

Preparation and investigation of some possible applications of ecological lubricants based on transesterified vegetable oils with polyvalent alcohols

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Abstract. The use of Metal Working Fluids or Cutting Fluids (MWF/CFLs) based on petroleum oils, as well as conventional additives to provide the desired properties of MWF/CFLs, creates serious environmental problems and threatens the health of people working in this industry. Vegetable oils and animal fats are a possible alternative for the oil component of MWF/CFLs. They are biodegradable and non-toxic, but their direct application is limited due to problems with thermo-oxidative stability, low-temperature properties, corrosion protection, and viscosity range. These problems are largely solved by chemical modifications of these natural lubricants. Replacing glycerol in triglycerides with another alcohol, as well as modification of the hydrocarbon chain, partially solves these problems. However, this does not solve the problem of additives, which are often serious environmental pollutants. The presented work aims to study the possibilities of using various environmentally friendly substances (natural products and their derivatives) as alternative additives in the composition of MWF/CFLs, by monitoring their physicochemical and tribological characteristics in comparison with MWF/CFLs based on mineral oils, as well as to determine the qualities of emulsions based on modified vegetable fatty acids, as an additive or substitute for water-paraffin emulsions in the metalworking industry. The realization of this goal is supported by the achieved results regarding the study of the physicochemical characteristics of vegetable oils, modified vegetable oils, and their mixtures.

1 Introduction

Metalworking is an integral part of modern industry. It involves processes of cutting, forming, rolling, turning, grinding, etc., of metals. These operations generate significant amounts of heat, chips, and dust. In addition, the contact between the metal surface and the processing tools can damage both the metal surface and the tool. In order to reduce friction

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and temperature in these processes, as well as to remove by-products from the processes, various MWF/CFLs are used. Most often, these are water-oil emulsions (3-10% oil/water).

Oils of petroleum origin are not biodegradable. In addition, additives often contain sulfur and phosphorus. This makes their disposal into the environment unacceptable, which accordingly requires their disposal, which is often more expensive than the MWF/CFLs themselves. In addition, when working with metal-cutting machines, part of the MWF evaporates and forms a mist that can cause certain diseases in machine operators, such as dermatitis, asthma, allergies, cancer, etc.

Vegetable oils and animal fats are a possible alternative for the oil component of MWF/CFLs. They are biodegradable and non-toxic, but their direct application is limited due to issues with thermo-oxidative stability, low-temperature properties, corrosion protection, and viscosity range [1].

Lubricants and, in particular, cutting fluids (MWF/CFLs) are widely used in metalworking, as the functions they perform are: to lubricate friction surfaces, to remove heat, and to facilitate the separation of chips and their removal from the contact areas. In addition, MWF/CFLs must also perform other functions such as corrosion prevention, power transmission, and sealing. For this purpose, the following are used: MWF/CFLs based on pure mineral or synthetic oils, MWF/CFLs based on water/oil emulsions, and gases [2, 3].

Depending on their chemical composition, they are divided into three groups: MWF/CFLs based on pure mineral or synthetic oils, MWF/CFLs based on water/oil emulsions, and gases.

According to their purpose, they are divided into: MWF/CFLs suitable for low pressures in metal processing by cutting (turning, milling, gear cutting, etc.); MWF/CFLs suitable for high pressures in plastic processing of metals (forging, stamping, rolling, etc.); coolants for hardening metals.

Mineral and later synthetic oils have been used only since the 19th century, but the rapid development of industry and the introduction of products from the oil refining industry led to the widespread use of petroleum-based lubricants. These are complex mixtures of C₂₀-C₅₀ hydrocarbons with aliphatic, aromatic, or cyclic structures.

The alternative is natural lubricants based on vegetable and animal fats, which are C₈-C₂₂ esters of higher fatty acids (HFAs) and glycerol-triacylglycerols. However, they must meet the requirements of modern technologies regarding physicochemical, tribological, and economic requirements.

