




Article

Technical Performance and Chemical–Physical Property Assessment of Safflower Oil Tested in an Experimental Hydraulic Test Rig

Luisa Ugolini ^{1,*} , Roberto Matteo ^{1,*} , Luca Lazzeri ¹, Lorena Malaguti ¹, Liliana Folegatti ², Paolo Bondioli ³ , Daniele Pochi ⁴, Renato Grilli ⁴, Laura Fornaciari ⁴, Stefano Benigni ⁴ and Roberto Fanigliulo ⁴

¹ Research Centre for Cereal and Industrial Crops, Consiglio per la Ricerca in Agricoltura e l'Analisi dell'Economia Agraria (CREA-CI), Via di Corticella 133, 40128 Bologna, Italy

² Innovhub-Stazioni Sperimentali per l'Industria Srl Area Oli e Grassi, Via G. Colombo 79, 20133 Milano, Italy

³ Freelance Expert, 20133 Milano, Italy

⁴ Research Centre for Engineering and Agro-Food Processing, Consiglio per la Ricerca in Agricoltura e l'Analisi dell'Economia Agraria (CREA-IT), Via della Pascolare 16, Monterotondo, 00015 Rome, Italy

* Correspondence: luisa.ugolini@crea.gov.it (L.U.); roberto.matteo@crea.gov.it (R.M.)

Abstract: Safflower (*Carthamus tinctorius* L.) is an underestimated and multipurpose crop resistant to environmental stresses. Its oil presents useful chemical–physical properties, potentially exploitable for industrial purposes as a bio-based lubricant. In this work safflower oil was applied as a less toxic alternative to mineral-based hydraulic fluids. The extracted oil was partially refined and the antioxidant tert-butylhydroquinone (TBHQ) was added at two concentrations (0.25 and 3.00 mg kg^{−1}). Efficiency tests of the obtained oil were carried out using an experimental test rig capable of simulating a real hydraulic system and performing severe short-duration work cycles with the aim of strongly accelerating the ageing of the tested oil. Oil performance was verified by monitoring hydraulic and chemical–physical parameters, which were correlated to the main lubricant properties through sensor detection and laboratory analysis in parallel. The results indicated that the safflower oil behaved well at both TBHQ concentrations and showed good technical performance (operating pressure and temperature; flowrate and transmitted hydraulic power), though a higher TBHQ concentration was necessary to protect the oil's chemical–physical properties from worsening. In fact, the higher TBHQ concentration allowed the test to be extended to 270 h, an improvement compared to the 150 h that was achieved with the lower TBHQ concentration. Finally, the use of safflower oil for industrial and agricultural purposes seems feasible and would contribute toward the sustainability of the whole crop rotation in a prospective valuable circular economy.

Keywords: semi-refined vegetable oil; biolubricants; high-pressure pump; tert-butylhydroquinone; agricultural hydraulic applications; green chemistry; circular economy



Citation: Ugolini, L.; Matteo, R.; Lazzeri, L.; Malaguti, L.; Folegatti, L.; Bondioli, P.; Pochi, D.; Grilli, R.; Fornaciari, L.; Benigni, S.; et al. Technical Performance and Chemical–Physical Property Assessment of Safflower Oil Tested in an Experimental Hydraulic Test Rig. *Lubricants* **2023**, *11*, 39. <https://doi.org/10.3390/lubricants11020039>

Received: 23 December 2022

Revised: 12 January 2023

Accepted: 17 January 2023

Published: 20 January 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The total global demand for lubricants reached 37 million metric tons in 2020 and is expected to grow to 38.1 million metric tons by 2028 [1]. As mineral oil supply has limits, biolubricants have recently been developed as alternatives. These lubricants are characterized by high biodegradability and low toxicity, and their use is particularly advised in sectors where high dispersion causes environmental and safety risks [2].

Agriculture plays a central role as a source of raw materials and determines the development of sustainable agricultural practices that form the base of a circular economy. Oleaginous crops are a renewable source of bio-products such as vegetable oils and biomasses rich in bioactive molecules and proteins. The potential use of vegetable oils in different green chemistry sectors is particularly important today in terms of environmental sustainability and is in line with the European Green Deal goals thanks to the low toxicity

and eco-compatibility of the oils. Vegetable oils are known for their potential applications as hydraulic fluids thanks to their high lubricity, low evaporative loss, high viscosity index, and flash point, which are factors that permit safe use, transportation, and storage [3]. The most used vegetable oil in Europe for industrial applications is rapeseed, and vegetable oils can be obtained from more than 300 oilseed crops and different forms of agricultural waste [3]. Recently, processed crambe oil and pomace oil were tested as hydraulic fluids and, when subjected to extreme work cycles in an experimental test rig, promising results were obtained in terms of hydraulic performance and stability [4,5]. Corn oil was evaluated for its wear and friction behavior and performed better than a reference mineral hydraulic fluid [6]. Oils obtained from berry seeds via supercritical extraction were successfully tested as working fluids in laboratory and bench tests [7]. A mixture of vegetable and mineral oil was also evaluated by Hilal et al., and the presence of vegetable oil was shown to enhance the flow properties of the fluid in a closed hydraulic circuit [8]. Even if the blending of mineral and vegetable oils provides benefits from the better properties of both fluids, these mixtures cannot be correctly reprocessed at the end of their operating life, neither along the recycling chain of vegetable oil nor mineral oil, and must be destroyed or disposed of. On the contrary, the recycling of pure fluids is an efficient example of fluid life cycle closure. In the near future, it is likely that the increasing awareness of environmental safety will help to widen the uses of vegetable oils, thus lowering their price and enhancing technology in hydraulic system applications. Vegetable oil's low oxidative stability is a major shortcoming that depends on its composition and could be overcome by chemical modifications or formulation development with an antioxidant additive [9]. In fact, fatty acid composition and, in particular, the fatty acid unsaturated forms, determine the oil's oxidative stability. Oleic acid, for example, is particularly stable and provides oxidative stability and resistance to polymerization of the oil. Chemical modification of natural oils and fats, i.e., esterification of natural fatty acids with neoglycols to modify kinematic viscosity and to improve thermal stability, is possible but the use of unmodified oil should be encouraged as it shortens the chain between the field and the application.

Safflower (*Carthamus tinctorius* L.), from the Asteraceae family, is an annual crop. This xerophilous species, native to Asia and the Mediterranean basin, grows well in arid and semi-arid regions [10,11] and is defined as a climate-smart crop that is adaptable to variable environmental growing conditions [12]. Despite it being a multipurpose crop that could be used as a medicinal plant, in tea production, and for foraging purposes [13,14], in recent years safflower has been cultivated mainly for food and feed purposes due to its highly polyunsaturated fatty acids profile [15]. Furthermore, safflower has traditionally been cultivated for its flowers, which were used as a colorant for textiles and food until the end of the 1800s [16,17] due to the presence in the floret of Carthamin, a red alcohol-soluble pigment, and Carthamidin, a yellow and water-soluble pigment. After renewed interest in "coloring foods" and natural dyes, cultivation was rapidly re-embraced in the EU [18]. Currently, safflower oil is mainly imported from Asia, especially China, though interesting perspectives are emerging from research into the selection of varieties of safflower for the purposes of adaptation to the Mediterranean climate, both during summer [19] or winter cycles, given its tolerance to low temperatures [20]. The oil's fatty acid composition is highly variable, with the main fatty acids represented by the unsaturated oleic and linoleic acids, which are present at different ratios in relation to the environmental growth conditions. The industrial uses of safflower oil are poorly studied and mostly limited to the use of the oil as biofuel [21]. A possible tool to improve the oxidative stability of the oil and its performance for industrial purposes as biodiesel or a biolubricant is through genetic engineering that enables the selection of high oleic safflower varieties [22]. A super high oleic safflower with improved properties in terms of industrial applications was developed by the Australian Grain Research & Development Corporation (GRDC) and the Commonwealth Scientific and Industrial Research Organisation (CSIRO) [23].

Safflower is an under-utilized crop whose adaptability should be further exploited, with its oil's industrial applications also deserving of more investigation. In this work,

open-field safflower cultivation, the subsequent extraction of oil from harvested seeds, chemical treatments, and additivation studies on the same oil are described. At a later stage, a partially refined safflower oil was tested as a hydraulic fluid in an experimental fluid test rig (FTR) capable of simulating a real hydraulic system to explore its possible application in industrial and agricultural sectors. The FTR, previously used to test vegetable oils [24], was further enhanced with sensors to continuously monitor the oil's behavior and to make the efficiency test more robust and safe.

2. Materials and Methods

2.1. Safflower Cultivation and Oil Extraction

Safflower seeds (*Carthamus tinctorius* L.), variety Montola 2000, were obtained from cultivated plants growing at the experimental fields of CREA-CI in Budrio (Bologna, Italy; 44°32'00'' N, 11°29'33'' E; 28 m above sea level). Sowing was carried out in spring (March 2017) on a 1100 m² plot previously plowed and fertilized with cattle manure amendment (C/N 15%, 600 kg ha⁻¹). A treatment of DECIS® + CONFIDOR® was applied for containment of the safflower fly (*Acanthophilus helianthi*) at a rate of 0.2 and 0.3 L ha⁻¹, respectively. Seeds were harvested in the third decade of July and cleaned and defatted via heating at 80 °C and the application of mechanical pressure (MIG srl, Fornovo San Giovanni, Bergamo, Italy). The obtained oil was paper-filtered and stored at room temperature while protected from light. Seeds and defatted seed meal were characterized for dry matter, oil, and nitrogen content as described in [5].

2.2. Oil Chemical Treatment and Additivation Studies

Extracted safflower oil was degummed in an acid environment for the removal of phospholipid, calcium, and phosphorous or metallic contamination. The procedure consisted of oil hydration and homogenization with a 10% citric acid aqueous solution at 70 °C, precipitation of phospholipids, and a final washing of the solution with water as described in [5]. To avoid excessive foam formation, a drop of silicon antifoam agent (active silicon polymer, Merck KGA, Darmstadt, Germany) was also added at the beginning of the degumming process. The obtained oil was finally filtered on cotton wool and through a paper filter press (7-µm) to remove residual water.

