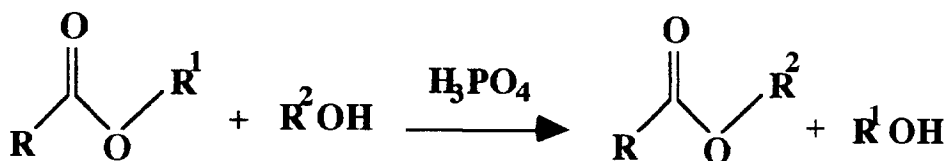


**SUNFLOWERATES 1: SYNTHESIS OF ALKYL OLEATES
BY TRANSESTERIFICATION OF OLEIC SUNFLOWER OIL
WITH C8-ALCOHOLS CATALYSED BY HYDRATED H₃PO₄.**

Corinne Dufaure and Zéphirin Mouloungui*,
E.N.S.C.T. - Laboratoire de Chimie Agro-Industrielle - U.M.R. INRA,
Route de Narbonne 118, 31077 - Toulouse Cedex 4, France
Fax : + 33 5 62 88 57 30 ; e-mail : zmouloungui@ensct.fr

Abstract :

Hydrated phosphoric acid is used to catalyse the transesterification of triglycerides by C8-alcohols (2-ethyl hexanol and octanol). Its catalytic activity is enhanced by the hydrodynamic nature of the reaction medium which is organised into hydrophobic/hydrophilic phases with the catalyst partitioned between the two phases. Esters yields exceeding 99% are obtained in 3-4 h at 130°C and 16% by weight of phosphoric acid using 2-ethyl hexanol at three times the stoichiometric amount.



R : fatty chain

2-Ethyl hexyl oleate and octyl oleate produced by the described process are submitted to qualifying tests to evaluate their ability to be used as base oils for biolubricants. The thermogravimetric analysis under N₂ and air show that the C8-sunflowerates are thermally stable as they decompose at temperatures around 320°C. They exhibit good resistance to hydrolysis (ASTM D2619). Their viscosities, viscosity index, pour point and flash point are measured together with their surfactant properties. The 2-ethyl hexyl and octyl sunflowerates possess the required characteristics for use as a base oil or additive for metalworking lubricants.

Résumé :

Le transfert d'acyle des triglycérides (TG) de l'huile de tournesol oléique vers les alcools gras (AG) est effectif par une réaction de transestérification réversible catalysée par l'acide phosphorique en réacteur agité. Dans des conditions expérimentales suivant les rapports molaires H₃PO₄ / TG : 0,29 à 1,48 ; AG / TG : 9/1, les températures 130 - 170 °C et des durées de l'ordre de 4 - 4,5 h, les oléates d'alkyles sont les produits formés avec des rendements de l'ordre de 85 - 98 %. La répartition de l'acide phosphorique entre les phases hydrophobe et hydrophile crée un milieu organisé. La réaction est interfaciale. Sa vitesse est augmentée. Sa sélectivité est élevée. Les rendements sont élevés.

Par analyse thermique différentielle les monooléates d'alkyle montrent une stabilité thermique sous hélium (gaz non réactif). Leur stabilité à l'hydrolyse est démontrée par le test d'hydrolyse réalisé selon la norme ASTM D2619.

Le domaine de la lubrification et notamment celui de l'usinage des métaux est ouvert à l'utilisation des oléates d'alkyles qui ont également des propriétés filmogènes.

* Auteur à qui toute correspondance doit être adressée

The transesterification of fats and oils is of industrial importance (1-2). This reaction requires a catalyst that may be protic or Lewis acids, bases and enzymes (3-6). Acidic protic catalysts are, in general, little used. Only sulfuric acid and sulfonic acids exhibit sufficient catalytic activity, if added in high proportions (5-6). The kinetics of the acid-catalysed reaction are therefore slow. In addition these strong acids accumulate various disadvantages such as the induction of side reactions on the unsaturated fatty chains, severe corrosion of the equipment used in the manipulations and difficult elimination of the catalyst in the post-reaction phase.

