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Research Article

Synthesis of Plant-Based Ester for Metalworking Fluids and Tribological Performance

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ABSTRACT

Lubricants derived from plant-based raw materials offer great potential for the development of environmentally friendly and renewable esters due to their easier and faster biodegradability, reducing dependence on petrochemical raw materials and creating new synthesis processes. The increasing burden of environmental regulations and the depletion of petroleum-derived raw materials have prompted many industries to opt for products based on natural raw materials. Due to these positive effects, vegetable oil-based esters have recently been considered as potential candidates for industrial use. In this context, ester synthesis from cottonseed oil, a natural biodegradable raw material source, was carried out by transesterification with isopropyl alcohol. The structure of the synthesized ester was elucidated by GC-FID and FTIR and important physical parameters such as acid number, saponification number, viscosity and density of the ester were investigated. The synthesized isopropyl cottonseed oil ester was used to formulate a synthetic metalworking fluid at concentrations of 2%, 4% and 6%. The tribological properties of the formulated metalworking fluid were evaluated using the Reichert test and the chip corrosion test. It was found that the addition of 6% isopropyl cottonseed oil ester to the synthetic metalworking fluid exhibited the best tribological properties.

Keywords: *Cottonseed oil, Metalworking fluid, Transesterification, Tribology.*

Metal İşleme Sıvısında Kullanılan Bitkisel Yağ Bazlı Ester Sentezi ve Tribolojik Performansı

ÖZ

Bitkisel bazlı hammaddelerden elde edilen yağlayıcılar, daha kolay ve daha hızlı biyolojik olarak parçalanabilmeleri, petrokimyasal hammaddelere bağımlılığı azaltmaları ve yeni sentez süreçleri yaratmaları nedeniyle çevre dostu ve yenilenebilir esterlerin geliştirilmesi için büyük bir potansiyel sunmaktadır. Çevresel düzenlemelerin artan yükü ve petrol türevi hammaddelerin tükenmesi, birçok endüstriyi doğal hammaddelere dayalı ürünleri tercih etmeye yöneltmiştir. Bu olumlu etkiler nedeniyle, bitkisel yağ bazlı esterler son zamanlarda endüstriyel kullanım için potansiyel adaylar olarak değerlendirilmektedir. Bu bağlamda, biyolojik olarak parçalanabilen doğal bir hammadde kaynağı olan pamuk tohumu yağından ester sentezi, izopropil alkol ile transesterifikasyon yoluyla gerçekleştirilmiştir. Sentezlenen esterin yapısı GC-FID ve FTIR ile aydınlatılmış ve esterin asit sayısı, sabunlaşma sayısı, viskozitesi ve yoğunluğu gibi önemli fiziksel parametreleri incelenmiştir. Sentezlenen izopropil pamuk tohumu yağı esteri, %2, %4 ve %6 konsantrasyonlarında sentetik bir metal işleme sıvısı formüle etmek için kullanılmıştır. Formüle edilen metal işleme sıvısının tribolojik özellikleri Reichert testi ve talaşlı korozyon testi kullanılarak değerlendirilmiştir. Sentetik metal işleme sıvısına %6 izopropil pamuk tohumu yağı esteri ilavesinin en iyi tribolojik özellikleri sergilediği bulunmuştur.

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Anahtar Kelimeler: *Pamuk yağı, Metal işleme sıvısı, Transesterifikasyon, Triboloji.*

I. INTRODUCTION

In recent years, vegetable oils have been widely used in both academic and industrial research.The components of vegetable oils have many highly reactive sites as they contain double bonds, carboxylic groups. This different structure and functionality offer a great opportunity for the creation of various reactions [1]. Vegetable oils, especially biodegradable lubricants such as rapeseed, canola, jatropha, coconut, palm, cotton, hazelnut are some of the more possible and promising alternatives as basic feedstocks for biodiesel and cutting fluids. They are easily biodegradable and less costly than synthetic base oils [2], [3]. The global production of vegetable oils is estimated at more than 100 million tons, which covers only 10% of the demand for diesel fuel [2].