Before testing in the FTR, tert-butylhydroquinone (TBHQ) (CAS1948-33-0, 97%, Merck KGA, Darmstadt, Germany) at two concentrations was added to the degummed oil. The first addition was kept to a low concentration of 0.25 g kg⁻¹, while the second one of 3.00 g kg⁻¹ was chosen as the optimum concentration according to a TBHQ dose–response study on oil stability and was measured using Rancimat equipment at lab scale (Section 2.5). TBHQ addition was performed by preparing a stock concentrated solution in oil at 60 °C, which was then diluted in the rest of the oil to be used for the FTR trials performed at the two final TBHQ concentrations.

2.3. Experimental Fluid Test Rig

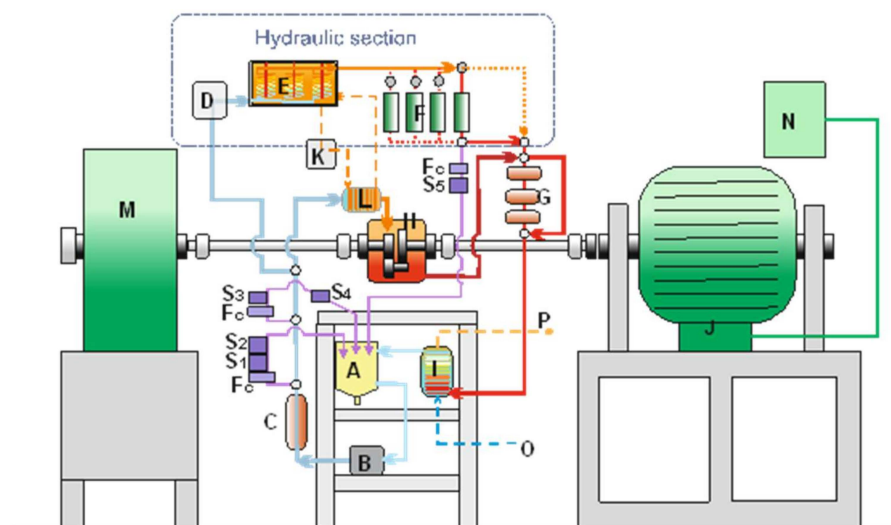
The FTR, designed and realized at the CREA-IT workshop, applied severe hydraulic workloads to the tested fluids. The FTR consisted of a lower pressure section, for fluid circulation and filtering, and a high-pressure section, for application of the hydraulic workload [24,25].

The main components of the FTR's sections are summarized in Table 1.

Table 1. Main components of the hydraulic section of the fluid test rig (FTR).

FTR Section	Component	Manufacturer	Model	Measurement Range/Setting
Low pressure	Oil reservoir	Self-made at CREA	-	Volume: 30 dm ³
	Horizontal multistage pump	Ebara Pumps Europe (Vicenza, Italy)	MATRIX3 5T/0.75M HT	Max flowrate: 80 dm ³ min ⁻¹ ; max pressure: 0.5 MPa; power: 0.75 kW
	Digital pressure gauge	Kobold Instruments (Milano, Italy)	SEN-329701/2B065	Measurement range: 0–6 MPa
	Flow meter	Kobold Instruments (Milano, Italy)	DON-215H	Measurement range: 15–550 dm ³ h ⁻¹
	Main filter	Donaldson Company (Minneapolis, USA)	P171533	Cartridge filtration mesh: 23 µm
	Oil-to-water heat exchanger	Pacetti S.r.l. (Ferrara, Italy)	BV 50–40 plate	Fluid operating temperature: 60 °C
High pressure	High-pressure radial piston pump	Atos Group (Sesto Calende, Italy)	PFR203	Displacement: 3.5 dm ³ ; max speed: 1800 min ⁻¹ ; max pressure: 50 MPa; max power: 5 kW
	Digital inverter	Toshiba (Tokyo, Japan)	VF-AS1 4055 PL-WP	-
	Fluid heating unit	Self-made at CREA	-	Thermal leap up to 40 °C
	Distributor with four solenoid valves	Self-made at CREA	-	-
	Four overpressure valves	Bosch Rexroth (Lohr am Main, Germany)	DBDS 6G 1X	10, 20, 30, 40 MPa
	Digital pressure gauge	Kobold Instruments (Milano, Italy)	SEN-329701/2A165	Measurement range: 0–60 MPa

The cooling system was set to keep the temperature of the oil entering the high-pressure pump (HPP) lower than 60 °C in order to comply with the operating limits of the pump. A fluid heating unit was installed between the HPP and the overpressure valves. This was designed to create additional thermal stress on the fluid. Due to the combined effects of the HPP and the fluid heating unit, the oil in the HP section underwent a thermal leap of 40 °C, and the temperature of the oil outflowing the overpressure valve exceeded 100 °C. The FTR was also equipped with thermocouples and pressure gauges to monitor oil conditions at the reservoir output, circulation pump, and overpressure valves. Figure 1 shows the experimental setup of the FTR, which was integrated within a tractor testing room featuring a dynamometric brake capable of assessing the dynamic–energetic balance of tractors [26].

**Figure 1.** Fluid test rig experimental setup. (A) Oil reservoir; (B) low-pressure circulation pump; (C) main filter; (D) HP piston pump; (E) hydraulic section fluid heater; (F) distributor block with four

solenoid valves and four pressure valves (10, 20, 30, 40 MPa); (G) series of three fine filters (3, 6, 10 μm filtration mesh) and a bypass; (H) transmission group; (I) heat exchanger; (J) 40 kW electric engine; (K) pump circulating the water–ethylene glycol solution of section E; (L) transmission section fluid heater; (M) dynamometric brake; (N) digital inverter controlling the electric engine; (O) cooling water inlet; (P) cooling water outlet; (Fc) fluid flow controllers; (S1) Parker “FPS 2810” at the main filter outlet; (S2) Parker “i-Count”; (S3) Argo-Hytos “LubCos H2O plus”; (S4) Argo-Hytos “OpCom FerroS”; (S5) Parker “FPS 2810” at the high-pressure valve outlet. Solid line arrows indicate the oil flow’s direction. Dashed blue line arrows indicate the flow of the cooling solution. Purple lines indicate the fluid flowing through the sensors.

The latter was used to apply mechanical loads to an oil bath transmission and was operated by an electric engine. This “transmission section” also allowed the FTR to be used in tests of transmission lubricants and multifunction fluids, such as UTTO (Universal Tractor Transmission Oils) [27].

Control of the FTR’s technical parameters (pressure, flowrate, temperature) allowed real-time calculation of the hydraulic power developed, the hydraulic work performed, and the heat dissipated by the fluid. The repeatable test conditions permitted comparisons of the technical performances of different fluids and the evolution of their main chemical–physical properties. The working conditions applied to the safflower oil in the FTR are summarized in Table 2.

Table 2. Working conditions applied to the safflower oil in the fluid test rig (FTR).

Technical Parameters	Unit	FTR Working Conditions
Tested oil volume	dm^3	22
Pressure in the low-pressure section	MPa	0.15
Oil temperature in the reservoir ¹	$^{\circ}\text{C}$	≤ 60
Oil temperature after lamination ²	$^{\circ}\text{C}$	$\cong 100$
Flow rate	$\text{dm}^3 \text{ min}^{-1}$	5.4
Pressure applicable in the HP section ³	MPa	40
HPP maximum speed	min^{-1}	1800
Hydraulic power	kW	3.8

¹ Before HPP. ² At 40 MPa. ³ The test was carried out at the highest pressure.

Regarding the duration of the test, the intensity of the work cycle was assessed based on both the hydraulic work performed and the thermal energy dissipated by the volume unit of the fluid, i.e., the total specific energy (kWh dm^{-3}). According to such an approach, some correspondence was found between a work cycle of 150 h in the FTR with 20–25 dm^3 of oil under the settings described in Table 2 and the work done by the hydraulic system of a tractor with medium power containing 80–100 dm^3 of oil in a period of use of 800–1000 h (approximately corresponding to one year of work and the time oil should be replaced) [25]. However, it must be considered that most tractors adopt UTTO fluids. These, in addition to operating the hydraulic system, also work as transmission lubricants and undergo workloads and ageing processes significantly heavier than those of normal hydraulic fluids whose lifetime is commonly very long. For this reason, the duration of the test where safflower oil was used as a hydraulic fluid in the FTR was extended beyond 150 h with the aim of observing its behavior and the occurrence of any variation in technical performance and/or chemical–physical parameters. To this purpose, all working parameters and data from sensors (see below) were continuously monitored (frequency of acquisition: 1 Hz). One-minute data averages were stored for subsequent data processing.

2.4. FTR Sensors and Fluid Chemical–Physical Parameter Acquisition

The FTR was equipped with a series of multiparametric sensors (S1 to S5 in Figure 1) for in-line monitoring of fluid status, which was performed through the measurement of some chemical–physical parameters which correlated to the main lubricant properties [28]. The most significant parameters detected by sensors were compared to confirm the correctness of their

measurements, with corresponding parameters measured by standard analytical methods in the laboratory using fluid samples periodically withdrawn from the FTR. In particular:

- Dynamic viscosity, VD (mPa s^{-1}), and density, D (g cm^{-3}), were determined by sensor S1 and S5.
- Kinematic viscosity, KVs (cSt or $\text{mm}^2 \text{s}^{-1}$), was provided by the ratio of VD to D . KVs was directly compared to the reference laboratory KV values measured by the viscometer according to ASTM D445-06 [29] at the reference temperatures of 40°C (KV_{40}) and 100°C (KV_{100}).
- Relative permittivity, P_R (or relative dielectric constant), was detected by S1, S5, and S3 and was compared to the peroxide value (PV), determined according to the ISO 3960:2017 standard method [30], and total acid number (TAN), evaluated following the ISO 660:2020 method [31].
- Electric conductivity, EC (pSi m^{-1}), was detected by sensor S3 and (for P_R) was also compared to the PV and TAN determined in the laboratory.
- Relative humidity, RH (%), describes the amount of water in the fluid as a percentage of the maximum soluble amount and is a value that increases with fluid temperature. This was detected by sensor S3. In parallel, the fluid's water content was measured in the laboratory (Karl Fisher method) by using a Karl Fischer automatic titrimeter (Metrohm, Herisau, Switzerland) according to the ISO 8534:2017 standard [32], which thus provided the absolute concentration in mg kg^{-1} (KF).
- Ferromagnetic particles, FMP, which could indicate the presence of wear processes, were detected by sensor S4 and their intensity is described by their amount and dimensions. S4 featured a magnetic head capable of attracting any ferromagnetic particles suspended in the fluid, with the captured particles classified as fine particles, coarse particles, or chunks. The amount of fine and coarse particles is expressed as a percentage of the occupancy rate (maximum total amount attractable by the magnetic head), while for the chunks their number is provided. When 100% of the occupancy rate was reached, the magnetic head automatically discharged, releasing the material. The detection then restarted. The trend in occupancy rate during the test was compared to that of the Fe concentration observed in fluid samples.
- Particle contamination was monitored by sensor S2. The level of contamination depends on the number of particles per fluid volume unit within certain dimensional classes, which is counted by the mean of automatic laser counters. The contamination is then expressed as "class of contamination", which is described by numbers (codes) according to international standards such as NAS 1638 [33] and ISO 4406:2021 [34]. In this study, the latter was considered, whose classification is based on three dimensional classes: $< 4 \mu\text{m}$, $< 6 \mu\text{m}$, $< 14 \mu\text{m}$. The relative codes vary from 1 to 22 depending on the number (n) of particles per ml of oil detected in each class. Therefore, oil status is described by three numbers. Despite the ISO 4406 codes ranging from 1 to 22, the range between 7 and 22 is the most frequently considered in practical applications.