Metal processing is most often carried out in boundary friction conditions. The function of oil is to lubricate, and of water to remove heat from the contact surface, which allows for reducing the tension between the rubbing surfaces. When processing metals, their surfaces rub in the contact zone between them. Reducing the adverse effect of friction and scuffing on the surface of the metal during cutting, high pressures during plastic processing of metals, the release of a large amount of heat, and the release of chips during cutting are achieved with a technology in which the different components vary, both in terms of their type and in terms of their content. In addition to the main components, additives also play an important role, which, through their mechanism of action, would reduce the adverse effect without negatively affecting the environment. They are added to the lubricating and cooling fluid in a certain concentration and contain surface-active substances that adsorb on the working surfaces of the parts and reduce the coefficient of friction in the contact zone.

The positive effect of the main components and additives in MWF/CFLs is due to the formation of a large contact support area due to the increased plasticity of the surface layers, and in some cases, the formation of intermediate films. The main components and additives in MWF/CFLs reduce the risk of galling, provide lubrication of friction surfaces, heat removal, and facilitate the separation of chips and their removal from the contact areas.

In addition, MWF/CFLs must perform other functions such as corrosion prevention, power transmission, and sealing, as well as ensure the preservation of the machined surfaces and the quality of the metals, their surfaces, and the contact areas between them.

Mineral and synthetic oils are widely used in all areas of industry, including in the composition of various types of MWF/CFLs. There is a well-developed mechanism for their recycling as regards motor, hydraulic, transmission, industrial oils, etc., after their resource is exhausted. This greatly reduces their environmental impact [4].

However, the possibilities for recycling CFLs are limited and pose a problem, as they are an additional source of water and soil pollution [5].

Another negative aspect of using MWF/CFLs is the effects of conventional MWF/CFLs on the health of operators. Workers who are exposed to aerosols daily suffer from skin irritations and allergies, and prolonged exposure can even cause cancer [6].

Health problems are also caused by microorganisms that grow in MWF/CFL emulsions [7].

These problems are largely solved by chemical modifications of these natural lubricants. Replacing glycerol in triglycerides with another alcohol, as well as modification of the hydrocarbon chain, partially solves these them [8].

The indicated modifications are applied through the use of various strategies and synthesis methods [9-11].

Our research aims to investigate the properties of methanol and trimethylol propane (TMP) esters with higher fatty acids (HFAs), in particular oleic acid, as base oils in the composition of emulsions for the production of environmentally friendly and non-toxic MWF/CFLs.

In connection with the aim of the study, the following tasks were set:

1. To study the kinetics of the esterification reaction of TMP with oleic acid at different molar ratios and amounts of catalyst to optimize the synthesis conditions of trioleyltrimethylolpropane, which can be used as a component for obtaining suitable emulsions based on modified vegetable fatty acids.
2. To compare the conditions of alkali-catalyzed and acid-catalyzed transesterification in the production of biodiesel, i.e., modified vegetable fatty acids, as a starting component included in the composition of MWF/CFLs, from low-quality vegetable oils with a high acid number.
3. To study the physicochemical indicators of the obtained emulsions containing vegetable oils, modified vegetable oils (TMP esters, methyl esters) separately, such as density, viscosity, emulsion stability, and corrosion resistance.
4. To study the physicochemical parameters of vegetable oils with increased acidity: density, viscosity, emulsion stability, and corrosion resistance.
5. To study the influence of vegetable oil mixtures with ME, as well as vegetable oil mixtures with TMP esters in different percentages, on the studied physicochemical parameters.
6. To study the influence of vegetable oil mixtures with ME and with TMP esters in different percentages on the studied physicochemical parameters.

2 Experimental procedure

The Methodology for the synthesis of trioleyltrimethylolpropane is as follows. In a Dean and Stark type apparatus equipped with a 1000 cm³ round-bottomed flask, condenser and cuvette, 250g (279.33 ml, $d_{20}^4=0.895$, $n=0.885$ mol, $M=282.4614$ g/mol) of oleic acid, 100 cm³ of cyclohexane ($T_k = 80.74^\circ\text{C}$ and $M= 84.16$ g/mol), 38.3g of trimethylolpropane ($n=0.285$ mol, $M=134.17$ g/mol) for the molar ratio is 3.1:1 and 36.5g ($n=0.272$ mol, $M=134.17$ g/mol) for the molar ratio is 3.25:1 are placed. The mixture was heated to 60°C,

and thereafter, 3% (7.5g) of p-toluenesulfonic acid (catalyst) and 1% (2.5g) by weight of oleic acid were added. The reaction was then carried out with continuous heating of the reaction mixture. After the reaction had stopped (at the end of the kinetic experiment), the reaction mixture was cooled, the cyclohexane was distilled off, and the reaction mixture was washed with saturated NaHCO₃ solution and then with saturated NaCl solution.

