Evaluation of the Use of Vegetable Oils and Formulations as a Cutting Fluid in the Grinding of AISI 4340 Steel

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Abstract

Machining processes are responsible for the manufacture of various mechanical components (screws, shafts, gears, bearings and prosthetics). However, the large volume of mineral oil-based cutting fluids consumed in machining processes causes enormous damage to the environment and human health. Therefore, this work evaluated the use of cutting fluids based on vegetable oils (soybean and corn) as a substitute for mineral cutting fluids. The physical-chemical analyses showed that the oils and cutting fluids had their viscosity changed after storage for 600 and 720 hours, indicating changes in their physical-chemical properties. The infrared spectroscopy showed possible signs of oxidation of the fluids after storage, nevertheless, did not affect their performance. The thermal analyses showed that the mineral cutting fluid degraded from (93 °C), while the corn oil (104.7 °C), corn-A5 (110.2 °C), soybean (114 °C), soybean-A5 (122.7 °C), Mix-1 (111.2 °C) and Mix-2 (107.8 °C). The machining parameters evaluated indicated that Mix-1, SN, and CR-A5 are promising candidates to replace mineral cutting fluid in the grinding of metal parts. Given the above, this study compared the physical, chemical and roughness properties of mineral cutting fluid with vegetable oils from soybean, corn and their formulations to find possible promising candidates to replace mineral oils widely used in industrial machining.

1. Introduction

The large volume of petroleum-based cutting fluids consumed by machining processes causes great environmental damage owing to the high toxic potential and low biodegradability of this fluid type [1–3]. The high toxic potential and prolonged contact with these cutting fluids cause carcinogenic, genetic, respiratory problems, and skin irritations that affect human health [4, 5]. They also cause environmental contamination owing to incorrect and sometimes premature disposal of these fluids [6–9].

Companies operating in the competitive industrial market, such as manufacturers of machined parts, have a greater environmental awareness than ever before; therefore, they seek to adopt more efficient, cheaper, and environmentally friendly manufacturing methods [10]. In light of this, Pusavec et al. [11] stated that sustainable measures of production offer the machining industry a viable economic path to improve economic, social, and environmental performance. Regarding petroleum-based cutting fluids, Cheng et al. [12] reported that the world's machining industries consume 2 billion litres of cutting fluids annually. According to Lukoil [13], the global demand for liquid hydrocarbons has grown by an average of 1.2% annually, and projections show that this growth will reach 105 million barrels/day by 2025.

In this context, the best solution is to seek alternative cutting fluids that have the appropriate characteristics to meet rigorous machining requirements in terms of production and surface quality as well as social and environmental requirements [14–17]. Pereira [18] analysed the feasibility of two types of biodegradable oils (sunflower and castor bean) in terms of their rheological and tribological characteristics through the machining process of Inconel 718. Rapeti et al. [19] proposed using molybdenum disulphide nanosuspensions in coconut, canola, and sesame oils in the turning of AISI 1040 steel. The results showed that the oils used have appropriate machining characteristics compared to

conventional cutting fluids. Coconut oil showed better performance in the tests. Following this approach, Lawal et al. [20] compared the efficiency of cotton and palm oils to that of mineral oil by machining AISI 4340 steel. The results showed that the tested formulations could improve the roughness and decrease the cutting force during turning with coated hard-metal tools. In addition, the vegetable oils tested presented no risk to the operator's health [21, 22]. The researchers evaluated a mixture of vegetable oils such as castor, Soybean, and Corn oils in the GH4169 nickel alloy grinding process. The results showed that the assessed mixtures effectively reduced viscosity and improved the flow, atomisation, heat exchange, and wetting properties. On the other hand, the castor oil/Soybean mixture presented an excellent lubricant effect, a relationship between the tangential and normal grinding forces, and a reduction of the specific grinding energy and roughness values. Silva et al. [23] proposed a mineral oil/Soybean oil mixture in the proportion (1:1 v/v) in the grinding of AISI 4340 steel. The results showed promise concerning the roughness (3D) and residual stress compared to pure mineral oil. The authors also highlighted that the formulation is biodegradable, less toxic, and produced from a renewable source, contributing to environmentally friendly and sustainable manufacturing. Choudhury and Muaz [24] stated that new ecological cutting fluids will be developed aiming at high lubrication capacity and good machining performance in terms of process parameters and the environment. It should be noted that although vegetable oils in their natural form are not suitable for machining processes, the mixtures of these vegetable oils and/or the addition of particles, combined with the minimal quantity lubricant technique, enables new formulations to be obtained that perform well concerning petroleum-based cutting fluids.

This work we investigated the use of vegetable oils as cutting fluids to replace mineral cutting fluids, which are harmful to the environment and human health. For this, after each grinding step, the fluids were collected, stored and evaluated for their physical, chemical and machining properties.

2 Materials And Methods

2.1 Materials

The mineral oil used in this work was paraffinic-based Mecafluid 14SC (PETRONAS) containing inactive sulfochlorinated additives indicated for cutting operations in general. The vegetable oils soybean and corn were acquired from the CAMPESTRE industry and used without further treatment. The extreme pressure additive used was Liovac 580. For a cooling agent, Liovac PLO was used. The antioxidant used was Naugalube 438-L. Table 1 shows the soybean (SN) and corn (CR) oils without additives and additivation (SN-A5), and (CR-A5), and the mixture of the mineral cutting fluid with soybean oil (Mix-1) and corn oil (Mix-2).

Table 1
Formulations for cutting fluids with (SN-A5, CR-A5, Mix-1, and Mix-2) and without additives (SN, CR, and mineral).

Additive concentration (% v/v)	Fluid
5% Liovac 580/1% Liovac PLO/0.1% Naugalube 438-L/Soybean oil	SN-A5
5% Liovac 580/1% Liovac PLO/0.1% Naugalube 438-L/Corn oil	CR-A5
50% Soybean oil (S-A5) + 50% mineral oil	Mix-1
50% Corn oil (C-A5) + 50% mineral oil	Mix-2
Without additives	SN
	CR
	mineral

The procedure to obtain the additive formulations was performed using a final volume of 5.0 L for each sample of SN-A5, CR-A5, and Mix-1, and Mix-2 fluids. The agitation of the system was performed with a mechanical agitator model TE 139-Tecnal at a speed of 700 rpm for 10 min at room temperature (25°C). Then, the formulations remained at rest for 30 min before the tests began. The material used was AISI 4340 steel with an average hardness of 52 ± 2 HRC (Rockwell C Hardness) hardened and tempered with dimensions of Ø 37 × 42 mm. The chemical composition in percentages is shown in Table 2.

Table 2
Chemical composition of AISI 4340 steel

C	Mn	P	Si	S	Cr	Ni	Mo	V	Cu	Co	Fe
0.38	0.66	0.03	0.21	0.01	0.74	1.66	0.22	0.04	0.05	0.04	95.96

2.2 Methods

2.2.1 Machining conditions

The machining tests were performed by using an external cylindrical grinder, power equivalent to 9 kW, and a conventional aluminium oxide wheel (Al_2O_3) with the following dimensions and designation: 355.6 mm × 50.8 mm × 127 mm, FE 38A60KV. Table 3 shows the process parameters of the three tested machining conditions.

Table 3
Machining parameters

Parameter	Experimental condition		
	1	2	3
Plunge rate (mm/min)	1.2	0.8	1.2
Spark-out (s)	10	10	5
Cycle numbers	6	9	36
Cycle time (s)	60	60	10
On metal (mm)	1.2	0.8	0.2
Fluid flow rate (L/min)			
Mineral/Mix-1/Mix-2	12.4	12.4	12.4
SN/SN-A5/CR/CR-A5	11.6	11.6	11.6

After machining the parts, the used cutting fluids were collected and stored. Therefore, after preliminary tests, and studies carried out the cutting fluids: CR, CR-A5 and Mix-2 were analyzed after 600 h of storage. On the other hand, the cutting fluids: mineral, SN, SN-A5 and Mix-1 were analyzed after 720 h of storage.

3. Characterisations

3.1 Acidity index

For acidity index analysis, the standard ASTM D974-14 [25] was used. To this end, approximately 2.0 g of the sample was weighed in an Erlenmeyer flask, and 25 mL of alcohol-ether solution (2:1) previously neutralised with a 0.1 M potassium hydroxide solution was added. Two drops of phenolphthalein indicator were added and titrated with 0.1 M potassium hydroxide solution until pink colouration appeared.