Vegetable oils and their esters are also used as lubricants, corrosion inhibitors and high-pressure additives in metalworking fluids (MWF). Lubricants based on plant-based renewable raw materials offer great potential for the development of ecological and renewable esters, as they are environmentally friendly, much easier and faster to degrade, and create new synthesis processes by reducing dependence on petrochemical raw materials [4]. The increasing obligations imposed by environmental regulations and the depletion of petroleum-based raw materials have directed many industries towards products derived from natural raw materials. Vegetable oil-based esters recently been increasingly used industrially due to their advantageous properties, such as excellent lubricity, high viscosity index, and low toxicity [5].

The increasing use of metals due to technological advancements has made the process from metal processing to the final product extremely important in industry. In addition, environmental concerns that have arisen in recent years have encouraged the metal and metalworking industry to use environmentally friendly and more efficient natural raw materials in the production of final metal products [6].

In particular, the ecological nature of oils and emulsions used in metalworking has gained significant importance. The main characteristic of fluids used in metal processing is to provide excellent lubrication, enabling the easy shaping of metal. Emulsifiers, which ensure the homogeneous mixing of oil and water in oil-water emulsions, are essential components of a good MWFs. Another crucial feature of MWFs are their ability to protect against corrosion during and after metal processing [7]. Corrosion is an unavoidable natural process and all metals are subject to corrosion according to the laws of thermodynamics. Even the slightest corrosion during the shaping of metals can lead to in the complete loss of material. Therefore, methods to protect metal materials against corrosion are widely used in the metal and metalworking industries. In MWF, one of the most important components is corrosion inhibitors. The materials used in new-generation MWF fulfill not only one feature but also more than one feature [8]. El-Din et. al. produced five different hydrophilic-lipophilic balance (HLB) values (10, 9.5, 9, 8.5, 8) using environmentally friendly ingredients and castor oil in a study to produce a new MWF. Performance evaluations showed that the prepared cutting fluid (E1) reduced the cutting force from 500 N to 280 N on a dry high-speed steel sample, while the commercial cutting fluid recorded this value as 340 N [9]. He et. all, cottonseed oil (CSO) was converted into a bio-based lubricant of branched nonyl isodecyl esters (NIEs). Pour point (-47 °C), kinematic viscosity (200.3 mm^2/s) and viscosity index (141) of NIEs were superior to CSO. The oxidation onset temperature (307.21°C) and oxidation induction time (21 minutes) are also higher than CSO. The coefficient of friction (0.07), wear track diameter (132 μm) and oil film coverage (100%) are better than CSO and commercial lubricants. This bio-based lubricant has the potential to replace mineral oils, according to the study [10].

Isopropyl cottonseed oil ester was synthesized by transesterification of cottonseed oil, a vegetable oil source, with isopropyl alcohol. Various derivatives of synthesized product have been reported in the literature as lubricants in MWF [11]. In this study, the structure of the synthesized iso-propyl cottonseed oil ester has been elucidated using FTIR spectroscopy and a GC-FID device. The acid number, saponification number, density, kinematic viscosity and flash point of the synthesized product have been measured. In the study, the synthesized ester has been added to a synthetic MWF formulation at certain ratios (2%, 4%, 6%). The lubrication performance test (Reichter Test) and the corrosion properties of MWF were examined by machining corrosion test, which is the preferred simple method for determining the corrosion rate in the industry.

II. MATERIAL AND METHOD

A. MATERIAL

The cottonseed oil used in the synthesis was supplied by the Pam Yağ Gıda ve Kimya Inc. Co., isopropyl alcohol and sodium methylate were purchased From Sigma- Aldrich and used without purification. Agilent 8890 GC instrument was used for GC-FID spectra of the synthesised esters. The PerkinElmer Spectrum Two 4000-400 cm-1 ATR instrument was used for Fourier transform infrared spectroscopy (FTIR). The BIOLAB Viscol-10A automatic kinematic viscometer was used to measure viscosity and the Normalab NCL 440 was used for flash point.