We propose the use of hydrated phosphoric acid (85% in water) which is a milder acid, to catalyse the production of esters by transesterification of triglycerides by lipophilic alcohols in a free solvent media. We think that the strength of the undissociated phosphoric acid is enhanced by the traces of water. This results in the reversible desired reactions taking place in a hydrodynamic system organised into hydrophobic/hydrophilic phases with the phosphoric acid partitioned between these phases (7-8). We conducted a study of the chemical reactivity occurring between triglycerides obtained from crude oleic sunflower oil (9-10) and 2-ethyl hexanol to produce 2-ethyl hexyl esters. 2-Ethyl hexanol was chosen as the model alcohol. Octanol was used in a second time. We then shown that 2-ethyl hexyl oleates and octyl oleates exhibit good resistance to heat and hydrolysis, together with desired viscosity and surfactant properties. The 2-ethyl hexyl esters possess the required characteristics for use as a base oil or additive for metalworking lubricants.

Experimental part :

Chemicals : The oil was obtained by cold pressing of oleic sunflower seeds (La Toulousaine de Céréales, St Orens, France ; harvested 1996) in a twin-screw extruder BC21 (Cletral, Firminy, France) (9). The acid value of this oil was 1.65 mg KOH/g oil, the water content 0.05% and the phosphorus content was about 98 mg/kg of oil. The fatty acids of the triglycerides (TG) were palmitic acid (3.2%), stearic acid (2.4%), oleic acid (89.9%) and linoleic acid (4.5%). 2-Ethyl hexanol (2EH, 99%), octanol (OCT, 99%) and phosphoric acid (H3PO4, 85%) were purchased from Prolabo (Gradignan, France).

Study of the transesterification of the oleic oil : 8.80 g of oil (0.01 mol TG) were heated in a 100 ml 3-necked flask equipped with a mechanical stirrer (250 rpm) and a condenser, with 2EH and H3PO4 in various proportions (see table 1) under nitrogen for 3 h. After cooling at the end of the reaction, the released glycerol, that had been acidified by H3PO4, settled out. This permitted rapid separation of the hydrophobic ester-alcohol phase from the hydrophilic glycerol-water phase. The reaction was followed by thin layer chromatography-flame ionisation detection (TLC/FID) system and the esters quantified (11). We calculate the esters yield which is the ratio of the mass of esters produced to the potential mass of esters which would be produced if all the triglycerides had been transformed into esters.

$$R \text{ (as \%)} = 100 * (\text{mass of esters produced} / \text{potential mass of esters})$$

Qualificating tests : samples of 2-ethyl hexyl sunflowerate and octyl sunflowerate have been produced by transesterification of the oleic sunflower oil catalysed by H3PO4 (200 g of oleic oil, molar ratio alcohol/TG of 6/1, molar ratio H3PO4/TG of 1/1, 7 h at 130°C, 500 rpm). After separation by decantation, the hydrophilic phase containing the esters is desacidified by elution on an adsorbent resin (Amberlyst IRA 93SP). The remaining alcohol is then distilled out.

Results and discussion :

Transesterification reaction : The results are summarised in table 1.

Entry	Molar ratio 2EH/TG	Molar ratio H3PO4/TG	Temperature (°C)	Esters yield (%)
1	6:1 ^a	1.48	130	95
2	9:1 ^b	1.48	130	99
3	9:1 ^b	0.29	170	90

a : twice the stoichiometric amount ; b : three times the stoichiometric amount. ; reaction time : 3h ; 250 rpm.
Table 1 : Esters yields for the transesterification of oleic sunflower oil by 2-ethyl hexanol catalysed by H3PO4.

The conversion of triglycerides by 2-ethyl hexanol was achieved with high esters yields above 90% in 3 hours. A moderate temperature of 130°C, a molar H₃PO₄/TG ratio of 1.48 and a low amount of alcohol (2 times the stoichiometric amount) ensured adequate operating conditions and esters yields exceeding 95% (test 1). The reaction equilibrium was completely displaced after a reaction time of 3 hours at 130°C as 99% of the oil was converted in test 2 when 3 times the stoichiometric amount of 2-ethyl hexanol and a molar H₃PO₄/TG ratio of 1.48 were used. The reaction also proceeded well with a catalytic amount (0.29 equiv.) of H₃PO₄ when a higher temperature was tested (test 3).