3.2 Refractive index

The refractive indices of the vegetable oils (SN, SN-A5, CR, and CR-A5) and cutting fluids (mineral, Mix-1, and Mix-2) were measured using the ABBE Refractometer, model RTA-100 (INSTRUTHERM), refractive index: 1.300-1.720 and, scale 0 to 95% Brix. The scale reading was obtained directly for the absolute refractive index at 40°C. The refractive index was calculated using Equation 1.

$$R = R^{'} + K(T^{'} - T)$$

1

where R = refraction index at room temperature, R’ = refraction index at working temperature, T = reference temperature (°C), T’ = working temperature (°C), and K = constant used for oils (0.0003885) and fats (0.000365).

3.3 Density

The fluid density was determined employing the standard ASTM 1298-12b [26]. The empty pycnometer was weighed. The sample was carefully added through the pycnometer walls to prevent the formation of air bubbles, immediately covered, and placed in a water bath at a temperature of (25.0°C ± 0.1). After 5 min, the full dry pycnometer was weighed on an analytical balance.

3.4 Viscosity

Viscosity measurements were obtained using a Brookfield rotational viscometer model DVE VISCOMETER (AMETEK BROOKFIELD), with a 1-200000 cP viscosity range. The final viscosity value was obtained following the standard ASTM D227-04 [27]. The analysed cutting fluids were added to the container connected to the digital thermostatic bath for 10 min at a temperature of 40°C.

3.5 Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

The infrared analyses were determined using an absorption spectrophotometer in the infrared region with an ATR accessory, model IR Prestige-21, equipped with Fourier FTIR-84005. Spectra were recorded between 4000 and 500 cm^{-1} by the accumulation of 40 scans and a resolution of 4 cm^{-1}.

3.6 Thermogravimetric analysis (TGA)

The thermal and oxidative stability of vegetable and mineral oils were analysed using DTG-60H equipment. The thermal analyses were performed in a temperature range of 25 to 600°C, under an airflow of 50 mL/min, and at a heating rate of 10°C.min^{-1}.

3.7 Differential scanning calorimetry (DSC)

The oxidative thermal stability of vegetable and mineral oils was analysed using DSC Q2000 (TA Instruments) equipment. The analyses were performed under an oxygen atmosphere of 50 mL/min with a heating sweep from 30 to 300°C at a heating rate of 10°C.min^{-1}.

3.8 Grinding wheel wear

The diametrical wear of the wheel was obtained by employing the Pt parameter of the rugosimeter Mitutoyo model SJ-301. To evaluate the grinding wheel wear, AISI 1020 steel samples were used, where printing of the worn region of the grinding wheel was performed on the sample surface to obtain the marking of the worn profile of the grinding wheel. This step was performed after the end of each machining test.

3.9 Arithmetic mean deviation (Ra)

The roughness was defined by the arithmetic mean deviation according to DIN 4776, and the cut-off sampling length used was 0.8 mm. The measurements were made with a roughness meter, Mytutoyo model SJ-301. Roughness was measured at four radial and equidistant positions at approximately 90°.

3.10 Contact angle

The contact angle analysis was performed on DROP Shape Analyser equipment, model DAS 100 (Kruss Scientific) The drop was obtained by programming the equipment after depositing 6.0 µL of oil precisely on the surface of the metal plate.

3.11 Statistical analysis

All statistical analyses were performed using One-way (ANOVA) Origin Pro software 8.5, and the results were expressed as mean ± errors. ANOVA analysed statistically significant differences (p) using Tukey's test. The difference was considered statistically significant when the value was $p \leq 0.05$.

4. Results And Discussion

4.1 Acidity index

Figure 1(a) Value of acidity index of cutting fluids CR, CR-A5, and Mix-2 after 600 h of storage. Figure 1(b) mineral, SN, SN-A5, and Mix-1 after 720 h of storage. Average followed by the same letter on the graph does not differ by Tukey's 95% confidence level test.

It was observed that the Mix-2 cutting fluid showed oscillatory behaviour throughout the test corn oil showed significant variation at all times; on the other hand, CR-A5 showed a smaller index at time 0 h. At other times, it tended to decrease and is considered statistically equal. The search for comparative analysis of the data by applying the hypothesis test contributed to evaluating the behaviour of the fluids during the storage. Figure 1(b) presents the results obtained for the acidity index of mineral oils, SN, SN-A5, and Mix-1 during the 720-h storage time.

In general, Figure 1(b) shows that none of the cutting fluids presented an increasing or decreasing variation in their values concerning time. It was also observed that the mineral fluid showed the highest acidity indexes, followed by Mix-1. For SN and SN-A5 additive oils, it was observed that at time 0 h, we have lower values for SN and higher values for SN-A5 than at other storage times. However, for SN-A5, this variation was not statistically significant. It can be observed that SN oil presented a considerable variation of values, evidenced by an oscillatory tendency. This behaviour is very similar to that of the Mix-1 oil. In this sense, it is noticed that the mineral cutting fluid presented the highest acidity index, and this high value probably refers to the use of additives in its formulation. A small variation of values was observed during the 720 h of use, indicating fluid stability. Concerning the SN-A5 cutting fluid, the values also did not undergo statistical changes during the 720 h of storage in the grinding tests, probably owing to additivation. This indicates this fluid's stability under the operating conditions used. Because of the results presented, it is possible to observe that mineral cutting fluid, vegetable oils with and without

additives, and Mix-1 and Mix-2 did not demonstrate significant evidence of degradation during the grinding tests for the monitored period.

4.2 Refractive index

Figure 2(a) Refractive index value for CR, CR-A5, and Mix-2 after 600 h of storage. Figure 2(b) mineral, SN, SN-A5, and Mix-1 after 720 h of storage. Average followed by the same letter on the graph does not differ by Tukey's 95% confidence level test.

It is observed that the value of the refractive index of CR oil increased between 0h and 240 h, and remained constant after 240 h, as shown in Figure 2(a). At 0 h, the fluid presented the highest refraction value, and at 120 h it presented the lowest value. It was also noted that these values are considered statistically different, and at other times, the values are equal. On the other hand, for CR-A5, the same values were observed a 0 h and 120 h. At other times there was a slight statistical increase. The Mix-2 cutting fluid presented the highest value at 240 h and the lowest at 0 h; all times are considered statistically equal.

Figure 2(b) shows the values obtained for the refraction index of the mineral, SN, SN-A5, and Mix-2 cutting fluids after 720 h of storage during machining tests. In this case, the highest refraction value was observed for the mineral cutting fluid at 360 h and the lowest at 0 h; however, all times are considered statistically equal. In the case of SN oil, there was an oscillating tendency between the values where the lowest value occurred at 180 h. From 360 h onward, there is a slightly increasing tendency of these values, and the highest value was found at 720 h. The SN-A5 cutting fluid showed a somewhat pendulous behaviour, with no behavioural tendency of the fluid. Its highest value occurred at 540 h and the lowest value at 0 h. These are considered statistically distinct. In the Mix-1 fluid, the highest value was observed at 180 h when compared to the initial time (0 h). It was also noted that only at time 0 h was there a statistically significant difference from other times. By applying the hypothesis test, it is possible to perform a more careful study of the data, thus contributing to fluid behaviour evaluations during machining tests.

In general, it was observed that over time, the refractive index value begins to oscillate, sometimes in an increasing, decreasing, or random manner over time. This is probably owing to changes in the homogeneity of the system as a function of particles in suspension from the grinding process in which they are incorporated into the fluid, as its use increases. This parameter is considered a positive indication of the feasibility and quality of the fluid used.

4.3 Viscosity

Figure 3(a) shows the viscosity results during storage of the cutting fluids in the grinding tests after 600 h. Corn oil presented the highest viscosity values at 0 h and 600 h. For CR-A5, a statistically significant difference between the storage times was noted. In the Mix-1 and Mix-2 cutting fluids, there are intermediate viscosity values and different values between the fluids. However, the values found are considered equal for their different test times.

Figure 3(b) shows the viscosity results during storage of the cutting fluids in the grinding tests after 720 h. It is observed that SN and SN-A5 oils presented similar viscosity values to CR oil at 720 h. However, these are considered statistically equal to those at 0 h. Mineral fluid values in the initial time at 0 h and final time at 720 h are the lowest of all slice fluids studied and do not present significant changes; they are considered statistically equal. The Mix-1 and Mix-2 cutting fluids have intermediate values of viscosity that are different from those of the other fluids. However, the values found are deemed equivalent in their different test times.

