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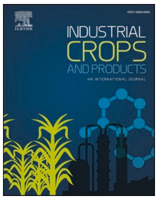

Potential valorization of waste cooking oils into sustainable bio-lubricants

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ABSTRACT

This work explores the feasibility of using waste cooking oils (WCO) as eco-lubricants. Five WCO from different food facilities were studied. Three of them were fractionated into both lighter and heavier fractions by molecular distillation. A comprehensive chemical characterization (fatty acids distribution, polar compounds and acidity) was carried out on all WCOs and their fractions, which led to set relationships with the oils' properties (such as viscosity index, low temperature viscous flow behavior, oxidation resistance, etc.). It is worth mentioning the high viscosity index values found in waste cooking oils with both low total polar compounds and acidity level, as well as the benefit which acidity had on their fluidity at low temperature and their lubricity. Moreover, it was also noteworthy that the lighter fractions, merely constituted by free fatty acids (FFA), presented an improved oxidative resistance. The largest OOT enhancement, 12.4%, was found for the light fraction of a non-segregated oil. Moreover, a better thermal stability was shown by the heavier fractions. Finally, both fractions exhibited enhanced friction-reducing capability as compared to their parent WCO. The light fractions from a non-segregated oil, a fast food restaurant oil and a deep-fried food establishment oil yielded wear reductions of 11.7%, 44.3% and 36.8%, respectively. Therefore, molecular distillation has been proved to be a key strategy to obtain more efficient liquid eco-lubricants.

1. Introduction

According to the Organization for Economic Cooperation and Development (OECD) countries, the petroleum demand fell by a 9.1 million barrels per day in 2020, the lowest level since 2011. However, the total world consumption of oil is still quite large, ca. 1300.9 million barrels per day (Bp, 2021). The worldwide concern on the massive use of petroleum-based products is such that the lubricant industry, on its part, is continually stepping up efforts in order to develop more sustainable formulations. With respect to the lubricant market, governmental directives such as the European Commission Decision 05/360/EC on environmental preservation has turned biodegradability into one critical design parameter in terms of the selection of base oils and lubricity improvers (Battersby, 2000; Lawate, 2006). It is noteworthy that the US and Europe account for 85–90% of bio-based lubricants production and consumption worldwide, and that the bio-lubricants global market was expected to grow at a compound annual growth rate of 5.4% from 2016 to 2024 (Tsagaraki et al., 2017).

As many researchers have previously pointed out (Erhan and Asadaukas, 2000; Lawate, 2006; Quinchia et al., 2010; Jahromi et al., 2021), different vegetable oils have been demonstrated to be suitable as base oils for lubricant applications. However, the large crop areas devoted to oilseeds with industrial purpose, which compete with the usage of lands for food production, is a huge controversial issue (Li and Wang, 2015). Thus, the growing production of bio-lubricants, based on either edible or non-edible vegetable oils, has been lately deemed to be an unsustainable practice. Apart from that, vegetable oil-based lubricants are up to 20% more expensive than conventional mineral oil-based lubricants (Miller, 2008).

Edible vegetable oils are widely used in deep-frying around the world. For a great variety of fried products, the frying process is normally carried out between 160 and 180 °C and in the presence of both air and moisture (Chatzilazarou et al., 2006). Chemical alterations, as a consequence of thermal oxidative and hydrolytic reactions, isomerization of double bonds, oligomerization and degradation of triglycerides, occur (Dobarganes and Márquez-Ruíz, 1998). Thereby, used deep-frying oils chemical composition differs from their parent fresh oils (Knothe and Steidley, 2009; Mannu et al., 2020). The specific impact of the

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deep-frying process depends on the type of processed food, frying temperature, number of frying cycles and total period of usage. In addition, vegetable oil compounds break down forming peroxides, acids and other radicals, which increase their polarity (Hassanien and Sharoba, 2014). Hence, deep-frying vegetable oil undergo undesirable physico-chemical changes (color, odor, viscosity, acidity, total polar compounds, among others). According to the European Healthy Authorities, a vegetable oil used in deep-frying must be replaced with a fresh one when the total polar compounds reach 25–27 wt% (Dobarganes and Márquez-Ruíz, 1998). Then, it becomes a waste classified as municipal waste under the code CER 20 01 25 (Directive 2006/12/EC), according to the European Waste Catalogue.

Over the last decades, the amount of waste cooking oil (WCO) generated from food industries, restaurants, fast-food establishments and homes has continuously increased, with a rate of up to 2% per year, due to the increment in food and, above all, fast-food consumption by the human population (Kulkarni and Dalai, 2006; Iglesias et al., 2012; Mannu et al., 2020). The Food and Agriculture Organization of the United Nations estimates that the annual average consumption of vegetable oil for food use will reach 23.5 kg per capita, with a prediction to grow by 0.9% per year until 2025 (OECD/FAO (2016). It is estimated that around 1–2.5 million metric tons per year of WCO are generated in the European Union (EU) countries (Talens Peiró et al., 2008; Borugadda and Goud, 2014; Mannu et al., 2020). However, the current level of collection is very low, as it varies between 0.7 and 1 million metric tons per year (Kulkarni and Dalai, 2006; Iglesias et al., 2012; De Feo et al., 2020). There exists an inadequate disposal of WCO through the sewage system that causes both economic problems and rivers and soils pollution (De Feo et al., 2020). On one hand, the irrational disposal of waste cooking oils into the drains yields operation and maintenance problems in the municipal sewage treatment plants which significantly increase their treatment costs (Kulkarni and Dalai, 2006). On the other hand, one liter of waste cooking oil poured into the environment may pollute 0.5 million liters of water, thus yielding serious environmental problems (Vidal-Benavides et al., 2017). Therefore, a proper handling of WCOs is mandatory to reduce its impact on the global environment and to improve their availability with a view to their reutilization in different industrial processes, such as bio-lubricants, biodiesel, additives for asphalts, animal feed, among others (Mannu et al., 2020).

Under such circumstances, governmental authorities in environment preservation matter worldwide have strongly encouraged the WCO collection and their potential valorization into value-added products. For example, their utilization as feedstock in biodiesel production plants is an established practice (Kulkarni and Dalai, 2006). In fact, biodiesel is cost-effectively produced from WCO, apart from other vegetable oils such as palm, rapeseed, sunflower or jatropha, among other seeds (Knothe and Steidley, 2009; Li et al., 2015). However, the biodiesel demand is currently declining for the sake of reducing harmful emissions, and lot of biodiesel plants are closing around the world. Therefore, other ways of reutilization need to be investigated, such that the negative effect of WCO on the environment, and the greenhouse gases emission are both mitigated.

With this in mind, bio-lubricants may become an attractive way to valorize waste cooking oils, with a twofold purpose: (a) first, it may prevent the above mentioned non-food usage of lands; (b) second, it may reduce the WCO management costs and prevents their potential impact in case of disposal to the environment. Apart from that, it is a cost-effective strategy because waste cooking oils are inexpensive and of fully availability anywhere. The lubricant industry could be a potential consumer of WCO, since they are between 2 and 3 times cheaper than fresh vegetable oils (Yaakob et al., 2013). Moreover, their use is a public evidence of commitment to environmental preservation, thereby counting on social acceptance.

