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The use of rosemary extracts in vegetable oil-based lubricants

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ABSTRACT

The use of vegetable oils as basestocks represents an important alternative to mineral lubricants. However, vegetable oil oxidation is a serious disadvantage for its use as a lubricant. In this sense, the use of natural antioxidant additives, which were obtained by different extraction processes from the rosemary plant, has been investigated to prevent the oxidation process in two selected potential vegetable oil-based lubricants (high oleic sunflower (HOSO) and castor (CO) oils). A variety of rosemary extracts with a different distribution of phenolic diterpene compounds have been obtained depending on the solvent used (n-hexane, methanol or 50% (v/v) methanol–water). The antioxidant resistance of these oils containing rosemary extract has been analyzed under accelerated conditions using both the ASTM D942-02 and ASTM E2009-08 standards. The results showed that the rosemary extracts are better solubilized in CO than in HOSO, obtaining the highest oxidation onset temperatures in CO. In addition to this, the rosemary extracts obtained with polar solvents had the highest concentration of rosmarinic acid, and showed a better antioxidant activity in CO; whereas the extract obtained with a non polar solvent had the highest concentration of carnosic acid, showing a better antioxidant activity in HOSO than the rest of rosemary extracts studied.

1. Introduction

Vegetable-based oils and fats were used as lubricant basestocks until the second half of the 19th century, when lubricants derived from crude oil were used almost exclusively due to their large range of performance, despite of being toxic, non-biodegradable, and a limited resource (Wagner et al., 2001; Verhé et al., 2004). Every year, around 2.5 million tonnes of used lubricants in Europe end up polluting the environment as result of total-loss lubrication or leaks, emissions, spillages or other problems (Luther, 2007). Consequently, during the last 25 years special attention has being paid to the protection of the environment against pollution caused by mineral-based lubricants. This worldwide environmental concern has resulted in a growing interest for the use of renewable and environmentally friendly lubricant formulations. Biodegradability has become one of the most important design parameters in the selection of the base fluid and the additives (Willing, 1999; Erhan and Asadauskas, 2000; Lazzeri et al., 2006; Quinchia et al., 2011). Thus, vegetable oil-based lubricants are being actively demanded for many green industrial activities.

In general, vegetable oils have some excellent properties for their potential use as lubricant basestocks, such as high viscosity index, high lubricity, low volatility, high flash point, and, specially, both low toxicity and high biodegradability (Erhan and Asadauskas, 2000; Bartz, 1998; Lea, 2002). However, some limitations should be technologically improved to allow their use in many industrial activities, particularly those related to their low thermal and oxidative stabilities (Quinchia et al., 2011; Erhan et al., 2006; Aluyor and Ori-Jesu, 2008).

Several attempts have been made to improve oxidative stability of vegetable oil-based lubricants using synthetic antioxidants additives, i.e., butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT), tert-butyl-hydroquinone (TBHQ) or 4,4′-methylenebis (2,6-di-tert-butylphenol) (MBP) (Becker and Knorr, 1996; Fox and Stachowiak, 2007; Merrill et al., 2008; Andréa et al., 2010; Quinchia et al., 2011). Nevertheless, there is an increasing interest in the use of natural antioxidant extracts because they avoid the toxicity problems which may arise from the traditionally used synthetic antioxidants. Vegetable extracts have been studied in relation to their antioxidant activity (Madsen and Bertelsen, 1995; Lindberg and Bertelsen, 1995; Hras et al., 2000; Briante et al., 2002; Malheiro et al., 2013), although most of the studies

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that highlighted the effects of the addition of natural antioxidants to vegetable oils are focused on edible oils (Khan and Shahidi, 2001; Shaker, 2006; Shyamala et al., 2005; Bera et al., 2006). In consequence, in this work, the greatest attention was paid to natural antioxidants from vegetable origin, particularly from rosemary (*Rosmarinus Officinalis* L.) extracts, which could show a powerful antioxidant activity on vegetable-based lubricants (Hras et al., 2000; Zhang et al., 2010).

The antioxidant activity of rosemary extracts is related to the presence of phenolic diterpene compounds, which block free radical chain reactions by hydrogen atom donation. A variety of previous studies have examined the antioxidant activity of rosemary extracts and isolated and identified a great variety of antioxidant compounds: monoterpenes and diterpenes like rosmanol, epirosmanol, isorosmanol, methyl carnosate, methoxyepirosmanol, rosmariquinone and rosmaridiphenol, phenolic acids, flavonoids and triterpenic acids, like ursolic, oleanolic, and betulinic acids (Wu et al., 1982; Frankel et al., 1996; Basaga et al., 1997; Hras et al., 2000; Arráez-Román et al., 2006; Thorsen and Hildebrandt, 2003; Wellwood and Cole, 2004; Hernández-Hernández et al., 2009; Zhang et al., 2010). Among them, the major phenolic diterpenes are carnosic acid (CA), carnosol (CAR) and rosmarinic acid (ROS) (Okamura et al., 1994; Frankel et al., 1996; Thorsen and Hildebrandt, 2003).