In general, it was observed that the cutting fluids used in the grinding tests showed increased viscosity; this suggests a change in their physical-chemical property after 600 and 720 h of use.

4.4 Density

Figures 4(a), and 4(b) presents the results obtained for the density after the storage of the grinding tests after 600 and 720 h, respectively. The results obtained from all fluids used in the grinding tests are statistically different among all types of fluids and those analysed after 600 and 720 h. Of the cutting fluids used in the 0 h time, the mineral had the lowest density value and CR-A5 the highest. On the other hand, after hours of use, the fluids indicated that the mineral fluid maintained the lowest value and soybean oil the highest. It is worth mentioning that the values of the replicas are close since the standard deviation was low.

Figure 4(a) shows in general that the fluids analysed at the storage times of 600 and 720 h have an oscillating behaviour and that this behaviour is less pronounced for fluids evaluated after 600 h of storage. This difference is probably owing to the number of ground parts, where the total volume of material removed was 27.8×10^4 mm^3 for the fluids stored at 600 h and 55.7×10^4 mm^3 for the fluids observed at 720 h.

After hours of use, the density values were higher in all of the cutting fluids, a result considered acceptable in all oils submitted to the grinding process, where the fluid tends to accumulate particles during its use. It was also noticed that the addition of SN-A5 and CR-A5 oils promoted a significant increase for this parameter. It was observed that for viscosity, higher absolute values were obtained after hours of use; however, they did not present a statistical difference. On the other hand, this difference was statistically significant; it was then perceived that this parameter is a good indicator for monitoring cutting fluids.

4.5 ATR-FTIR analysis

The analyses of the infrared spectra first sought to investigate the cutting fluids used and stored after 600 e 720h. Then, the cutting fluids' spectral differences were compared looking for signs of their oxidation. Figure 5(a) shows the ATR-FTIR spectra for CR, CR-A5 and Mix-2 at the initial time 0 h of use of the fluids and after storage 600 h. On the other hand, Figure 5(b) shows the spectra for mineral, SN, SN-A5 and Mix-1 at 0 and 720 h.

Comparing the spectra of SN-A5 and CR-A5 it is observed that both fluids presented differences originated by the additivation, which promoted a reduction in the intensity of the 3008 cm^{-1}, 1235 cm^{-1}, and 1158 cm^{-1} bands for SN-A5 and an increase in the intensity of the 1373 cm^{-1} and 1454 cm^{-1} bands when compared to SN oil. For the CR and CR-A5 cutting fluids, the changes in spectra were subtler and signalled a small reduction in intensity in the bands 1416 cm^{-1} and 1465 cm^{-1}, and an increase in the bands 1654 cm^{-1} and 1378 cm^{-1}. According to Navarra et al [28], and Sharma et al. [29] bands in the 1400-to-1200-cm^{-1} regions are mainly attributed to the bending of CH_2, CH_3, and aliphatic groups. The only strong carbonyl peak from the vibrational elongation of triglyceride carbonyl groups was observed in vegetable oil spectra at about 1750 cm^{-1}. Another feeble band was observed at about 1654 cm^{-1} [28].

It is also noted in Figure 5(b) that the mineral cutting fluid had bands at 3089 cm^{-1} associated with vibrations of double trans links of (C=C) and at 2521 cm^{-1} and 2359 cm^{-1}, a characteristic of symmetric vibrations of the aliphatic C-H of CH_2 and terminal groups of CH_3, respectively, as described by [30, 31]. For the Mix-1 and Mix-2 cutting fluids, discrete bands were observed at 3008 cm^{-1}, accentuated at 2926 cm^{-1}, and specific vegetable oil bands at 1744 cm^{-1} (C=O), 1452 cm^{-1}, 1382 cm^{-1}, 1159 cm^{-1}, and 736 cm^{-1}. In general, the characteristics of vegetable oils prevailed in the mixture with mineral cutting fluid.

In general, little change was noticed between the spectra in the fluids used. In the vegetable oil spectra, the 3006 cm^{-1} bands were evidenced at 3008 cm^{-1} and did not change after storage, thus signalling that the cutting fluids did not oxidise. Another region of the spectrum highlighted was 1163 cm^{-1}, and in agreement with De la Mata [30], these differences are a consequence of the presence of triglyceride groups. For Navarra et al. [28], the oxidation processes begin with the formation of unstable hydroperoxide molecules degraded into secondary oxidation products such as alcohols, aldehydes, and ketones, and spectral modifications were shown at 3530 cm^{-1}, 3006 cm^{-1}, and 1163 cm^{-1}. Furthermore, Guillén and Cabo [32] showed that the 3006 cm^{-1} band is a fingerprint of the oxidation process and is associated with the C-H vibration elongation of the *cis* connection (=CH) where the band position remains almost unchanged or undergoes a low wave change during the first oxidation time.

It was observed by a general evaluation of the obtained spectra that there were no significant spectral changes concerning the oxidation of cutting fluids. To investigate the potential oxidation of the cutting fluids used after the machining steps, we sought to evaluate the potential increase of the spectral band areas (ATR-FTIR) through the integralisation of these bands. Thus, it was possible to observe that a small increase in the carbonyl band area occurred after 600 and 720 h of use. An increase in the carbonyl band (C=O) area is an indication of the beginning of the oxidation of vegetable oils. Table 4 lists the differences between the areas of the bands as analysed by ATR-FTIR.

Table 4
Evaluation of oxidation process of cutting fluids through the relationship between band areas in the infrared region.

Fluid	Band (806-1540 cm^{-1})	Band (1550-1860 cm^{-1})
	Value	Value
CR	43.28	28.16
CR-A5	58.00	26.70
Mix-2	69.40	29.20
Mineral	138.89	27.18
SN	66.00	31.70
SN-A5	51.12	29.21
Mix-1	74.05	31.40

The increase in the band areas of the mentioned regions indicated that there was a small change in all samples after 600 and 720 h during the use of cutting fluids in the machining tests that were not observed in Figures 5(a-b). It was observed that the mineral, Mix-1, and Mix-2 cutting fluids suffered more significant differences between the values of the initial and final areas in the region of 806 cm^{-1} to 1540 cm^{-1}. From 1550 cm^{-1} to 1840 cm^{-1}, the most significant difference was noticed in SN oil and the smallest in CR-A5. It is worth mentioning that the additives provided a delay in oxidation between SN oil for SN-A5 and CR for CR-A5 since the difference was smaller for the additive fluids. Furthermore, Guillén and Cabo [32] stated that no band modifications were detected in the spectral region between 700–1500 cm^{-1}, which showed that structural changes occur only at a late stage of oxidation. According to Sherazi et al. [33], it is possible to accurately, safely, and quickly monitor oil changes using the ATR-FTIR method, with the advantage of not using solvents. It is concluded that the performance of the cutting fluids monitored after the machining conditions tested did not show significant changes when compared to the mineral cutting fluid.

4.6 TGA analysis

TGA analyses of the additive and nonadditive vegetable oils, mineral, Mix-1, and Mix-2 cutting fluids were performed to select and investigate their oxidative behaviour. The data obtained showed the stages of mass variation identified with the aid of the TGA curve. Regarding the mineral cutting fluid, two losses of mass were observed, the first between 107.7°C and 283.2°C with a loss of mass of 85% in weight, probably owing to the degradation of volatile materials. The second step, determined between 283.2°C and 570.0°C with a loss in mass of 13.9% by weight, results from the polycondensation and carbonisation of the compounds formed [34, 35].

In the case of vegetable oils (soybean and corn), were also observed two stages of thermal degradation: the first stage, determined between 200-230°C, can be attributed to the thermal decomposition of triglycerides, composed mainly by polyunsaturated fatty acids [36]. In the second stage, the initial temperature was approximately 380°C, and the most significant loss in mass occurred above 47% owing to the probable degradation of the carbon chains. This loss in mass is owing to the decomposition of polyunsaturated, and saturated fatty acids, respectively [37]. It is also interesting to note that the mineral cutting fluid presented the lowest temperature for the beginning of degradation (107°C) and the highest loss of mass (85% by weight) in the first step. In comparison, the SN oil sample presented the highest temperature concerning the beginning of the degradation process (232°C). Among the vegetable oils, SN oil showed the highest degradation temperature. The behaviour of additive oils showed significant variation. For the SN-A5 and CR-A5 oils, where the antioxidant was added, there was an increase in the degradation temperature from 232 to 248.2°C, and 221 to 255.1°C, respectively. The Mix-1 and Mix-2 cutting fluids were obtained by mixing mineral cutting fluid with vegetable oils. Three stages of thermal degradation were identified. The first step started above 150°C, and a loss in mass of approximately 60% was observed. The second step started at around 390°C, and the third step above 420°C, noting that the mixing of vegetable oils with the mineral cutting fluid provided thermal gains since the mineral fluid started its thermal degradation at 107°C. This was a positive factor for the use of Mix-1 and Mix-2 cutting fluids. In general, it was observed that the additives used increased the thermal stability of SN oil, as represented in Figure 6.

