

Article

Rheological Study and FTIR Analysis of Thermally Degraded Mineral and Biodegradable Hydraulic Fluids

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Abstract

In this work, three hydraulic fluids—a paraffinic mineral hydraulic oil (H46) and two biodegradable oils (HETG46—hydraulic oil based on natural esters and HF-E46—hydraulic oil based on synthetic esters derived from fatty acids extracted from vegetable oils)—were studied in both fresh and thermally degraded states. The study of these oils was performed both from a rheological and spectroscopic point of view using Fourier transform infrared spectroscopy (FTIR). The thermal degradation process consisted of repeated heating and cooling cycles at four different temperatures for 15 min performed eight times. The rheological characterization was initially performed for the fresh oils, and the results obtained were compared with those of the thermally degraded samples. For the rheological characterization, two rheological models (the Newtonian model and the power law model) were used, following which the rheological parameters were determined. At the same time, this work highlights how thermal degradation influences the rheological behavior and chemical structure of hydraulic fluids. The results obtained showed that the Newtonian model best describes the rheological behavior of the analyzed fluids. From a chemical point of view, FTIR analysis did not reveal significant changes between fresh fluids and those subjected to thermal degradation.

Keywords: biodegradable oils; rheology; FTIR analysis; thermal degradation



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1. Introduction

Starting from the wide range of applications in which hydraulic oils are used, the common point they have is represented by the operating conditions, which, the more demanding they are, accelerate the degradation of the fluid and affect the performance of the hydraulic system [1]. To extend the life of these systems and keep the components in optimal condition, it is essential to understand the degradation process, as well as to test them in specialized laboratories [2,3].

During use, hydraulic fluids are exposed to degradation processes, such as oxidation, contamination, and loss of functional additives, which leads to the formation of varnish and sludge, reduced efficiency of anti-wear, anticorrosion, and antifoaming additives, and

implicitly to poor lubrication. These effects accelerate the wear of hydraulic components and alter the mechanical properties of the system [2,4,5].

Hydraulic fluid performance directly influences system operation [6]. Its degradation is determined by factors such as high temperatures, friction, particle contamination, and the presence of water, which leads to a decrease in the efficiency of the entire assembly [7]. In this context, an in-depth understanding of the behavior of the materials used in plant components in the presence of hydraulic fluids becomes essential [8,9].

The degradation of hydraulic fluids, whether mineral or biodegradable, is a process caused by contamination, oxidation, and thermal degradation that is achieved by controlled heating and cooling of the fluid [10,11]. Exceeding the working temperature of the fluids from the data sheet results in accelerated thermal degradation [12] of the fluid. Oxidation produces changes in the physical properties of the fluid and can negatively affect the proper functioning of hydraulic installations, emphasizing the importance of monitoring the condition of the fluid and the quality of the working environment [13].

Vegetable oil-based fluids are considered an environmentally friendly alternative to mineral oil-based fluids due to their high biodegradability [14], a factor that contributes to reducing environmental pollution in the event of oil leaks [15], which occur in the equipment used in the hydraulic systems of agricultural and forestry machinery [12].

Hydraulic installations are used in a wide range of applications, where hydraulic fluid plays an essential role in their operation, providing lubrication of components, energy transfer, and the removal of heat from the system. The correct choice of hydraulic oil is very important to increase the reliability and service life of the facility [8,16]. To meet the functional requirements, hydraulic fluids must exhibit very good physicochemical properties, such as thermal and oxidative stability, good performance at low temperatures, and good biodegradability, while also providing corrosion protection and reducing wear of the contacting surfaces under tribological conditions [7,17].

An important property of fluids is viscosity, which influences the charge capacity of the fluid film, tightness, and also internal friction in the fluid. If the viscosity of a fluid varies as a function of the shear stress, this behavior indicates that the fluid is non-Newtonian and requires the study from rheological viewpoints [18].

Following the rheological study of the fluids, the rheological properties are determined, which describe their behavior under the action of external forces, necessary for the manufacturing process, handling, storage, and for the efficient design of hydraulic systems [19].

Fourier transform infrared spectroscopy (FTIR) is known as the best method for determining types of lubricating oils with similar chemical compositions due to its ability to highlight differences in the molecular structure of lubricant bases and additives by analyzing the relevant spectral regions [20]. The equipment for FTIR analysis is characterized as sensitive equipment, with high efficiency, very fast in processing the results, and ease of use. Also, through the FTIR analysis microscope, several types of sampling can be performed, such as transmission, reflection, ATR (Attenuated Total Reflectance), and grazing angle [21].

