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Recovery, Purification, Analysis and Chemical Modification of a Waste Cooking Oil

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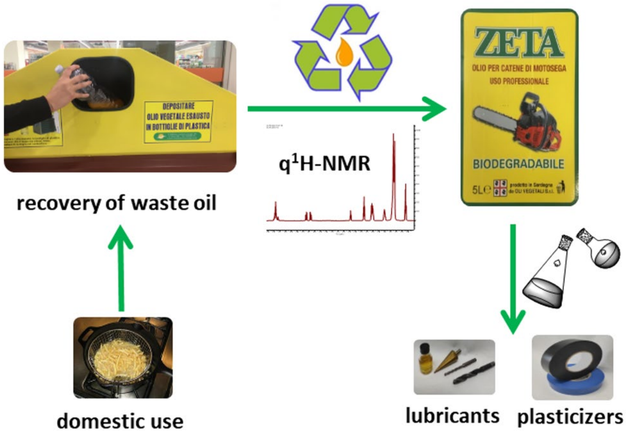
Abstract

Disposing of residual cooking oil is a major environmental concern, so its conversion into commercial products is a desirable goal. To design the chemical modification of a domestic waste oil into valuable biochemicals other than biodiesel, we analyzed a series of its samples, collected over a period of three years, using quantitative ^{1}H-NMR. This analysis, allowing a quick determination of its main chemical characteristics, has rendered the image of a vegetable oil with an almost constant composition over time and with a relative low content of saturated fatty acids. To make this collection protocol more economical, we projected its chemical transformation into esters and epoxidized esters of long chain and branched alcohols, which could find employment as biolubricants and/or bioplasticizers. The one-pot transesterification of the waste cooking oil into esters of commercially available and biodegradable Guerbet alcohols was obtained under environmentally friendly conditions by employing commercial CaO as a catalyst. Additionally, microwave irradiation of this reaction allowed to optimize the energy expenditure by significantly reducing the reaction time as compared with reactions run under conventional heating. To improve their oxidation stabilities, the resulting esters were epoxidized under conditions useful to minimize side-reactions. An investigation of their main rheological properties shows that some of the resulting products display characteristics that make their use as biolubricants or bioplasticizers predictable. The entire process represents a virtuous example of circular economy.

Graphical Abstract



Keyword Waste cooking oil –Quantitative ^{1}H-NMR—Microwave-assisted transesterification – Epoxidation – Plasticizers – Biolubricants

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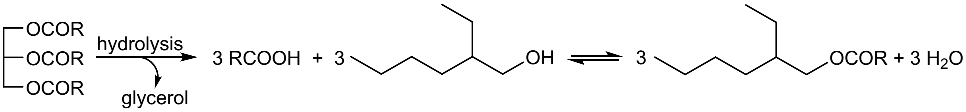


Scheme 1 Synthesis of 2-EtC_6H_{12}OH esters of fatty acids via hydrolysis/esterification; R = fatty acid chain

Statement of Novelty

Thanks to an original harvesting protocol, we have recovered as a secondary raw material a pre-purified waste cooking oil with a chemical composition almost constant over time, containing a high percentage of mono and polyunsaturated fatty acids.

To aid in designing its transformation into biochemicals other than biodiesel, several pre-purified samples were analyzed using a non-destructive control method that significantly reduces the analysis time and the amount of sample required.

Accordingly, its chemical modification under low impact conditions afforded valuable biochemicals, as supported by the determination of the physico-chemical properties of some of the resulting products.

Introduction

The valorisation of wastes [1, 2] is a key concept in reducing the environmental impact and costs of chemical productions. Waste cooking oil (WCO) is a widely available and inexpensive renewable resource whose uncontrolled disposal is responsible for severe environmental pollution, with ample potential to be transformed into a variety of useful biochemicals [3–8]. In 2018, around 1,400,000 tons of vegetable oils and fats were consumed for food purposes in Italy. A significant share of these oils, around 20%, was disposed of after the cooking process, which means a supply potential of 260,000 tons of WCO. In the same year, the WCO recovery was 76,000 tons, three to four times lower than the supply potential; 90% of the treated and cleaned WCO was sold to a biodiesel producer and the remaining 10% was used in the production of biolubricants, soaps, waxes, inks, or cosmetics [9].

In Sardinia, one of the two main islands of Italy, consuming approx. 7500 ton/year of vegetable oils and not furnished with plants for the production of biodiesel, WCO is successfully collected by a local company, Il Gabbiano Industria Ecologica s.r.l. (Porto Torres, Italy), that developed an original harvesting system differentiating WCO produced by commercial activities from WCO produced by domestic use. Whilst WCO from commercial activities is conferred to the production of biodiesel, WCO from domestic use is purified and locally marketed as an oil for chainsaw chains (120 tons/year) and other biochemicals (100 tons/year), such as lubricants and release agents for concrete.

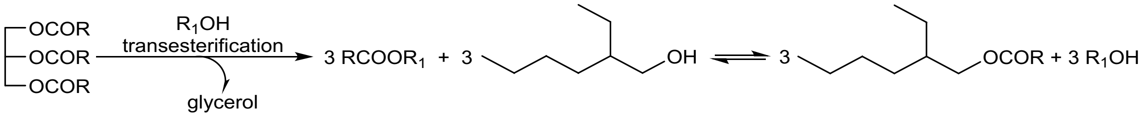
In this article we report our efforts to make this harvesting protocol even more cost effective by designing the chemical modification of the chainsaw chain oil into valuable biochemicals other than biodiesel [8]. To this end, we further characterized this purified oil by means of quantitative ^{1}H-NMR (q ^{1}H-NMR). As an advantage over the most common protocols, this spectroscopic technique affords an almost complete characterization of vegetable oils within short times, consuming extremely small quantities of samples and of a single solvent [10–12]. According to thus obtained analytical results, we designed the chemical modification of this renewable resource into valuable biochemicals, namely esters and epoxidized esters of 2-ethyl-1-hexanol (2-EtC_6H_{12}OH) and 2-butyl-1-octanol (2-BuC_8H_{16}OH), two commercially available Guerbet alcohols [13, 14] which are considered biodegradable [15].