Among these parameters, KVs , P_R , EC , and RH are strongly temperature dependent. Thus, information regarding fluid status obtained by measuring the fluids can be useful only if the values refer to the same temperature conditions. In this case, their variations could signal some form of oil alteration. Information on sensors is reported in Table 3 together with the main parameters they monitored, the corresponding parameter measured in the laboratory, and the fluid alterations which could cause their variations.

Table 3. Sensor descriptions, measured parameters, corresponding laboratory parameters, and possible fluid alterations connected to parameter variations. VD: dynamic viscosity (mPa s^{-1}); KV₄₀ and KV₁₀₀: kinematic viscosity at 40 °C and 100 °C (cSt); D: fluid density (g cm^{-3}); P_R: relative permittivity; PV: peroxide value ($\text{meq O}_2 \text{ kg}^{-1}$); TAN: total acid number (mg KOH g^{-1}); T: temperature (°C); RH: relative fluid humidity (%); KF [H₂O]: water content according to the Karl Fisher method (mg kg^{-1}); EC: electric conductivity (pS m^{-1}); ISO 4406:2021 [34]: classification of fluid contamination levels in the particle classes < 4 μm , < 6 μm , and <14 μm ; FMP, ferromagnetic particles; [Fe]: concentration of Fe (and other elements).

Manufacturer	Sensor		Measured Parameters	Laboratory Parameters	Possible Fluid Alterations
	Model	Symbol			
Parker	FPS 2810	S1–S5	VD D P _R T	KV ₄₀ , KV ₁₀₀ PV, TAN -	Primary oxidation, secondary oxidation Oxidation Thermal stress
Parker	i-Count	S2	Particles	ISO 4406:2021	Contamination with particles of various origin
Argo-Hytos	LubCos H2O plus	S3	RH P _R	KF [H ₂ O] PV, TAN	Contamination with water Primary oxidation, secondary oxidation
			EC	PV, TAN, KF [H ₂ O]	Primary oxidation, secondary oxidation, polar products, contamination with water and/or other substances
			T	-	Thermal stress
Argo-Hytos	OPCom FerroS	S4	Fine FMP occ. rate Coarse FMP Chunk	[Fe]; other metals	Wear of materials

The sensors were placed in different points on the FTR, as shown in Figure 1 where they are labeled with the symbols indicated in Table 3. To this purpose, they were suitably grouped and installed in fluid lines that were each provided with a flow controller, Fc, that allowed specific flowrate values to be maintained so that the sensors worked correctly.

The first group of sensors, comprising Fc, S1, and S2, was in the delivery line after the main filter. Here, the flowrate was adjusted to allow the fluid (at about 60 °C) to partially cool down and maintain its temperature at 40 °C. Fluid VD, D (and relative KVs), and P_R were detected by S1. The fluid then entered the area monitored by S2, where a laser scanner detected the suspended particles and classified them by their dimensions and number as described above. Each hydraulic machine had characteristic ISO codes. To ensure proper operation of the machines, the fluid used to operate them must not exceed these codes.

The second group of sensors was formed by Fc, S3, and S4. It was also placed on the delivery line; however, in this case, it worked on the fluid at about 60 °C (the exercise temperature in the reservoir). S3 detected the fluid T and RH at 20 °C and P_R and EC at 40 °C, while S4 attracted, classified, and discharged any ferromagnetic particles suspended in the fluid.

The third group of sensors only consisted of Fc and S5 and was placed downstream of the overpressure valve, where it received the fluid at about 90 °C after it had already partially cooled from the 100 °C measured by a thermocouple at the valve outflow. Similarly to S1, S5 measured VD and D, which were used to calculate KVs at about 90 °C.

2.5. Oil and FTR Fluid Laboratory Chemical–Physical Characterization

Crude, treated oil, and the FTR fluids were analyzed for fatty acid composition (%), metal and contaminant element content (mg kg^{-1}), free fatty acid content (% oleic acid), TAN (mg KOH g^{-1}), PV ($\text{meq O}_2 \text{ kg}^{-1}$), water content (KF) (mg kg^{-1}), KV at 40 and 100 °C (cSt); viscosity index (VI), oxidation stability at 120 °C (Rancimat test), and TBHQ fluid content (g kg^{-1}) (HPLC analysis) using standard methods and equipment as described in [5].

2.6. Statistical Analysis

Analyses were repeated twice independently after a repeatability check. Each standard method measurement is reported with a 95% confidence level. For all other analyses, the standard deviation (SD) was determined. Comparisons between the series of values obtained by sensors and the laboratory equipment were based on Pearson's tests for linear correlation.

3. Results and Discussion

3.1. Safflower Seed Production, Oil Extraction, Characterization, and Partial Refining

After harvest and seed cleaning, 275 kg of available seeds were obtained from a 1100 m² plot with a potential yield of 2.5 t ha⁻¹, which is higher than a yield of the same variety previously cultivated in Italy [19]. Considering the reduced effort required for cultivation in terms of energy and fertilizer input and the interest that this crop has been gaining over the last few years in southern EU countries, this represents an interesting starting point for vegetable oil-based lubricant production. As discussed in the introduction, yield and net income could increase in the near future through increased research on genetic improvements and agronomical techniques [12,20,35]. The seeds' oil content was 31.9% based on dry weight (DW), which is comparable to other values found in the literature [19,36]. Oil extraction was performed two times (2018 and 2020) through a mechanical process and heat was applied to the seeds before extraction to improve oil extraction yield. A high yield of oil (81.2–84.9% of the initial content) and defatted seed meal with low residual oil content (6.2–8.8% based on DW) were obtained from the two trials. Seed oil quality was evaluated and fatty acid composition showed a high percentage of monounsaturated omega-9 oleic acid and polyunsaturated omega-6 linoleic acid, which represents 54% and 36% of total fatty acids, respectively (Table 4).

Table 4. Safflower oil fatty acid composition. Fatty acid percentage is reported as the average value of two independent analyses \pm uncertainty of measurement. M = mean. Ue = expanded uncertainty associated with a test result based on a coverage factor of K = 2 and a level of confidence of 95%.

Fatty Acids		M \pm Ue %
Miristic acid	C 14:0	0.09 \pm 0.01
Pentadecanoic acid	C 15:0	0.01 \pm 0.02
Palmitic acid	C 16:0	5.86 \pm 0.24
Palmitoleic acid	C 16:1	0.13 \pm 0.02
Eptadecanoic acid	C 17:0	0.03 \pm 0.01
Stearic acid	C 18:0	2.23 \pm 0.16
Oleic acid	C 18:1	54.24 \pm 2.44
Linoleic acid	C 18:2	36.07 \pm 2.41
Linolenic acid	C 18:3	0.08 \pm 0.05
Arachidic acid	C 20:0	0.40 \pm 0.03
Eicosenoic acid	C 20:1	0.25 \pm 0.03
Behenic acid	C 22:0	0.28 \pm 0.03

The high ratio of oleic acid to linoleic acid found in safflower oil is considered beneficial for industrial applications as it is known to indicate that the oil has higher oxidative stability [22].

Crude oil elemental analysis showed the absence of metals or contaminants, possibly due to plants or components with potential oxidative activity (Table 5).

Table 5. Elemental analysis of crude and degummed safflower oil derived from the first and second extractions (2018 and 2020). Results are reported as the average value of two independent analyses \pm uncertainty of measurement.

Elements		Crude Oil 1st	Crude Oil 2nd	Degummed Oil 1st	Degummed Oil 2nd
Wear metals					
Fe	mg kg ⁻¹	<1.0	<1.0	<1.0	<1.0
Ag, Al, Cr, Cu, Mn, Ni, Ti, Sn, Pb	mg kg ⁻¹	<1.0	<1.0	<1.0	<1.0
Contaminant elements					
K	mg kg ⁻¹	6.6 \pm 1.6	14.0 \pm 2.5	<1.0	<1.0
Na	mg kg ⁻¹	<1.0	2.0 \pm 0.5	<1.0	<1.0
V	mg kg ⁻¹	<1.0	<1.0	<1.0	<1.0
Si	mg kg ⁻¹	<1.0	<1.0	3.1 \pm 0.1	<1.0
Additive elements					
P	mg kg ⁻¹	23.1 \pm 0.9	60 \pm 6.3	5.0 \pm 0.7	<4.0
Ca	mg kg ⁻¹	9.6 \pm 0.2	18 \pm 0.2	1.7 \pm 0.2	<1.0
Mg	mg kg ⁻¹	5.6 \pm 0.5	13 \pm 0.5	<1.0	<1.0
Mo, Zn, Ba	mg kg ⁻¹	<1.0	<1.0	<1.0	<1.0
Free fatty acids	% oleic acid	0.57 \pm 0.07	1.4 \pm 0.05	0.55 \pm 0.07	1.13 \pm 0.05

The oils showed low free fatty acid content, especially the one obtained after the first extraction, thus demonstrating that the oil has good quality in terms of being a starting raw material.

Element analysis also revealed high Ca and P content, which is related to phospholipid content and dangerous in terms of potential oil sludge formation [37]. This high content was probably due to the heat applied during the extraction process, as observed in previous work [5]. An acid degumming step for phospholipid removal via precipitation was then followed and led to a strong reduction in the oil's Ca and P content without altering other parameters, as shown in Table 5.