B. METHOD

B. 1. Ester Synthesis

Cottonseed oil, isopropyl alcohol and sodium methoxide (1:6.7:0.1) were mixed and placed in a 250 mL three-necked flask. The reaction was kept at a temperature of 75 °C and stopped after 3 hours. After the reaction, the excess alcohol was removed from the mixture using vacuum. The resulting product was transferred to a separatory funnel and allowed to settle. The glycerol formed during the reaction was separated from the product and the free glycerol remaining in the product was removed by washing the product three times. After removal of water and free glycerol from the reaction product, the final product was characterized by GC-FID and FTIR.

B. 2. Physical Properties for Synthesized Ester

B.2.1. Determination of acid and saponification number

The acid number of the synthesized ester was determined according to the official AOCS method Cd 3d-63 [12] , the saponification value was determined according to the official AOCS method TI 1a-64 [13].

B.2.2. Determination of kinematic viscosity, density and flash point

The kinematic viscosity of the synthesized product was measured according to ASTM D445 [14]. The density of the synthesized product was measured according to ASTM D891-18 [15] and the flash point was determined according to ASTM D1310 [16].

B.2.3. GC-FID test

Reaction products were monitored by capillary column gas chromatography, using a Agilent 8890 GC (Fig 1) equipped with a flame ionization detector (FID) according to AOCS Ce 1a-13 method [17]. CP-Sil 88 for FAMEs GC Columns has been used. The injection system was split-splitless. The carrier gas was helium at a flow rate of 1mL/minutes. The internal standard technique was used to quantify the amount of the chemical species.

Figure 1. *Agilent 8890 GC.*

B.2.4. FTIR

FTIR characterization is used to determine the changes in functional groups that occur before and after the esterification reaction. These changes can be observed by a shift in specific wave numbers or the appearance of new absorption peaks. Characteristic peaks in the FTIR spectrum of esters, especially bands such as the C=O ester group and the C-O ester group, help to determine the presence and identity of the compound. These peaks are important for assessing the accuracy and purity of the samples [18]. In addition, the peaks in the FTIR spectrum of esters enable the monitoring of chemical reactions. PerkinElmer Spectrum Two 4000-400 cm-1 ATR device has been used for FTIR spectra (Fig 2).

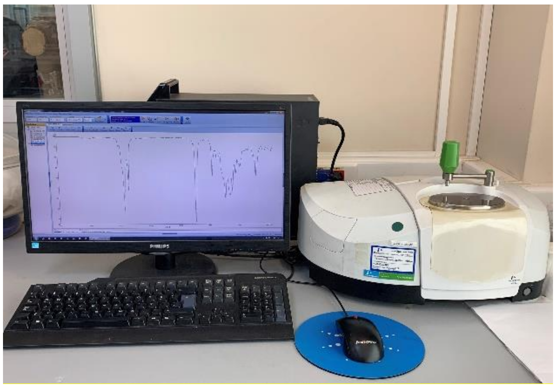

Figure 2. PerkinElmer Spectrum Two FTIR device.

B. 3. Tests on MWF

B.3.1. Lubrication performance test (Reichtert Test)

The Reichert test is used to determine the wear properties (WP) and extreme pressure properties (EP) of lubricants and additives in MWF. The effect of the synthesized ester on the lubrication performance in MWF and its quality-enhancing impact on the machined metal surface was tested using the Reichert Test device (Fig 3) [19]. The metal bearing tested is AISI 52100 steel. In the Reichert test, 25 mL of MWF is placed in the reservoir, and a rotating bearing is semi-immersed in it. An untreated roller is placed in the indentation and the test is started with a pressure of 200 Newton. The test duration is 100 seconds. Throughout the test, the rotating metal bearing is treated with the MWF, and the fluid remains between the bearing and the roller. The better the MWF protects the roller during the test, the fewer wear marks will appear on the roller. At the end of the test, the roller is removed from its position, and the length and width of the wear mark (in millimeters) are measured and calculated according to Equality is given 1.

$$Lubrication\ performance\ test = \frac{Scar\ (length) \times Scar\ (width) * 3.14}{4} \quad (1)$$