Infrared spectroscopy (IR) consists of transmitting infrared radiation through a test sample [22]. Part of the radiation is absorbed by the sample, and the rest is transmitted through it. The interaction of radiation with the molecules of the sample generates an absorption and transmission spectrum, which reflects the unique molecular fingerprint of the analyzed substance [12]. Because the molecular structure of each substance is specific, the resulting infrared spectrum is distinct, making IR spectroscopy extremely useful for various types of analyses [23].

In the literature, several authors have investigated the degradation of hydraulic fluids and lubricants, as well as their impact on the components of technical systems. Hnilicová

et al. [24] evaluated the wear of hydraulic equipment by analyzing five oil samples taken over the course of a year. The physicochemical properties (viscosity at 40 °C, water content, total acid number) and FTIR spectroscopy indicated a progressive degradation of the fluid, manifested by the increase in oxidation products, aromatic hydrocarbons, and contaminants resulting from the overheating of the oil, favoring the wear of the system components. Tulik et al. [25] tested a new biodegradable poly-alpha-olefin (PAO)-based fluid under accelerated laboratory conditions. FTIR analysis and ICP (Inductively Coupled Plasma) spectroscopy showed good thermal stability and minimal degradation of the additives, but early signs of oxidation were observed, with no significant changes in the essential properties of the fluid. In another study, Santos et al. [26] investigated the thermal degradation of oils used in automotive engines, using IR, MRI (Magnetic Resonance Imaging), and GC/MS (Gas Chromatography–Mass Spectrometry) methods. The results showed the occurrence of oxidation reactions, generating carboxylic acids and ketones, while the GC/MS analysis did not reveal major structural changes between degraded and non-thermally degraded oils. The study of Xu et al. [20] demonstrated that the use of FTIR spectroscopy can be used as a fast and reliable alternative method to classical laboratory methods in the analysis of the chemical composition of lubricants.

Based on the previous premises, the main objective of this research work is to determine the rheological parameters (viscosity, consistency index, and flow behavior index) and to evaluate the changes in the chemical structure using Fourier transform infrared spectroscopy (FTIR) for three hydraulic fluids. The three hydraulic fluids used are a paraffinic mineral hydraulic oil (H46), widely used in hydraulic installations, a biodegradable hydraulic oil based on vegetable oils (HETG46), and a biodegradable hydraulic oil based on synthetic esters (HF-E46), analyzed as possible sustainable alternatives. Their choice was made in the context of increasingly strict environmental regulations, which require the use of lubricants with reduced environmental impact. In modern applications, where hydraulic systems operate in sensitive environments (agriculture, forestry, hydrotechnical works, construction equipment), it is necessary to replace conventional mineral oils, which are difficult to degrade and can cause soil and water pollution, affecting ecosystems and human health [17].

The analyzed fluids were initially tested in the fresh state and then compared with the same fluids subjected to thermal degradation at temperatures ranging from 130 °C to 220 °C. To determine the rheological parameters, two models were applied: the Newtonian model and the power law model. Regarding the changes in the chemical structure, these were investigated by FTIR spectroscopy, comparing the spectra of the fresh fluids with those of the thermally degraded fluids. The results revealed that the rheological model that best describes the behavior of the fluids is the Newtonian model. Additionally, no significant differences were observed in the chemical structure of the fresh and the thermally degraded fluids, suggesting that they were formulated to withstand temperatures greater than 130 °C, as is commonly encountered in hydraulic systems. No similar studies conducted on these oils were identified to compare the results, highlighting the novelty of the study.

2. Materials and Methods

2.1. Materials

Three types of hydraulic oils were tested in the study, namely, the following:

- H46—paraffinic mineral hydraulic oil [27];
- HETG46—hydraulic oil based on natural esters [28];
- HF-E46—hydraulic oil based on synthetic esters derived from fatty acids extracted from vegetable oils [27].

Table 1 shows the physicochemical properties of the oils tested, according to the manufacturer's technical sheets.

Table 1. Physicochemical properties of the oils tested [29–31].

Properties	H46	HETG46	HF-E46
ISO viscosity class	46	46	46
Density at 15 °C, max [kg/m ³]	876	918	921
Viscosity index, min	98	210	188
Kinematic viscosity at 40 °C [mm ² /s]	44	-	47.2
Kinematic viscosity at 100 °C [mm ² /s]	6.6	10	9.41
Flash point, min [°C]	226	>270	320
Pour point, max [°C]	−24	−30	−42
Copper strip corrosion, 3 h, max 100 [°C]	1A	-	-
Acid number [mgKOH/g]	-	0.5	-
Parts of renewable raw materials, according to ASTM D 6866 [%]	-	95	>80
Biodegradability in 28 days, according to OECD 301B [%]	-	>80	76
Auto-ignition temperature [°C]	-	-	>400

2.2. Thermal Degradation

Depending on the flash point of each oil described in its technical data sheet, the temperatures at which the oils are thermally degraded are as follows:

- For the mineral hydraulic fluid, 130 °C and 150 °C;
- For the two biodegradable hydraulic fluids, 150 °C, 200 °C, and 220 °C.