4.7 DSC analysis

The DSC technique is based on measuring the heat flow generated by the oil sample during heating and/or cooling of the sample. It is then possible to evaluate the crystallisation of triglycerides, which translates into a peak where the enthalpy (peak area) and lower and upper temperatures of the process can be measured [38]. It was noted Tan and Che [39] that the transfer of an oxygen molecule to unsaturated fatty acids requires the release of energy. In this sense, [40, 41] determined the oxidative stability of vegetable oils by employing the DSC technique.

In this context, the dynamic oxidative study for cutting fluids via DSC showed two exothermic peaks for all the fluids analysed; these peaks were more evident for the soybean and soybean-A5 oils. The temperatures of (Tonset) were obtained by extrapolating the baseline with the exothermic curve's tangent [39]. Figure 7 shows the thermal behaviour for the mineral, SN, SN-A5 and Mix-1, CR, CR-A5, and Mix-2 fluids at times 0h, 600 and 720h.

It is noted that the mineral cutting fluid presented the lowest temperature for the beginning of degradation at 92.8°C and SN-A5 oil showed the highest at 122.7°C, followed by SN oil at 114°C, CR at 104.7°C, and CR-A5 at 110.2°C. This behaviour was also observed by Smith et al. [42] for vegetable oils without additives. The Mix-1 and Mix-2 cutting fluids reached 111.2°C and 107.8°C, respectively; these were higher values than those found for mineral cutting fluid. Tan and Che [39] stressed that it is possible to evaluate the differences and similarities of oils to investigate the initial and final transition temperature

and maximum reaction temperature. This study corroborates and reaffirms the oxidative behaviour of vegetable and mineral fluids. Similar studies Gloria and Aguilera [43] and, Márquez-Ruiz et al. [44] noted that the higher the linolenic and linoleic acid content, the higher the value obtained for the temperature of (Tonset). However, easier oxidation of vegetable oils was observed owing to the unsaturation present in their molecular structure. On the other hand, the mineral cutting fluid presented the lowest Tonset, mainly owing to its chemical structure composed of alkane carbon chains. The process of decomposition and combustion occurs easily, according to [45]. Table 5 presents the calorimetric data of vegetable and mineral fluids evaluated during the machining tests.

Table 5
Thermal behaviour (thermal event, Tonset, and maximum temperature) of vegetable oil (SN, CR), and cutting fluids (SN-A5, CR-A5, Mix-1, Mix-2, and mineral) via DSC analysis.

Fluid	Thermal event	Temperature onset (°C)	Maximum temperature (°C)
Mineral	Exothermic	92.8	127.2
SN	Exothermic	114.0	159.3
SN-A5	Exothermic	122.7	167.9
CR	Exothermic	104.7	146.2
CR-A5	Exothermic	110.2	146.8
Mix-1	Exothermic	111.2	157.9
Mix-2	Exothermic	107.8	145.9

Per Kowalski et al. [46], the investigation of kinetic analysis and oxidation of vegetable oil by DSC has become a relatively popular technique. It is also worth mentioning that in tests where induction times are measured, one can use the oil oxidation speed and temperature constants for thermal and kinetic parameters.

In general, the DSC technique contributed to the investigation of the initial degradation temperature of the monitored cutting fluids, where we have SN-A5 > SN > Mix-1 > CR-A5 > Mix-2 > CR > mineral. The evaluated data allowed for the investigation of the initial reaction temperature according to the energy flow.

4.8 Diametric grinding wheel wear

The cutting tool’s performance in the grinding of the AISI 4340 steel samples was evaluated by the diametrical grinding wheel wear after the three grinding conditions were tested using the cutting fluids employed. Figures 8(a-b) show the results for the grinding wheel wear after the machining conditions were tested.

As shown in Figures 8(a-b) the statistical analysis performed for cutting fluids (SN, SN-A5, CR, CR-A5, Mix-1, and Mix-2) in different conditions show that the corn oil presented a lower wear value in machining condition 3 and a higher value in condition 1. Regarding CR-A5 oil, a lower value was observed in machining condition 3 and a higher value in condition 1. Mix-2 cutting fluid showed statistically distinct values for the three conditions. Machining condition 2 produced the lowest value, and condition 3 showed the highest grinding wheel wear value. There was no standard behaviour concerning vegetable cutting fluids. In the case of fluids storage for 720 h, the mineral cutting fluid had its lowest value in machining condition 2, whereas in machining conditions 1 and 3 the results were more extensive and considered statistically equal. For SN-A5 cutting fluid, the results showed less wear for machining condition 2 and higher wear for condition 1. However, statistically, these values are considered equal for the three machining conditions tested. Finally, for the Mix-1 cutting fluid, we had in machining condition 2 the lowest wheel wear value. Condition 1 showed the highest; however, statistical analysis shows us that these values were not distinguishable between the three machining conditions tested.

In general, it was noticed that the different machining conditions present different results of diametrical grinding wheel wear. Machining condition 1 required a more aggressive grinding wheel to remove material on the part owing to the shorter period. It was noted that Mix-1 fluid showed better performance in machining conditions 1 and 3, signalling a gain for this cutting fluid when compared with the mineral cutting fluid that showed higher grinding wheel wear in these two conditions. In machining condition 2, Mix-1 fluid showed similar values to the mineral fluid when considering its standard deviation. It should be noted that machining condition 3 is similar to the grinding conditions used in the industrial environment. Dressing conditions and cutting penetration greatly influence the grinding wheel wear. It was also noticed that CR-A5 and SN oil presented values close to the mineral cutting fluid in machining condition 3.

4.9 Arithmetic mean deviation (Ra)

The surface quality of AISI 4340 steel machined parts was evaluated using the roughness parameter (Ra) after the three grinding conditions were tested using the cutting fluids employed. Figures 9(a) and 9(b) show the result of the Ra during the use of the cutting fluids CR, CR-A5, Mix-2 and mineral, SN oil, N-A5, and Mix-1 in the machining conditions tested.

According to Figure 9(a), a statistical analysis performed for CR and, CR-A5 under different machining conditions revealed that the corn oil presented its lowest roughness value in machining condition 2 and its highest in machining condition 3. On the other hand, it was observed that the CR-A5 presented its lowest value in machining condition 3 and highest in machining condition 1. The Mix-2 cutting fluid showed its best performance in machining condition 2 and worst in condition 3. Regarding the cutting fluids monitored during 720 h, Figure 9(b), the mineral fluid presented in machining condition 1 showed its lowest value and highest roughness value in condition 3. SN oil gave a better performance in machining condition 1 and a worse value in machining condition 2. It is also observed that machining condition 3 is considered similar to condition 1. SN-A5 oil had its best performance in machining

condition 1; its worst performance was in machining condition 3. Mix-1 revealed in machining condition 2 its lowest roughness value and in condition 1 its highest value.

In general, it was observed that for cutting fluids monitored up to 600 h, the best performance was for CR-A5 oil and Mix-2 fluid in machining condition 3. There were also gains concerning the additivation of corn-A5 oil, in machining condition 3, which showed a considerable reduction in roughness from 0.52 µm to 0.31 µm. It was also observed concerning the monitored cutting fluids up to 720 h that the mineral fluid presented a lower value for roughness only in machining condition 1. By contrast, Mix-1 fluid had its best performance in machining conditions 2 and 3. SN oil showed the highest values, i.e., the worst performance in machining conditions 1 and 2, while SN-A5 oil had its best performance in machining condition 3. He noted that soybean oil showed higher roughness than SN-A5 oil for machining conditions 1 and 2, thus signalling gains obtained by the additivation of soybean oil in these machining conditions.