Indeed, 2-EtC_6H_{12}OH is one of the most important synthetic alcohols [16], and its esters with saturated and monounsaturated fatty acids found employment as non-toxic and biodegradable low viscosity solvents, in the production of biolubricants, as well as in the cosmetic and pharmaceutical industries [17–21]. On the other side, 2-BuC_8H_{16}OH, which comes naturally in safflower oil [22], is used as a solvent and an emollient in the cosmetic industry [23, 24].

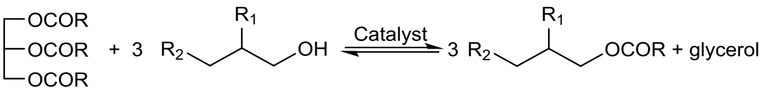
Among epoxidized esters of vegetable oils, epoxidized isooctyl soyate (E-2-EtC_6H_{12}Soyate, Vikoflex® 4050) is employed as a low temperature plasticizer providing heat and light stability in vinyl formulations [25], as a scavenger for the hydrochloric acid released from PVC at high temperatures [26], or as a component of a biocide to protect PVC from attack by microorganisms [27]. Additionally, epoxidized esters of WCOs with 2-EtC_6H_{12}OH proved to be effective alternatives to dioctyl phthalate as plasticizers for PVC [28], as well as valuable biolubricants with good oxidation stability and low-temperature properties [29].

As an additional advantage, according to the European Chemicals Agency (ECHA) non-epoxidized [30] and epoxidized [31] esters of 2-EtC_6H_{12}OH with unsaturated fatty acids are readily biodegradable.

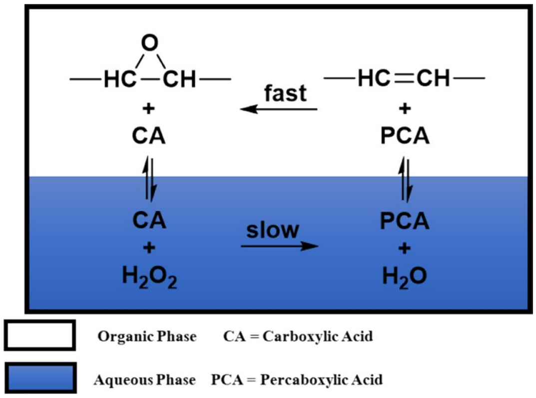
Esterification of vegetable oils with 2-EtC_6H_{12}OH, is usually run in two steps. A first methodology involves the hydrolysis of vegetable oils followed by esterification of the resulting fatty acids catalyzed either by enzymes [21], or by acidic homogeneous [32] or heterogeneous [33] catalysts (Scheme 1).



Scheme 2 Synthesis of 2-Et$C_6H_{12}OH$ esters of fatty acids via a double transesterification procedure; R = fatty acid chain; $R_1 = CH_3$ or C_2H_5



Scheme 3 Synthesis of Guerbet alcohols esters of fatty acids via a direct transesterification procedure; R = fatty acid chain; 2-Et$C_6H_{12}OH$: $R_1 = C_2H_5$, $R_2 = C_3H_7$; 2-Bu$C_8H_{16}OH$: $R_1 = C_4H_9$, $R_2 = C_5H_{11}$; Catalyst: CH_3ONa or CaO



Scheme 4 Schematic diagram of the epoxidation reaction with a percaboxylic acid (PCA) generated in situ from a carboxylic acid (CA) and aqueous H_2O_2, and mass transfer between phases; adapted from ref. 38

As an alternative, 2-Et$C_6H_{12}OH$ esters are obtained by a transesterification of the vegetable oils with methanol (or ethanol), followed by transesterification of thus obtained biodiesel with 2-Et$C_6H_{12}OH$ in the presence of a basic catalyst (e.g., CH_3ONa [18] or K_2CO_3 [20], Scheme 2). A comparable procedure was successfully applied to the synthesis of the epoxidized 2-Et$C_6H_{12}OH$ ester of a WCO catalyzed by CaO, a particularly cheap and easily available base [29].

Interestingly, a single example involves the one-pot transesterification of soybean oil with 2-Et$C_6H_{12}OH$ [34]. As a distinct advantage, operating such a transformation in a single step maximizes atom economy, increases energy efficiency, and minimizes both reaction waste and the employment and wear of the necessary equipment's. On the other side, such a reaction was catalysed with CH_3ONa, a strong base usually generated under harsh reaction conditions, e.g., by reacting dry CH_3OH with Na metal.

To set-up an environmentally friendlier synthetic approach, we investigated the one-pot transesterification of our WCO's with Guerbet alcohols catalyzed by commercially available CaO (Scheme 3). To optimize the energy expenditure, the results obtained under conventional heating were compared with results obtained under microwave irradiation.

Besides transesterification, epoxidation is one of the most widely applied chemical modifications of vegetable oils. Despite the availability of several efficient methodologies to synthesize epoxidized vegetable oils, the Prilezhaev reaction is probably the most widely employed methodology, mostly at the industrial level [35–37]. The overall reaction is a two-step process occurring in a biphasic system, as diagrammatically shown in Scheme 4.

In the first, rate determining step [39], the peracid is generated by the reaction of a carboxylic acid, usually CH_3COOH or HCOOH, with a concentrated aqueous solution of H_2O_2 (30–60% w/w). Formation of peracetic acid usually requires the presence of catalytic amounts of a strong Brønsted acid which, on the other side, is unnecessary to generate performic acid [39]. In the second step, formation of the oxirane ring occurs after migration of the peracid to the organic phase, where it reacts with the carbon–carbon double bonds leading to a highly exothermic (-55 kcal/mol for each double bond) reaction [40].

Numerous research works are dedicated to the optimization of the selectivity of this reaction, with particular attention to the set-up of useful conditions to avoid runaway reactions [40–42], to substitute homogeneous with heterogeneous acidic catalysts [38, 43, 44], to evaluate the activity of these last catalysts under conventional or microwave heating [45], and to avoid the formation of by-products due to the acid-catalyzed ring opening of the oxiranes [12, 38, 39, 43, 46–48].