The H46 mineral oil was also intended to be thermally degraded at temperatures of 200 °C and 220 °C, but these temperatures are too close to its flash point (226 °C). When the temperature got close to 200 °C, the H46 oil changed its color to dark brown and started to emit heavy smoke, risking catching fire.

Thermal degradation was achieved by heating the oils to the above-mentioned temperatures and then leaving them to cool until room temperature. The thermal degradation was carried out on a heating device with a circulating air enclosure.

The oils were heated for 15 min to set the temperature and then cooled until they reached the ambient temperature of 22 °C. This cycle was repeated 8 times. Each sample of oil that was heated measured 200 mL.

2.3. Rheological Study

The rheological testing of the fluids was performed with the help of the Brookfield CAP2000+ Couette rotary viscometer, with cone-plate geometry, controlled by CAPCALC 32 software through which the numerical data processing and the setting of the working parameters of the viscometer were performed.

The procedure for testing oils on the viscometer is to insert the lubricant between the rotating cone and the plate that has the controlled temperature. To obtain the characteristic rheograms, a shear rate-imposed type measurement program was used with 40 measurement steps for both the loading and unloading cycles. The fluids were tested at a constant temperature of 20 °C, in a shear rate range between 100 s^{−1} and 2000 s^{−1}. During the measurements, the shear rate increased by 48–50 s^{−1}, and the soaking time at each measurement step was 60 sec. The technical characteristics of the cone used are a radius of 15.11 mm and a tip angle of 3°.

The determination of the rheological parameters (viscosity, flow index, consistency index) was achieved using the Newtonian rheological Equation (1) and the power law Equation (2) as follows:

$$\tau = \eta \cdot \dot{\gamma}, \quad (1)$$

where

- τ —shear stress [Pa];
- η —viscosity [Pa·s];
- $\dot{\gamma}$ —shear rate [s^{−1}].

$$\tau = m \cdot \dot{\gamma}^n, \quad (2)$$

where

- m and n are material constants— m is the consistency index [Pa·s ^{n}] and n is the flow index (dimensionless).

The studied fluids belong to the category of time-dependent non-Newtonian fluids, which, once subjected to shear changes, occur in their structure over time, both in shear stress and viscosity. This category of time-dependent non-Newtonian fluids includes thixotropic fluids.

Thixotropy is a time-dependent rheological behavior [32] in which a fluid exhibits a decrease in viscosity under shear stress, followed by a gradual recovery of the initial structure and viscosity upon removal of shear, over a characteristic period of time.

2.4. FTIR Spectroscopy

FTIR analyses were performed using the Nicolet iS50R spectrometer at room temperature using the Attenuated Total Reflectance (ATR) module.

Total attenuation reflection is a sampling method frequently used in FTIR analyses because it can be used on solid or liquid test products, does not require prior sample preparation, is easy to use, and is very fast. The method involves the use of a crystal, on which the test sample is applied. The test sample absorbs some of the infrared (IR) radiation that has penetrated beyond the crystal and is subsequently translated into the IR spectrum of the sample. The crystal used has a high refractive index and very good transmission properties [21].

In total, 32 scans of samples between 4000 and 400 cm^{−1} were performed at a resolution of 4 cm^{−1}. The recording of the spectra and the processing of the data were carried out through OMNIC 32 software.

3. Results and Discussion

3.1. Rheological Study Results

Table 2 presents rheological parameters of hydraulic fluids determined using the Newtonian rheological model and the power law rheological model.

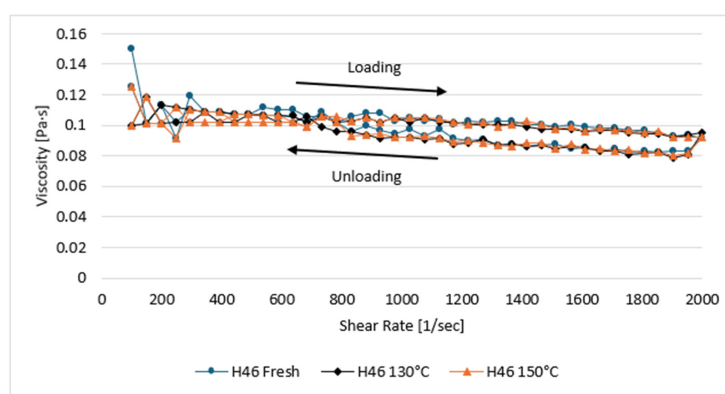
By comparing the correlation coefficients obtained for the two models, it is observed that the Newtonian model best describes the rheological behavior of fluids, both in the fresh state and after thermal degradation.