Regarding the roughness parameter Ra, it was observed that the Mix-1 cutting fluid was superior to the mineral cutting fluid in the second and third conditions of the machining test. The CR-A5 cutting fluid was also superior to mineral in the third condition, which showed that Mix-1 and corn-A5 cutting fluid are viable options for obtaining machined surfaces with a quality surface finish while being environmentally friendly since these cutting fluids have biodegradable characteristics. Machining condition 3 was the least severe of the grinding tests because, in this machining condition, the wheel advances over the workpiece surface, removing less material in a shorter space of time. It is worth mentioning that the third machining condition is the most used by industries that grind hardened steel parts. In this sense, it was observed that the total volume of material removed was 27.8×10^4 mm^3 for the fluids monitored for 600 h and 55.7×10^4 mm^3 for the fluids monitored for 720 h.

Generalising the results showed that the fluids used showed values very close and even lower than the mineral cutting fluid, which is a positive factor for its use since these fluids are obtained from renewable sources and less aggressive to the operator.

4.10 Contact angle

A contact angle test was performed to evaluate the wetting behaviour and performance of the tested cutting fluids. Table 6 shows the contact angle values of AISI 4340 steel's surface after grinding using the cutting fluids analysed. Given this, it was observed that the formulations proposed through the additivation of vegetable oils obtained different values for the contact angle, where the mineral oil showed higher wettability when compared to other fluids.

Table 6
Value of contact angle of the surface of AISI 4340 steel after machining conditions using CR, CR-A5, Mix-2, Mineral fluids, SN, SN-A5, and Mix-1.

Fluid	Contact angle (°)
CR	21.54 ± 0.05
CR-A5	20.53 ± 0.14
Mix-2	20.10 ± 0.21
Mineral	11.90 ± 0.11
SN	28.44 ± 0.18
SN-A5	23.68 ± 0.04
Mix-1	21.20 ± 0.28

Analyzing Table 6, it was observed that the mineral cutting fluid has a lower contact angle value when compared to other fluids. The difference between the mineral and the Mix-2 formulation is approximately 68%. On the other hand, Mix-1 cutting fluid showed the best performance in machining parameters (diametric wheel wear and Ra) in machining condition 3, which showed that the chemical interaction of the Mix-1 formulation provided significant gains among the tested formulations. Mix-1 showed an approximately 78% greater contact angle than mineral oil and 10% greater than that of Mix-2. According to Gajrani et al. [47] cutting fluid, wettability is mainly influenced by the chemical interaction of the cutting fluids with the surface of the cutting tool and the workpiece, which substantially affects the lubricating capacity during machining. According to Li et al. [48] and, Zhang et al. [49], the wettability of cutting fluids on the surface of the cutting tool is one of the essential factors since it substantially affects the lubricating capacity during machining, where the stability of the lubricating oil film at the workpiece/roller interface also plays a vital role in the lubricating effect.

Therefore, the results obtained from the diametrical grinding wheel wear and roughness (Ra) showed that the mineral oil's best wettability (lower contact angle value) did not provide the best results for the machining parameters in the third grinding condition. In this sense, Zhang et al. [49] showed that the machined part's surface quality could be correlated to the viscosity and contact angle. Thus, the results obtained from viscosity and contact angle were associated with diametrical grinding wheel wear and Ra parameter to evaluate the performance of the tested formulations. Thus, the mineral oil presented the lowest values for viscosity and contact angle, which indicated that the lubricant film formed in the cutting zone is thinner. At high temperatures, the generated film breaks and evaporates easily. Thus, there is no formation of an effective lubricant film in the cutting zone in the region of contact between the part and wheel. Thus, the dry friction becomes pronounced, causing the lubricant effect to be lost. Given this situation, the surface quality of the machined part is compromised [50, 51]. On the other hand, Mix-1

presented higher values for viscosity and contact angle. Given this, the high viscosity of Mix-1 fluid reduces fluidity and increases the thickness of the lubricating oil film so that the stability of the film and the lubricating effect improve in the cutting area. This promotes greater surface quality to the machined part. According to Zhang et al. [52], the fluid's high viscosity allows it to flow slowly, which can improve the lubrication properties in the cutting zone when machining the part, thus improving friction and wear between the part and cutting tool.

The results obtained in the third machining condition proved that Mix-1 fluid achieved the best performance for the Ra and diametric wheel wear parameters. Given the above, although the Mix-1 cutting fluid did not present the best wettability compared to mineral oil, Mix-1 gave the best performance for the machining parameters analysed. Therefore, the proposed formulation for Mix-1 offers great potential for applying this cutting fluid in the ecologically sustainable machining industry.

5. Conclusion

According to the characterisations carried out and the results, it was observed that the oils and cutting fluids evaluated presented higher values for viscosity after storage for 600 and 720 hours, indicating possible changes in their physicochemical properties. The FTIR bands showed possible signs of oxidation of the fluids after storage, however, did not affect their performance. The TGA and DSC analyses indicated that the mineral cutting fluid degraded at a lower temperature compared to the vegetable oils, showing that the vegetable oils (SN and CR) have superior thermal stability. Furthermore, the CR-A5 and SN-A5 additive fluids showed greater thermal stability compared to CR and SN. Regarding the machining parameters, it was observed that the Mix-1 cutting fluid obtained the best performance in machining conditions 1 and 3. On the other hand, SN and CR-A5 also presented values close to the mineral in machining condition 3, being these fluids considered a promising alternative in replacement to the mineral fluid. As for roughness, it was observed that the Mix-1 cutting fluid showed better performance compared to the mineral fluid. It is worth noting that machining condition 3 is the one used by the industry. Thus, the results found indicate that the vegetable oils used are a promising alternative to mineral oils because they are biodegradable, low cost, non-toxic and environmentally friendly. It is noteworthy that in this study the results obtained suggest that Mix-1, SN, and CR-A5 are promising candidates to replace mineral cutting fluid in the grinding of parts.

Declarations

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Figures

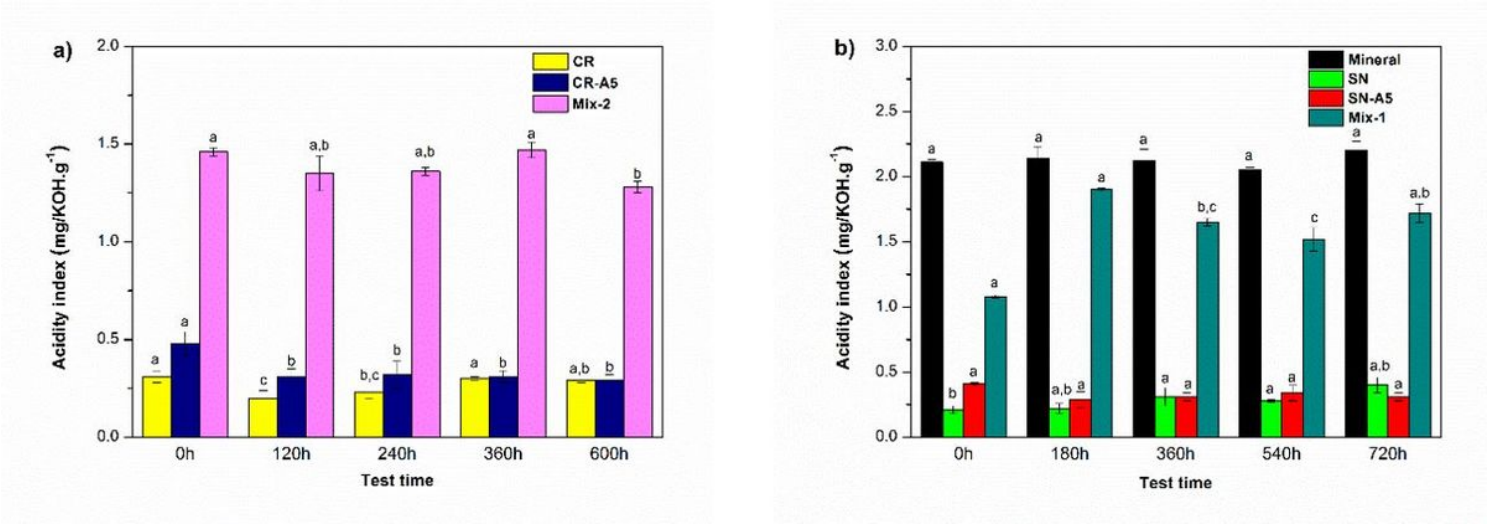

Figure 1

(a) Value of acidity index of cutting fluids CR, CR-A5, and Mix-2 after 600 h of storage. Figure 1(b) mineral, SN, SN-A5, and Mix-1 after 720 h of storage. Average followed by the same letter on the graph does not differ by Tukey's 95% confidence level test.