Finally, seed oil extraction provided a co-product (the residual defatted seed meal) with interesting potential for different applications in the food, feed, and agriculture sectors [12,38,39] due to its interesting protein content of 23.5% of DW.

3.2. Antioxidant Additivation

The food-grade antioxidant TBHQ was chosen from analogous previous experiments performed on crambe oil [5] and was added to the safflower degummed oil to preserve the biodegradability of the mixture. TBHQ was added at two different concentrations: 0.25 g kg⁻¹ (to the oil from the first extraction batch) and a higher concentration (to the oil from the second extraction batch) established by evaluating the oil's oxidative stability in relation to TBHQ concentration. The study was performed using the Rancimat method, which determines Rancimat induction time (RIT) at increasing TBHQ concentrations, thus obtaining the optimal TBHQ concentration of 3.00 g kg⁻¹ (Figure 2).

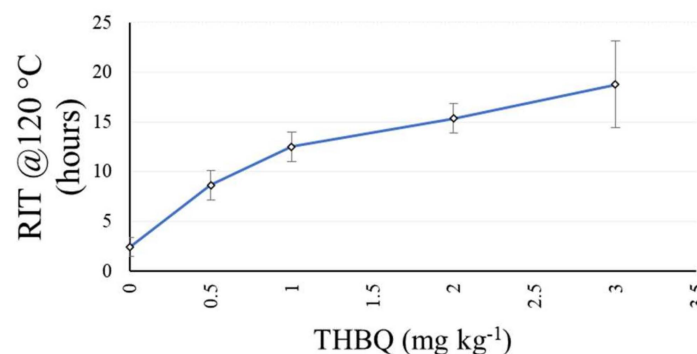


Figure 2. Correlation between safflower oil TBHQ concentration (g kg⁻¹) and Rancimat induction time, RIT (hours), determined at 120 °C. Results represent the average value of two independent analyses \pm measurement uncertainty.

Higher TBHQ quantities were not tested to avoid possible solubility problems. The two final oils with the two added TBHQ concentrations were tested in the experimental FTR.

3.3. Safflower Oil Efficiency Tests

The FTR was designed to apply intense hydraulic, mechanical, and thermal stresses (pressure up to 40 MPa; temperature up to 100 °C) to a small volume of fluid (20 to 25 dm³) with the aim of accelerating its ageing. The ageing of hydraulic fluids is achieved through the combined effects of the mechanical stress caused by continuous lamination in the high-pressure valves and the thermal stress emphasized by the fluid heater. The FTR was usefully employed in previous hydrodynamic tests on hydraulic biofluids based on vegetable oils [4,5], multifunction fluids, transmission lubricants, and hydraulic fluids such as UTTO [27]. The partially refined oils with different TBHQ concentrations added, 0.25 and 3.00 g kg⁻¹, were tested in the FTR and their technical performance was evaluated. The results in Figure 3 show that some small differences in pressure and flowrate were observed between the low and high TBHQ tests (Figure 3a), likely due to different calibrations of the 40 MPa overpressure valve. However, the values of hydraulic HPP (high-pressure pump) power in both cases were very similar and constant (Figure 3b). The same behavior was observed for fluid temperatures before and after the 40 MPa valve, which were always around 60 and 100 °C, respectively (Figure 3b).

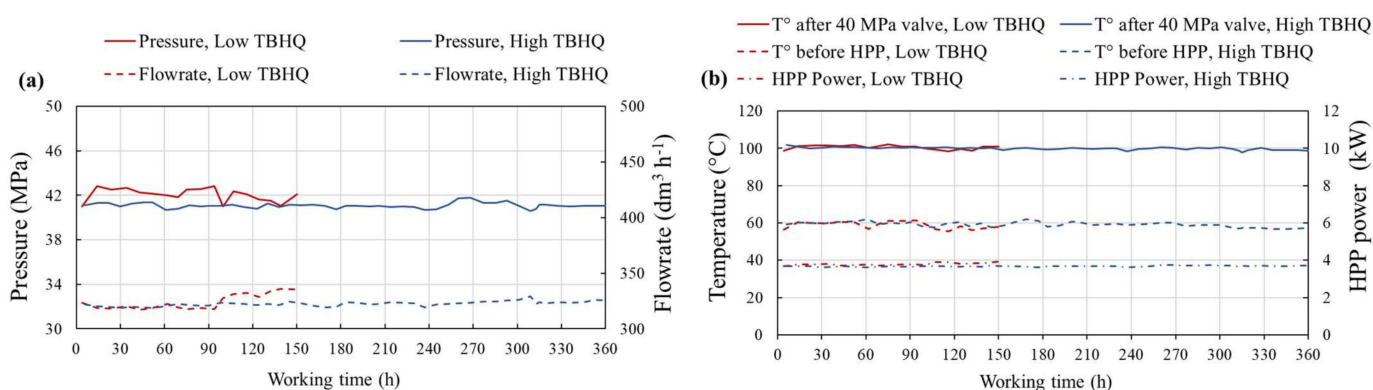


Figure 3. Technical performance of safflower oils with two added TBHQ concentrations (0.25 (low-TBHQ) and 3.00 g kg⁻¹ (high-TBHQ)) during the respective work cycles in the fluid test rig. (a) Operating pressure (MPa) and flowrate (dm³ h⁻¹); (b) operating temperature (°C) after the 40 MPa valve and before the HPP (high-pressure pump) and hydraulic HPP power (kW).

During the entire work cycle, both of the tested fluids maintained the preset values of observed parameters, as also confirmed by the statistical indices reported in Table 6 that demonstrate low coefficient of variation (CV) and standard error (SE) values and limited differences between maximum and minimum values.

Table 6. Statistical indices of the technical performance of the safflower oils with two TBHQ concentrations (0.25 (low-TBHQ) and 3.00 g kg⁻¹ (high-TBHQ)) evaluated during the fluid test rig cycles. SD (standard deviation); SE (standard error).

Test	Statistical Indices	Pressure (MPa)	Flowrate (dm ³ h ⁻¹)	HPP Power (kW)	T° before 40 MPa Valve (°C)	T° after 40 MPa Valve (°C)
Low-TBHQ	Average	42.10	324.40	4.46	58.80	100.50
	SD	3.00	2.87	0.08	1.32	0.47
	CV	0.71	0.89	1.75	2.24	0.47
	SE	0.05	0.04	0.02	0.02	0.01
	Max value	43.30	340.40	4.61	61.40	101.70
	Min value	40.90	310.10	4.34	54.40	98.50

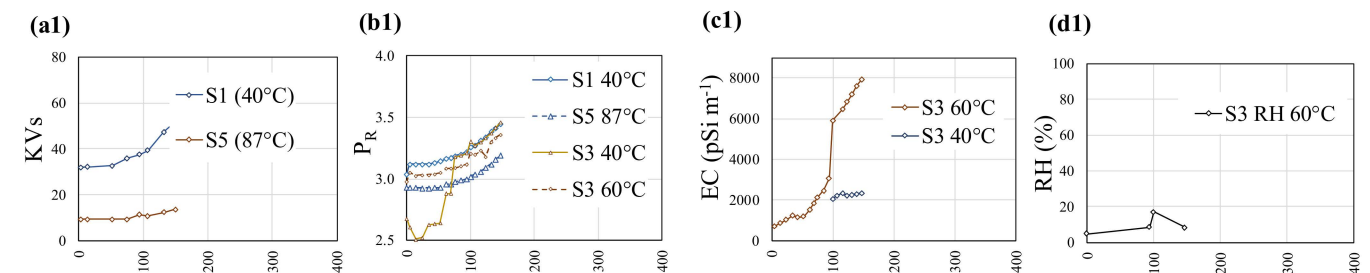
Table 6. Cont.

Test	Statistical Indices	Pressure (MPa)	Flowrate (dm ³ h ^{−1})	HPP Power (kW)	T° before 40 MPa Valve (°C)	T° after 40 MPa Valve (°C)
High-TBHQ	Average	41.10	322.50	4.33	58.40	100.00
	SD	2.35	2.46	0.04	1.26	0.51
	CV	0.57	0.76	0.89	2.16	0.51
	SE	0.03	0.02	0.01	0.02	0.01
	Max value	42.50	339.40	4.41	62.00	101.40
	Min value	40.60	314.50	4.25	53.60	98.80

The key parameters of operating pressure and flowrate remained rather stable, which suggests that the fluids did not undergo changes that could affect the hydraulic power transmission. In addition, the oil was able to withstand high thermal stress. In fact, the outlet temperature of the 40 MPa relief valve stayed constant at about 100 °C during all tests.

Indeed, the main noticeable difference from Figure 3 between the two tests concerned their duration, which was 150 h in the low-TBHQ test and 360 h in the high-TBHQ test. This difference can be explained by the observations of the fluid's physical parameters that were recorded by sensors and, in parallel, by the results from the laboratory analysis of collected samples during the tests, as described below. Sensor recordings were promptly detected and the data related to low and high-TBHQ concentrations are reported in Figure 4.

Low [TBHQ]



High [TBHQ]

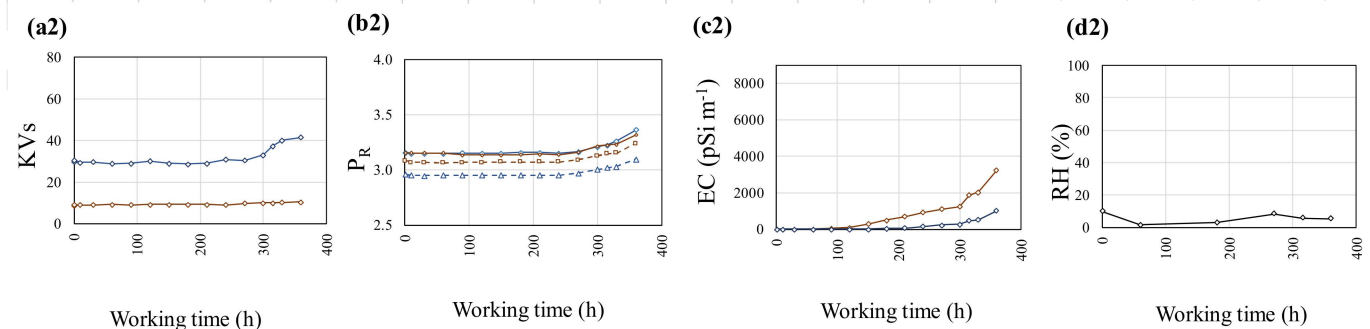


Figure 4. Diagrams of the parameters measured by the sensors. Low [TBHQ]: oil with lower TBHQ concentration (0.25 g kg^{−1}) in the 150 h work cycle (a1–d1). High [TBHQ]: oil with higher TBHQ concentration (3.00 g kg^{−1}) in the 360 h work cycle (a2–d2). (a1,a2): Curves of kinematic viscosity (KV) measured by S1 and S5 at 40 and 87 °C, respectively; (b1,b2): curves of the relative permittivity (P_R) measured by S1 at 40 °C, S3 at 40 and 60 °C, and S5 at 87 °C; (c1,c2): curves of the electric conductivity (EC) measured by S3 at 40 and 60 °C; (d1,d2): curves of the relative humidity (RH) measured by S3 at 60 °C.