Figure 1 shows the comparative viscosity curves of the H46 mineral hydraulic fluid in the fresh state, as well as in the thermally degraded states after it was heated at a temperature of 130 °C and 150 °C, respectively.

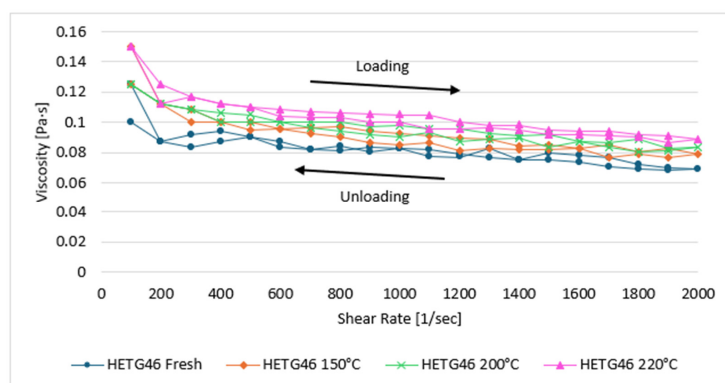
The variation in viscosity as a function of temperature, at different shear rates, for the mineral hydraulic fluid H46 (fresh and thermally degraded), can be observed in the range 100–800 s^{−1}. In this area, the thixotropy effect is insignificant, which means that the hysteresis loop is absent.

Table 2. Rheological parameters of hydraulic fluids at a temperature of 20 °C.

Oil Type	Oil Condition	Rheological Model				
		Newtonian		Power Law		
		Viscosity, η [Pa·s]	Correlation Coefficient [%]	Consistency Index, m [Pa·s ⁿ]	Flow Index, n	Correlation Coefficient [%]
H46	Fresh	0.0936	99.29	0.199	0.897	94.20
	130 °C	0.0922	99.32	0.167	0.919	93.90
	150 °C	0.0927	99.34	0.165	0.922	94.00
HETG46	Fresh	0.0752	99.49	0.190	0.874	96.00
	150 °C	0.0836	99.55	0.279	0.834	96.90
	200 °C	0.0882	99.59	0.229	0.869	97.60
	220 °C	0.0947	99.62	0.280	0.851	97.60
HF-E46	Fresh	0.0817	99.67	0.220	0.864	97.50
	150 °C	0.0835	99.64	0.229	0.861	98.10
	200 °C	0.0941	99.67	0.283	0.848	98.30
	220 °C	0.0998	99.79	0.195	0.908	98.30

**Figure 1.** Viscosity curves for the H46 mineral hydraulic fluid—fresh and thermally degraded at temperatures of 130 °C and 150 °C.

These comparative curves were also performed for the biodegradable hydraulic oils HETG46 (Figure 2) and HF-E46 (Figure 3).

**Figure 2.** Viscosity curves for the HETG46 biodegradable hydraulic oil—fresh and thermally degraded at temperatures of 150 °C, 200 °C, and 220 °C.

For HETG46 and HF-E46 biodegradable hydraulic oils, the viscosity behavior differs depending on the condition of the fluid. Thus, in the fresh form, the viscosity varies in the range of 100–1250 s^{−1} for HETG46 and 100–900 s^{−1} for HF-E46, without significant manifestations of thixotropy. In the case of thermally degraded HETG46 fluid, the relevant range is reduced to 100–700 s^{−1}, while also remaining in the zone without visible thixotropy.

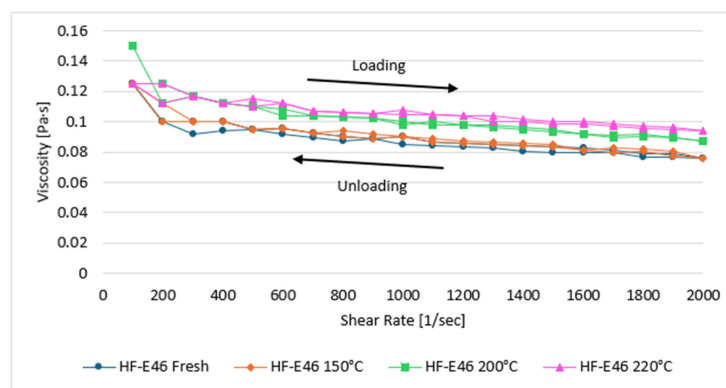


Figure 3. Viscosity curves for the HF-E46 biodegradable hydraulic oil—fresh and thermally degraded at 150 °C, 200 °C, and 220 °C.