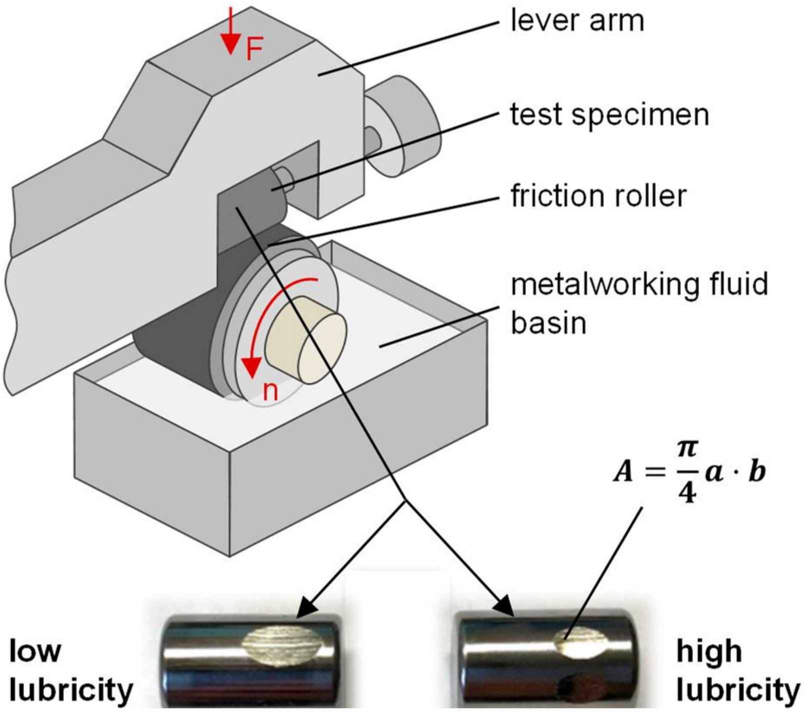

Figure 3. *Reichert tribology test [19].*

B.3.2. Corrosion test

Corrosion test of 1%, 2% and 3% emulsions of MWF was carried out according to DIN 51360-2 standard[20].

III. RESULTS AND DISCUSSION

A. ESTER CHARACTERISATION AND PHYSICAL PROPERTIES

Isopropyl cottonseed oil ester was synthesized under the specified conditions and the structure of this ester has been elucidated by GC-FID and FTIR. Cottonseed oil contains myristic acid in a range of 0.6-1%, palmitic acid in a range of 21.4-26.4%, stearic acid in a range of 2.1-3.3%, oleic acid in a range of 14.7-21.7%, and linoleic acid in a range of 46.7-58.3% [21]. Figure 4 shows the GC-FID chromatogram of the synthesized ester. When the chromatogram was analyzed, the GC chromatogram showed five different peaks with two different intensities; the peaks at retention times 16.5, 22.94 and 24.37 (Figure 4) have a lower intensity (122 to 294 pA) compared to the peaks at 19.3 and 26.85 minutes with intensities of 12.18 to 86.5 pA. The GC chromatogram of the fatty acid isopropyl ester standards shows peaks at retention times between 15 and 28 minutes.