3 Results and discussion

3.1 Study of the physicochemical parameters of the obtained emulsions containing vegetable oils, modified vegetable oils (TMP esters, methyl esters) separately

The resulting emulsions had the following basic composition: Emulsol with vegetable oil 5 kg: vegetable oil - 3.65 kg (3.35 kg), blank - 0.25 kg, PMK - 0.4 kg (0.35 kg), TEA - 0.3 kg, NaNO₂ - 0.25 kg, SLOVASOL (slovazol) - 0.5 kg (0.45 kg), with variations in terms of vegetable oil (rapeseed oil or sunflower oil) and its mixtures with ME, as well as with TMPE in different mass percentages.

TABLE 1. Characteristics of the obtained emulsions containing vegetable oils, modified vegetable oils (TMP esters, methyl esters), separately.

Types of emulsions containing vegetable oils or their derivatives	Density at 15°C ρ_{15} (g/cm ³) BDS EN ISO 3675	Kinematic viscosity at 40°C ν_{40} (mm ² /s) BDS EN ISO 3104	Copper plate corrosion (level) BDS EN ISO 2160	Emulsion stability (hours) BDS EN ISO 20783
ROE	0.945	35.5	Class 1	9
SFOE	0.930	32.0	Class 1	10
MEE (RO)	0.885	4.75	Class 1	14
MEE (SFO)	0.875	4.45	Class 1	16
TMPEE	0.893	9.50	Class 2	21

RO – Rapeseed Oil, ROE – Rapeseed Oil Emulsion, SFO – Sunflower Oil, SFOE – Sunflower Oil Emulsion, MEE – Methyl Esters Emulsion, TMP – Trimethylolpropane, TMPEE – TMP Esters Emulsion.

Table 1 shows that the density of the obtained emulsions from vegetable oils and their derivatives varies between 0.875-0.945 g/cm³, respectively, and the kinematic viscosity at 40°C (ν_{40} (mm²/s) varies from 4.45 mm²/s to 35.5 mm²/s. It can be seen that the greatest stability is achieved by the emulsion from TMPE (21 hours), while the emulsions from ME (16 hours from SFO and 14 hours from RO) have intermediate stability values. From this follows the conclusion that the emulsions obtained with the esters of fatty acids, and especially those with branched alcohol residues (TMPE), have greater stability compared to the emulsions from RO. This is also evident from Fig. 1.

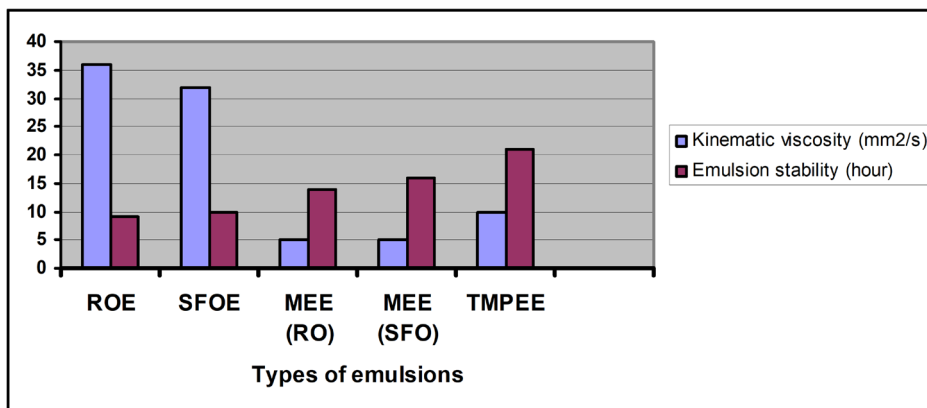


Fig. 1. Characteristics of the obtained emulsions (kinematic viscosity at 40°C and emulsion stability) containing vegetable oils, modified vegetable oils (TMP esters, methyl esters) separately.