Among them, KV is probably the most important characteristic for hydraulic fluids and lubricants, while P_R is an indicator of a fluid's polarity that can increase due to increased water content, a higher amount of contaminants, and/or greater presence of polar products resulting from (both primary and/or secondary) fluid ageing [40]. Increases in P_R that

exceed 10–20% of the fresh oil value require fluid control. EC, besides fluid contamination (with solids and liquids), can vary due to oil changes, refills, and mixing with other oils. As for P_R , oxidation processes can cause increased EC. Therefore, both P_R and EC could be associated to PV and TAN, as discussed below.

Looking at the diagrams in Figure 4, in the low-TBHQ test, the sensors started to detect the first variations in several parameters, such as KV, P_R , and EC, after about 30 h of work and continued with an increasing trend (Figure 4a1–c1). After 150 h, the obtained values suggested that the test should have been stopped to avoid damage to the system, despite no variations being noticed in the technical parameters described before. On the other hand, during the high-TBHQ test, the oil conditions remained sensibly constant until about 300 h. After 300 h, an initial increase in KV, P_R , and EC was detected by the sensors (even in the high-TBHQ test) and the upward trend continued up to 360 h when the test was stopped (Figure 4a2–c2). Conversely, RH (Figure 4d1,d2), measured by S3 at 60 °C, was always below 20% and 10% for the low-TBHQ and high-TBHQ concentrations, respectively. In Figure 4b1 (low-TBHQ), an anomalous trend in P_R at 40 °C can be observed, which is a parameter calculated by S3 based on the values measured at 60 °C and which thus indicates the poor reliability of such calculated measurements. However, in Figure 4b2 (high-TBHQ) P_R at 40 °C was regular.

Additionally, changes were also observed in the chemical–physical properties of fluid taken during the efficiency tests, as described in Figure 5 and Tables 7 and 8 where the starting and final values of each parameter are reported alongside the relative differences.

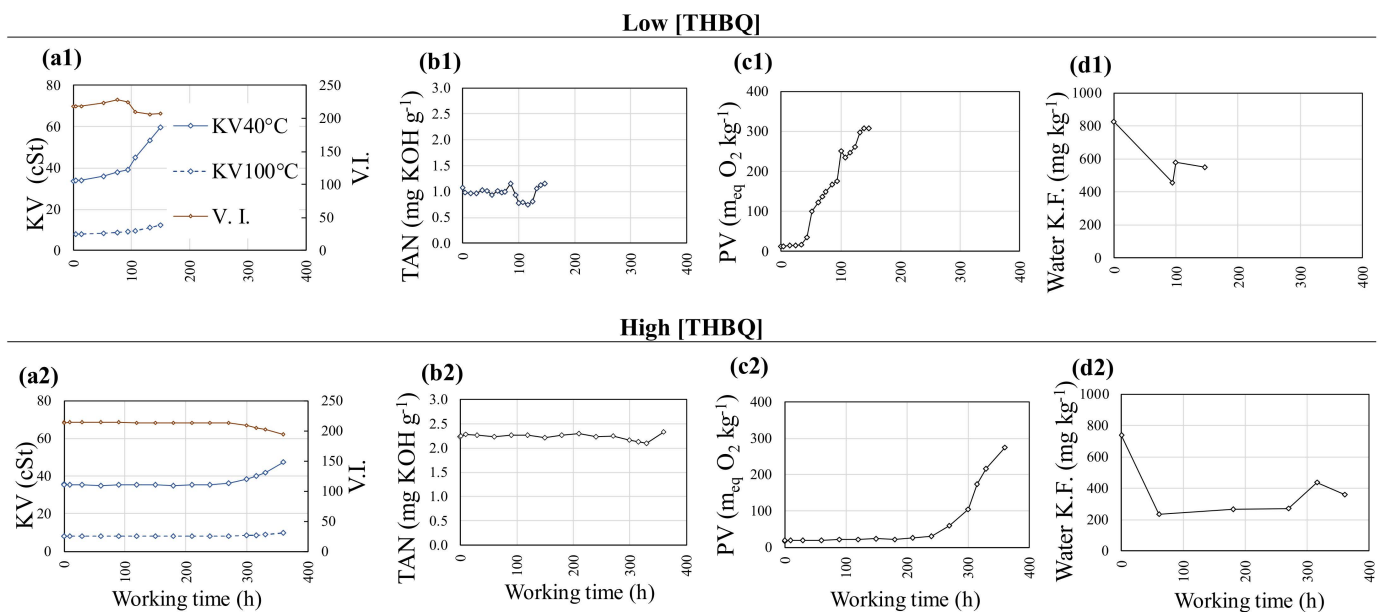


Figure 5. Results of the lab analyses of safflower oil with TBHQ added. Low [TBHQ]: oil with lower TBHQ concentration (0.25 g kg⁻¹) in the 150 h work cycle (a1–d1). High [TBHQ]: oil with higher TBHQ concentration (3.00 g kg⁻¹) in the 360 h work cycle (a2–d2). (a1,a2): kinematic viscosity (KV) at 40 °C and 100 °C (cSt) and viscosity index (VI); (b1,b2): total acid number (TAN) (mg KOH g⁻¹); (c1,c2): peroxide value (PV) (meq O₂ kg⁻¹); (d1,d2): water content according to the Karl Fisher method (mg kg⁻¹).

Table 7. Main parameters of the safflower oil with 0.25 g kg^{−1} of TBHQ added as measured at the beginning (T₀) and end (T₁₅₀) of the test. Kinematic viscosity (KV) at 40 °C and 100 °C, viscosity index (VI), total acid number (TAN), peroxide value (PV), and density (D) were measured.

Properties	T ₀	T ₁₅₀	Differences (T ₁₅₀ − T ₀)
KV ₄₀ (cSt)	33.48	59.65	26.17 (78%)
KV ₁₀₀ (cSt)	7.87	12.26	4.39 (56%)
VI	219.00	208.00	−11.00 (−5%)
TAN (mg KOH g ^{−1})	1.08	1.16	0.08 (7%)
PV (meq O ₂ kg ^{−1})	13.69	308.38	294.69 (2152%)
D at 20 °C (g cm ^{−3})	0.90	0.91	0.01

Table 8. Main parameters of the safflower oil with 3.00 g kg^{−1} of TBHQ added as measured at the beginning (T₀) and end (T₃₆₀) of the test. Kinematic viscosity (KV) at 40 °C and 100 °C, viscosity index (VI), total acid number (TAN), peroxide value (PV), and density (D) were measured.

Properties	T ₀	T ₃₆₀	Differences (T ₃₆₀ − T ₀)
KV ₄₀ (cSt)	35.55	47.29	11.74 (33%)
KV ₁₀₀ (cSt)	8.15	9.62	1.48 (18%)
VI	214.00	194.00	−20.00 (9%)
TAN (mg KOH g ^{−1})	2.24	2.33	0.09 (4%)
PV (meq O ₂ kg ^{−1})	17.00	275.30	258.30 (1521%)
D at 20 °C (g cm ^{−3})	0.91	0.92	0.01

Figure 5a1, shows that the KV at 40 °C for the low-TBHQ oil remained unchanged until 43 h, after which it started to increase and exceeded 10% variation at about 70 h and 20% variation after 95 h of the work cycle. The test was suspended after 150 h when viscosity variation reached 78% (Table 7). Regarding the high-TBHQ oil, no significant viscosity variations were observed in the first 270 h at both 40 and 100 °C (Figure 5a2). After 270 h, oxidative degradation occurred very rapidly: viscosity variation was 20% at 340 h and 33% when the test was stopped (360 h) (Table 8). The same considerations, in terms of viscosity variations, can be made for KV at 100 °C (Figure 5a1,a2). Consequently, the VI decreased for both oils (Figure 5a1,a2). The ISO 4263-3: 2015 standard [41] for the evaluation of an oil's oxidation stability establishes that oil should be replaced when the increase in viscosity at 40 °C exceeds 20%.

The diagrams in Figure 5b1,b2, show that TAN remained nearly constant during the tests for both fluids. The low-TBHQ oil had a TAN starting value of 1.08 mg KOH g^{−1}, while the high-TBHQ oil had a TAN that exceeded 2.00 mg KOH g^{−1}, probably due to different refinement processes and/or storage conditions. This latter value is commonly considered dangerous due to the possible corrosion of hydraulic components. However, considering the inherent acidic properties of vegetable fluids, TAN increases compared to the TAN of the new oil were taken as a reference when defining the following TAN variation thresholds: “caution limit” equal to +0.60 mg KOH g^{−1} and “critical limit” equal to +1.00 mg KOH g^{−1}. According to such indications, the TAN variations stayed far underneath the caution limit in both tests (Tables 7 and 8), which means that the oil did not undergo a primary oxidation process. The trends for PV (Figure 5c1,c2) differed from those of TAN and were quite similar to those of KV. In the low-TBHQ oil, PV started to increase after 45 h of work (from 13 to 36 meq O₂ kg^{−1}) and its value at the end of the 150 h work cycle was 308 meq O₂ kg^{−1} (Table 7). In the high-TBHQ oil, PV doubled in value (from 17 to 36 meq O₂ kg^{−1}) after 270 h of work and, at the end of the test, reached the value of 275 meq O₂ kg^{−1} (Table 8). The massive formation of peroxides was the consequence of the primary oxidation of fatty acid chains. This process was accompanied by the formation of polymerized structures related to the increased viscosity. Such a behavior suggested that 0.25 g kg^{−1} of TBHQ did not protect the oil from secondary oxidation negatively affecting viscosity and lubricity, while at the TBHQ concentration of 3.00 g kg^{−1} protection was significantly extended to

240–270 h of the rig test without any apparent effect. The diagrams in Figure 5d1,d2, show that water content remained nearly constant during the tests for both fluids.