The reaction system consisted of two phases. The main hydrophobic phase was composed of triglycerides and 2-ethyl hexanol at the beginning of the reaction and of 2-ethyl hexyl esters and 2-ethyl hexanol at the end of the reaction. 2-Ethyl hexanol served both as a reagent and as diluent for the triglycerides. It exhibits co-surfactant properties because of its C₈ structure and is an isomer of octanol. Its interfacial tension at equilibrium with water is in fact 13.5 mN/m at 25°C (compared with 8.3 mN/m for octanol) (7). The hydrophilic phase consisted of phosphoric acid and water at the beginning of the reaction and of a glycerol-phosphoric acid-water mixture at the end of the reaction. This hydrophilic phase increased as the reaction progressed, and partitioning of the phosphoric acid between the hydrophilic and hydrophobic phases improved. Thin Layer Chromatography/Flame Ionisation Detection (TLC/FID) analysis of the hydrophobic phase revealed the transient presence of diglycerides and monoglycerides amongst the components of the reaction medium. These partial glycerides and the 2-ethylhexyl esters help to structure the interface of the reaction system. The constitution of the heterogenic hydrophobic/hydrophilic medium is propitious to the catalytic activity of phosphoric acid.

Qualifying tests

- The thermal behaviour of the esters is evaluated under nitrogen (inert gas) and air (reactive gas) with thermogravimetric analysis coupled with differential thermal analysis (TGA/DTA) (12). Results are shown in table 2.

Compound	Atmosphere	Onset of weight loss (°C)	Onset of degradation (°C) ^a
2-ethyl hexyl oleate	nitrogen	180	330
	air	190	320
octyl oleate	nitrogen	200	330
	air	210	320

a: indicated on the DTA curves.

Table 2: TGA-DTA analysis of 2-ethyl hexyl oleate and octyl oleate.

The 2-ethyl hexyl and octyl oleate produced are thermally stable compounds. The presence of the double bond on the fatty chain does not badly influence the thermal behaviour of our products (12).

- The hydrolysis stability of the esters is determined according to the ASTM D2619 method (table 3). The viscosity and acid value of the products remain constant after the test (48 h heating at 93°C of a water/esters mixture (25/75) in the presence of copper). The hydrolysis stability of the 2-ethyl hexyl oleate and octyl oleate is therefore very good.

Compound	Viscosity changing (%)	Total acidity changing (mg KOH/g)	Total acidity of water (mg KOH/g)	Weight loss for copper (mg/cm ²)
2-ethyl hexyl oleate	+0,1	+0,38	6,32	-0,67
octyl oleate	+0,3	+0,23	2,47	-0,36

Table 3: Hydrolysis stability tests (ASTM D2619) for 2-ethyl hexyl oleate and octyl oleate.

The total acidity of water after the test and the value of the weight loss for copper are high. This shows that the synthesised esters are aggressive against metals in the experimental conditions of the test that are drastic and far from the usual metalworking operating conditions. As for petrochemical base oils, the C₈-sunflowerates produced have to be formulated with additives such as metal passivators for their use as biolubricants.

- The cinematic viscosities at 40°C and 100°C (ASTM D-445), the viscosity index (ASTM D-2270), the pour point (ASTM D-97) and the flash point (ASTM D-93) of the 2-ethyl hexyl

oleate and octyl oleate have been measured (table 4). Reference values are also given to evaluate the ability of the C8-sunflowerates to be used as base oils for lubricants.

Properties	2-ethyl hexyl oleate	octyl oleate	Petrochemical base oil ^a	2-ethyl hexyl stearate (b)
Viscosity at 40°C (cSt)	8,30	8,63	7	10
Viscosity at 100°C (cSt)	2,66	2,85	1	3,1
Viscosity index	177	207	100	180
Pour point (°C)	-31	-4	<-18	7 ^c
Flash point (°C)	160	178	>152 ^c	215

(a) : commercial petrochemical base oil for lubricants ESSO 60 NEUTRAL (b) : RADIA 7131 (FINA) ; (c) : method not specified ;

Table 4 : Properties of the 2-ethyl hexyl oleate and octyl oleate.