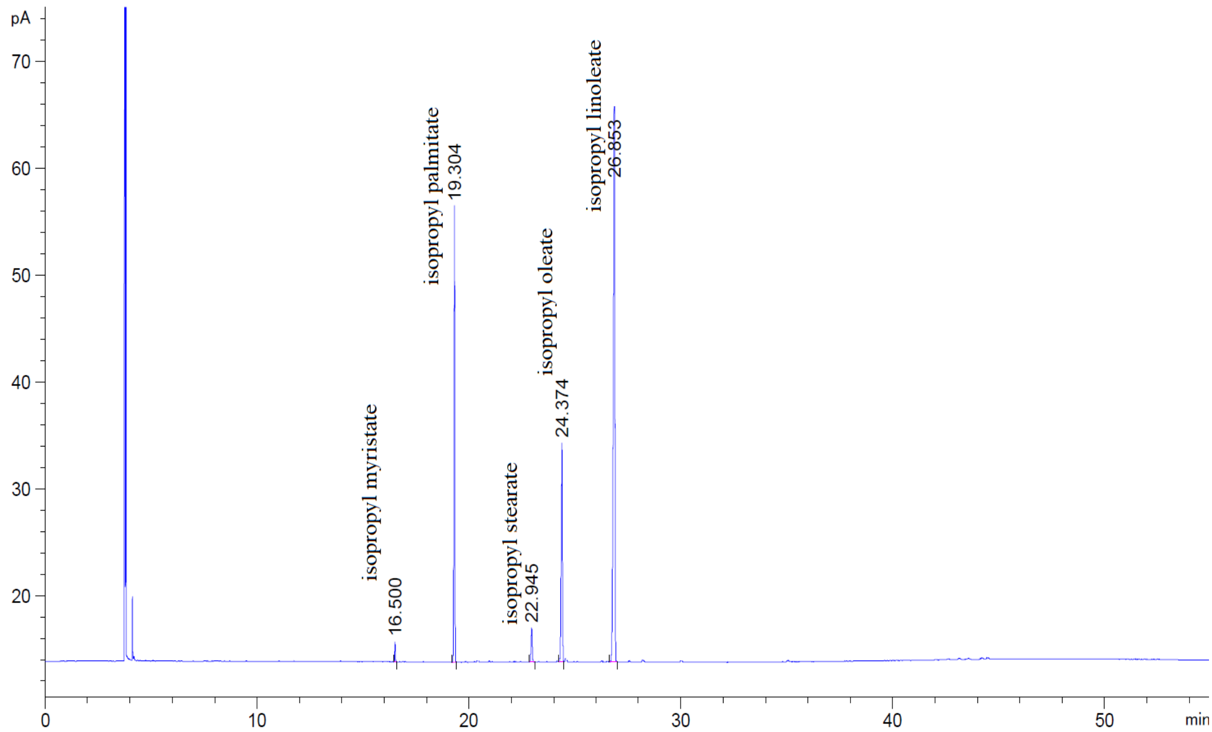

Figure 4. *GC chromatogram for Isopropyl cotton fatty acid ester.*

According to these data, the transesterification process is considered successful because the majority of the reaction product consists of the desired products. Accordingly, the peak at 16.5 belongs to isopropyl myristate, the peak at 19.3 to isopropyl palmitate, the peak at 22.94 to isopropyl stearate, the peak at 24.37 to isopropyl oleate and the peak at 26.85 to isopropyl linoleate.