Such considerations were confirmed for both oils by the different values of SD, CV, and SE reported in Table 9.

Table 9. Statistical indices of the chemical–physical analyses of fluid sampled during the test rig experiments performed with two TBHQ concentrations (0.25 and 3.00 mg kg^{−1}) in two work cycles. Kinematic viscosity (KV) at 40 °C and 100 °C, viscosity index (VI), total acid number (TAN), and peroxide value (PV) were measured. Statistical indices include standard deviation (SD) and standard error (SE).

Test	Statistical Indices	KV ₄₀ (cSt)	KV ₁₀₀ (cSt)	VI (N)	TAN (mg KOH g ^{−1})	PV (meq O ₂ kg ^{−1})
TBHQ 0.25 g kg ^{−1}	Average	41.50	9.27	217.00	0.97	151.00
	SD	8.45	1.52	7.75	0.12	110.61
	CV	20.37	16.45	3.56	12.53	73.25
	SE	1.94	0.51	2.58	0.03	25.38
	Max value	59.65	12.26	228.00	1.16	308.69
	Min value	33.48	7.87	206.00	0.75	13.69
THBQ 3.00 g kg ^{−1}	Average	36.94	8.31	211.00	2.24	71.35
	SD	3.43	0.44	5.67	0.06	86.18
	CV	9.27	5.34	2.69	2.71	120.74
	SE	0.86	0.11	1.42	0.02	21.55
	Max value	47.29	9.62	214.00	2.33	275.32
	Min value	35.06	8.04	194.00	2.10	16.98

Finally, in both tests, the results of laboratory analyses were compared to the sensor data collected on the same day, and a certain correspondence between some parameter trends was noticed when looking at the recorded diagrams of Figures 4 and 5. This correlation was further confirmed by the results of the Pearson test reported below (Tables 10–13).

Table 10. Absolute (cSt) and percent (%) variations (Δ) in kinematic viscosity (KV) at 40 and 100 °C in terms of fluid temperature (T) as measured at the end of each oil test performed using two TBHQ concentrations (0.25 and 3.00 g kg^{−1}). Correlation coefficient “ r ” and probability of not being correlated “ p ” between the laboratory KV values and sensor S1 measurements. The red underlined values refer to $r > 0.60$. The green underlined values refer to $p < 0.05$.

TBHQ Concentration	Fluid T (°C)	Δ KV (cSt)		Δ KV (%)		Correlation Lab/S1	
		Lab.	S1	Lab.	S1	r	p
Low (0.25 g kg ^{−1})	40	26.17	19.82	75.39	62.00	<u>0.99</u>	<u>1.2×10^{-6}</u>
	100	4.39	4.23	53.70	44.60	<u>0.95</u>	<u>3.2×10^{-4}</u>
High (3.00 g kg ^{−1})	40	12.23	12.91	33.04	38.89	<u>0.96</u>	<u>3.1×10^{-9}</u>
	100	1.58	1.72	18.12	19.49	<u>0.88</u>	<u>6.9×10^{-6}</u>

Table 11. Correlation coefficient “ r ” and probability of not being correlated “ p ” between the relative permittivity (P_R) values measured by sensors S1 (40 °C), S5 (88 °C), and S3 (60 and 40 °C) and the laboratory-measured total acid number (TAN) and peroxide value (PV) values. The red underlined values refer to $r > 0.60$. The green underlined values refer to $p < 0.05$.

TBHQ Concentration	Lab Parameters	P_R –S1 (40 °C)		P_R –S5 (87 °C)		P_R –S3 (60 °C)		P_R –S3 (40 °C)	
		r	p	r	p	r	p	r	p
Low (0.25 g kg ^{−1})	TAN	0.072	7.8×10^{-1}	0.187	4.7×10^{-1}	−0.057	8.2×10^{-1}	−0.068	7.9×10^{-1}
	PV	<u>0.95</u>	<u>8.3×10^{-10}</u>	<u>0.92</u>	<u>1.8×10^{-8}</u>	<u>0.96</u>	<u>2.7×10^{-9}</u>	<u>0.96</u>	<u>3.4×10^{-11}</u>
High (3.00 g kg ^{−1})	TAN	−0.119	6.7×10^{-1}	−0.203	4.7×10^{-1}	−0.177	5.3×10^{-1}	−0.205	4.6×10^{-1}
	PV	<u>0.96</u>	<u>7.4×10^{-9}</u>	<u>0.98</u>	<u>1.9×10^{-10}</u>	<u>0.97</u>	<u>2.5×10^{-9}</u>	<u>0.96</u>	<u>2.0×10^{-8}</u>

Table 12. Correlation coefficient “*r*” and probability of not being correlated “*p*” between the electric conductivity (EC) value provided by S3 (60 and 40 °C) and the total acid number (TAN) and peroxide value (PV) from lab analyses. The red underlined values refer to $r > 0.60$. The blue underlined values refer to $r < -0.6$. The green underlined values refer to $p < 0.05$.

TBHQ Concentration	<i>r/p</i>	EC (S3)–TAN		EC(S3)–PV	
		EC (60 °C)	EC (40 °C)	EC (60 °C)	EC (40 °C)
Low (0.25 g kg ^{−1})	<i>r</i>	−0.08	−0.05	<u>0.94</u>	<u>−0.62</u>
	<i>p</i>	7.8×10^{-1}	8.4×10^{-1}	<u>1.2×10^{-8}</u>	<u>4.7×10^{-3}</u>
High (3.00 g kg ^{−1})	<i>r</i>	−0.24	−0.14	<u>0.95</u>	<u>0.97</u>
	<i>p</i>	3.9×10^{-1}	6.2×10^{-1}	<u>4.5×10^{-8}</u>	<u>3.7×10^{-9}</u>

Table 13. Correlation coefficient “*r*” and probability of not being correlated “*p*” between the relative humidity (RH) values provided by S3 (60 °C) and the total acid number (TAN), peroxide value (PV), water content (KF), and electric conductivity (EC) values from S3. The red underlined values refer to $r > 0.60$. The blue underlined values refer to $r < -0.6$.

TBHQ Concentration	<i>r/p</i>	RH (S3)–TAN	RH (S3)–PV	RH (S3)–KF	RH (S3)–EC (S3)	
					RH–EC (60 °C)	RH–EC (40 °C)
Low (0.25 g kg ^{−1})	<i>r</i>	−0.336	0.202	<u>0.724</u>	0.160	0.100
	<i>p</i>	0.203	0.454	0.104	0.531	0.690
High (3.00 g kg ^{−1})	<i>r</i>	<u>−0.825</u>	0.590	−0.426	−0.150	−0.080
	<i>p</i>	0.175	0.411	0.574	0.580	0.770

Indeed, a very strong correlation was observed between the KVs values determined by S1 (at 40 °C) and S5 (87 °C) and the KV₄₀ and KV₁₀₀ values from laboratory measurements (Table 10). At the same time, the increasing trend in P_R, measured by sensors S1 (40 °C), S5 (87 °C), and S3 (60 and 40 °C), and EC, measured by S3 (60 and 40 °C), compared to lab analyses revealed some correlations to the trends in PV (Tables 11 and 12). On the contrary, the TAN level remained quite constant in both tests, while the trend in RH measured by S3 at 60 °C showed some similar traits to that of laboratory-measured KF but was not correlated to it or any of the other parameters (Table 13). However, the KF value was more variable, probably due to the effect of atmospheric humidity which could have contaminated the oil samples during sampling.

These results suggest that the fluid in both tests underwent an important primary oxidation process which led to an increase in peroxides (as well as in P_R and EC) and their polymerization, thus resulting in viscosity increase. The TAN remained substantially stable, though secondary oxidation would likely have started if testing continued. Furthermore, the comparison between lab and sensor data confirmed the importance of using sensors to continuously monitor the conditions of the fluid during the tests in order to promptly detect any variations in its basic parameters and to preserve the FTR from damage.

Regarding the elemental analysis performed in sampled fluids during the tests, the results of the two trials are reported in Tables 14 and 15. The results indicated no significant metal contamination, especially during the test performed with the higher TBHQ concentration. A small accumulation of Zn was observed in both tests, with a lower amount found in the second one that is lower than previous tests performed on crambe oil [5]; however, the origin is still not clear and deserves further investigation. Low metal content was also confirmed also by sensor acquisitions during the tests, particularly by sensor S4. In the case of plant materials suffering from wear, the sensors would have detected ferromagnetic particle accumulation.

Table 14. Element analysis of safflower oil with 0.25 g kg^{−1} of THBQ added using samples taken during the first endurance test at different times (0, 93, 100, 150 h). Results are reported as the average value of two independent analyses ± uncertainty of measurement.

Elements		T ₀	T ₉₃	T ₁₀₀	T ₁₅₀
Wear metals					
Cu	mg kg ^{−1}	<1.0	1.7 ± 0.2	14.4 ± 0.9	6.3 ± 0.9
Ag, Al, Cr, Fe, Mn, Ni, Ti, Sn, Pb	mg kg ^{−1}	<1.0	<1.0	<1.0	<1.0
Contaminant elements					
K, Na, V	mg kg ^{−1}	<1.0	<1.0	<1.0	<1.0
Si	mg kg ^{−1}	3.1 ± 0.1	3.1 ± 0.1	2.9 ± 0.1	2.8 ± 0.1
Additive elements					
P	mg kg ^{−1}	5.0 ± 0.7	19.6 ± 0.9	18.1 ± 0.9	17.9 ± 0.7
Ca	mg kg ^{−1}	1.7 ± 0.2	37.6 ± 2.6	37.5 ± 2.6	35.9 ± 2.6
Mg	mg kg ^{−1}	<1.0	<1.0	<1.0	<1.0
Zn	mg kg ^{−1}	<1.0	101.0 ± 0.1	114.0 ± 0.1	108.0 ± 0.1
Ba, Mo	mg kg ^{−1}	<1.0	<1.0	<1.0	<1.0

Table 15. Element analysis of safflower oil with 3.00 g kg^{−1} of TBHQ added using samples taken during the second endurance test at different times (0, 60, 180, 270, 315, 360 h). Results are reported as the average value of two independent analyses ± uncertainty of measurement.