Despite that more than 36.8 million tons per year of lubricants are demanded around the world (Sönnichsen, 2021), the number of research works on the reuse of WCO in lubricants applications is less than expected. In that sense, Pehan et al. (2009) pointed out that biodiesel produced from waste cooking oils may improve the lubrication conditions in pump plungers. Chowdhury et al. (2013) obtained octyl esters-based bio-lubricants by esterification of the free fatty acids obtained by enzymatic hydrolysis of WCO. Borugadda and Goud (2014, 2016) and Li and Wang (2015) carried out the epoxidation of methyl esters from waste cooking oils. They showed contrary effects on their kinematic viscosity as compared to their parent neat WCO, but the same enhancement of both the thermo-oxidative stability and the low-temperature properties, which indicated that they could be used as possible substitutes for the conventional lubricant base stocks. Sun et al. (2017) produced pentaerythritol fatty esters by transesterification of WCO-derived fatty acid methyl esters with trimethylolpropane. Abdulbari et al. (2011) and Rajvanshi and Kumar Pandey (2016) formulated a lubricating grease using WCO as base oil. In general, most research works related to waste cooking oils focus on the use of their fatty acids methyl esters for the production of WCO-derived molecules, and present their physico-chemical characterization. Even so, only a few of them report a full physico-chemical characterization of the WCO used, and none of them analyzed the relationship between its physico-chemical properties and tribological performance.

This work explores the potential use of WCO as bio-lubricant and, as a novel approach, their fractions from molecular distillation as lubricant base stock. A comparative evaluation of waste cooking oils from a variety of food facilities is reported. The effect of their physico-chemical properties on the tribological behavior is analyzed.

2. Materials and methods

2.1. Materials

Five waste cooking oils from a variety of food facilities in the city of Huelva (Spain) have been studied: common restaurant (CR-WCO), fast-food restaurant (FF-WCO), deep-fried food establishment (FR-WCO), shop selling fritters (CH-WCO) and, finally, a mixture of used cooking oils from varying unidentified origins, with no segregation (WM-WCO). They all were kindly supplied by the authorized waste manager (GRU 2066) BIOLIA. (Huelva, Spain). These used cooking oils, from palm and sunflower oils mainly, may have been subjected to very different conditions in terms of frying temperature, cycles of frying and total period of usage.

All waste cooking oils were previously filtered in order to eliminate suspended particles. Moreover, moisture was removed in a rotary evaporator under vacuum.

2.2. Waste cooking oils molecular distillation

WCO fractionation was performed using a short path distillation (KDL5, UIC GmbH, Alzenau, Germany), which is an agitation-featured variation of a falling-film molecular distiller. The set-up consists of a jacketed evaporator (circulating oil is used as heating fluid) and an internal condenser. The heat transfer areas of the evaporator and the internal condenser are 0.048 and 0.065 m^2, respectively. They are set to 220 °C (distillation temperature) and 40 °C, respectively. The feed entered the distiller at 50 °C, with a flow rate which varied between 1.0 and 5.0 mL/min. All distillations were performed at an extremely low pressure of 0.007 mbar. The WCO were fractionated into two, light and heavy, fractions, which were stored at − 18 °C for subsequent analysis.

2.3. Analytical determinations

Free fatty acids (FFA) contents (% oleic acid) and fatty acids compositions were determined following the AOCS standard methods (AOCS, 1997). Fatty acid composition was determined after transesterification of the oils with KOH in methanol. Fatty acid methyl esters (FAME) were analyzed using a Hewlett-Packard 6890 Series gas chromatograph (GC) equipped with a DB-23-fused silica capillary column (60 m, l, 0.25 mm, i.d. 0.25-µm film thickness) and a flame ionization detector (FID). The detector and injector temperatures were held at 240 °C while the column temperature remained isothermal at oven temperature of 185 °C. The FAMEs were calculated based on the retention times and peak areas with a rapeseed oil reference mix. Each fatty acid was expressed as a percentage of mass fractions.

The amount of polar compounds was determined by silica column chromatography following IUPAC method 2.507 (Ruiz-Méndez et al., 2008). Briefly, starting from 1 g of oil, a non-polar fraction containing unoxidized triacylglycerols was first eluted with a mixture of hexane and diethylether 90:10 (v/v) and then a second fraction, comprised of total polar compounds was eluted with diethyl ether. The polar fraction was further analyzed by high-performance, size-exclusion chromatography, and oxidized triacylglycerol monomers, triacylglycerol dimers, triacylglycerol oligomers, diacylglycerols, and free fatty acids concentrations were determined. Polar fractions were dissolved in tetrahydrofuran at 20 mg/mL and analyzed in an Agilent 1200 Infinity Series liquid chromatograph equipped with a quaternary pump VL (G1311C), a standard autosampler (G1329B), a thermostatted column compartment (TCC) (G1316A), and a refractive index detector (G1362A). The separation was performed on two 100- and 500-Å columns (25 cm x 0.77 cm i.d.) packed with porous, highly cross-linked styrene-divinylbenzene copolymers (Agilent Technologies, Palo Alto, CA, USA) connected in series, with tetrahydrofuran (1 mL/min) as the mobile phase.

2.4. Fourier transform infrared (FTIR) spectroscopy

A FT/IR-4200 spectrometer (JASCO) was used to obtain FTIR spectra with a wavenumber range from 400 to 4000 cm^{-1}, at 4 cm^{-1} resolution, in transmission mode. All samples were analyzed as thin layers on KBr disks (32 mm × 3 mm).

2.5. Thermogravimetric analysis

WCO thermal degradation was determined in a Q-50 thermobalance (TA Instruments Waters, USA). Samples (10 ± 1 mg) were analyzed using open aluminum pans under nitrogen atmosphere (flow rate of 60 mL/min), and applying a heating rate of 10 ºC·min^{-1}, within a temperature range of 25–600 °C. All these measurements were done at least twice.

2.6. Oxidation resistance analysis by DSC

The oxidation onset temperature (OOT) tests were performed according to ASTM E 2009-08 standard, using a Q-100 differential scanning calorimeter (TA Instruments Waters, USA) under oxygen atmosphere (flow rate of 50 mL/min). Oil samples (3.0–3.3 g) were placed in open aluminum pans and heated from 100 °C to 250 °C, at a heating rate of 10 °C·min^{-1}. All these measurements were done at least twice.

2.7. Viscosity and density measurements

Dynamic viscosities were measured with a Physica MCR 301 rotational controlled-stress rheometer (Anton-Paar, Austria), at selected temperatures of 25, 40 and 100 °C. Steady state viscous flow tests were carried out, in a shear rate range of 0.1–100 s^{-1}, using a smooth plate-plate geometry (50 mm diameter; 1 mm gap). Kinematic viscosity values were calculated as the ratio of the dynamic viscosity relative to the density, at every temperature studied. For this purpose, a DMA-5000 capillary densimeter (Anton Paar, Austria) was used to measure the sample densities at 25, 40 and 100 °C. Viscosity index (VI) values were then determined according to ASTM D-2270. For each oil, three replicates were carried out on fresh samples such that results shown have statistical significance at the 95% confidence level.

Additionally, the evolution of the dynamic viscosity at 1 s^{-1} with temperature between 25 and − 80 °C was monitored, in order to analyze the effect of crystallization on the low-temperature viscous flow behavior of the WCO studied. Measurements were done at a cooling rate of − 1 °C·min^{-1}, using a rotational controlled-strain rheometer, model ARES G2 (TA Instruments, USA) coupled to a freezing system.