At this level of our research, with the aim of using a relatively simple procedure able to avoid the formation of by-products, we decided to perform the epoxidation of both the WCO and the Guerbet esters with HCOOH and H_2O_2 in the presence of an organic co-solvent, thus avoiding the addition of other acids [39].

Finally, we will report on some of the physicochemical properties (cloud point, kinematic viscosity, viscosity index and oxidation stability) of the starting material and some of the corresponding esters and epoxidized esters to envisage their possible applications.

Experimental

Materials Information

Four different samples of WCO (termed as WCO_1 to WCO_4) were provided by Il Gabbiano Industria Ecologica srl (Porto Torres, Italy) within a three-year span of time. Al_2O_3 (neutral, Brockmann® I), Celite, CaO (99.9%), dry Na_2SO_4 and $CDCl_3$ (99.8% atom D), were purchased from Sigma-Aldrich. AcOEt (> 98%), 2-ethyl-1-hexanol (> 99.5%), 2-butyl-1-octanol (> 98%) and HCOOH (> 99.5%) were purchased form TCI. 30% H_2O_2 was purchased from VWR BDH Chemicals.

Preliminary Purification of WCOs

WCO, which is conferred in capped plastic bottles, is drained from the bottles and coarsely filtered through a 2 mm stainless steel strainer filter to remove the macroscopic solid residues, washed with water in a counter-current washing tower (400 mm diameter, 5000 mm high) and decanted by means of a series of 3 successive stainless-steel tanks (10 m^3 each). The oil separated from the washing water is thereafter filtered twice, first through a 10-micron bag filter and, after vacuum dehydration (600 mmHg, 70 °C), through a 5-micron paper filter with a 1 atm maximum differential pressure. The resulting product is collected in 5 L sealed plastic tanks and labelled as biodegradable chainsaw chain oil. During this work, four different WCO samples (purified as described above and referred to as WCO_1-WCO_4) were collected and used as starting materials over a three-year span of time.

Titration and Deacidification of WCO

The free fatty acid content (%FFA) of WCOs was determined according to IUPAC's recommendation [49]. Deacidification was run in a 3 L Erlenmeyer flask by dissolving 1 L of WCO into 760 mL of AcOEt followed by the addition of 100 – 200 g of neutral Al_2O_3. The resulting mixture was slowly stirred (to avoid excessive fragmentation of Al_2O_3 particles) at rt overnight, then filtered over Celite, dried (Na_2SO_4) and the filtrate evaporated to afford the deacidified WCO.

NMR Experiments

^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz spectra were recorded with a Bruker Ascend 400 spectrometer in $CDCl_3$ (99.8% D content) solution with the residual peak of $CHCl_3$ as reference for the chemical shift values. Quantitative ^{1}H-NMR analyses of WCOs were run in agreement with literature data (Fig. S1, Supporting information) [10–12].

CaO Catalysed Transesterifications Under Conventional Heating

CaO from a freshly opened container (Sigma-Aldrich, 99.9%) was stored in an oven at 120 °C during 48 h and chilled to rt in a desiccator immediately before use. Transesterification of WCO_3 with 2-$EtC_6H_{12}OH$ is illustrative of a general procedure.

The reaction was run under dry Ar in a 500 mL two-necked round-bottom flask equipped with magnetic stirrer, dropping funnel and reflux condenser connected with an Ar inlet. The reactor was immersed in a thermostatic bath oil. Dry CaO (15 or 25 mol % of WCO) was added to a mixture of 100 g (0.11 mol) of deacidified WCO_3 and 2-$EtC_6H_{12}OH$ (1.1 to 2.0 equivalents) and the resulting mixture was vigorously stirred at the temperature and during the time reported in Table V. The resulting mixture was filtered over Celite, separated from glycerol, washed several times with brine until neutrality, dried with Na_2SO_4 and evaporated to recover excess of 2-$EtC_6H_{12}OH$. The reaction product was characterized by ^{1}H- and ^{13}C-NMR.

Microwave-Assisted CaO Catalysed Transesterifications

Microwave-assisted reactions were run in a CEM Discover microwave apparatus, consisting of a continuous microwave power delivery system with operator selectable power output from 0—300 watts., a self-adjusting single mode microwave cavity and an infrared temperature control system, located below the microwave cavity floor, that monitors reaction temperature and pressure and maintains the desired temperature (between 0 and 300 °C) by computer control. The transesterification of WCO_3 with 2-$EtC_6H_{12}OH$ is illustrative of a general procedure.

In a 10 mL vial were charged under dry Ar 0.9 g (1.5 mmol) of deacidified WCO_3, 1.1 to 2.7 equivalents of 2-$EtC_6H_{12}OH$ and dry CaO (15 to 25 mol %). The vial was inserted into the microwave apparatus and irradiated at 200 W for the time and at the temperature reported in Table

VI. The resulting mixture was filtered over Celite, separated from glycerol, washed several times with brine until neutrality, dried with Na_2SO_4 and evaporated to recover excess of 2-EtC_6H_{12}OH. The reaction product was characterized by ^{1}H- and ^{13}C-NMR.

Characterization of CaO

Characterization of dry CaO by Infrared spectroscopy was performed with a Jasco FT-IR 4600 spectrophotometer operating in ATR mode.

Epoxidation

Epoxidation of WCO_3 is illustrative of a general procedure. The reaction was run in a 250 mL three-necked spherical glass reactor (internal maximum diameter 95 mm) immersed in a thermostatic bath oil and equipped with an egg-shaped magnetic stir bar (length 25 mm, diameter 12 mm), dropping funnel, internal thermometer and reflux condenser. 50 g of the substrate (WCO_3, 5.6×10^{-2} mol, 3.81 C = C/mol) was dissolved in 100 mL of toluene and chilled at 0 °C. To this mixture were successively dropwise added 7.9 mL of HCOOH (9.6 g, 2.1×10^{-1} mol); the mixture was then conditioned at 0 °C for 5 min. Next, under stirring, 64.3 ml of hydrogen peroxide (30% w/w, 6.3×10^{-1} mol) were added dropwise during 30 min. Once the addition was finished, the mixture was stirred at 1400 rpm (onset of the vortex at 550 rpm) and heated at 60 °C ($\Delta T = \pm 8$ °C) for 6 h, then chilled at rt and the biphasic solution separated. The organic phase was washed with saturated $NaHCO_3$ (100 ml), saturated NaCl (100 ml) and H_2O (100 ml). The resulting organic phase was then dried with anhydrous $MgSO_4$ and, after filtration, distilled under vacuum to remove the toluene. The reaction product was characterized by ^{1}H- and ^{13}C-NMR.