Elements		T ₀	T ₆₀	T ₁₈₀	T ₂₇₀	T ₃₁₅	T ₃₆₀
Wear metals							
Cu	mg kg ^{−1}	<1.0	<1.0	<1.0	<1.0	2.0	2.0
Ag, Al, Cr, Fe, Mn, Ni, Ti, Sn, Pb	mg kg ^{−1}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Contaminant elements							
K, Na, V	mg kg ^{−1}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Si	mg kg ^{−1}	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Additive elements							
P	mg kg ^{−1}	6.2 ± 0.9	5.9 ± 0.9	6.0 ± 0.9	6.1 ± 0.9	6.7 ± 0.9	6.3 ± 0.9
Ca	mg kg ^{−1}	1.0 ± 0.2	1.0 ± 0.2	1.0 ± 0.2	1.0 ± 0.2	1.0 ± 2.6	1.0 ± 2.6
Mg	mg kg ^{−1}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Zn	mg kg ^{−1}	1.0 ± 0.1	9.0 ± 0.1	22.0 ± 0.1	35.0 ± 0.1	54.0 ± 0.1	74.0 ± 0.1
Ba, Mo	mg kg ^{−1}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0

3.4. THBQ Endurance in FTR-Sampled Fluids

The THBQ concentration in fluids sampled during the second FTR test decreased with time until reaching a value of less than 30 mg kg^{−1} after 315 h (Figure 6).

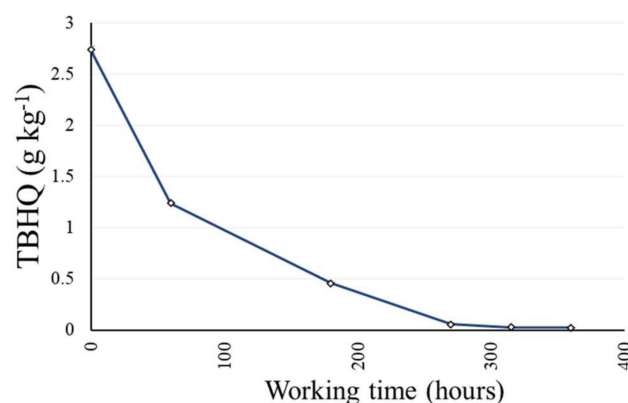


Figure 6. TBHQ concentration (g kg^{−1}) in fluid test rig fluids sampled at different times (hours) during the second test performed with the 3.00 g kg^{−1} concentration. The reported results represent the average value of two independent analyses ± measurement uncertainty.

According to a previous study [5] in which the authors established a positive correlation between residual TBHQ concentration and oxidative stability, as measured by the Rancimat test, it can be confirmed that the fluid was exhausted in terms of its hydraulic function.

The results indicate that the safflower oil behaved well from the point of view of technical performance (operating temperature and pressure, flowrate, hydraulic power), which remained substantially constant across the two tests. On the other hand, antioxidants played a key role in the evolution of the oil's chemical–physical properties and, at higher concentration, protected the safflower oil used in the second test for 270 h, despite the oil's lower quality with respect to the oil from the first test. After 270 h, the TBHQ concentration became negligible and its protective effect on the oil ceased, leading to the massive increase in peroxide value and viscosity. The use of an oil with a lower initial TAN in the second test would probably have reduced the consumption of TBHQ and extended the oil's life span. This aspect should be explored in further studies, as well as the optimal concentration of antioxidant, which could vary from oil to oil.

As to the intensity of the work cycles for the FTR, intensity was based on previous research regarding the utilization of agricultural tractors [42,43]. A previous study indicated that a 150 h work cycle would correspond to the work performed by the hydraulic system of a medium-power tractor in about 1 year, with major thermal stress also used to represent the normal hydraulic oil temperature inside the tractor [24]. This means that a 270 h work cycle, without significant variations in technical performance and chemical–physical properties caused by the safflower oil with 3.00 g kg^{-1} of antioxidant, would amount to 1.8 years of normal farm use, on average, in an agricultural tractor hydraulic system.

The above assessment was based on “specific energy” (kWh dm^{-3}), i.e., the global energy (kWh) “conveyed” by the fluid volume unit (dm^3) in a given time interval. In the case of hydraulic plants, this represents the specific hydraulic work carried out and the specific thermal energy dissipated by the oil. The “specific energy” calculated based on the 150 h work cycle (Table 3) was compared to the specific energy mentioned for the work cycles prescribed by the ASTM D7043-17 and IP 281 standards [44,45] (assessment of the anti-wear properties of hydraulic fluids). The energy required for the cycle in this paper was higher, justifying the severity of our tests and confirming the prospective use of safflower oil as a hydraulic fluid that can properly protect against oxidation and other factors that affect tribological properties.

4. Conclusions

The excellent tribological properties of many vegetable oils have been known for a long time, but the use of these oils as lubricants or hydraulic fluids has been substantially hindered by their susceptibility to oxidative phenomena that cause the aforementioned decline in properties and put plant efficiency at risk.

The current growing sensitivity towards the issues of environmental protection and the use of resources from renewable sources has rekindled the interest in using vegetable oils as possible base stocks so that the lubricants and hydraulic fluids of fossil origin (mineral oils and synthetic esters) can be replaced.

In light of the results of the present work, which were provided with intense work cycles, safflower oil was shown to suitably protect against oxidative degradation and seems to be a promising basis for the realization of efficient hydraulic fluids with low environmental impact.

The use of specific test rigs to apply repeatable work cycles, thus allowing researchers to monitor both the working conditions and the evolution of fluid characteristics, represents an important contribution to studies aimed at introducing bio-based hydraulic fluids and lubricants. Integrating test rigs with proper sensors for continuous monitoring of oil status further improved the reliability and accuracy of the test systems, which were thus capable of promptly providing information regarding any variation in the main tribological parameters. This allows the characteristics of the oil and the effects of different additives (and different additive concentrations) to be better defined. In addition, damage to the

test plant can be avoided or limited. Finally, given the high adaptation of safflower to Italian climate conditions and cultivation techniques, the use of safflower oil for industrial purposes seems feasible and would contribute toward the sustainability of the whole crop rotation. Considering this, the present paper showed a potential use of safflower oil in the agricultural tractor sector that could allow farmers to produce their own plant-based rough vegetable oil, thus reducing the level of dependency on oil-based economies and suggesting the possibility of a valuable circular economy based on green chemistry.

Author Contributions: Conceptualization, L.U., L.L., P.B., D.P. and R.F.; methodology, L.U., L.M., P.B., D.P. and R.F.; validation, L.U., L.M., D.P. and R.F.; formal analysis, L.U., D.P. and R.F.; investigation, L.U., L.M., L.F. (Liliana Folegatti), P.B., D.P., R.G., L.F. (Laura Fornaciari), S.B. and R.F.; resources, L.U., L.M., L.F. (Liliana Folegatti), P.B., D.P. and R.F.; writing—original draft preparation, L.U., R.M., D.P. and R.F.; writing—review and editing, L.U., R.M., L.L., L.F. (Liliana Folegatti), P.B., D.P. and R.F.; visualization, L.U., D.P. and R.F.; supervision, L.L., P.B., D.P. and R.F.; project administration, L.L., P.B., D.P. and R.F.; funding acquisition, L.L. and D.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the AGROENER Research Project, WP4—Integrated biorefineries in agro-food production chains, granted by MASAF (Italian Minister of Agriculture, Food Sovereignty and Forests), ex-MiPAAF (Italian Ministry of Agriculture, Food and Forestry Policies) (D.D. n. 26329).

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy restrictions.

Acknowledgments: The authors thank Nerio Casadei (CREA-CI) for supporting safflower reproduction and oil extraction in Bologna.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Global Demand for Lubricants from 2000 to 2020, with a Forecast for 2023 and 2028. Available online: <https://www.statista.com/statistics/411616/lubricants-demand-worldwide/> (accessed on 5 January 2023).
2. Mendoza, G.; Igartua, A.; Fernandez-Diaz, B.; Urquiola, F.; Vivanco, S.; Arguizoz, R. Vegetable oils as hydraulic fluids for agricultural applications. *Grasas Aceites* **2011**, *62*, 29–38. [\[CrossRef\]](#)
3. Ohifuemen, A.; Fagbemi, E.A.; Fasina, K.A. Bio-lubricants: A renewable alternative to mineral oils. *Int. J. Agric. Environ. Bioresearch* **2020**, *05*, 22–32. [\[CrossRef\]](#)
4. Fanigliulo, R.; Bondioli, P.; Fornaciari, L.; Folegatti, L.; Grilli, R.; Benigni, S.; Calderari, I.; Pochi, D. Bench Test of a Hydraulic Biofluid Based on Refined Pomace Oil. *Eur. J. Lipid Sci. Technol.* **2021**, *123*, 2100116. [\[CrossRef\]](#)
5. Fanigliulo, R.; Pochi, D.; Bondioli, P.; Grilli, R.; Fornaciari, L.; Folegatti, L.; Malaguti, L.; Matteo, R.; Ugolini, L.; Lazzeri, L. Semi-refined *Crambe abyssinica* (Hochst. EX R.E.Fr.) oil as a biobased hydraulic fluid for agricultural applications. *Biomass Convers. Biorefin.* **2021**. [\[CrossRef\]](#)
6. Jabal, M.; Abdulmunem, A.; Abd, H. As a potential hydraulic fluid: Corn oil behavior characteristics examination. *J. Therm. Eng.* **2021**, *7*, 215–221. [\[CrossRef\]](#)
7. Olszak, A.; Osowski, K.; Musiałek, I.; Rogoś, E.; Kęsy, A.; Kęsy, Z. Application of Plant Oils as Ecologically Friendly Hydraulic Fluids. *Appl. Sci.* **2020**, *10*, 9086. [\[CrossRef\]](#)
8. Hilal, A.H.; Merzah, A.S.; Khadom, A.A.; Abdul-Mtaleb, M.R.; Ali, S.K. Experimental, statistical, and numerical investigations for influence of using vegetable oil with mineral oil to enhance the flow characteristics through a closed hydraulic circuit. *Results Eng.* **2022**, *15*, 100608. [\[CrossRef\]](#)
9. Woma, T.Y.; Lawal, S.A.; Abdulrahman, A.S.; Olutoye, M.A.; Ojapah, M.M. Vegetable oil based lubricants: Challenges and prospects. *Tribol. Online* **2019**, *14*, 60–70. [\[CrossRef\]](#)
10. Beyyavas, V.; Haliloglu, H.; Copur, O.; Yilmaz, A. Determination of seed yield and yield components of some safflower (*Carthamus tinctorius* L.) cultivars, lines and populations under the semi-arid conditions. *Afr. J. Biotechnol.* **2011**, *10*, 527–534.
11. El-Lattief, E.A.A. Evaluation of 25 safflower genotypes for seed and oil yields under arid environment in upper Egypt. *Asian J. Crop Sci.* **2012**, *4*, 72–79. [\[CrossRef\]](#)
12. Emongor, V.E.; Emongor, R.A. Safflower (*Carthamus tinctorius* L.)—Future Smart Food. In *Neglected and Underutilized Crops*; Muhammad, F., Kadambot, S., Eds.; Nikki P. Levy: London, UK, 2022; pp. 683–731. ISBN 978-0-323-90537-4.
13. Corleto, A.; Alba, E.; Polignano, G.B.; Vonghio, G. A multipurpose species with unexploited potential and world adaptability. In *Proceedings of the 4th International Safflower Conference*; Corleto, A., Mündel, H.-H., Eds.; Adriatica Editrice: Bari, Italy, 1997; p. 373.
14. Ekin, Z. Resurgence of safflower (*Carthamus tinctorius* L.) utilization: A global view. *J. Agron.* **2005**, *4*, 83–87. [\[CrossRef\]](#)