2.8. Friction and wear measurements

Friction tests, at rotational speeds in the interval 0.01–1000 rpm, under a normal load of 10 N (0.8 GPa Hertzian pressure) and at 25 °C, were done with a ball-on-three plates tribology cell coupled to a rotational controlled-stress rheometer, model Physica MCR 501 (Anton Paar, Austria). The set-up consisted of a lower measuring geometry with three 45º pitched steel plates (1.4301 AISI 304) and an upper part which sustains a fixed 6.35 mm radius bearing ball (1.4401 grade 100). All friction tests were performed under pure sliding conditions. For each oil, tests were conducted at least five times using a fresh sample such that results shown have statistical significance at the 95% confidence level.

Moreover, wear was evaluated at a normal load of 10 N and a constant rotational speed of 40 rpm (or equivalently, at a sliding velocity of 16 mm/s) for 1800 s at room temperature. The selected rotation condition corresponded to the so-called mixed friction regime (both fluid and solid friction take place). All steel plates were properly cleaned with ethanol and ambient dried before being used. Both morphology and diameter of wear scars in the plates were examined by using a BX51 optical microscope (Olympus, Japan), equipped with a C5050Z camera (Olympus, Japan). For each oil, at least three replicates were carried out on fresh samples such that results shown have statistical significance at the 95% confidence level.

3. Results and discussion

3.1. Waste cooking oil chemical analysis

Table 1 shows the WCO compositions, in terms of their main fatty acids. Their polar compounds distribution and their acidity are also presented. Fatty acid composition and acidity of sunflower oil (most used deep-frying oil in Western Europe) was included for the sake of comparison.

WCO studied showed noticeably variations in unsaturated fatty acid contents but just minor variations in the saturated fatty acid composition. FF- and FR-WCO oils showed acidity (6.76 and 7.51 wt%, respectively), and by far, the largest values of total polar compounds (33.5 and 37.22 wt%, respectively) over passing the EU regulations (25%). Conversely, CR-WCO seems to be the less degraded WCO (acidity of 0.52 wt% and total polar compounds of 9.83 wt%). It is difficult to attribute the causes because several variables are involved such as temperature and heating time in the frying conditions, the frequency of oil replacement and, of course, the initial quality of the oil. Thermal degradation during their lifespan provoked significant differences with respect to both polar compounds and acidity (Ruiz-Méndez et al., 2008).

The final acidity of the used oil is usually due to the processed foods. Thus, the predominance of deep-frozen foods, with a high water content, favors the hydrolysis of triglycerides, giving rise to the highest contents of both diglycerides and monoglycerides (Ruiz-Méndez et al., 2008). This fact could explain the high content of free fatty acids in FF- and FR-WCO oils (Table 1). On the other hand, FR- and CH-WCO oils presented the highest content of major molecules (oligomers +dimers, and polymers), the most revealing compounds of temperature action in the presence of air and during a long processing time (Steel et al., 2006). This result is probably due to a higher number of "in/out" cycles of the food, which favors the entry of air. Even so, CH-WCO showed a rather low acidity (0.78 wt%), a result indicating a lower degree of hydrolysis probably due to the type of fried food processed.

Table 1
Composition (wt%) in terms of main fatty acids, polar compounds and acidity of the WCO studied.

Waste cooking oils	Sunflower oil[a]	Non- segregated (WM)	Fast food restaurant (FF)	Deep-fried food establishment (FR)	Common restaurant (CR)	Shop selling fritters (CH)
Palmitic (C16:0)	6.18	7.26	5.53	6.95	7.18	6.65
Stearic (C18:0)	3.41	3.45	3.54	3.46	3.47	3.70
Oleic (C18:1)	25.60	31.37	58.70	40.29	31.79	47.23
Linoleic (C18:2)	63.80	54.15	29.07	45.63	54.08	37.05
Linolenic (C18:3)	0.08	0.08	0.09	0.05	0.06	0.03
Others	0.93	3.69	3.07	3.62	3.42	5.34
Acidity (wt% oleic ac.)	0.81	1.27	6.78	7.51	0.52	0.78
Total polar comp. (wt %)		19.00	33.5	37.18	9.83	27.25
Olig[b] + dimers		5.53	9.13	12.34	3.45	15.51
oxTG[b]		6.82	4.32	3.37	2.60	7.64
DG[b]		5.07	12.77	15.23	2.82	3.39
MG[b]		0.44	0.61	1.21	0.70	0.08
Free fatty acids		1.09	6.67	5.03	0.26	0.63
Polymers (wt%)		7.08	6.05	13.62	3.29	17.39

[a] Data extracted from Quinchia et al. (2010) and Konuskana et al. (2019).
[b] Olig: triglyceride polymers; oxTG: oxidized triglycerides, DG: diglycerides; MG: monoglycerides

FF- and FR-WCO oils, with the highest FFA contents, were submitted to molecular distillation. Moreover, the non-segregated waste oil (WM-WCO) was also molecular distilled, because it represents the most common way of collection. WCO distillation does not demand too much energy, thus it can be considered to be feasible from an economical standpoint (Mannu et al., 2020). Molecular distillation yielded two fractions: a lighter fraction enriched with free fatty acids, and a heavier fraction including the most polar compounds and a low fraction of non-distilled free fatty acids. Both fractions are liquid at room temperature. The low acidity of WCO used brought about poor light fractions yields of 10.8 and 13.6 wt% (with respect to the initial distillation charge) for FF- and FR-WCO oils, respectively. As for WM-WCO, only 7.6 wt% was obtained. It is worth pointing out that under the mild distillation conditions used (220 °C and 0.007 mbar) no thermal decomposition is expected to occur. Hence, as can be appreciated in Table 2, both light and heavy fractions showed quite similar fatty acid distributions as compared to their parent WCO, with the exception of WM light fraction, with significantly higher and lower contents of C16:0 and C18:2, respectively. Polar compounds of the starting oils and their corresponding heavy fractions differ not only in the lower content of free fatty acids, which is to be expected, but also in the removal of 22.8–56.8% of the diglycerides present, which may affect their rheological properties.

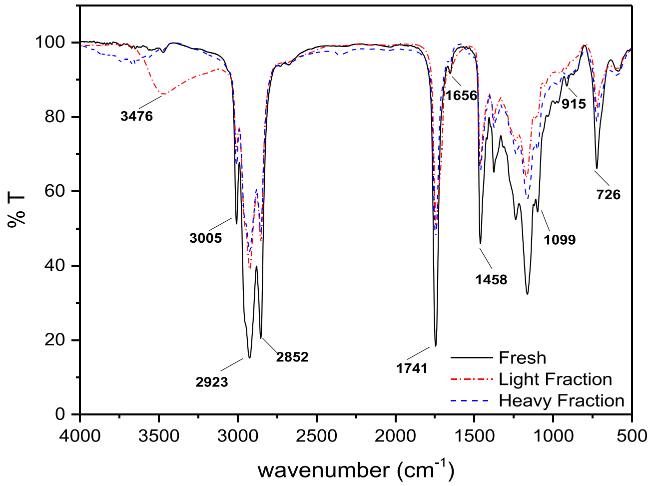

Fig. 1. FTIR spectra of WM-WCO and its fractions as obtained by molecular distillation.

