Oleins as a source of estolides for biolubricant applications

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1. INTRODUCTION

Interest in biolubricants derived from renewable sources, like vegetable oils, is growing due to their biodegradability, low toxicity and environmentally benign nature. In this sense, the synthesis of a new class of bio-based esters derived from vegetable oils that exhibit excellent flow properties at low temperatures and oxidative stability has been reported (Kodali, 2002). These advances are also possible due to progress in both vegetable oil biotechnology and chemical modifications, which can be used to apply these natural esters as components of high performance biolubricants. Thus, lubricants may contain a significant number of additives, which are used to either enhance an already existing useful property or impart desirable new characteristics. This is especially important in the case of vegetable oils (Maleque et al., 2003), which usually show some technical disadvantages, such as low thermo-oxidative stability, poor low-temperature properties, and a limited range of viscosity.

Soapstock and deodorizer distillates are the major by-products from vegetable oil refining. They have little commercial value and are sold at a fraction of the oil cost (Dumont and Narine, 2007). The use of fatty acids from soapstock as a thickener for multigrade lubricating grease has been investigated by El-Adly (2000) and Al-Wakeel and El-Adly (2005). Fatty acids are the major component of soapstock, after water has been extracted. They represent approximately 10% of the soapstock composition on a wet basis. As fatty acids are mainly used in animal feed, the extraction process must be cheap in order to be justified. Soapstock splitting using a mineral acid is the most common process and the oily phase is sold as olein.

Estolides are a class of ester resulting from the reaction between a carboxylic group in a fatty acid molecule and an unsaturation in another fatty acid molecule to form an ester linkage (Isbell et al., 1994, Isbell et al., 2000, Cermak et al, 2001). The number of these linkages determines the structure and properties of estolides. Different molecular parameters (e.g., molecular weight, branching, etc...) and physical properties (e.g. viscosity and density) are obtained by modifying the nature of the base material and reaction conditions. Moreover,
these products can improve thermal oxidative stability (Becker et al., 1996, Cermak et al., 2003), and low temperature properties of vegetable oils (Isbell et al., 1994).

Previous results have shown that oleic acid can be used to obtain estolides with remarkable viscosities, a fact that make them promising compounds for biolubricant applications (García-Zapateiro et al., 2008).

On the other hand, the use of olein as a base material for the synthesis of estolides may have additional benefits, mainly from an environmental point of view. This work deals with the synthesis and characterization of estolides derived from high-oleic sunflower oil oleins. These chemical products could be used as additives to increase the viscosity of vegetable oils for lubricant applications. Specifically, the effect of reaction time on estolide viscosities was analyzed.

2. MATERIALS AND METHODS

2.1. Materials

Oleins resulting from the refining treatment of high-oleic sunflower oil, supplied by COREYSA (Sevilla, Spain), were used as base material to obtain the estolides. Olein composition is shown in Table 1. The quantification of acidity, unsaponifiable matter and fatty acid composition was performed according to the IUPAC Standard Methods.

Highly concentrated sulphuric acid (98%), monobasic and dibasic phosphates, tetrahydrofuran (THF) and sodium sulphate, from Panreac (Spain), were also used to synthesize the estolides.

2.2. Synthesis of estolides

Estolides were obtained from olein by following the sulphuric acid-catalyzed method described elsewhere (Isbell et al., 1994). Fatty acid (100 g) was equilibrated at 50 °C for 10 min, followed by the addition of concentrated sulphuric acid (in stoichiometric proportion) in a stirred vessel. After 3-24 h, the reaction was quenched by pouring the blend into a separating funnel with 200 mL hexane. The hexane layer was washed twice with 100 mL portions of a 1M Na2HPO4 aqueous solution. The second wash with phosphate turned the black solution to yellow and formed an emulsion that was broken with THF (100 mL). The estolide solution was then washed twice with 100 mL of an aqueous phosphate buffer (pH 3.7, 129.7 g monobasic phosphate and 0.85 g dibasic phosphate in 1 L H2O), dried over Na2SO4, filtered and concentrated using vacuum distillation (120 to 160 °C; 0.5 torr) to yield 60.04 g of a dark colored product.

2.3. Viscosity measurements

Viscous flow tests were carried out in a rotational controlled-strain ARES rheometer (Rheometrics Scientific, UK), at temperatures between 10 and 120 °C, using a coaxial cylinder geometry (inner diameter: 32 mm, outer diameter: 34 mm, cylinder length: 33.35 mm). The shear rate range studied was between 5 and 1000 s⁻¹. All the samples show Newtonian behavior.