Oxidation Stability

Pressurized differential scanning calorimetry (PDSC) experiments were accomplished using a Sensys calorimeter by Setaram (Lione, France) equipped with stainless steel hermetic high-pressure cells. Typically, a sample mass between 35 and 60 mg was placed in the crucible of the high-pressure cells, that was closed under air. As a reference, a high-pressure empty cell was used. The cells were pressurized at 9 bars of pure dry oxygen (99.999%; provided by SOL S.p.A, Monza, Italy). A 10 °C min^{-1} heating rate from 25 °C to 250 °C was used during each experiment. The oxidation onset (OT, °C) and signal maximum temperatures (SMT, °C) were obtained from the calorimetric profile for each experiment. Each sample was run in triplicate and the average values rounded to the nearest whole degree are reported together with their standard deviation values.

The oxidation onset temperature is a relative measure of the degree of oxidative stability in a material evaluated for a given heating rate and oxidation environment. The signal maximum temperature is the temperature at which maximum heat output is observed in the sample during oxidative degradation. The calorimeter was calibrated with pure indium before the temperature evaluations.

Results and Discussion

Collecting and Purification of WCOs

WCO was collected in capped plastic bottles delivered either through a door-to-door collection system or by depositing the capped bottles in special street containers. The purpose of this collection method is to avoid mixing the oil from domestic users with that from commercial activities. Indeed, the latter usually contains a high percentage of palm oil whose relatively high content of saturated fatty acids determines its relatively high melting point. As described below, this selection allows to recover a WCO containing a relatively low percentage of saturated fatty acids (< 17%). After filtering, washing and drying, recovered WCOs were submitted to titration to determine their %FFA. Indeed, it is well known that WCOs usually contain a relatively high %FFA and these impurities negatively affect the efficiency of base-catalysed transesterifications [50].

Therefore, we determined the %FFA of all WCOs under investigation according to IUPAC's recommendation [50]. The results, as reported in Table 1 (column 3), show a relatively high content of FFA, thus suggesting the need to

Table 1 Deacidification of WCOs with neutral Al_2O_3[a]

Entry	Sample	%FFA before deacidification	%FFA after-deacidification
1	WCO_1	0.822	0.069
2	WCO_2[b]	1.860	1.045
3	WCO_2[c]	1.045	0.372
4	WCO_2[d]	1.045	0.055
5	WCO_3	0.700	0.062
6	WCO_4	0.692	0.062

[a] All deacidification procedures were run with a WCO/EtOAc = 1.3:1.0 (v/v) and a WCO/Al_2O_3 = 10:1 (w/w) unless otherwise indicated. [b] First run; [c] Second run. [d] Second run with a WCO/Al_2O_3 = 5:1 (w/w)

submit the different samples to an efficient deacidification procedure.

By modifying a patented procedure [51], the oil was dissolved in AcOEt (WCO/AcOEt = 1.3:1.0 v/v) and deacidified with neutral alumina (WCO/Al_2O_3 = 10:1 w/w), followed by filtration and evaporation of the solvent. The results, as reported in Table 1 (column 4), show the efficiency of this protocol leading to recover WCOs with %FFA < 0.2 in all cases but one (Table 1, entry 2). Partially deacidified WCO_2 was therefore submitted to a second deacidification procedure, either with a WCO_2:Al_2O_3 = 10:1 or 5:1 (w/w), leading to satisfactory results (Table 1, entries 3 and 4).

According to the original procedure [51], spent Al_2O_3 can be reactivated by washing with 1 M aqueous NaOH and water, followed by drying to remove moisture.

Characterization of WCOs

Quantitative ^{1}H-NMR (q^{1}H-NMR) was employed to determine significant chemical properties of the different batches of the deacidified WCOs: molecular weight (MW), iodine value (IV), average Carbon–Carbon double bond/mole (C = C/mol), % molar composition of saturated fatty acids (%SFA), mono-unsaturated fatty acids (%MUFA) and poly-unsaturated fatty acids (%PUFA), and the molar ratio between unsaturated fatty acids and saturated fatty acids (%UFA/%SFA, with %UFA = %MUFA + %PUFA) [10–12].

The results, as reported in Table 2, show that the main physico-chemical characteristics of the recovered WCOs do not vary to a great extent within the analysed batches, thus affording a picture of a secondary raw material [52] with an almost constant chemical composition, and demonstrating the effectiveness of the harvesting method.

To validate the above reported results, the fatty acid compositions of WCO_2 and WCO_3 were determined by GC analysis of the transesterification products of the oils with methanol (CH_3WCO_2 and CH_3WCO_3, respectively) according to IUPAC's recommendation [53] (Table 3).

Table 2 Significant physico-chemical properties of WCO oils.[a]

Property	WCO_1	WCO_2	WCO_3	WCO_4
MW	888.05	898.87	892.29	889.12
IV	111.2	109.27	108.37	109.90
C = C/mol	3.89	3.87	3.81	3.85
%SFA	16.2	15.0	15.6	14.2
%MUFA	40.4	43.4	43.0	42.7
%PUFA	43.4	41.6	41.4	43.1
%UFA/%SFA	83.8/16.2	85.0/15.0	84.4/15.6	85.8/14.2

[a] As determined by quantitative ^{1}H-NMR spectroscopy

Table 3 Fatty acid profile of WCO_2 and WCO_3.[a]

Fatty Acid	WCO_2 (% mol)	WCO_3 (% mol)
Palmitic	8.9	9.4
Stearic	3.2	3.7
Oleic	44.7	44.1
Linoleic	41.8	41.3
Linolenic	0.5	0.8
Behenic	0.6	0.7
Lignoceric	0.3	-

[a] As determined by GC of the corresponding methyl esters

Starting from the fatty acid profiles, we calculated the corresponding MW, IV, C = C/mol, %SFA, %MUFA, %PUFA and %UFA/%SFA data, which were compared with the results obtained by q^{1}H-NMR analysis of the same samples.