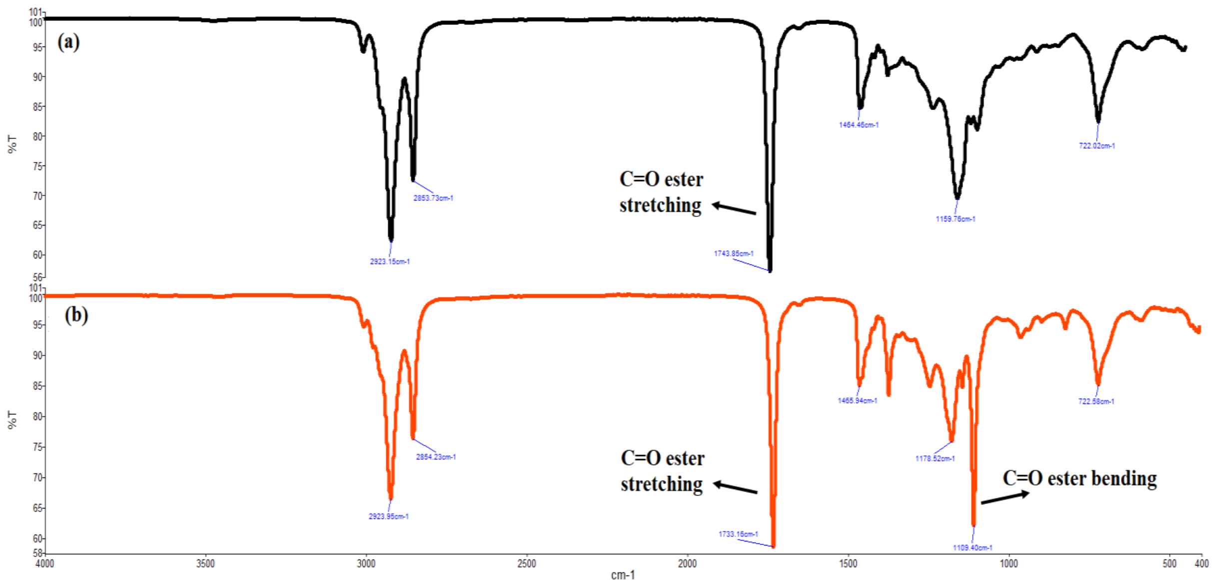

Figure 5. *Comparison between IR spectra of cottonseed oil (a) and isopropyl cottonseed oil ester (b).*

The spectra of cottonseed oil (Fig. 5(a)) and isopropyl cottonseed oil ester (Fig. 5(b)) are shown in comparison. The wavelength of the alcohol, -OH (3300-3100 cm-1) is not seen in the isopropyl cottonseed oil ester. This suggests that the OH bond in the isopropyl alcohol has completely reacted with the oil to form the ester. There is also a shift from a wavelength of 1743 cm-1 for the spectrum of cottonseed oil to a wavelength of 1733 cm-1 for the spectrum of isopropyl cottonseed oil ester. There is also a wavelength of 1109 cm-1 after transesterification, indicating the CO bond functional group as a result of the formation of the ester isopropyl cottonseed oil ester [22].

Tests such as saponification number, acid number, viscosity, density and flash point of the synthesized ester were performed and the results are given in Table 1.

Table 1. *Some parameters of the synthesized ester*

Sample	**Acid number** *(mgKOH/g)*	**Saponification number** *(mgKOH/g)*	**Viscosity** *(cSt) (40 C°)*	**Density** *(g/cm³)*	**Flash point** *(C°)*
Iso-propyl cottonseed oil ester	0,25	185,5	3,3	0,87	175

The saponification number of esters, acid number, density, viscosity and flash point are important criteria for determining the performance and stability of lubricants. These parameters are critical to understanding both the chemical and physical properties of lubricants and their suitability for the application [23]. The saponification number is used to determine the amount of the esters and triglycerides present in the oil. The saponification number of the esters is important for assessing the biodegradability and environmental impact of lubricants [24]. Acid number indicates the amount of free fatty acids in a lubricant and is used to assess the oxidation stability of the oil. The density determines the mass and volume of the lubricant. It is also a critical parameter in understanding how lubricants behave under different temperature and pressure conditions [25]. Viscosity refers to the fluid resistance of the lubricant and determines the effect of the oil on friction, wear and energy loss [26]. Flash point indicates the ignition temperature of a lubricant's vapours and is used to assess the risk of fire [27].

B. MWF PERFORMANCE TESTS

MWF contain pH regulators, lubricants, anti-wear additives, extreme pressure additives, metal passivators, metal chelating agents, antifoaming agents, boron compounds, emulsifiers, ionic and non-ionic surfactants and corrosion inhibitors[19]. Some physical properties of the original metalworking fluid and the metalworking fluid with % Isopropyl cottonseed oil ester (2%, 4%, 6%) are given in Table 2.

Table 2. *Some parameters of the MWF*

Sample	**Viscosity** *(cSt) (40 C°)*	**Density** *(g/cm³)*
Original MWF	33,5	0,84
2% Isopropyl cottonseed oil ester added MWF	33,1	0,83
4% Isopropyl cottonseed oil ester added MWF	33,3	0,84
6% Isopropyl cottonseed oil ester added MWF	33,5	0,85

Reichert Test device was used to measure the effect of the synthesized isopropyl cottonseed oil ester on the lubrication performance in metal processing fluids and the quality enhancing effect on the treated metal surface. Fewer scars caused by metal-metal friction ensures a smaller average area. For this reason, synthesized isopropyl cottonseed oil ester was used in different ratios in the metal treatment liquid and Reichert test was performed. The synthesized cotton oil ester was added as 2%, 4% and 6% in the formulation of a synthetic MWF. The scar width and length measurements caused by metal-metal friction in the Reichert test device are given in Table 3. Figures of the rollers processed in the Reichert test machine are given in Figure 6.

