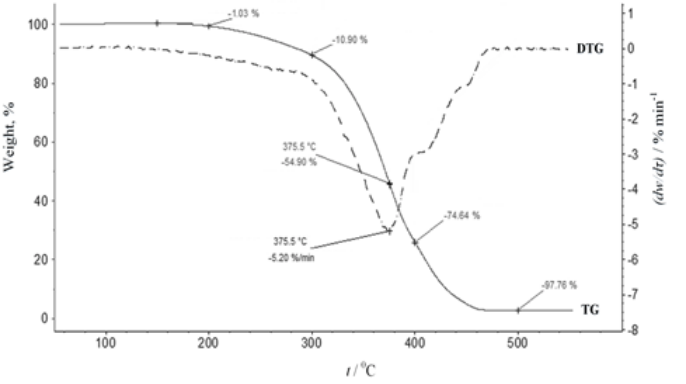

Fig. 8. TG and DTG curves of CO (50%) - C2 (50%) in nitrogen atmosphere

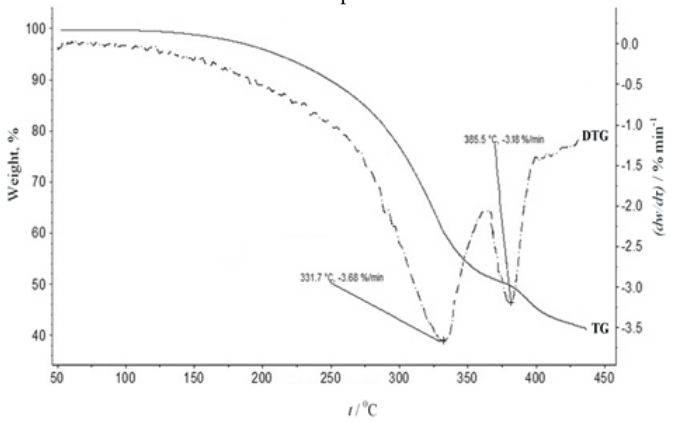

Fig. 9. TG and DTG curves of CO (50%) - C2 (50%) in synthetic air

From the TG/DTG curves of CO (fig. 3) we notice that no major decomposition takes place up to 317.0°C, compared to the curves recorded in a nitrogen atmosphere. Above this temperature there is a new amendment to the 407.5°C, which is probably associated with the double bonds oxidation process.

In figure 7 are shown two decomposition processes. The first major decomposition is recorded at 325.3°C and corresponds to C1, and the second one, at 365.4°C corresponds to CO. The total decomposition is recorded at 440°C.

In figure 9 are also shown two decomposition processes. The first major decomposition is recorded at 331.7°C and corresponds to C2, and the second one, at 385.5°C corresponds to CO. The total decomposition is recorded at 460°C.

Following the thermal results we conclude that the thermal stability of the studied mixtures is better than that of the castor oil and the two esters.

Conclusions

The two adipic diesters C1 and C2 have typical lubricant properties [17]. Castor oil is a raw material with optimum quality for lubricants [22, 23]. The mixtures of castor oil and adipic esters (C1 and C2) can also be a source of raw materials with improved quality for lubricants. They are physical homogeneous mixtures. Characteristics of the studied mixtures have shown that they are superior to mineral oils. With proper viscosity and viscosity indices, they can be used as lubricants for engines and machines demanding.

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