The results, as reported in Table 4, show a pretty good agreement between data determined either by GC or by q^{1}H-NMR analyses of the different methyl esters.

Interestingly, the presence of relatively low percentages of saturated fatty acids lowers the pour point temperature of the products that can be obtained from the chemical modification of these vegetable oils, an important feature for products that are used as lubricants and/or plasticizers. On the other side, the presence of high percentages of mono- and poly-unsaturated fatty acids requires their conversion into the corresponding epoxides to improve their oxidation stabilities [29, 43, 54, 55].

Transesterification Reactions

All reactions were run under Ar atmosphere with an excess of the appropriate alcohol and in the presence of variable amounts of the catalyst. The transesterification of deacidified oil WCO_3 (%FFA = 0.062) with an excess of 2-EtC_6H_{12}OH in the presence of a catalytic amount of dry CaO was first investigated.

The extent of the transesterification reaction was monitored by ^{1}H-NMR spectroscopy of crude reaction mixtures, by comparing the integration of the newly formed multiplet centred at 3.96 ppm, corresponding to the CH_2O of the esterified 2-EtC_6H_{12}O chain, with the integration of the (overlapped) triplet(s) at 2.33–2.27 ppm, corresponding to the CH_2 in the α-position with respect to the carbonyl group(s). Complete disappearance of the hydrogen resonances of the trialkyl glyceride backbone (one multiplet at 5.43–5.34 and two doublets of doublets at 4.33 and 4.10 ppm) was also indicative of a good conversion of the starting materials.

Selected results, as reported in Table 5, show that under conventional heating conditions the transesterification reaction is quite slow. Additionally, although complete conversion of the starting material was observed under conditions reported in Table 5, entries 3 and 4, an accurate analysis of ^{1}H-NMR spectra of crude reaction mixtures have shown that the 2-EtC_6H_{12}OH ester of WCO_3 (2-EtC_6H_{12}WCO_3) was contaminated by non-negligible quantities of the intermediate products of mono- and di-transesterification. Indeed, products of incomplete transesterification, *i.e.*, diglycerides (DG) and monoglycerides (MG), give rise to several multiplets within the 4.35–3.55 ppm region.

Although purification of 2-EtC_6H_{12}WCO_3 from relatively small amounts of mono- and di-glycerides can be achieved by storing the impure compounds in the fridge (6 °C) for 2–3 days, followed by filtration of the resulting heterogeneous mixtures, we decided to investigate the possibility to overcome such a problem and to reduce the reaction time by running the transesterification reaction under microwave (MW) irradiation. Indeed, it is well known that MW irradiation has been used extensively to accelerate a variety of chemical reactions, significantly reducing reaction times [56].

Accordingly, a new set of reaction was run under MW irradiation. Selected results, as reported in Table 6, show that

Table 4 Comparison between physico-chemical properties of CH_3WCO_2 and CH_3WCO_3 as determined by GC or by q^{1}H-NMR analyses

Property	CH_3WCO_2, as determined by GC	CH_3WCO_2, as determined by q^{1}H-NMR	CH_3WCO_3, as determined by GC	CH_3WCO_3, as determined by q^{1}H-NMR
MW	293.99	302.71	293.67	301.03
C = C/mol	1.30[a]	1.27	1.29[a]	1.25
IV	112.17[b]	106.48	111.49[b]	105.39
%SFA	13.0	15.1	13.8	15.6
%MUFA	44.7	43.9	44.1	43.0
%PUFA	42.3	41.0	42.1	41.4
%UFA/%SFA	87.0/13.0	84.9/15	86.2/13.8	84.4/15.6

[a]Determined as ∑[%mol oleate + (2 × %mol linoleate) + (3 × %mol linolenate)]/100; [b]Determined as (100/MW) × (C = C/mol) × 253.80

Table 5 CaO-catalyzed transesterification of WCO_3 with 2-EtC_6H_{12}OH under conventional heating.[a]

Entry	CaO (mol %)	2-EtC_6H_{12}OH (equivalents)	t (°C)	T (h)	Conversion (%)[b]	Selectivity 2-EtC_6H_{12}WCO_3/DAG + MAG (%)[b]
1	15	1.1	100	24	< 5.0	-
2	15	2.0	180	24	44.3	n.d.[c]
3	25	2.0	190	24	> 95.0	90.3/9.7
4	25	2.0	190	48	> 95.0	90.5/9.5

[a]All reactions were run under an Ar atmosphere. [b]Determined by ^{1}H-NMR analyses of crude reaction mixtures. [c] n.d. = not determined

Table 6 Microwave-assisted CaO-catalyzed transesterification of WCO_3 with 2-EtC_6H_{12}OH.[a]

Entry	CaO (mol %)	2-EtC_6H_{12}OH (equivalents)	t (°C)	T (h)	Conversion (%)[b]	Selectivity 2-EtC_6H_{12}WCO_3/DG + MG(%)[b]
1	15	1.1	180	1	> 95.0	79.0/21.0
2	15	2.0	180	1	> 95.0	87.5/12.5
3	15	2.7	180	1	> 95.0	91.0/9.0
4	25	2.0	180	1	> 95.0	91.3/8.7
5	25	2.0	190	1	> 95.0	94.5/5.5
6	25	2.0	190	2	> 95.0	95.0/5.0
7	25	2.0	190	3	> 95.0	> 95.0/< 5.0

[a]All reactions were run under an Ar atmosphere at 200 W. [b]Determined by quantitative ^{1}H-NMR analyses of crude reaction mixtures

all the investigated reaction parameters (oil to 2-EtC_6H_{12}OH molar ratio, relative amount of the catalyst, reaction temperature and time) affect the overall conversion of the starting material to the desired 2-EtC_6H_{12}OH ester. With an oil to 2-EtC_6H_{12}OH molar ratio = 1:6 and in the presence of a 25 mol % of the catalyst, high conversion and selectivity of the starting material were obtained after 3 h at 190 °C (Table 6, entry 7), thus demonstrating the good performance of the MW-assisted process.