As can be seen from Figure 1, the curves for the thermally degraded samples of the H46 mineral oil overlap the curve of the fresh one. This indicates that the thermal degradation process performed at set temperatures of 130 °C and 150 °C had no influence on the viscosity of the H46 mineral oil. On the other hand, analyzing Figures 2 and 3, it is obvious that the HETG46 and HF-E46 biodegradable oils do not exhibit this behavior when they are thermally degraded. The increase in degradation temperature leads to higher values of shear stress and, implicitly, to a higher viscosity.

After exceeding these values of the shear rate, the thixotropic effect becomes evident, which makes the results regarding the viscosity variation with temperature no longer experimentally relevant. On the other hand, for the thermally degraded HF-E46 fluid, no thixotropic behavior was observed in any of the analyzed intervals.

The overlapping comparative rheological curves for the H46 mineral hydraulic fluid in the fresh state and thermally degraded states presented in Figure 1 highlight the fact that its viscosity is the same regardless of the state of degradation in which the fluid is. On the other hand, for the HETG46 (Figure 2) and HF-E46 (Figure 3) biodegradable oils, the viscosity recorded after thermal degradation is higher compared to that of the fresh oil. This is because, through the evaporation of compounds, structural reorganization at the molecular level or adjustments to the functional composition occur in the fluid structure.

Figure 4 shows the variation of viscosity for the fresh and thermally degraded hydraulic oils at temperatures of 130 °C, 150 °C, 200 °C, and 220 °C. For the biodegradable oils (HETG46 and HF-E46), it is observed that viscosity increases with the increase in degradation temperature. In the case of the H46 mineral oil, there is an insignificant difference in terms of viscosity values (the viscosity of the fresh sample is slightly higher than that of thermally degraded oil at temperatures of 130 °C and 150 °C, respectively).

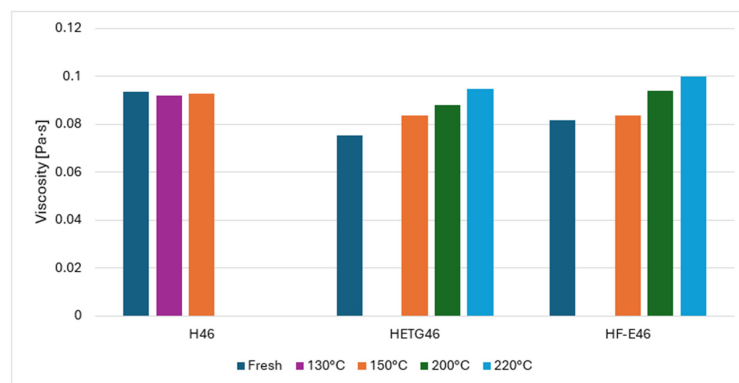


Figure 4. Viscosity variation depending on oil condition.

The viscosity of the two biodegradable oils increased by approximately 20% after thermal degradation. Such a variation exceeds the typically acceptable limits for hydraulic oils (± 10 – 15%) and may negatively influence system performance by reducing pumpability, slowing system response, and increasing energy consumption. Nevertheless, under normal operating conditions (40 – 80 °C) of the industrial or mobile machinery, oil overheating up to 200 °C can only occur accidentally in the case of malfunction or failure of the oil cooling systems. In these cases, after the defect is remedied, the oil is replaced as performance, lubrication, and component protection are compromised.

3.2. FTIR Spectroscopy Results

Figure 5 shows the FTIR spectrum for H46 mineral hydraulic oil in its fresh state and after thermal degradation at 130 °C and 150 °C.

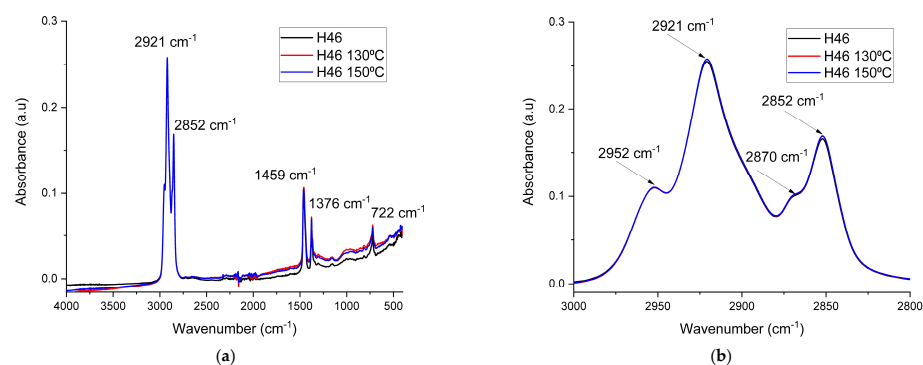


Figure 5. FTIR analysis for H46 mineral hydraulic fluid—fresh and thermally degraded at temperatures of 130 °C and 150 °C. Full spectra—(a) 2800 – 3000 cm^{-1} detail—(b).