As shown in Fig. 1, WM-WCO and its molecular distillation fractions yielded infrared absorption spectrum intensity maps comparable to other vegetable oils (Shi et al., 2017). The remaining WCO studied showed, qualitatively, exactly the same infrared absorption bands (data not shown) than WM-WCO. Minor differences between the light fraction and the fresh WCO/heavy fraction were observed, thereby corroborating the analyses results displayed in Table 2. Thus, the light fraction showed a highly pronounced band at 3476 cm^{-1} assigned to the stretching vibration of -OH groups in free fatty acids as a consequence of being almost wholly conformed by FFA (Shi et al., 2017; Ullah et al.,

Table 2
Composition (wt%) in terms of main fatty acids and polar compounds of selected WCO, as compared to their molecular distillation fractions.

	WM-WCO			FF-WCO			FR-WCO		
Waste cooking oils	Fresh WCO	Heavy fraction (H)	Light fraction (L)	Fresh WCO	Heavy fraction (H)	Light fraction (L)	Fresh WCO	Heavy fraction (H)	Light fraction (L)
Palmitic (C16:0)	7.26	7.33	10.25	5.53	5.44	6.12	6.95	6.77	7.73
Stearic (C18:0)	3.45	3.51	3.48	3.54	3.53	3.30	3.46	3.49	3.23
Oleic (C18:1)	31.37	31.92	30.43	58.70	58.54	59.81	40.29	40.28	41.15
Linoleic (C18:2)	54.15	53.95	50.91	29.07	29.21	27.90	45.63	45.82	44.82
Linolenic (C18:3)	0.08	0.08	0.11	0.09	0.10	0.10	0.05	0.05	0.05
Others	3.69	3.21	4.82	3.07	3.18	2.77	3.62	3.59	3.02
Total polar compounds (wt%)	19.00	19.01		33.5	17.89		37.18	28.1	
Olig+ dimers	5.53	7.12		9.13	8.45		12.34	9.20	
oxTG	6.82	6.53		4.32	3.42		3.37	2.46	
DG	5.07	3.82		12.77	5.51		15.23	11.76	
MG	0.44	0.83		0.61	0.21		1.21	0.82	
Free fatty acids	1.09	0.70		6.67	0.30		5.03	3.86	

2014). Moreover, the light fraction showed attenuated bands at 1656 (just a shoulder) and 1099 cm^{-1} with respect to both heavy fraction and fresh WM-WCO. The band at 1656 cm^{-1} corresponds to the cis -C=C bond, whilst that at 1099 cm^{-1} is associated to the stretching vibration of -C-O groups in triglycerides. Other remarkable stretching and bending vibrations bands remained roughly the same: stretching vibration bands assigned to -C-H of unsaturated carbon (3005 cm^{-1}), to -C-H symmetrical (2923 cm^{-1}) and asymmetrical stretching (2852 cm^{-1}) of the saturated carbon-carbon bond and to the ester carbonyl functional group in triglycerides (1741 cm^{-1}); bending vibration bands assigned to -CH_2 and -CH_3 aliphatic groups (1458 cm^{-1}); olefin reflector outside stretching vibration peaks (915 cm^{-1}); and the carbon skeleton vibration peak (726 cm^{-1}).

Therefore, FTIR spectra in Fig. 1 corroborates that the molecular distillation process performed, in the absence of moisture, on WCO did not yield further chemical alterations. Thereby, it was confirmed that only physical fractionation took place in the distiller according to the relative volatilities of the species initially present in the WCO studied. As a consequence, molecular distillation produced a heavier fraction slightly enriched on polar compounds with respect to the fresh WCO, and a lighter fraction merely consisting of FFA.

3.2. *Waste cooking oils thermal behavior as related to its potential application in sustainable lubrication*

Thermogravimetric analysis (TGA) enabled to monitor the thermal degradation events as the WCO studied were subjected to an increasing temperature program under controlled inert environment (Vecchio et al., 2008). Fig. 2a displays weight loss curves (and their first temperature derivatives) for the five different waste cooking oils studied. For the sake of comparison, the two fractions, heavy and light, obtained by molecular distillation of WM, FR- and FR-WCO oils were compared to their corresponding fresh WCO in Fig. 2b, c and d, respectively. Under N_2 atmosphere, all WCO presented similar thermal decomposition profiles, characterized by a main decay being located within the temperature interval between 350 and 400 °C and the offset temperature at ca. 500 °C. No residue remained upon completion of the tests. Additionally, FF- and FR-WCO oils exhibited a former decomposition peak at lower temperature, around 244 °C. Thereby, CR-, CH- and WM-WCO showed a higher thermal stability than FF and FR. In fact, FF- and FR-WCO oils, from fast-food restaurants and deep-fried establishments, respectively, presented acidity values of 6.78 and 7.51 wt%, respectively. In contrast, the other three used oils only had 0.52, 0.78 and 1.27 wt% for CR-, CH- and WM-WCO oils, respectively. Consequently, the higher the acidity (i.e., the FFA content) is, the lowest the onset of decomposition of the WCO, because the free fatty acids are more susceptible to temperature than mono, di or triglycerides. Interestingly enough, such a thermal event at 244 °C was missed in the heavy fractions from WCO tested because the FFA located in the lighter fraction. Therefore, molecular distillation was found to be a method that yields a heavy fraction with improved thermal stability.

Oxidation onset temperature (OOT) tests, according to ASTM E2009-

Table 3
Relevant decomposition temperatures (onset and peak maximum), weight loss percentage and onset oxidation temperature (OOT) for selected WCO and their fractions from molecular distillation.

	1st peak		2nd peak	
	T_{onset}/T_{max} (°C)	Weight loss (wt. %)	T_{onset}/T_{max} (°C)	OOT (°C)
CR	–	–	349.3 / 412.3	152.0 ± 0.7
CH	–	–	348.7 / 411.7	139.7 ± 5.7
FF	189.8 / 244.2	8.40	370.4 / 420.9	165.5 ± 6.1
Light-FF	191.6 / 250.0	46.38	371.4 / 406.5	170.7 ± 0.8
Heavy-FF	–	–	348.0 / 418.6	164.3 ± 1.3
FR	190.9 / 245.0	7.40	345.7 / 418.2	159.4 ± 3.4
Light-FR	183.8 / 248.6	40.62	378.6 / 407.4	161.2 ± 2.7
Heavy-FR	–	–	346.2 / 413.2	159.5 ± 2.7
WM	–	–	363.8 / 420.4	153.0 ± 1.7
Light -WM	198.1 / 253.2	37.61	386.3 / 410.8	172.0 ± 0.2
Heavy-WM	–	–	376.5 / 419.0	157.5 ± 1.7