The main objective of this work has been developing new environmentally friendly lubricant formulations based on vegetable oil potentially usable as lubricant basestock (high oleic sunflower (HOSO) and castor (CO) oils) and rosemary extracts. With this aim, different solvent extraction techniques on rosemary plant were analyzed and the distribution of polyphenolic compounds in rosemary extracts were quantified using high-performance liquid chromatography (HPLC). Moreover, the antioxidant resistance of oil/rosemary extract blends were analyzed under accelerated conditions using both the ASTM D942-02 and ASTM E2009-08 standards, also comparing the antioxidant effect of these rosemary extracts with others synthetic antioxidants.

2. Materials and methods

2.1. Materials

Castor oil (CO) was submitted from Guinama (Spain) and high-oleic sunflower oil (HOSO), with 85 wt.% oleic acid and submitted to degumming, neutralization, bleaching, and deodorization processes, was kindly supplied by the "Instituto de la Grasa", CSIC (Spain). Vegetable oils fatty acid compositions and some physico-chemical properties are shown in Table 1.

Rosemary samples were collected in Huelva (region in the south-west of Spain) within the summer season. Rosemary's leaves and flowers were separated from the sticks, and then dried in a convection oven, model Digitronic (Selecta, Spain), at 30–33 °C for 24 h, according to the experimental procedure proposed elsewhere (Boutekedjiret et al., 1997).

Solvents employed in the experiments were HPLC grade: methanol (CAS RN: 67-56-1; density: 0.79 g/cm^3; boiling point: 64.5 °C) and n-hexane (CAS RN: 110-54-3; density: 0.66 g/cm^3; boiling point: 68 °C) from Scharlau (Spain). Also, a methanol–water mixture (50%, v/v) was used, being the distilled water obtained at our laboratory (conductivity at 20 °C, 1.6 μS/cm).

2.2. Extraction of antioxidant compounds and vegetable oil additivation

Dried rosemary leaves and flowering parts were subjected to Soxhlet extraction using methanol or n-hexane as solvent. Ten grams of rosemary leaves and 200 mL of solvent were used in a nine cycles extraction procedure. The concentrated solution was then filtered and the solvent was vacuum-distilled at 40 °C in a rotary evaporator, model Laborota 4001 (Heidolph Instruments, Germany). The remaining extract was finally dried in a conventional oven, model Digitronic (Bromatos S.L., Spain), at 30 °C for 2 h to ensure the total removal of any residual solvent. Dry extracts were stored in a freezer at −20 °C until use. When the 50% (v/v) methanol–water mixture was used as solvent, a direct extraction procedure was carried out: ground dried rosemary leaves and flowers were extracted in a bath with 200 mL of the methanol–water mixture at room temperature for 7 h 50 min. The extract was filtered, concentrated, dried, and stored as described above.

Table 1
Fatty acid composition and physical–chemical properties of the different vegetable oils studied.

Physico-chemical properties	Vegetable oils	
	HOSO	CO
Dynamic viscosity (Pa s) (40 °C)	0.0359	0.2293
Dynamic viscosity (Pa s) (100 °C)	0.0087	0.0187
Kinematic viscosity (cst) (40 °C)	38.55	211.05
Kinematic viscosity (cst) (100 °C)	9.99	21.00
Viscosity index	257	116.00
Peroxide value (meq O_2/kg)	23.11	3.76
Acidity (% oleic acid)	0.39	1.46
Iodine value	6.69	8.35
Polyphenols (mg/kg cafeic acid)	1067.23	637.16
Palmitic (C16:0)	3.84	1.70
Stearic (C18:0)	4.42	1.96
Oleic (C18:1)	83.66	5.34
Ricinoleic (C18:1:OH)	TRACE	82.48
Linoleic (C18:2)	8.08	7.01
Linolenic (C18:3)	TRACE	1.51

In relation to the vegetable oil additivation process, vegetable oils were blended with 1% (w/w) of each rosemary extract in batches of 55 cm^3. Rosemary extracts were added to the vegetable oils studied by stirring at 300 rpm during 90 min at temperature below 100 °C. A homogeneous single phase was obtained for n-hexane extract, but a certain degree of sedimentation was observed for both methanol and methanol–water mixture (50%, v/v) extracts. Consequently, the insoluble substances had to be removed by centrifugation. This fact was logically due to the non-polar nature of vegetable oils, which make easier the solubility of rosemary extract obtained with n-hexane than those extracted using polar solvents. Afterwards, samples were cooled down to room temperature. Resulting formulations were named according to the next rule: vegetable oil + solvent used in the extraction method. Therefore, COMe is castor oil with rosemary extract using MeOH; COHe is castor oil with rosemary extract using n-hexane; COMeW is castor oil with rosemary extract using a 50% (v/v) methanol–water mixture; the same criteria was assumed for HOSO.

2.3. Characterization methods

2.3.1. HPLC analysis

A high-performance liquid chromatographic analysis of rosemary extracts specifically to detect and quantify carnosic acid, carnosol, and rosmarinic acid was done. The analysis was performed with a Thermo Separation Products HPLC system (ThermoQuest, USA) equipped with a P4000 pump, an AS3000 autosampler and an UV/Vis photodiode array detector, model UV6000, with 50 mm lightpipe flow cell. The column was a reverse-phase Hypersil Gold C_{18} type with a 5 μm particle size, 250 mm × 4 mm i.d (Thermo Fisher Scientific, USA). The analytical mobile phases consisted of solvent A (840 mL water, 8.5 mL acetic acid, and 150 mL acetonitrile) and solvent B (methanol). The separation was carried