The viscosity of the 2-ethyl hexyl oleate and octyl oleate are similar to those of commercial base oils (8.30 and 8.63 cSt compared to 7 cSt at 40°C). Their viscosity indexes are higher, showing that the temperature has only little influence on the viscosity of C8-sunflowerates. The temperatures associated with the pour point and the flash point are also good.

If we compare with 2-ethyl hexyl stearate, the double bond of the oleic chain decreases the viscosities and the pour point of the C8-oleates, permitting an use at low temperatures.

The viscosities of the branched alkyl esters (2-ethyl hexyl esters) are lower than the viscosities of the linear alkyl esters (octyl esters). The arrangement of the ramified molecules is less compact leading to a higher mobility of the molecules and an increase of the volatility of the ramified product (flash point lower for the 2-ethyl hexyl esters). The behaviour at low temperatures for the 2-ethyl hexyl esters is better than for the octyl esters as their pour point is lower.

• The surfacting properties of the 2-ethyl hexyl oleate and octyl oleate have been evaluated by measuring of the interfacial tensions at the interface water/soya oil by I.T.Concept (Longessaigne, France). For each ester tested, the evolution of the interfacial tension as a function of time and for different massic concentration of the esters in the soya oil (10 to 100%) is presented on figures 1 and 2.

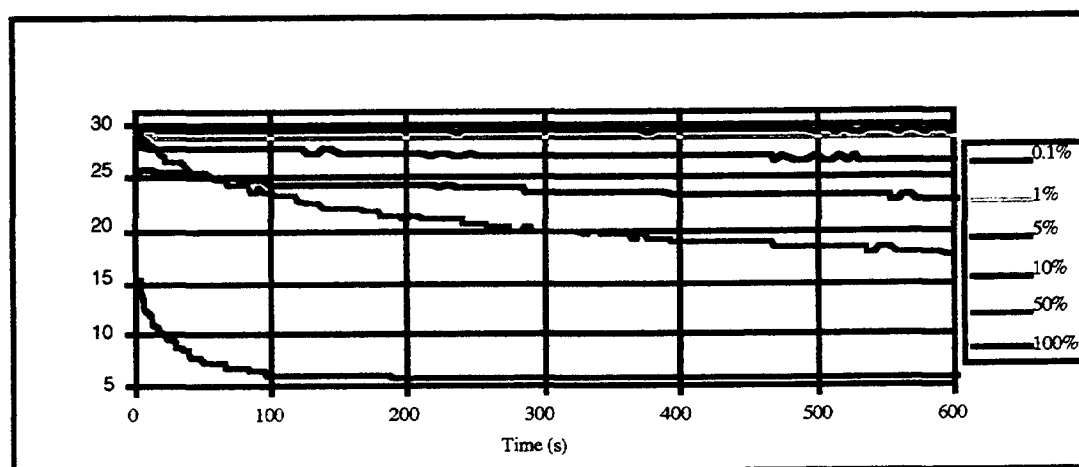


Figure 1 : Evolution of the interfacial tension as a function of time for 2-ethyl hexyl oleate in soya oil.