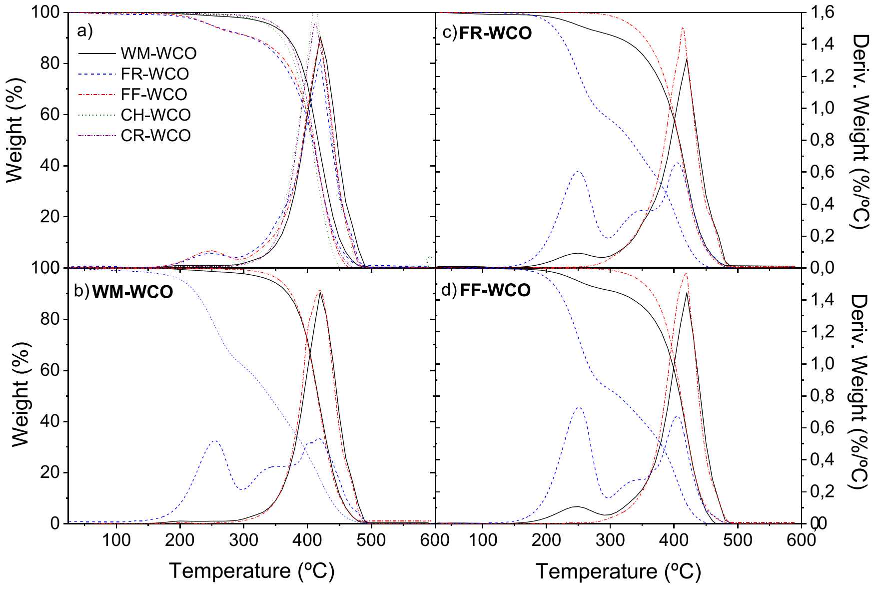

Fig. 2. Comparative evaluation of the weight loss curves and their first temperature derivatives (curves which shown a maximum peak) of all WCO studied (a); WM-WCO and its fractions (b); FR-WCO and its fractions (c); and FF-WCO and its fractions (d). In b), c) and d): fresh WCO (black solid lines), light fractions (blue dashed lines), and heavy fractions (red dashed-dotted lines).

08 standard (Quinchia et al., 2011), were carried out on the WCO studied. Their respective OOT values are listed in Table 3. Such a parameter is a quality indicator on the expected oxidation resistance of the WCO tested in real-life application (Borugadda and Goud, 2014). The WCO studied showed OOT values between 139.7 and 165.5 °C. FF-WCO (from fast food restaurant) presented the highest oxidative resistance, which is in accordance with its lowest PUFAs content, i.e., linoleic fatty acid (29.07 wt%). Furthermore, it is noteworthy that WCO molecular distillation produced a light fraction with improved resistance to oxidation. The largest OOT enhancement, 12.4%, was found for WM-light fraction, which showed an OOT value of 172.0 °C as compared to 153.0 °C for fresh WM-WCO. FF- and FR-light fractions showed less noticeable improvement, of around 3.2% and 1.7%, respectively. Therefore, molecular distillation has been shown to produce a light fraction with improved oxidative resistance.

3.3. *Waste cooking oils viscosity as related to its potential application in sustainable lubrication*

Cloesen et al. (1998) demonstrated that vegetable oils viscosity increased with ageing. In their studies, sunflower oil viscosity was found to rise 60% of its initial value after 100 h ageing under oxygen-enriched environment and 90 °C. Such outcome has motivated us to consider the feasibility of using WCO from diverse origins in sustainable lubricant applications, which may demand base oils involving a range of viscosities. On these grounds, both their viscous flow behavior and tribological performance were evaluated.

The influence of the fatty acid composition on the viscosity of vegetable oils has been analyzed by Kim et al. (2010) and Yalcin et al. (2012). They demonstrated that vegetable oils viscosity mainly depend on their major components, i.e., oleic and linoleic fatty acids. Moreover, Hassanien and Sharoba (2014) pointed out that WCO kinematic viscosity was directly proportional to the percentage of polymers, oligomers or dimers, among other high molecular weight compounds. On this basis, a viscous flow analysis of the five waste cooking oils studied and their fractions (only for FF, FR and WM) is hereby presented, in order to explore and establish its dependence on composition.

All WCO studied showed a well-defined Newtonian viscous flow behavior, characterized by a constant value of the dynamic viscosity within the shear rate interval between 1 and 100 s^{-1}. Moreover, they all showed very similar density values within the temperature range tested, in such a way that no significant differences were found at the 99% confidence level. Thereby, average density values of 921.82 ± 2.88, 911.50 ± 2.86 and 871.04 ± 2.83 g/L were calculated at 25, 40 and 100 °C, respectively. It is worth pointing out that the WCOs studied showed both higher densities and kinematic viscosities than other vegetable oils-based lubricants found elsewhere (Sarma and Vinu, 2022). Table 4 shows the kinematic viscosities for the different WCO studied, calculated as the ratio of the dynamic viscosity relative to the density. As can be observed, CH-WCO, with the largest polymers and olig + dimers content (17.39 wt% and 15.51 wt%, respectively) and relatively low PUFAs content (37.05 wt%) showed the highest kinematic viscosity. Conversely, CR-WCO with the lowest polymers and olig + dimers content (3.29 wt% and 3.45 wt%, respectively), and high PUFAs content (54.08 wt%) showed the lowest kinematic viscosity (Tables 1 and 4). Consequently, the higher the percentage of polymers, oligomers and dimers, and the lower the PUFAs content were, the higher the kinematic viscosity. These results match the studies by Kim et al. (2010) and Hassanien and Sharoba (2014).

Table 4 displays the viscosity index (VI) values of the five WCO studied and their fractions (only for FF-, FR- and WM-WCO), which were calculated from their kinematic viscosities at 40 and 100 °C, as described in ASTM D2270. Many applications may demand the lubricant to perform across a wide range of conditions. Thus, lubricant's viscosity may be required to remain stable over temperature fluctuations, i.e., a high viscosity index. Hassanien and Sharoba (2014) pointed out that the viscosity temperature-sensitivity of vegetable oils was related with the number of double bonds in the fatty acids chains. Thus, they analyzed the viscosity temperature dependence of different vegetable oils subjected to deep frying based on both the oleic acid (C18:1) and the linoleic acid (C18:2) content. In our work, relatively high VI values of 210 and 208 were obtained for CR- and WM-WCO oils, respectively, with high content of C18:2. Moreover, a low VI value of 169 was obtained for FF-WCO, with low content of C18:2. However, FR-WCO with a high content of C18:2 also showed a low VI value of 179, whereas CH-WCO with lower C18:2 content displayed a higher VI value of 204. In this sense, it was found that both the total polar compound content and the acidity seem to have a direct effect on that property, and not the number of double bonds in the fatty acids chains. Thus, FF- and FR-WCO oils presented very high values of total polar compounds (33.5 and 37.18 wt%, respectively) and acidity (6.78 and 7.51 wt%, respectively), whilst CR- and WM-WCO oils presented low values of total polar compounds (9.83 and 19.00 wt%, respectively) and acidity (0.52 and 1.27 wt%, respectively).

On the other hand, WCO molecular distillation yielded heavy fractions with higher kinematic viscosity, and less viscosity-temperature dependent (higher VI values), than their corresponding fresh samples. Light and heavy fractions, with similar fatty acid compositions, noticeably differ in both their kinematic viscosity and their viscosity indexes. It can be, therefore, concluded that the nearly absence of free fatty acids is the reason behind the heavy fractions' high VI values. Molecular distillation has led to VI improvements of 19.9%, 7.3% and 14.9% for the FF-, FR- and WM-heavy fractions, respectively, as compared to their parent oils. If such heavy fractions were hypothetically used in any lubricant application, they would belong to API group IV as very high viscosity index lubricants (Delgado et al., 2017).