Table 3. *Isopropyl cottonseed oil ester Reichert test result.*

Sample, %	**Scar**		**Average area** *(mm^2)*
	Height *(mm)*	**Width** *(mm)*	
0	7,3	3,8	21,77
2	7,3	3,7	21,20
4	7,0	3,2	17,58
6	7,0	3,1	17,03

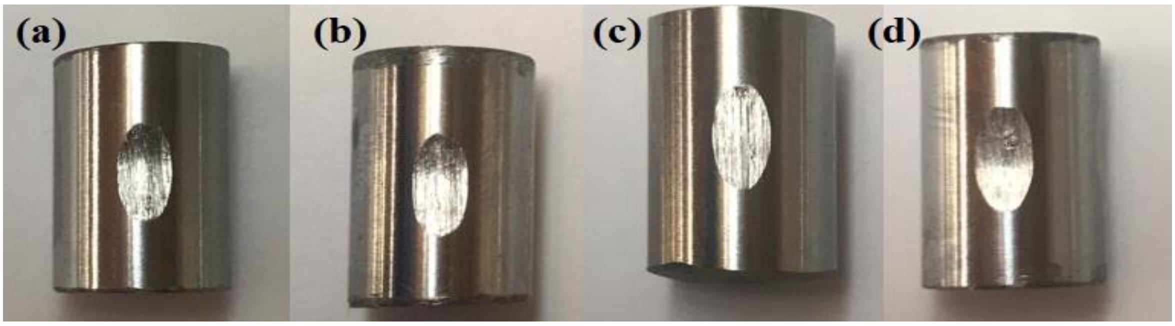

Figure 6. *Roller result from the Reichert test of isopropyl cottonseed oil ester with (a) without ester, (b) 2.0% ester, (c) 4.0%, (d) 6.0% ester.*

The Reichter test results in Table 3 show that when the synthesized isopropyl cottonseed oil ester was added to the MWF formulation, the area of the scars on the test rollers decreased. The best utilization rate of the synthesized ester in the developed synthetic MWF is 6%. It is known in the literature that vegetable oils and esters derived from them are more homogeneous than mineral oils [1], [5], [8], [28], [29], [30], [31]. Vegetable oil and ester derivatives have higher boiling point and larger molecular weight, which leads to increased stability in metalworking fluids and less product loss due to evaporation [29]. In addition, lubricating and wear properties of vegetable oils and vegetable oil-based esters are also known to be better than mineral oils [29]. Vegetable oil-based esters are generally obtained from unsaturated long-chain fatty acids and have a high lubricity due to this structure. Fox and Stachowiak reported in a study that vegetable oil-based esters enable energy savings by reducing friction between metal and metal and allowing operation at lower temperatures [32]. The polar groups of plant-based esters bind to metal surfaces and form a protective film. This film layer offers high abrasion resistance and extends the service life of the devices. In a study on these properties, it was shown that the anti-wear protection performance of esters from palm and sunflower oil is superior to that of esters from mineral oils [33]. In the Reichert test, the synthesized product added instead of a petroleum-derived mineral oil in the original formulation gave better results due to its good lubricity and anti-wear properties. The increase in the amount of the synthesized product was proportional to the decrease in wear in the Reichert test. With the increase of vegetable oil based ester in the metal working fluid, the metal surface was less abraded. This indicates that the synthesized ester has good lubricity and anti-wear properties. According to Reichert's test results, unsaturated long-chain fatty acids and polar groups in cottonseed oil improve the lubricity and anti-wear properties of the metalworking fluid.