The FTIR spectroscopy for the H46 sample (Figure 5) presents the characteristic peaks for the C-H bonds in the region 2800 – 3000 cm^{-1} . As there are no peaks over 3000 cm^{-1} , we can conclude that all hydrogens are bonded to sp^3 carbons (saturated). The asymmetric stretching vibrations for C-H in $-\text{CH}_3$ and $-\text{CH}_2-$ are noticed at 2952 and 2921 cm^{-1} , respectively [33]. The relative intensity of these two peaks is sensitive to the CH_3/CH_2 ratio in the sample, indicating the presence of long-chain aliphatic hydrocarbons. The peak from 2852 cm^{-1} can be assigned to the symmetric stretching vibration for C-H in $-\text{CH}_2-$, while the corresponding symmetric stretching vibration for the C-H bond in the $-\text{CH}_3$ moiety can be identified as a small shoulder around 2870 cm^{-1} . The peaks from 1459 and 1376 cm^{-1} are assignable to $-\text{CH}_3$ asymmetric and symmetric bending deformation and overlapped with the CH_2 scissor vibration.

As the ratio between normalized absorbance from 2921 and 2952 cm^{-1} is sensitive to the methylene to methyl ratio, it can give information about eventual fragmentation or other degradation of the aliphatic chains. The calculated values (Table 3) indicate a slight increase in this ratio, less than 0.8% , confirming the high thermal stability of this oil sample, which remains virtually unchanged.

Table 3. The corresponding normalized areas for various peaks and their ratios for H46 samples.

Sample	A_{2952}	A_{2921}	A_{2921}/A_{2952}
H46	0.438	4.371	9.979
H46 130 °C	0.444	4.441	10.002
H46 150 °C	0.441	4.436	10.059

The corresponding FTIR spectra for the biodegradable hydraulic oils HETG46 and HF-E46 are shown in Figures 6 and 7.

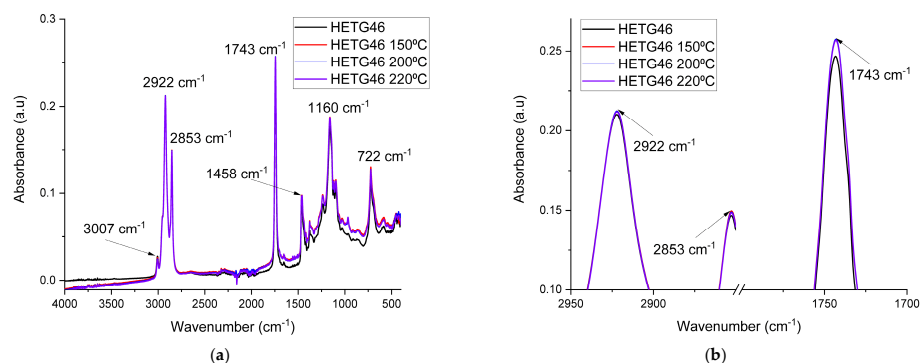


Figure 6. FTIR analysis for HETG46 biodegradable hydraulic fluid—fresh and thermally degraded at 150 °C, 200 °C, and 220 °C. Full spectra—(a) 1700–1800 and 2850–2950 cm^{-1} detail—(b).

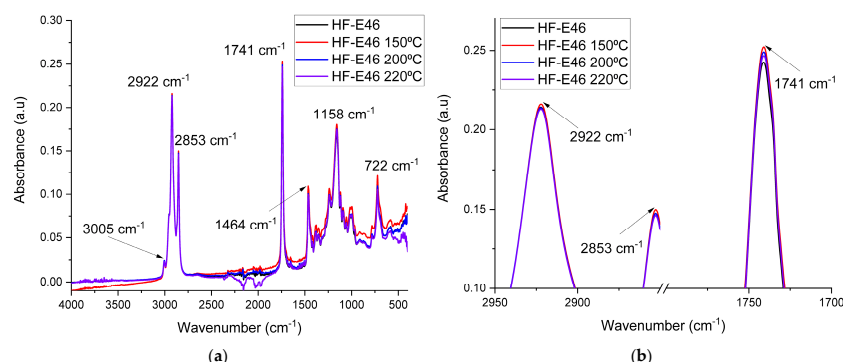


Figure 7. FTIR analysis for HF-E46 biodegradable hydraulic fluid—fresh and thermally degraded at temperatures of 150 °C, 200 °C, and 220 °C. Full spectra—(a) 1700–1800 and 2850–2950 cm^{-1} detail—(b).