3.3.1. *Viscosity-temperature dependence*

Assessing the viscous flow behavior of the waste cooking oils studied within a low temperatures window is also of outstanding importance

Table 4

Kinematic viscosities (in cSt) at 25, 40 and 100 °C, and viscosity index values for the five WCO studied. Light and heavy fractions of selected WCO are also presented.

Temperature (°C)	Sunflower oil[a]	Common restaurant (CR)	Fast food restaurant (FF)	Deep-fried food establishment (FR)	Shop selling fritters (CH)	Non- segregated (WM)
25	64.42 ± 0.81	63.72 ± 1.54	72.05 ± 1.25	78.40 ± 1.09	101.12 ± 2.16	74.23 ± 1.83
40	32.90 ± 2.30	36.37 ± 2.07	40.63 ± 0.67	44.29 ± 1.77	53.80 ± 0.83	40.66 ± 0.38
100	8.40 ± 0.10	8.25 ± 0.74	7.87 ± 0.81	8.70 ± 0.88	11.06 ± 1.04	8.90 ± 0.56
Viscosity index	248	210	169	179	204	208
	FF-WCO		**FR-WCO**		**WM-WCO**	
Temperature (°C)	**Light fraction (L)**	**Heavy fraction (H)**	**Light fraction (L)**	**Heavy fraction (H)**	**Light fraction (L)**	**Heavy fraction (H)**
25	50.00 ± 0.99	80.14 ± 4.68	57.52 ± 4.02	87.57 ± 3.03	62.65 ± 1.37	77.06 ± 6.51
40	28.16 ± 0.81	42.12 ± 1.83	30.29 ± 0.29	46.36 ± 0.64	33.61 ± 2.58	39.52 ± 1.09
100	5.94 ± 0.16	8.90 ± 0.31	6.16 ± 0.33	9.40 ± 0.56	6.93 ± 0.25	9.57 ± 0.68
Viscosity index	163	199	158	192	173	239

[a] Data extracted from Quinchia et al. (2010).

since lubricants may need to perform under such thermal conditions. Hence, Fig. 3 illustrates their viscous flow behavior (at a selected shear rate value of 10 s^{-1}) between room temperature and −60 °C, according to a previous protocol pointed out by Quinchia et al. (2012). This test provided valuable information on the WCO lowest operating temperature. In relation with the low-temperature flow behavior displayed in Fig. 3, the evolution of the dynamic viscosity with temperature between room temperature and ca. 0 ºC corresponds to the typical Arrhenius-like dependence, as previously described in Quinchia et al. (2012) and Hassanien and Sharoba (2014) for a variety of fresh vegetable oils. In addition, on further cooling down to −60 °C, three thermal transitions were observed. Their related onset temperatures (T_{i1}, T_{i2} and T_{i3}) were summarized in Table 5. For the sake of comparison, sunflower oil results extracted from Quinchia et al. (2010) are also shown. T_{i1} denotes the beginning of the crystallization process, i.e., the nucleation step. At T_{i2}, a sudden fluidity loss (remarkable viscosity increase) was noticed because of the crystals growth process (Quinchia et al., 2012; Li and Wang, 2015). Below T_{i3} viscosity drastically increased because the WCO solidified. According to Erhan and Adhvaryu (2002) and Quinchia et al. (2012), a higher concentration of PUFAs delays the oil's fluidity loss down to lower temperatures. As shown in Fig. 3 CR- and WM-WCO oils, with 54.14 and. 54.23 wt% PUFAs, respectively, presented the highest values of fluidity loss temperature (T_{i2}), around of −10 °C. By contrast, FF-WCO, with just 29.16 wt% PUFAs, presented the highest values of T_{i2}, −5.5 °C. However, the PUFAs content by itself would not explain the low T_{i2} and T_{i3} values of −12.0 and −44.5 °C, respectively, found for CH-WCO (with only 37.08 wt%. PUFAs). Hence, it was found that the acidity may also affect the oil's fluidity at low temperature, given that FFAs have higher melting points than glycerides. Thus, CH-, CR- and WM-WCO oils, with the best fluidity at low temperature, presented the lowest values of acidity. Therefore, it suggest that free fatty acid molecules have a higher tendency to form macro crystalline structures at low temperatures than other chemical molecules presented in WCO, limiting its easy flow at lower temperatures.

As can be appreciated in Fig. 4, molecular distillation brought about light fractions which were more susceptible, in terms of fluidity loss, to temperature than their parent WCO. Such a low temperature flow behavior was due to a larger FFA content. Among them, FF light fraction showed the highest solidification temperature. This is due to its lower unsaturated/saturated fatty acid ratio of 6.86, as compared to 8.26 and 7.99 for FR- and WM-WCO light fractions, respectively (Quinchia et al., 2012). However, no significant differences were appreciated when heavy fractions and their parent WCO were compared, due to the low distillation yields above reported.

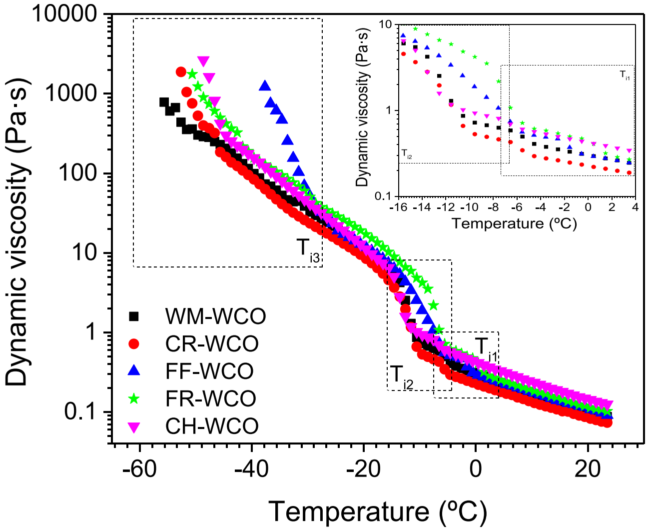

Fig. 3. Evolution of the dynamic viscosity, at 10 s^{-1}, with temperature for the WCO studied. Inlet plot show a magnification of the first onset temperatures.

Table 5
Characteristic temperatures from viscosity temperature evolution (Ti's) for the different WCO studied and their fractions (only FF, FR and WM).

Cooking oils	Onset temperatures of thermal events (°C)		
	T_{i1}	T_{i2}	T_{i3}
Sunflower Oil[a]	–	-8.5	–
CR	-4.8	-10.2	-46.1
FF	-1.0	-5.5	-28.0
FF-Light	6.2	-6.6	–
FF-Heavy	-4.1	-9.2	-34.5
FR	1.5	-5.6	-41.6
FR-Light	5.5	-2.9	-14.5
FR-Heavy	-0.9	-7.6	-43.5
CH	-5.6	-12.0	-44.5
WM	-5.0	-10.3	-53.0
WM-Light	10.7	–	-29.6
WM-Heavy	-6.2	-11.2	-49.0

[a] Data extracted from Quinchia et al. (2012).