2.4. Density measurements

Density measurements were performed in a capillary densimeter, model DMA-5000 (Anton Paar, Austria) at temperatures between 10 and 120 °C.

2.5. Gel permeation chromatography (GPC)

GPC determinations were performed with a Waters apparatus, equipped with styragel HR 4E columns (500Å-7.8 x 300 mm), at 35 °C, using THF as eluent. A Waters 2414 refractive index detector was used. The flow rate was 1.0 mL/min. The number-average molecular weight (Mn), the weight-average molecular weight (Mw), and polydispersity index (Mw/Mn) were calculated relative to polystyrene standards.

3. RESULTS AND DISCUSSION

Table 1 shows the main groups of chemical components of the olein sample used in these assays. As can be observed, the free fatty acid (FFA) content is above 70%, and the glyceridic fraction, which comprises triglycerides and partial glycerides, is 25%. These considerations, and the previous experience with oleic acid (García-Zapateiro et al., 2008), make this byproduct a potentially excellent raw material for the oleochemical industry. Little information about direct applications has been found. In particular, modifications of epoxide resin through synthesis of chlorinated fatty acid and glycidyl ester of fatty acid were proposed from sunflower oil olein (Yazicigil and Ahmetli, 2008).
Concerning the physical properties of the olein used, Table 2 shows densities, dynamic and kinematic viscosities for this base material, in a temperature range of 10-120 °C. In addition, the viscosity index (VI) is usually calculated to evaluate the thermal susceptibility of lubricating oils. VI was estimated from the kinematic viscosity values at 40° and 100 °C, according to the ASTM D2270 standard. Olein used in this work had a VI value of 193.

Craig Isbell et al. (1994). In fact, a certain degree of polymerization has been detected in the initial olein sample, which shows two peaks in the GPC chromatogram, one corresponding to the mixture of triglycerides and free fatty acid content (around 500 g/mol, as expected) and another one corresponding to a fraction of higher molecular weight (1270 g/mol) (Table 3). This polymerized fraction results from the previous acid and thermal treatments applied on the olein. Aiming to establish the optimum reaction time for estolide synthesis, different reaction times were monitored, i.e., 3, 6, 12 or 24 h, much longer than those usually associated with an esterification process. For all estolide samples, the peak corresponding to the non-polymerized fraction still appears, but, as can be seen in Table 3, both weight-(Mw) and number-average (Mn) molecular weights, related to the polymerized fraction, depend on reaction time. Thus, a dramatic increase in molecular weight was observed after 3 h. Further increments were noticed after 6 h of reaction. On the contrary, quite similar molecular weights were obtained for reaction times between 6-12 h. Finally, a slight decrease in Mw and Mn was observed after 24 h of reaction, probably due to a thermal degradation of the sample.

Estolides dynamic and kinematic viscosities, at different reaction times and in a temperature range of reaction, probably due to a thermal degradation of the sample.
between 10 and 120 °C, are listed in Table 4. As can be observed, increments in estolide kinematic viscosities of around 1000% and 500% at 40 °C and 100 °C, respectively, relative to the corresponding olein viscosities, were obtained after a reaction time of 3 h. However, the maximum viscosity values were obtained after reaction times of up to 12 h, matching estolide maximum number-average molecular weight. On the contrary, estolide viscosities significantly decrease after 12h reaction time, a fact related to a lower molecular weight. This result confirms that estolide viscosity is controlled by the oligomerization degree (Cermak et al., 2001). The viscosity index for the estolides synthesized in this work was 178 ± 5, regardless of reaction time, slightly lower (7%) than that obtained for olein.

4. CONCLUSIONS

Estolides derived from high-oleic sunflower oil oleins have been obtained. The reaction time for a sulphuric acid-catalyzed conversion of oleins into oligomers significantly affects the average-weight molecular weight and, consequently, the kinematic viscosity of the estolides synthesized. Thus, a dramatic increase in molecular weight was observed after 3 h of processing, when the largest level of oligomerization takes place. Nevertheless, the maximum viscosities were obtained for reaction times comprising between 6-12 h, coinciding with the maximum values of the average molecular weights. These chemical products could be used as additives to increase the viscosity of vegetable oils for lubricant applications.

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