Recovered 2-EtC_6H_{12}WCO_3 was characterized by ^{1}H-NMR spectroscopy as reported in Fig. 1, where a comparison between the ^{1}H-NMR spectra of WCO_3 and the corresponding 2-EtC_6H_{12}OH ester is reported.

^{13}C-NMR spectroscopy was employed to further characterize 2-EtC_6H_{12}WCO_3. Besides the disappearance of the resonances corresponding to the trialkyl glyceride carbons (69.0 and 62.2 ppm) and the the simplification of resonances relating to ester carbonyls (174.0–174.1 ppm), the main differences concern the appearance of resonances corresponding to the CH_2O (66.7 ppm), to the CH (38.9 ppm) and to the side chain CH_3 of the isooctylate (11.1 ppm) (Figure S2, Supporting Information).

Under comparable reaction conditions, we realized the transesterification of WCO_3 with 2-BuC_8H_{16}OH (Scheme 3), and the resulting product (2-BuC_8H_{16}WCO) was characterized by means of ^{1}H- and ^{13}C-NMR spectroscopies; as discussed above, the corresponding spectra are mainly characterized by the resonances of the CH_2O of the esterified alcohol chain and by the disappearance of the resonances of, respectively, the hydrogen and the carbon atoms of the trialkyl glyceride skeleton (Figures S3 and S4, Supporting Information).

It is finally worth noting that processing of all transesterification mixtures led, by evaporation at reduced pressure, to recover the excess of the different alcohols. Recovered alcohols (usually 80–85% mass recovery of the starting materials) were analytically pure by ^{1}H- and ^{13}C-NMR analyses and identical to commercial samples, thus allowing their successful recycling to successive runs without detrimental effects.

Characterization of Dry CaO

Dry CaO was characterized by means of FT-IR spectroscopy. CaO displays a strong band around at 550 cm^{-1} [57] and the reported IR spectrum (Fig. 2) allows to identify the presence of small amounts of impurities characteristic of an

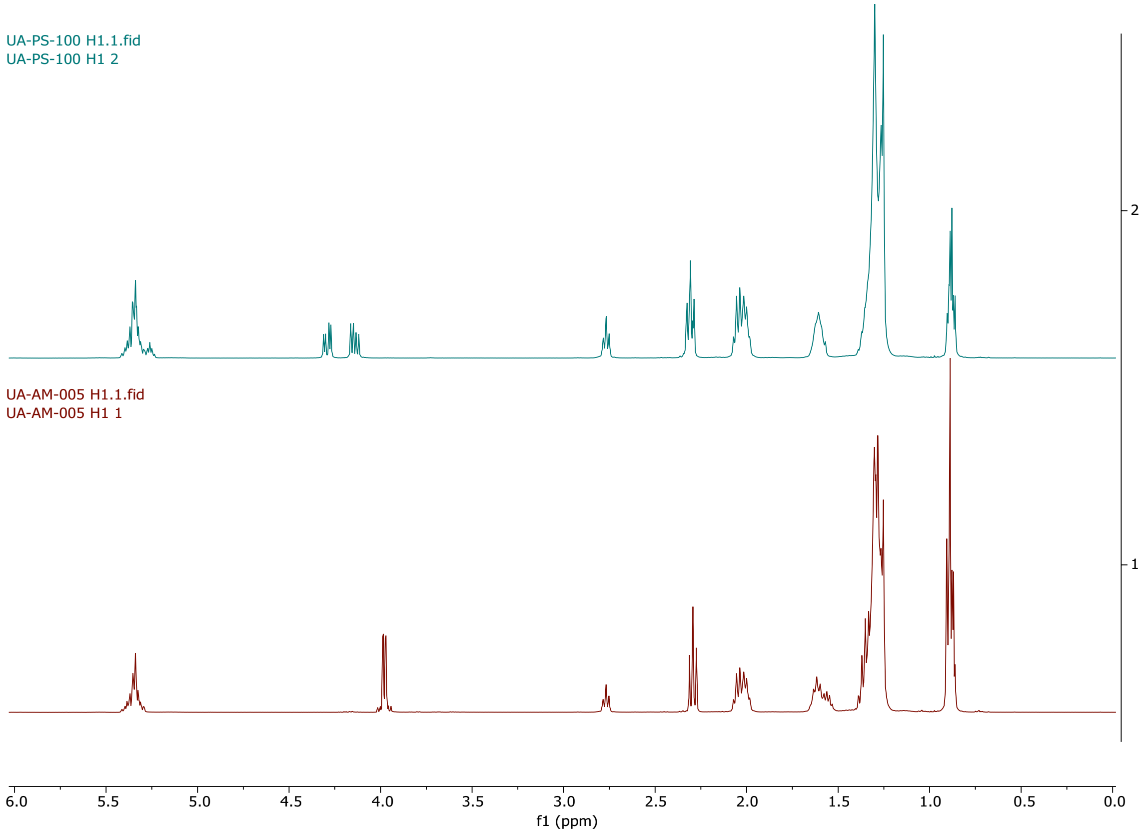
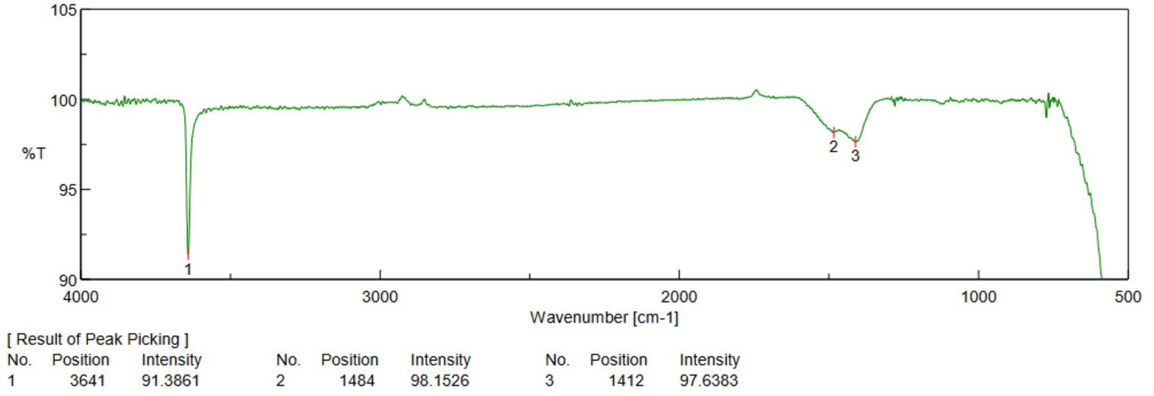