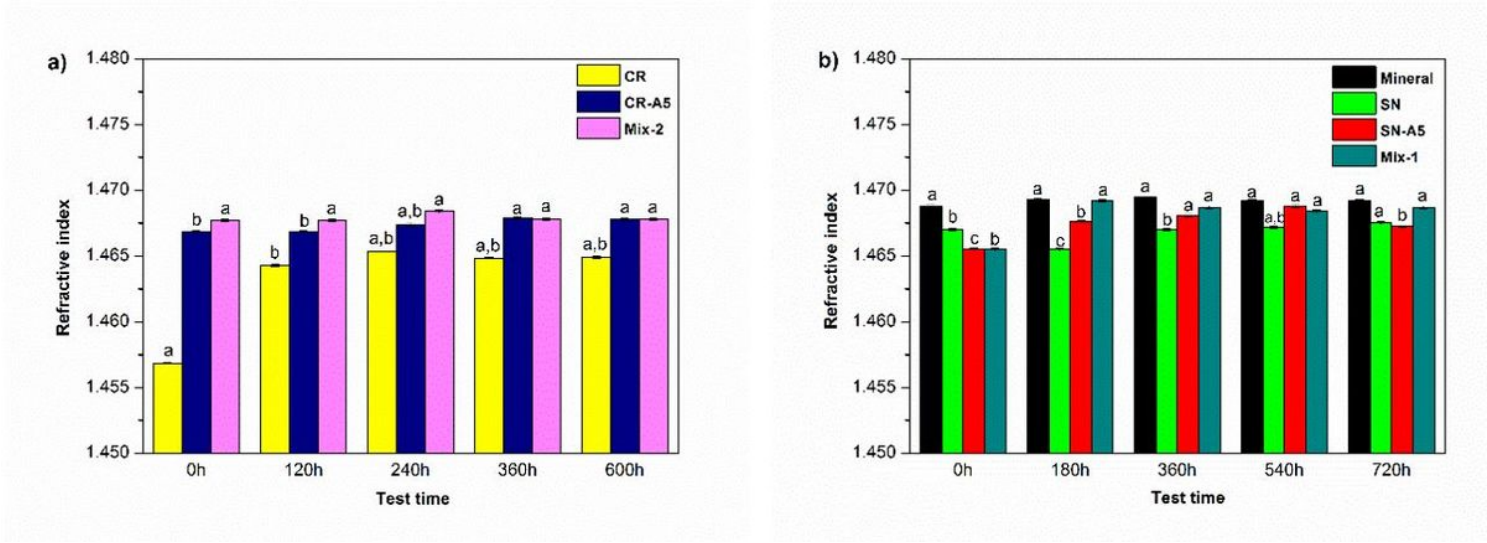

Figure 2

(a) Refractive index value for CR, CR-A5, and Mix-2 after 600 h of storage. Figure 2(b) mineral, SN, SN-A5, and Mix-1 after 720 h of storage. Average followed by the same letter on the graph does not differ by Tukey's 95% confidence level test.

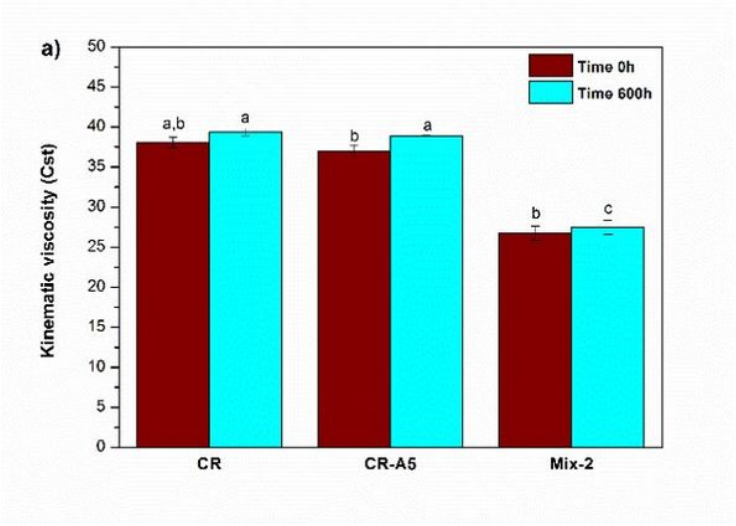

Figure 3

(a) Viscosity value of cutting fluids CR, CR-A5, and Mix-2 after 600 h of storage. Figure 3(b) Mineral, SR, SR-A5, and Mix-1 after 720 h of storage. Average followed by the same letter on the graph does not differ by Tukey's 95% confidence level test.

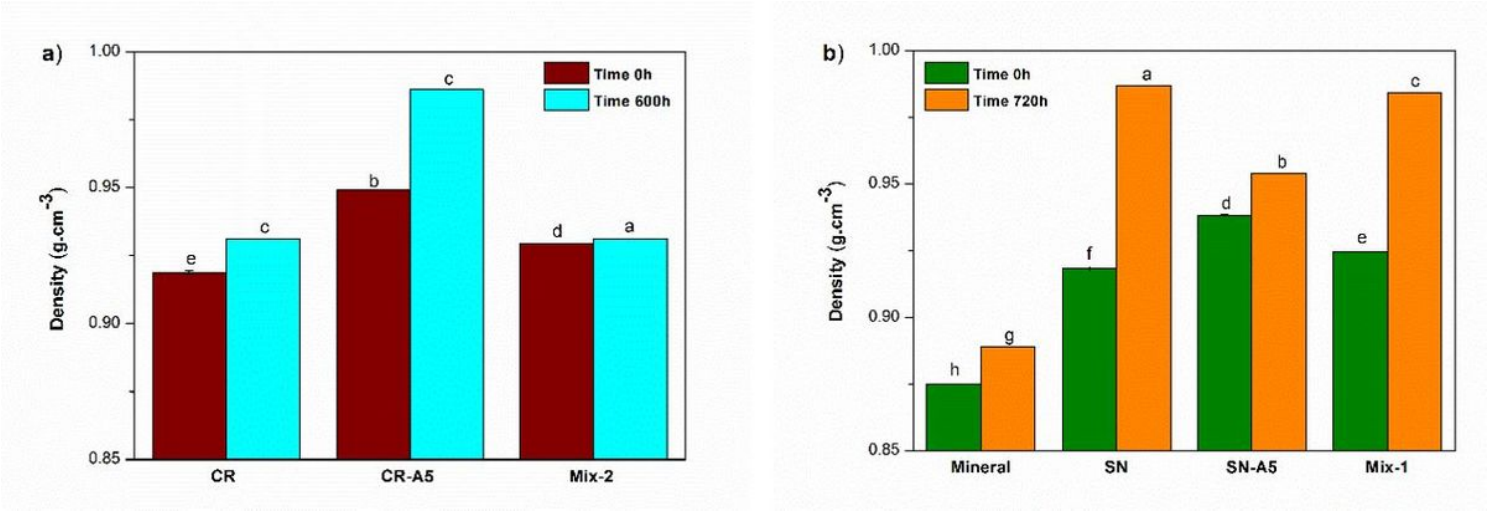

Figure 4

(a) Density value of cutting fluids CR, CR-A5, and Mix-2 after 600 h of storage. Figure 4(b) Mineral, SN, SN-A5, and Mix-2 after 720 h of storage. Average followed by the same letter on the graph does not differ by Tukey's 95% confidence level test.