In the FTIR spectrum for the HETG46 sample (Figure 6), a small peak at 3007 cm^{-1} can be noticed beside the peaks from the region $2800\text{--}3000\text{ cm}^{-1}$. This can be assigned to the C-H stretching vibration in unsaturated compounds, with unsaturated carbon (sp or sp^2). As there is a small peak at 1658 cm^{-1} that can be assigned to the C=C stretching vibration, we can assume that the 3007 cm^{-1} peak is from an alkene [34]. We can conclude that there are no aromatic rings in the structure of oil compounds, as for aromatic rings, there should be no peak above 1630 cm^{-1} and only a sharp one between 1630 and 1400 cm^{-1} . The presence of unsaturation is confirmed by the small peak from 1654 cm^{-1} assigned to the C=C bonds in unsaturated fatty acids [35]. As the wag of the =C-H bond is at 967 cm^{-1} , the isomer present is probably trans, not cis. The strong peak from 1743 cm^{-1} originates from the C=O stretching vibration, while the 1160 cm^{-1} can be assigned to the C-O stretching vibration. Together with the peaks from 1237 and 1096 cm^{-1} , this indicates the presence of an ester group [36].

For a quantitative analysis, we have measured the ratio between the absorbance at 1743 cm^{-1} , corresponding to C=O stretching (esters, aldehydes, ketones) and absorbance at 2921 cm^{-1} , assigned to C-H asymmetric stretching (Table 4) [37]. The peak around 2921 cm^{-1} (C-H asymmetric stretching vibration in $-\text{CH}_2-$) was observed to be relatively stable in all the spectra; therefore, it was used as an internal spectral reference. Additionally, we have determined the ratio for the normalized areas of 1160 cm^{-1} peaks (C-O stretching in esters) vs. 1458 cm^{-1} (CH_2 bending). The determined areas suggest a slight increase for the A_{1743}/A_{2921} ratio, $\sim 0.8\%$, and a higher increase for A_{1160}/A_{1458} , with $\sim 1.9\%$, which is significantly higher, a behavior that was reported previously in the literature for natural esters [38], although with a higher magnitude. This suggests the possibility of minor oxidation processes, leading to an increase in ester quantity in particular. A differential

normalized absorbance analysis for the A_{1743}/A_{2921} ratio, as indicated in [38], shows an increase of 0.4 to 0.7 units for samples heated at 150 and at 200 °C, respectively. These values are one magnitude of order smaller than those reported in [38]. Moreover, the increase in temperature to 220 °C does not lead to a further increase in the A_{1743}/A_{2921} ratio, indicating a possible plateau.

Table 4. The corresponding normalized areas for various peaks and their ratios for HETG46 samples.

Sample	A_{2921}	A_{1743}	A_{1743}/A_{2921}	A_{1458}	A_{1160}	A_{1160}/A_{1458}
HETG46	6.281	4.988	0.794	1.543	3.524	2.284
HETG46 150 °C	6.344	5.065	0.798	1.561	3.644	2.334
HETG46 200 °C	6.373	5.102	0.801	1.568	3.666	2.338
HETG46 220 °C	6.367	5.097	0.801	1.564	3.641	2.328

The FTIR for the HF-E46 sample (Figure 7) is very similar to the HETG46 sample, indicating the presence of the same functional groups in both samples. The peaks from 2956 and 2922 cm^{-1} correspond to the asymmetric stretching vibration for C-H in $-\text{CH}_3$ and $-\text{CH}_2-$, respectively. The higher intensity of the 2922 cm^{-1} peak indicates the presence of long-chain aliphatic hydrocarbons. The presence of the ester functional group is indicated by the sharp peak from 1741 cm^{-1} (C=O stretching vibration) and by the peak from 1158 cm^{-1} (C-O stretching vibration) [39]. The ester hydrocarbon chains are partially unsaturated, as indicated by the small peaks from 3004 cm^{-1} that can be assigned to the C-H stretching vibration with sp or sp^2 carbon. The 722 cm^{-1} absorption band can be assigned to the in-plane deformation vibration of the methylene group [40].