3.2 Study of the physicochemical parameters of vegetable oils with increased acidity

Vegetable oils with increased acidity were investigated in terms of their characteristics such as viscosity, acid number, color, emulsion stability and density. Table 2 shows the characteristics of vegetable oils (sunflower oil and rapeseed oil) with increased acidity, and Table 3 shows the emulsions obtained from the corresponding vegetable oils. The parameters of vegetable oils with the following AVs were examined: sunflower oil: AV = 175 mgKOH/g, 137 mgKOH/g, 80.1 mgKOH/g and 55.9 mgKOH/g, as well as rapeseed oil: AV = 145 mgKOH/g, 123 mgKOH/g, 75.8 mgKOH/g and 65 mgKOH/g. The density of the obtained emulsions from vegetable oils (sunflower oil and rapeseed oil) with increased acidity varies between 0.937-0.958 g/cm³, respectively the kinematic viscosity at 40°C (v_{40} (mm²/s) varies from 37.14 mm²/s to 52.33 mm²/s. The color on the ball system ranges between 1.0 and 3.5. It can be seen that the greatest stability is achieved by the emulsions from sunflower oil and rapeseed oil with the highest acid number values, respectively 175 mg KOH/g and 145 mg KOH/g (28 h from SFO and 29 h from RO).

TABLE 2. Characteristics of vegetable oils with increased acidity.

Characteristic	Units of measurement	Sunflower oil				Rapeseed oil			
Viscosity	mm ² /s	52.33	47.61	41.93	37.14	48.76	48.25	40.76	40.76
Acid value	mg KOH/g	175	137	80.1	55.9	145	123	75.8	65.0
Density	g/cm ³	0.948	0.935	0.925	0.917	0.936	0.928	0.922	0.921

From here it follows that the emulsions obtained from RO with higher acidity have greater stability, compared to emulsions from RO with lower acidity. This is also evident from Fig. 2 and Fig. 3. The reason probably lies in the fact that, thanks to the presence of free fatty acids, which act as good surfactants and especially their salts, the stabilization of the emulsion for a longer period of time is favored.

TABLE 3. Characteristics of the obtained emulsions from vegetable oils with increased acidity.

Characteristic	Units	Sunflower oil emulsion + ME				Rapeseed oil emulsion + ME			
		10	30	50	75	10	30	50	75
ME	% (w/w)	10	30	50	75	10	30	50	75
Viscosity	mm ² /s	50.24	46.86	35.39	32.41	48.76	45.52	34.87	33.89
Density	g/cm ³	0.955	0.927	0.912	0.889	0.956	0.924	0.909	0.892
Colour	white	1.0	2.5	3.5	4.5	1.5	2.5	3.5	4.0
Emulsion stability	(hour)	29	35	37	38	29	34	38	38
Copper plate corrosion	(level)	Class 1	Class 2	Class 2	Class 2	Class 1	Class 2	Class 2	Class 2

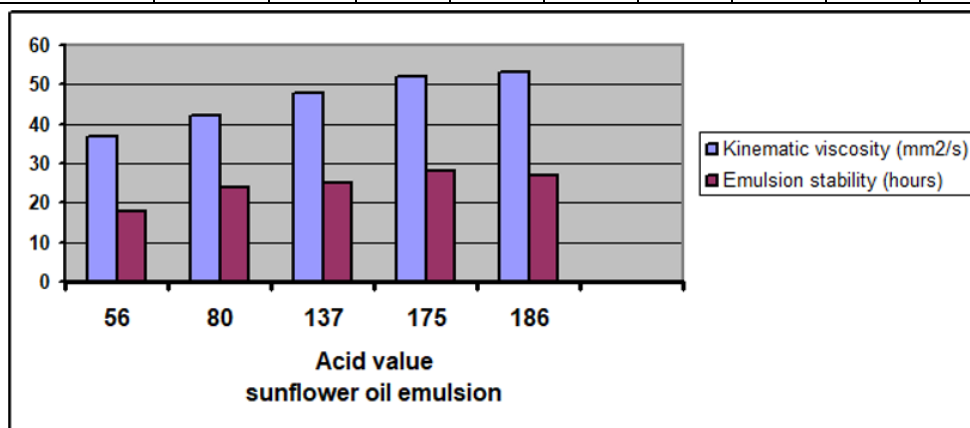


Fig. 2. Characteristics of the obtained emulsions (kinematic viscosity at 40°C and emulsion stability) from sunflower oil with increased acidity.