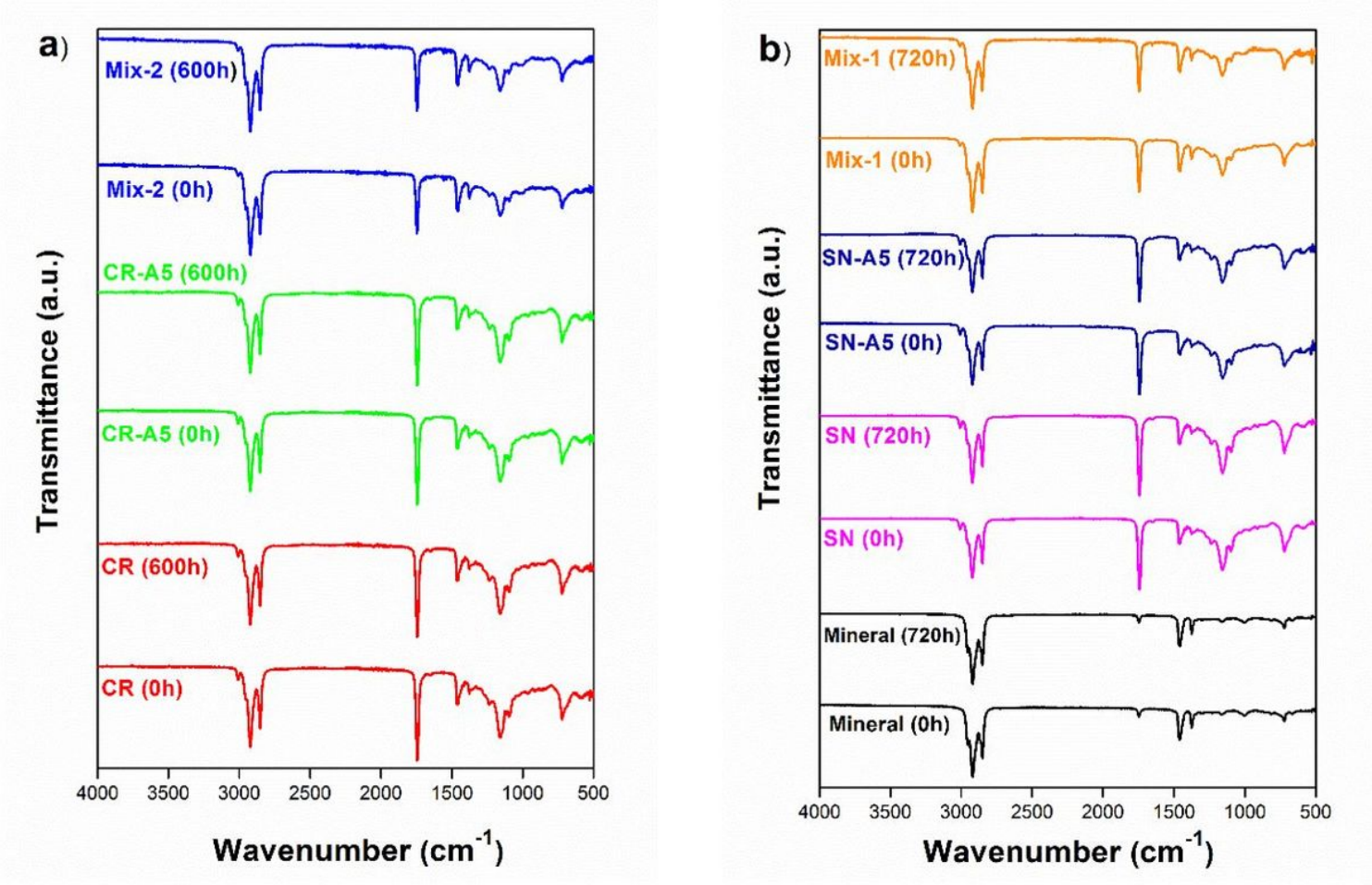

Figure 5

(a) ATR-FTIR spectrum for CR, CR-A5 and Mix-2, Figure 5(b) Mineral cutting fluid, SN, SN-A5, and Mix 1.

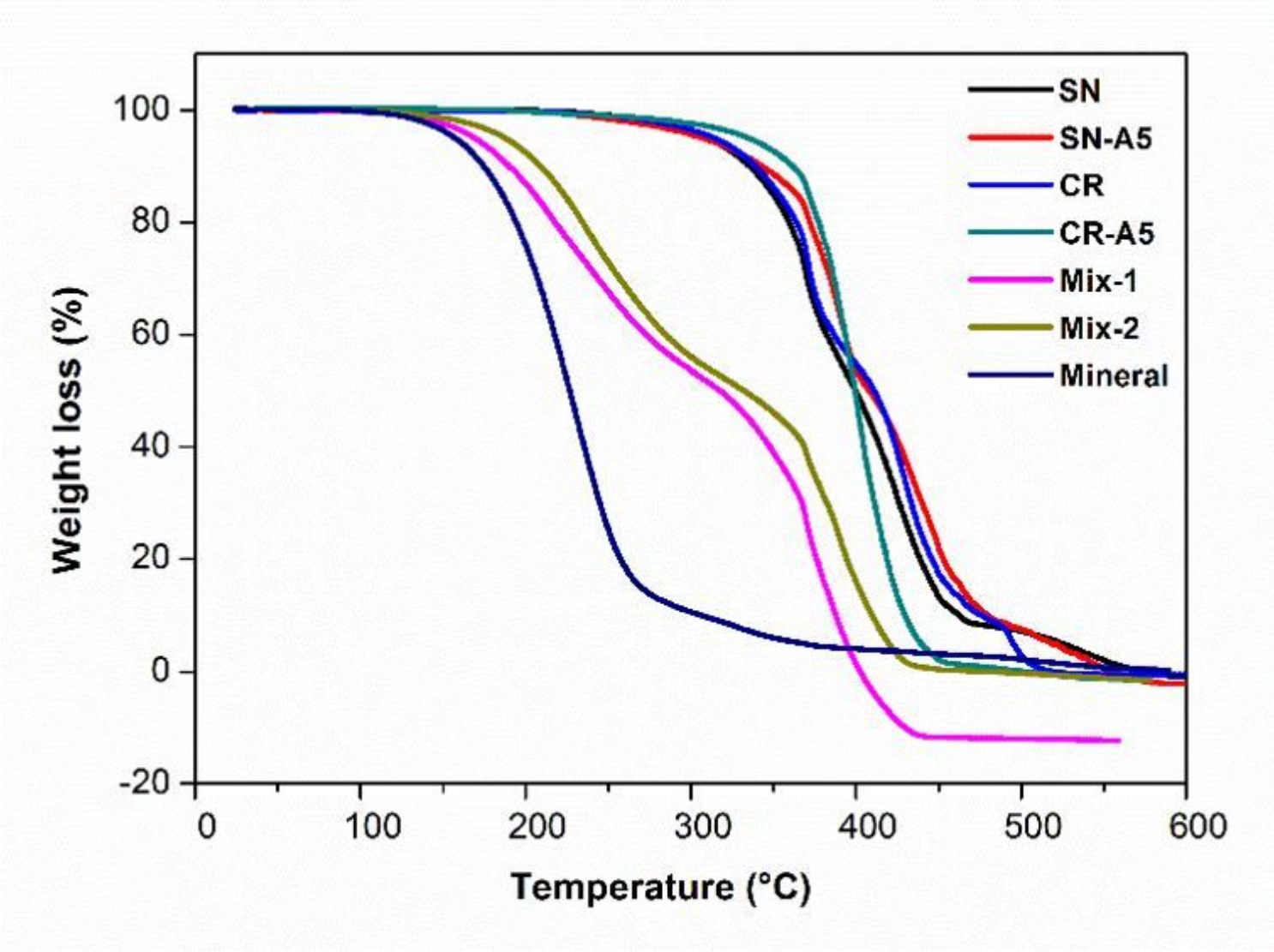

Figure 6

TGA curve of SN, SN-A5, CR, CR-A5 and mineral cutting fluids, and Mix-1 and Mix-2.