Fig. 1 Comparison between ^{1}H-NMR spectra of WCO_3 (above) and 2-EtC_6H_{12}WCO_3 (below)



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3641	91.3861	2	1484	98.1526	3	1412	97.6383

Fig. 2 IR spectrum of dry CaO

oxide marketed in packages unsealed under an inert atmosphere. The two weak bands at 1484 and 1412 cm^{-1} can be ascribed to asymmetric stretching bands of carbonate due to absorption of CO_2 on the surface of CaO as a monodentate ligand [58]. The sharp band at 3641 cm^{-1} can be attributed to free (non-hydrogen bonded) O–H stretching typical of calcium hydroxide [59]. The absence of broad absorption(s) in this region strongly suggests the absence of water molecules adsorbed to the oxide.

Epoxidation of WCO_3, 2-$EtC_6H_{12}WCO_3$ and 2-$BuC_8H_{16}WCO_3$

Epoxidized WCO_3 (E-WCO_3), epoxidized 2-$EtC_6H_{12}WCO_3$ (E-2-$EtC_6H_{12}WCO_3$) and 2-$BuC_8H_{16}WCO_3$ (E-2-$BuC_8H_{16}WCO_3$) esters were prepared by reacting the different starting materials with 30% H_2O_2 and HCOOH with a C = C/H_2O_2/HCOOH ratio = 1:3:1 at 60 °C during 6 h, using toluene as a diluent of the organic phase (1:1 v/v) to reduce viscosity, minimize side reactions [39, 43] and obtain efficient dispersion of the reaction heat [60].

Under these conditions, > 95% conversion of each starting material was obtained within 6 h, as determined by ^{1}H-NMR analysis of crude reaction mixtures. Indeed, epoxidation of C = C double bonds led to the disappearance of resonances due to the vinylic (multiplet at ca. 5.42–5.28 ppm), bisallylic (triplet at ca. 2.76 ppm) and allylic protons (multiplet at ca. 2.10–1.96 ppm). On the other side, the epoxidized compounds show new resonances due to the protons of the oxirane rings (multiplets at ca. 3.15–2.85 ppm) and to protons at the α-position of the oxirane rings (multiplet at ca. 1.55–1.40 ppm). Accordingly, ^{13}C-NMR spectra of epoxidized compounds are characterized by the disappearance of the resonances between 130.3 – 128.0 ppm due to the vinylic carbons and by the appearance of a series of new resonances at 57.3 – 54.2 ppm due to the carbons of the oxirane rings (Figures S5-S10, Supporting Information).

Pour Point, kinematic viscosity, viscosity index and oxirane oxygen content. Pour point, kinematic viscosity and viscosity index are key parameters to evaluate the efficiency of a vegetable oil derivative as a plasticizer or as a lubricant [54, 61, 62]. Pour points were determined according to ASTM D5950-14. Kinematic viscosities at 40 and 100 °C were determined for WCO_2 and WCO_3, E-WCO_3, 2-$EtC_6H_{12}WCO_3$, E-2-$EtC_6H_{12}WCO_3$, 2-$BuC_8H_{16}WCO_3$ and E-2-$BuC_8H_{16}WCO_3$ according to ASTM D445-19a; the corresponding viscosity indexes were determined according to ASTM D2270.

The results are reported in Table 7, where literature data for two commercially available plasticizers derived from soybean oil, i.e., epoxidized soybean oil (E-SoyOil, Vikoflex® 7170) [54, 63] and E-2-EtC_6H_{12}Soyate (Vikoflex® 4050) [25, 54] and for a proposed biolubricant for drilling fluids, i.e., 2-ethylhexyl palmitate (2-EtC_6H_{12}PO) [15], are also reported for comparison purposes. Due to the well-known increase of viscosity with epoxidation [64], the oxirane oxygen contents of epoxidized compounds are also reported.

As a first remark, it is worth noting that all investigated properties of the WCO batches under consideration are very similar (Table 7, entries 1 and 2), thus providing further evidence of the relative stability of their fatty acid composition over time.

As expected, the molecular weight differences between WCOs and E-WCO_3 on the one hand (Table 7, entries 1–3) and the corresponding Guerbet esters (Table 7, entries 4 and 6) and epoxidized Guerbet esters on the other (Table 7, entries 5 and 7), lead to a large decrease in both pour points and viscosity data for the lower molecular weight compounds. Additionally, epoxidation led to an increase of pour points and kinematic viscosities, as well as to a decrease of the viscosity

Table 7 Physical properties of WCOs and of transesterified and/or epoxidized derivatives

Entry	Sample	Pour Point (°C)[a]	Kinematic viscosity at 40 °C (mm^2/sec)[b]	Kinematic viscosity at 100 °C (mm^2/sec)[b]	Viscosity Index[c]	Oxyrane Oxygen Content (%)
1	WCO_2	-6	36.99	8.33	211.21	
2	WCO_3	-6	37.54	8.43	211.19	
3	E-WCO_3	-3	132.80	17.22	141.92	5.7[d]
4	2-$EtC_6H_{12}WCO_3$	-21	8.52	2.79	198.66	
5	E-2-$EtC_6H_{12}WCO_3$	-18	17.22	4.12	146.41	4.2[d]
6	2-$BuC_8H_{16}WCO_3$	-33	12.05	3.46	179.74	
7	E-2-$BuC_8H_{16}WCO_3$	-24	21.83	4.77	144.06	3.9[d]
8	E-SoyOil (Vikoflex® 7170)	3.0[e]/0[f]	174.9[e]	21.0[e]	142[e]	> 7[f]
9	E-2-EtC_6H_{12}Soyate (Vikoflex® 4050)	-4.5[e]	16.8[e]	4.0[e]	140	> 5.3 [g]
10	2-EtC_6H_{12}PO	-15 [h]	8.24 [h]	3.03 [h]		

[a] Determined according to ASTM D5950-14, detection interval: 3 °C. [b] Determined according to ASTM D445-19a; [c] Determined according to ASTM D2270; [d] Determined according to ref. [49], p. 92–93. [e] According to ref. [54]; [f] According to ref. [63]. [g] According to ref. [25]. [h] According to ref. [18]

indexes (Table 7, entry 2 versus entry 3; entry 4 versus entry 5; entry 6 versus entry 7).