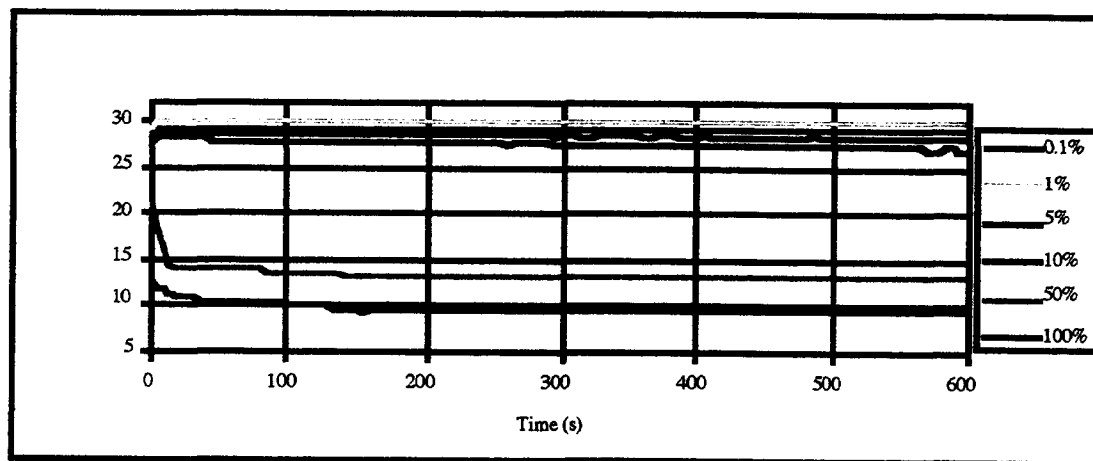


Figure 2 : Evolution of the interfacial tension as a function of time for octyl oleate in soya oil.

Interfacial surface tensions lower than 10 mN/m are obtained for an interface water/esters, showing the surfacting properties of the 2-ethyl hexyl and octyl sunflowerates.

Conclusion :

To summarise, phosphoric acid is an effective catalyst for the transesterification of vegetable oils. These first trials gave satisfactory yields under non-optimised experimental conditions. The key to the phosphoric acid activity is the nature of the biphasic hydrophobic/hydrophilic system. The present procedure has many advantages : (i) The catalytic activity of phosphoric acid permits the use of a low molar ratio of triglycerides/fatty alcohol, in the order of 2 to 3 times the stoichiometric value. (ii) Mild reaction conditions are used for a high weight alcohol (130°C). (iii) High conversion yields and a selective reaction towards the final esters are attained. (iv) The procedure is of general applicability. Phosphoric acid is an excellent catalyst of the envisaged lipochemical reactions which could be extended to any vegetable oil or fat and to any lipophilic alcohol.

The thermal and hydrolytic stabilities of the 2-ethyl hexyl sunflowerate and octyl sunflowerate obtained by the described process are very good. Thanks to their oleic unsaturated fatty chain, these products are fluid. Their viscosities, coupled with low pour points and high flash points, are very well adapted to the field of lubrication, specially as metalworking lubricants. The alkyl radical lowers the pour point of the fatty esters allowing an use at low temperature. The surfacting properties of this C8-sunflowerate base oil will moreover enhance the miscibility of the additives in the formulated biolubricant.

References :

- (1) MEFFERT A., J. Am. Oil Chem. Soc., 1984, 61, 255.
- (2) MAAG H., J. Am. Oil Chem. Soc., 1984, 61, 59.
- (3) OTERA J., Chem. Rev., 1993, 93, 1449 and references therein.
- (4) RANU B.C., DUTTA P., SARKA A., J. Org. Chem, 1998, 63, 6027.
- (5) SONNTAG N.O.V., J. Am. Oil Chem. Soc., 1979, 56, 751A.
- (6) FREEDMAN B., PRYDE E.H., MOUNTS T.L., J. Am. Oil Chem. Soc., 1984, 61, 1638.
- (7) LACAZE-DUFAURE C., PhD Thesis from the Institut National Polytechnique de Toulouse n°1438 (July 1998).
- (8) MOULOUNGUI Z., LACAZE-DUFAURE C., GASET A., RIGAL L. french patent n° 98/08062 : Process of Production of Alkyl Esters by Transesterification or Alcoholysis.
- (9) DUFAURE C., LEYRIS J., RIGAL L., MOULOUNGUI Z., J. Am. Oil Chem. Soc. Part I, 1999, 76, 1073.
- (10) DUFAURE C., MOULOUNGUI Z., RIGAL L., J. Am. Oil Chem. Soc. Part II, 1999, 76, 1081.
- (11) LACAZE-DUFAURE C., MOULOUNGUI Z., J. of High Resolution Chromatography, 1999, 22, 191.
- (12) DUFAURE C., THAMRIN U., MOULOUNGUI Z., Thermochim. Acta, 1999, 338, 77.
- (13) VERMEERSCH G., O.C.L., 1996, 3, 19.