Pour 4 g of corrosion chips onto the filter paper placed in the Petri dish using a precision balance. After pouring 5 ml of emulsion from 1%, 2% and 3% emulsion mixture of the prepared full synthetic MWF onto the corrosion sawdust with the help of a pipette, the petri dish was closed and kept in the laboratory environment. After 24 hours, the results of the corrosion stains formed on the filter paper were recorded. A corrosion cips test was performed on the product developed from the synthesized product with 6% full synthetic MWF formulation. The result of this process is shown in Figure 6.

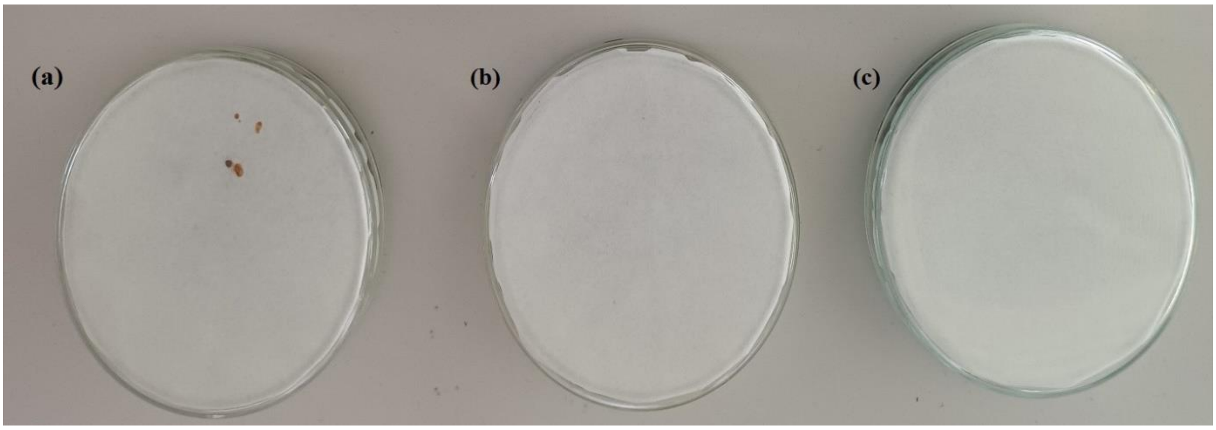

Figure 7. *Corrosion cips test results of 1% (a), 2% (b) and 3% (c) emulsions of prepared synthetic MWF.*

When testing the machining corrosion of the product developed from the synthesized product with a 6% MWF formulation (Figure 7), a corrosion unit is observed in the 1% emulsion of the synthetic MWF. No corrosion is observed in the 2% and 3% emulsions after 24 hours. This shows that the synthesized product has both an anticorrosive effect and lubricant properties.

IV. CONCLUSION

In this study, a high value-added ester was synthesized from cottonseed oil, a vegetable raw material. The structure of the ester synthesized by the transesterification method was elucidated by FTIR and GC-FID. Physical parameters such as acid number, viscosity and saponification number of this synthesized ester were also performed and reported in the literature. The synthesized ester was used to develop a synthetic MWF formulation that is used in the metalworking industry. The tribological properties of the MWFs developed by using the synthesized ester at different ratios (2%, 4% and 6%) were analyzed by Reichtert test and corrosion properties were also investigated. The results showed that the isopropyl cotton oil ester used at 6% in synthetic MWF had the best tribological properties. In the Reichtert test of the metalworking fluid containing mineral oil, 21.77 mm^2 of the roller surface was worn. In the metalworking fluid with synthesized isopropyl cottonseed oil ester additives (2%, 4%, 6%), the wear decreased to 21.2 mm^2, 17.58 mm^2 and 17.03 mm^2 respectively. This shows that vegetable-based fatty esters have good lubricants and anti-wear properties. At the same time, the results of the machining corrosion test show that vegetable oil-based esters protect the metal surface better than mineral based oils. The performance of vegetable oil-based esters can change depending on the workpiece and machining process, so the work can be extended to different workpiece materials and machining processes, which will expand the scope of the work in the future. In conclusion, further studies need to be conducted to obtain more conclusive results. Nevertheless, the data from this study can be used as a basis for further formulation studies using isopropyl cottonseed oil esters and other vegetable oil esters.

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