A similar analysis of the corresponding absorbance peak areas was performed for the HF-E46 samples (both fresh and treated), and the values are given in Table 5. In the case of HF-E46 samples, the A_{1741}/A_{2922} ratio increases by ~3.1%, a much higher percentage than that determined for HETG46 oil. This might point out the subtle differences between oil compositions, as the HF-E46 sample is more sensitive to oxidation. On the other hand, the increase in the A_{1158}/A_{1464} ratio by only ~2% indicates that the oxidation mechanism is different from the one of HETG46 oil. Esters are also formed in the case of the HF-E46 sample, but some other components are also oxidized to the corresponding ketones or aldehydes [41]. Nevertheless, the determined changes are small, and this indicates that for the duration of the thermal treatment, the oils can be considered as stable, as the other literature reports increases from 50 to 200% in the analyzed ratios [41].

Table 5. The corresponding normalized areas for various peaks and their ratios for HF-E46 samples.

Sample	A_{2922}	A_{1741}	A_{1741}/A_{2922}	A_{1464}	A_{1158}	A_{1158}/A_{1464}
HF-E46	6.487	5.112	0.788	1.813	3.802	2.097
HF-E46 150 °C	6.559	5.187	0.791	1.842	3.922	2.129
HF-E46 200 °C	6.454	5.239	0.812	1.804	3.856	2.137
HF-E46 220 °C	6.453	5.242	0.812	1.808	3.967	2.139

4. Conclusions

In the present work, three types of hydraulic fluids were tested both from a rheological and spectroscopic point of view, namely, an H46 mineral hydraulic fluid and two

biodegradable hydraulic fluids, HETG46 and HF-E46. They were studied in both fresh and thermally degraded states, and the results were compared.

From a rheological point of view, the data were analyzed under the assumption of the validity of two rheological models, namely, the Newtonian model and the power law model.

Using the regression analysis method, rheological parameters of the fluids were determined, and it was observed that the rheological model that best approximates the behavior of the three fluids is the Newtonian model, as it presents a correlation coefficient of over 99%, higher than the power law model, where the correlation coefficient is on average 96%.

From the results obtained by applying the power law model, it was observed that the flow index is less than 1, which means that the fluids have pseudoplastic behavior, meaning their viscosity decreases with the increase in the shear rate, and the fluids begin to flow regardless of the force applied to them. This pseudoplastic behavior is important in industrial applications where a decrease in viscosity can reduce the fluid's efficiency in hydraulic systems.

The studied fluids exhibit thixotropic properties (pseudoplastic fluids), as can be seen in the experimental results. However, to simplify the modeling of lubrication processes, it was recommended to use the Newtonian model, based on the classical Reynolds equations. The obtained results will be used in finite element analysis programs, which are based on the classical Reynolds equation implemented in most commercial simulation software. The modeling of fluid flow processes in hydraulic system components (pumps, valves, distributors, hydraulic cylinders, etc.) by means of these programs is usually performed based on the Navier–Stokes flow equations for Newtonian fluids. In this context, the use of the Newtonian model is recommended for convenience and compatibility with commercial software since they mainly implement the classical Reynolds and Navier–Stokes equations for Newtonian fluids. The same observation is valid for the modeling of lubrication processes specific to hydraulic systems. The results obtained represent useful information for design engineers and researchers specialized in the field of hydraulic installations.

The three hydraulic oils were also studied from a spectroscopic point of view by applying FTIR analysis, with the main purpose of identifying the structural changes of the oils when they are thermally degraded and comparing them with the fresh ones.

Since the FTIR spectra for the fresh biodegradable hydraulic oil sample HF-E46 and the thermally degraded samples at temperatures of 150 °C, 200 °C, and 220 °C are essentially the same, we can conclude that no new type of bonding occurs. The same can be observed for the fresh and thermally degraded H46 and HETG46 oil samples.

This is due to the following factors:

- The tested samples are designed to be resistant to high temperatures;
- The time in which thermal degradation was achieved was not long enough for structural changes to occur;
- The chemical stability of the hydraulic oil at normal temperature is ensured by the presence of additives (antioxidants, anticorrosive, antifoaming agents, etc.), which reduce the speed of chemical degradation reactions. At very high temperatures (during the test, up to 200–220 °C), biodegradable oils show an increase in viscosity, a phenomenon attributed to the formation of compounds identified by the absorption bands (peaks) highlighted in the FTIR spectra of the oils tested at different temperatures.

To be sure of this, further investigations should be made since the FTIR analysis will identify types of bonds and not the compounds in the oil, and this cannot be used as evidence that a compound or mixture has not undergone any transformation but only that no new types of bonds have appeared.

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Abbreviations

The following abbreviations are used in this manuscript:

ATR	Attenuated Total Reflectance
GC-MS	Gas Chromatography–Mass Spectrometry
FTIR	Fourier Transform Infrared Spectroscopy
ICP	Inductively Coupled Plasma
IR	Infrared
MRI	Magnetic Resonance Imaging
PAO	Poly-alpha-olefin

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