Among the synthesized derivatives of our WCO, 2-$BuC_8H_{16}WCO_3$ and E-2-$BuC_8H_{16}WCO_3$ show pour point temperatures significantly lower and relatively higher kinematic viscosities than those of the corresponding 2-$EtC_6H_{12}OH$ derivatives, most probably due to the superior steric hindrance of their alkoxy moiety [29], as well as to their relatively higher molecular weight.

As a comparison with commercially available plasticizers, it can be observed that epoxidized derivates of WCO synthesized in the present work (Table 7, entries 3, 5 and 7) compare well with epoxidized soybean oil derivates (Table 7, entries 8 and 9). Indeed, despite differences in kinematic viscosities between E-WCO_3 and E-SoyOil, viscosity indices of epoxidized WCO derivatives are comparable with those of the corresponding soybean oil derivative; additionally, there is a significant decrease of pour points when switching from soybean oil derivatives to those of the WCO, once again accounting for the relative differences in oxirane oxygen content [64] (Table 7, entries 3, 5, 8 and 10).

Finally, pour points, kinematic viscosities and viscosity indexes determined for 2-$EtC_6H_{12}WCO_3$ and 2-$BuC_8H_{16}WCO_3$ compare well with the corresponding properties of the 2-$EtC_6H_{12}OH$ ester of palm oil (2-$EtC_6H_{12}OPO$), which was proposed as a biolubricant for drilling fluids [18] (Table 7, entry 10).

Oxidative Stability

Pressure differential scanning calorimetry (PDSC) was used to evaluate the oxidative stability of two WCOs and all WCO derivatives, an important parameter to evaluate their possible employment as biolubricants or plasticizers. The results are reported in Table 8, where the literature data for E-SoyOil and E-2-EtC_6H_{12}Soyate are also reported for comparison purposes [54].

Table 8 The PDSC data for WCOs and for transesterified and/or epoxidized derivatives showing OT and SMT

Entry	Sample	OT (°C)	SMT(°C)
1	WCO_2	135 ± 1	205 ± 2
2	WCO_3	142 ± 2	198 ± 2
3	E-WCO_3	191 ± 3	210 ± 2
4	2-$EtC_6H_{12}WCO_3$	141 ± 1	200 ± 1
5	E-2-$EtC_6H_{12}WCO_3$	180 ± 2	212 ± 1
6	2-$BuC_8H_{16}WCO_3$	160 ± 2	212 ± 2
7	E-2-$BuC_8H_{16}WCO_3$	199 ± 2	228 ± 2
8	E-SoyOil (Vikoflex® 7170)	199[a]	233.6[a]
9	E-2-EtC_6H_{12}Soyate (Vikoflex® 4050)	192.75[a]	219.2[a]

[a] According to ref. [54]

As expected from their almost constant fatty acid composition, OT ed SMT recorded values are quite similar for our triglycerides WCO_2 and WCO_3 (Table 8, entries 1 and 2). From this point of view, it is interesting to notice that while no appreciable variations in the oxidative stability values are observed in passing from WCO_3 to 2-$EtC_6H_{12}WCO_3$, we observed a decidedly higher stability for the corresponding 2-$BuC_8H_{16}OH$ epoxidized ester (Table 8, entries 2, 4 and 6).

On the other hand, epoxidation of carbon–carbon double bonds of WCO_3, 2-$EtC_6H_{12}WCO_3$ and 2-$BuC_8H_{16}WCO_3$, was accompanied by a significant increase of the OT and

SMT values of the corresponding reaction products, i.e., E-WCO_3, E-2-Et$C_6H_{12}WCO_3$ and E-2-Bu$C_8H_{16}WCO_3$, respectively (Table 8, entry 2 versus entry 3; entry 4 versus entry 5; and entry 6 versus entry 7). It is worth noting that the highest OT and SMT values were obtained in the case of the 2-Bu$C_8H_{16}OH$ ester. These results strongly suggest a positive influence on the oxidation stability of an increase in the chain length of the carbon atoms and/or of the steric hindrance of the alkoxy portion of the monoester derivatives.

Finally, it is interesting to note that while the OT and SMT values obtained for E-WCO_3 and E-2-Et$C_6H_{12}WCO_3$ describe products with slightly lower oxidation stabilities than that reported for the corresponding commercially available soybean oil derivatives (Table 8, entries 8 and 9), the values obtained in the case of E-2-Bu$C_8H_{16}WCO_3$ (Figure S11, Supplementary Information) describe a product with oxidation stability characteristics that compare well with those of Vikoflex 4050.

Conclusion

Our report illustrates an original collection method of a WCO that allows the recovery of a secondary raw material with an almost constant composition over time, as well as its chemical modification into useful biochemicals.

The design of these useful chemical modifications was based on the rapid determination of the chemical characteristics of the oil, made possible by using quantitative ^{1}H-NMR as an analytical tool.

The key transesterification step of the triglyceride with long chain and branched primary alcohols was obtained for the first time by employing commercially available CaO as a basic catalyst. Additionally, MW irradiation allowed the optimization of energy expenditure.

The success of our protocol is evidenced by the determination of the main physico-chemical properties of the resulting products. Indeed, our Guerbet esters compare well in terms of pour points and kinematic viscosities with the 2-Et$C_6H_{12}OH$ ester of palm oil (2-Et$C_6H_{12}PO$), recently proposed as a biolubricant for drilling fluids, whilst the epoxidized Guerbet esters synthesized in the present work compare well with a commercially available plasticizers also in terms of oxidative stability.

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Declarations

Conflict of interest Angelo Montenero is Manager of Il Gabbiano Industria Ecologica s.r.l.

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