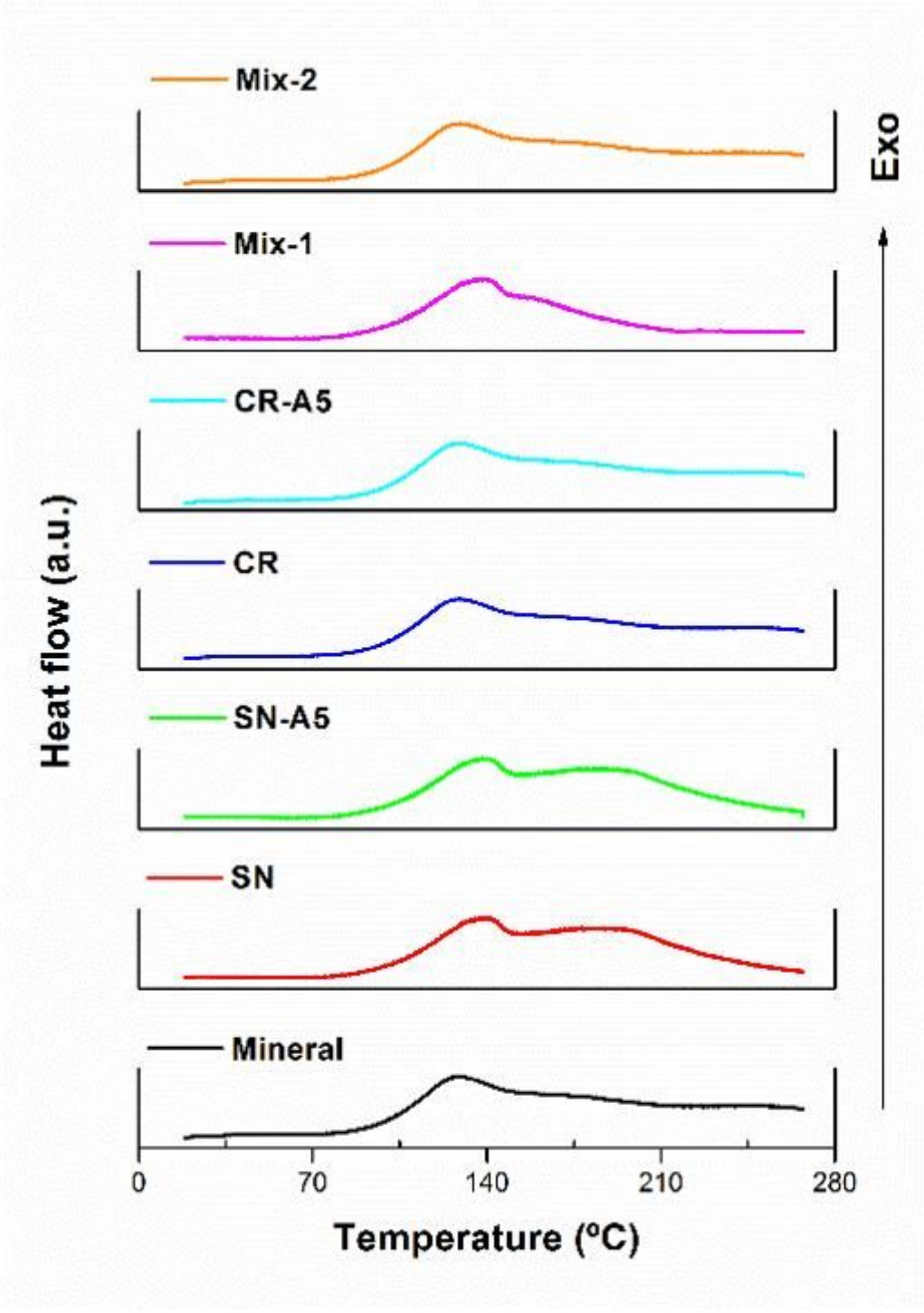

Figure 7

DSC curve for cutting fluids Mineral, SN, SN-A5, CR, CR-A5, Mix-1, and Mix-2, respectively.

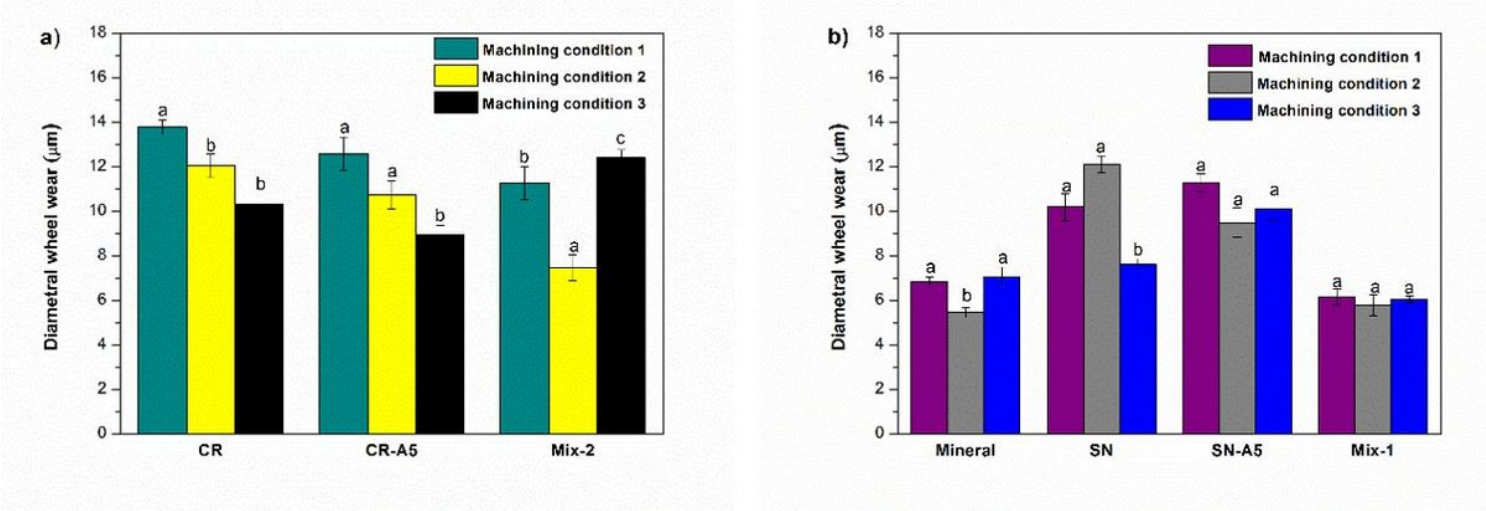

Figure 8

(a) Diameter wear value of grinding wheel (µm) for CR, CR-A5 oils, and Mix-2 cutting fluid and, Figure 8(b) mineral and Mix-1 and SN and SN-A5 cutting fluids analysed after three machining conditions were tested. Average followed by the same letter on the graph does not differ from Tukey's 95% confidence level test.

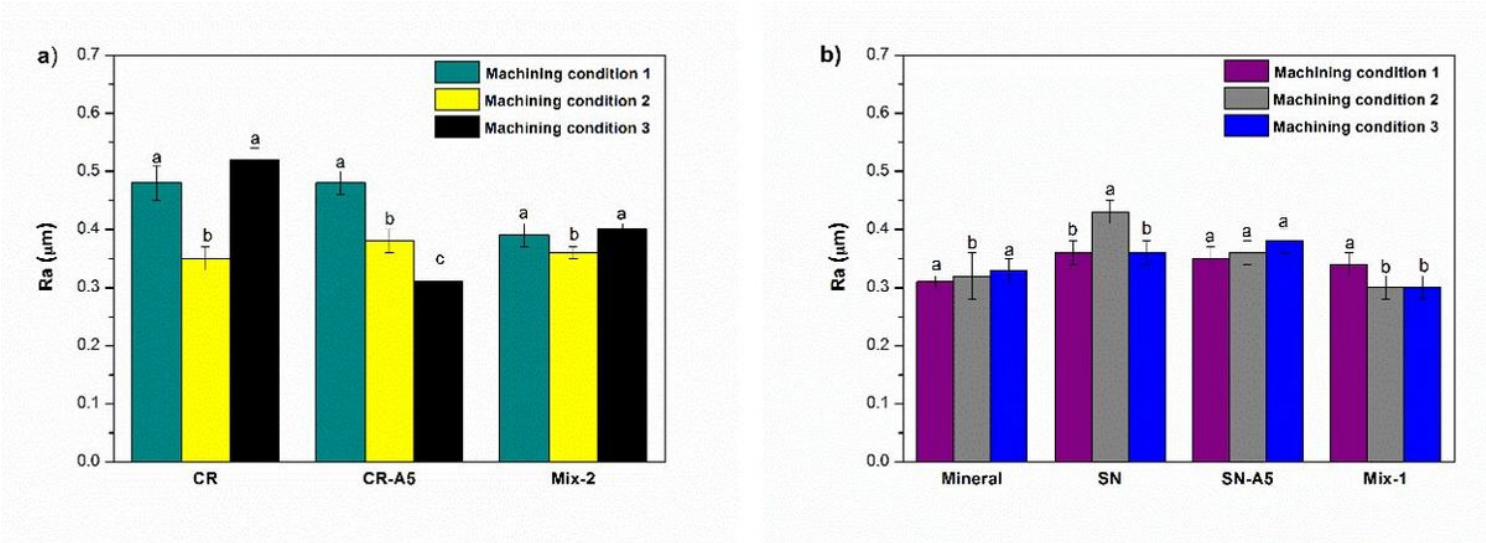

Figure 9

(a) Roughness value (Ra) for CR, CR-A5, and Mix-2 oil and, Figure 9(b) Mineral, Mix-1, SN, and SN-A5 analysed after three machining conditions were tested. Average followed by the same letter on the graph does not differ from Tukey's 95% confidence level test.