3.4. *Waste cooking oils tribological behavior as related to its potential application in sustainable lubrication*

Fig. 5 depicts the evolution of the friction coefficient with the sliding speed for the WCO studied, as obtained by using a steel-steel ball-on-three plates-based tribocell under a normal force of 10 N (0.8 GPa Hertzian pressure), at 25 °C. In general, all WCO studied fit the typical behavior shown by the Stribeck curve. Thus, the friction coefficient was relatively high and almost constant at the low sliding velocity range (values lower than 20 mm/s), i.e., in the boundary film lubrication regime (solid friction occurs between asperities of the mating surfaces). Such a behavior is subsequently followed by a substantial reduction in the friction coefficient in the mixed lubrication regime, when the fluid friction starts taking place. Within the boundary region, all WCO studied showed friction coefficient values between 0.11 and 0.13, which is in accordance with other average friction coefficients found in lubricated asperity contacts (Bhushan, 2013). It is worth pointing out that FF- and FR-WCO, with the largest unsaturated to saturated fatty acid ratios of 9.69 and 8.26, respectively, showed the lowest values of friction coefficient within the boundary region and also along the mixed friction regime. In contrast, CR- and WM-WCO oils, which presented ratios of 8.07 and 6.86, respectively, exhibited noticeable higher values of friction coefficient. This result is in accordance with Martin et al. (2013) and de Barros Bouchet et al. (2017), who manifested that unsaturated fatty acids yield the best performance in terms of friction reduction, while saturated fatty acids such as stearic or palmitic acid are less efficient within the boundary friction regime. Furthermore, both FR- and FF-WCO showed the highest total polar compounds contents, 37.18 and 33.5 wt%, respectively, as compared for example to CR-WCO with only 9.83 wt%. FR- and FF-WCO oils also showed the highest acidity values, 7.51 and 6.78 wt%, respectively. As Guangteng and Spikes (1997) and Padgurskas et al. (2011) pointed out, polar molecules experience van der Waals attraction forces toward the solid surfaces, thus concentrating close to the mating surface and reducing friction. Therefore, the high content of polar compounds present in FF- and FR-WCO oils also justifies the greater lubricity provided by these WCO in comparison with the others.

Among the total polar compounds analyses, special attention was paid to the free fatty acids, i.e., to the light fractions. It is noteworthy that an improved lubrication performance at both boundary and mixed friction regimes was reached by using the molecular distillation light fractions (Fig. 6). As reported by Kimura et al. (1994), favorable boundary lubrication with free fatty acids was achieved by their monomolecular films which are strongly attached to metal surfaces by chemical bonds between their polar group (head of the chains) and the

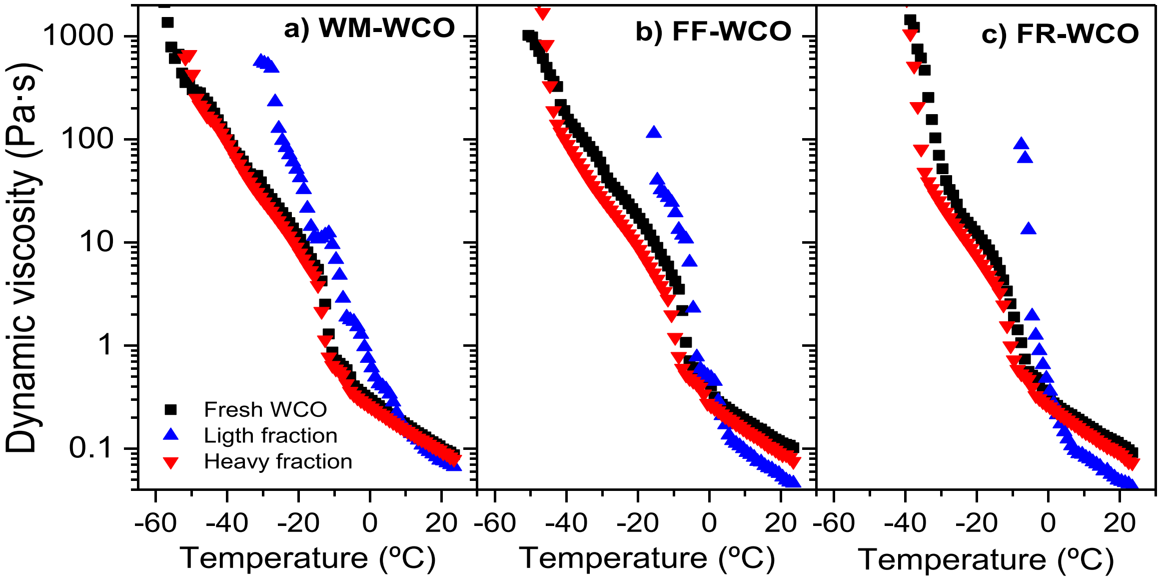

Fig. 4. Evolution of dynamic viscosity, at 10 s^{-1}, with temperature for: a) WM; b) FF; and c) FR. Their light and heavy fractions as obtained from molecular distillation are included for the sake of comparison.

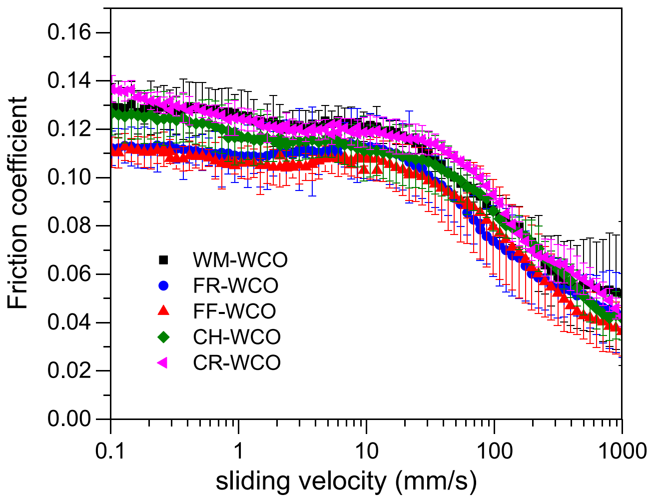

Fig. 5. Variation of the friction coefficient with the sliding velocity for all WCO studied upon application of a 10 N normal load at 25 °C.

surfaces, and by lateral attraction between their hydrocarbon chains. On the contrary, the heavy fractions revealed a worse lubrication performance at the boundary region, despite of their higher kinematic viscosity (Biresaw and Bantchev, 2008). However, with the exception of FF-WCO, the remaining heavy fractions exhibited an enhanced tribological performance within the mixed friction region with respect to their fresh WCO. At this region, fluid friction starts gaining importance such that the film thickness play a relevant role. In this sense, the coefficient of friction was greatly affected by the viscosity of the lubricant, which was in turn increased by the high molecular weight polar compounds (Guangteng and Spikes, 1997). Therefore, the lower viscosity and high polarity of the light fractions obtained by molecular distillation (consisting entirely of free fatty acids) resulted in a base-oil with noticeable friction-reducing properties within the entire lubrication regime (from the boundary to the hydrodynamic region). Thus, waste cooking oils molecular distillation has been proved to be a key strategy to obtain more efficient liquid lubricants, which could even be used as friction-reducing additive for other formulations.