15. Carvalho, I.S.; Miranda, I.; Pereira, H. Evaluation of oil composition of some crops suitable for human nutrition. *Ind. Crops Prod.* **2006**, *24*, 75–78. [\[CrossRef\]](#)
16. Dajue, L.; Mündel, H. *Safflower Carthamus tinctorius L. Promoting the Conservation and Use of Underutilized and Neglected Crops*; IPGRI; IPK: Rome, Italy, 1996; ISBN 9290432977.
17. Emongor, V. Safflower (*Carthamus tinctorius* L.) the underutilized and neglected crop: A review. *Asian J. Plant Sci.* **2010**, *9*, 299–306. [\[CrossRef\]](#)
18. Steberl, K.; Hartung, J.; Munz, S.; Graeff-Hönniger, S. Effect of row spacing, sowing density, and harvest time on floret yield and yield components of two safflower cultivars grown in southwestern Germany. *Agronomy* **2020**, *10*, 664. [\[CrossRef\]](#)
19. La Bella, S.; Tuttolomondo, T.; Lazzeri, L.; Matteo, R.; Leto, C.; Licata, M. An agronomic evaluation of new safflower (*Carthamus tinctorius* L.) germplasm for seed and oil yields under mediterranean climate conditions. *Agronomy* **2019**, *9*, 468. [\[CrossRef\]](#)
20. Zanetti, F.; Angelini, L.G.; Berzuini, S.; Foschi, L.; Clemente, C.; Ferioli, F.; Vecchi, A.; Rossi, A.; Monti, A.; Tavarini, S. Safflower (*Carthamus tinctorius* L.) a winter multipurpose oilseed crop for the Mediterranean region: Lesson learnt from on-farm trials. *Ind. Crops Prod.* **2022**, *184*, 115042. [\[CrossRef\]](#)
21. Shyurova, N.; Dubrovin, V.; Narushev, V.; Kozhevnikov, A.; Milovanov, I. Biofuel as an Alternative Energy Source for the Automobile Industry: The Experience of the Lower Volga Region (Russia). *J. Ecol. Eng.* **2020**, *21*, 29–35. [\[CrossRef\]](#)
22. Nogales-Delgado, S.; Encinar, J.M.; González Cortés, Á. High oleic safflower oil as a feedstock for stable biodiesel and biolubricant production. *Ind. Crops Prod.* **2021**, *170*, 113701. [\[CrossRef\]](#)
23. Hudson, D.; Richards, R. Super High Oleic Safflower—A Game Changer for Grain Growers. Available online: <https://grdc.com.au/resources-and-publications/grdc-update-papers/tab-content/grdc-update-papers/2019/08/super-high-oleic-safflower-a-game-changer-for-grain-growers> (accessed on 5 January 2023).
24. Pochi, D.; Fanigliulo, R.; Bisaglia, C.; Cutini, M.; Grilli, R.; Fornaciari, L.; Betto, M.; Pari, L.; Gallucci, F.; Capuzzi, L.; et al. Test rig and method for comparative evaluation of conventional and bio-based hydraulic fluids and lubricants for agricultural transmissions. *Sustainability* **2020**, *12*, 8564. [\[CrossRef\]](#)
25. Pochi, D.; Fanigliulo, R.; Grilli, R.; Fornaciari, L.; Bisaglia, C.; Cutini, M.; Brambilla, M.; Sagliano, A.; Capuzzi, L.; Palmieri, F.; et al. Design and assessment of a test rig for hydrodynamic tests on hydraulic fluids. In *Innovative Biosystems Engineering for Sustainable Agriculture, Forestry and Food Production, MID-TERM AIIA 2019. "Lecture Note in Civil Engineering" Book Series*; Coppola, A., Di Renzo, G., Altieri, G., D'Antonio, P., Eds.; Springer Nature: Cham, Switzerland, 2020; Volume 67, pp. 419–429.
26. Pochi, D.; Fanigliulo, R.; Pagano, M.; Grilli, R.; Fedrizzi, M.; Fornaciari, L. Dynamic-energetic balance of agricultural tractors: Active systems for the measurement of the power requirements in static tests and under field conditions. *J. Agric. Eng.* **2013**, *44*, 415–420. [\[CrossRef\]](#)
27. Pochi, D.; Fanigliulo, R.; Bisaglia, C.; Cutini, M.; Grilli, R.; Betto, M.; Fornaciari, L. Vegetable-based oil as UTTO fluid for agricultural tractors application. *Appl. Eng. Agric.* **2020**, *36*, 79–88. [\[CrossRef\]](#)
28. Pochi, D.; Grilli, R.; Fornaciari, L.; Betto, M.; Benigni, S.; Fanigliulo, R. Bench testing of sensors utilized for in-line monitoring of lubricants and hydraulic fluids properties. *Sensors* **2021**, *21*, 8201. [\[CrossRef\]](#) [\[PubMed\]](#)
29. ASTM D445-06; Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity). American Society for Testing and Materials: West Conshohocken, PA, USA, 2006.
30. ISO 3960:2017; Animal and Vegetable Fats and Oils-Determination of Peroxide Value-Iodometric (Visual) Endpoint Determination. The International Organization for Standardization: Geneva, Switzerland, 2017.
31. ISO 660:2020; Animal and Vegetable Fats and Oils-Determination of Acid Value and Acidity. The International Organization for Standardization: Geneva, Switzerland, 2020.
32. ISO 8534:2017; Animal and Vegetable Fats and Oils-Determination of Water Content-Karl Fischer Method (Pyridine Free). The International Organization for Standardization: Geneva, Switzerland, 2017.
33. NAS 1638; Cleanliness Requirements of Parts Used in Hydraulic System. National Aerospace Standard. Aerospace Industries of America: Washington, DC, USA, 2001.
34. ISO 4406:2021; Hydraulic Fluid Power-Fluids-Method for Coding the Level of Contamination by Solid Particles. The International Organization for Standardization: Geneva, Switzerland, 2021.
35. Abou Chehade, L.; Angelini, L.G.; Tavarini, S. Genotype and seasonal variation affect yield and oil quality of safflower (*Carthamus tinctorius* L.) under mediterranean conditions. *Agronomy* **2022**, *12*, 122. [\[CrossRef\]](#)
36. Arslan, B. The determination of oil content and fatty acid compositions of domestic and exotic safflower (*Carthamus tinctorius* L.) genotypes and their interactions. *J. Agron.* **2007**, *6*, 415–420. [\[CrossRef\]](#)
37. Gupta, M.K. Degumming. In *Practical Guide to Vegetable Oil Processing*; Elsevier Inc.: Lynnwood, TX, USA, 2017; pp. 41–78.
38. Ugolini, L.; Cinti, S.; Righetti, L.; Stefan, A.; Matteo, R.; D'Avino, L.; Lazzeri, L. Production of an enzymatic protein hydrolyzate from defatted sunflower seed meal for potential application as a plant biostimulant. *Ind. Crops Prod.* **2015**, *75*, 15–23. [\[CrossRef\]](#)
39. Canistro, D.; Vivarelli, F.; Ugolini, L.; Pinna, C.; Grandi, M.; Antonazzo, I.C.; Cirillo, S.; Sapone, A.; Cinti, S.; Lazzeri, L.; et al. Digestibility, toxicity and metabolic effects of rapeseed and sunflower protein hydrolysates in mice. *Ital. J. Anim. Sci.* **2017**, *16*, 462–473. [\[CrossRef\]](#)
40. Meijer, G.C.M. *Smart Sensor Systems*; Meijer, G., Ed.; John Wiley & Sons: West Sussex, UK, 2008.
41. ISO 4263-1:2003; Petroleum and related products-Determination of the ageing behavior of inhibited oils and fluids-TOST test-Part 1. Procedure for Mineral Oils. The International Organization for Standardization: Geneva, Switzerland, 2003.

42. Renius, K. *Tractors: Technology and Its Application*; BLV Publishing Society: Munchen, Germany, 1985.
43. Osinenko, P. *Optimal Slip Control for Tractors with Feedback of Drive Torque*; Technische Universität Dresden: Dresden, Germany, 2014.
44. ASTM D7043-17; Standard Test Method for Indicating Wear Characteristics of Non-Petroleum and Petroleum Hydraulic Fluids in a Constant Volume Vane Pump. American Society for Testing and Materials: West Conshohocken, PA, USA, 2017.
45. IP 281; Methods of Test for Petroleum and Its Products Part 281: Determination of Anti-Wear Properties of Hydraulic Fluids-Vane Pump Method. The Institute of Petroleum: London, UK, 2000.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.