Finally, wear was assessed in stationary friction conditions within the mixed lubrication regime (10 N as normal load and 16 mm/s as sliding velocity) for 30 min. For all WCO studied and their light (L) and

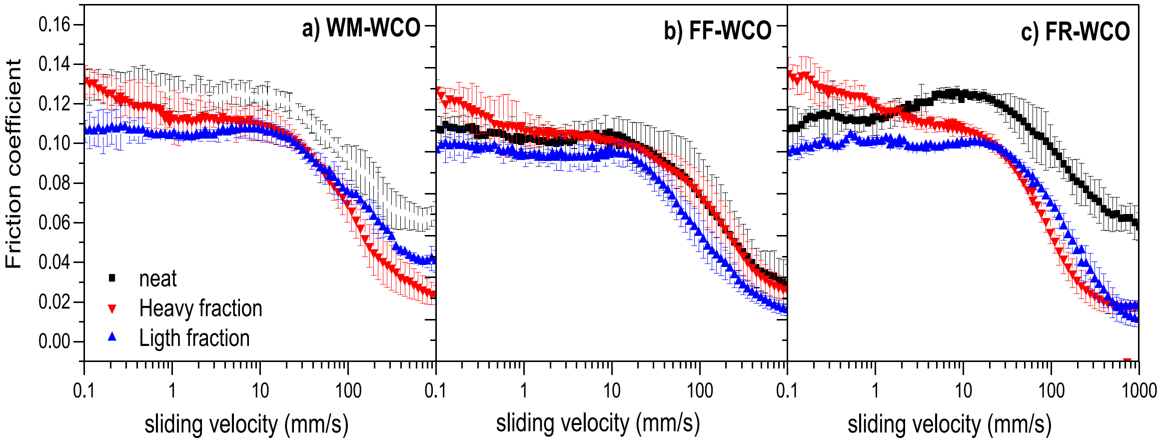

Fig. 6. Variation of the friction coefficient with the sliding velocity for the light and heavy fractions obtained from molecular distillation upon application of a 10 N normal load at 25 °C: a) WM-; b) FF-; c) FR-WCO oils. Parent WCO included for the sake of comparison.

heavy (H) fractions, Fig. 7 shows both the steady state friction coefficient values and the average diameters of the wear scars formed on the steel plates. Four out of five WCO showed wear scar diameters within the range 500–600 μm. However, very significant differences were found on their corresponding friction coefficient values. Thus, FF- and FR-WCO oils clearly showed the lowest friction coefficients at the mixed friction regime, as it was discussed above (Fig. 5). In addition, the molecular distillation fractions also showed improved tribological properties. Wear reductions of 11.7%, 44.3% and 36.8% were reached with the light fractions from WM-, FF- and FR-WCO oils, respectively, as compared to their parent WCO. As commented above, the free fatty acids existing in the light fraction contributed to such wear reduction by the formation of an adsorbed layer (Padgurskas et al., 2011). In addition, the light fractions developed a more stable lubrication, with less variation of the friction coefficient within the whole time interval analyzed. On the other hand, the heavy fractions from WM, FF- and FR-WCO oils displayed wear scar reductions of 28.2%, 43.9% and 28.0%, respectively, as a consequence of their higher viscosity (Guangteng and Spikes, 1997). Thus, it is worth concluding that molecular distillation led to two fractions, light and heavy, with improved tribological properties within the mixed friction regime as compared to their parent waste cooking oils.

4. Conclusions

WCO studied showed noticeably variations in theirs chemical composition, attributed to several variables involved in the different frying process studied. Thus, FF- and FR-WCO oils showed the high content of free fatty acids and diglycerides, due to the hydrolysis of triglycerides provoke by the deep-frozen foods. Moreover, FR- and CH-WCO oils presented the highest formation of major molecules (oligomers +dimers, and polymers), which revealed a higher number of "in/out" cycles of the food that favors the entry of air. Even so, CH-WCO showed a rather low acidity indicating a lower degree of hydrolysis probably due to the type of fried food processed.

These variations in chemical composition affected the studied properties in different ways. Thus, CH-WCO, with the highest molecules (oligomers +dimers, and polymers), and low PUFAs content showed the highest kinematic viscosity. On the contrary, CR-WCO with the lowest content of major molecules and high PUFAs content showed the lowest kinematic viscosity. In addition, FF- and FR-WCO oils, with the highest values of total polar compounds and acidity, showed the lowest viscosity index values (169 and 179, respectively), whereas CR- and WM-WCO, with the lowest values of total polar compounds and acidity, showed the highest viscosity index vales (210 and 208, respectively), thereby being less temperature susceptible. Moreover, it was found that acidity also affected the oils' fluidity at low temperature such that CH-, CR- and WM-WCO, with the best fluidity at low temperature, presented the lowest values of acidity. Finally, it was concluded that the high acidity and large unsaturated to saturated fatty acid ratio of FF- and FR-WCO oils endowed these WCO with the greatest lubricity.

The most outstanding result was that molecular distillation yielded two fractions, light and heavy, with highly enhanced tribological properties as compared to their parent waste cooking oils. Thus, the low viscosity and high polarity of the light fractions, enriched in free fatty acids, yielded an improved lubrication performance at both boundary and mixed friction regimes. Favourable boundary lubrication was achieved most probably due to the attachment of FFA to the metal surface by chemical bonds. Moreover, the heavy fractions, enriched in major molecules, exhibited an enhanced tribological performance within the mixed friction region, where fluid friction starts gaining importance. Furthermore, wear reductions of 11.7%, 44.3% and 36.8% were achieved with light fractions from WM-, FF- and FR-WCO oils, respectively. Finally, molecular distillation produced a light fraction with improved oxidative resistance (higher OOT values) and a heavy fraction with enhanced thermal stability. In consequence, molecular distillation has been proven to be a way to valorize waste cooking oils and obtain efficient liquid eco-lubricants.

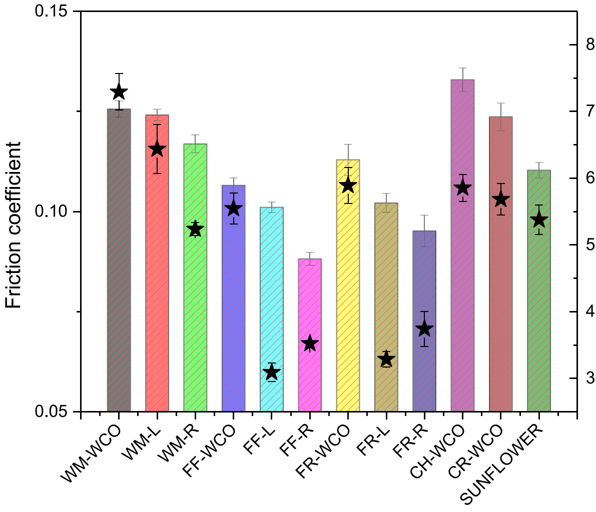

Fig. 7. Stationary friction coefficients (bars) and wear scar diameter (stars) obtained by applying a constant sliding velocity of 16 mm/s and normal load of 10 N at 25 °C.

CRediT authorship contribution statement

S.D. Fernández-Silva: Data curation, Investigation, Software. **M.A. Delgado:** Conceptualization, Data curation, Funding acquisition, Project administration, Supervision, Validation, Writing – original draft. **M. V. Ruiz-Méndez:** Data curation, Resources. **I. Giráldez:** Data curation, Investigation, Resources. **M. García-Morales:** Conceptualization, Formal analysis, Funding acquisition, Supervision, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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