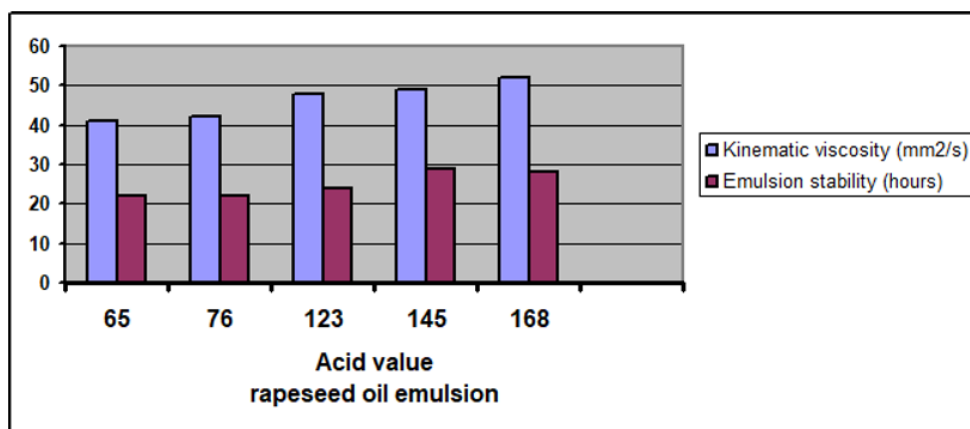


Fig. 3. Characteristics of the obtained emulsions (kinematic viscosity at 40°C and emulsion stability) from rapeseed oil with increased acidity.

3.3 Study of the influence of vegetable oil mixtures with ME and TMP esters in different percentages on the studied physicochemical parameters

Table 4 shows the emulsions from the respective mixtures of vegetable oils, ME, and TMPE. The indicators density, viscosity, emulsion stability, color, corrosion resistance, and thermo-oxidative stability were considered. The density of the obtained emulsions from the respective mixtures of vegetable oils (sunflower oil and rapeseed oil), ME, and TMPE varies between 0.893-0.946 g/cm³, respectively, and the kinematic viscosity at 40°C (ν_{40} (mm²/s) varies from 42.67 mm²/s to 33.54 mm²/s. The color on the ball system ranges between 1.5 and 4.5. The corrosion of a copper plate varies between Class 1 and Class 3.

It can be seen that the emulsion of a mixture of vegetable oil+ME+TMPE (20%:40%:40%) has the greatest stability, specifically between SFO+ME+TMPE (60 h) and RO+ME+TMPE (59 h). Also high stability is achieved by emulsions of mixtures between vegetable oil+ME+TMPE (40%:30%:30%), specifically between SFO+ME+TMPE (59 h), and RO+ME+TMPE (58 h), intermediate stability values are achieved by emulsions of mixtures between vegetable oil+ME+TMPE (60%:20%:20%), specifically between SFO+ME+TMPE (47 h), and RO+ME+TMPE (46 h), and the lowest stability is achieved by emulsions of mixtures between vegetable oil+ME+TMPE (80%:10%:10%), specifically between SFO+ME+TMPE (38 h), and RO+ME+TMPE (37 h).

TABLE 4. Characteristics of emulsions of vegetable oil mixtures with ME and with TMP esters in different percentages

Character istic	Units	Emulsion from sunflower oil + ME + TMPE				Emulsion from rapeseed oil + ME + TMPE			
		80:10:10	60:20:20	40:30:30	20:40:40	80:10:10	60:20:20	40:30:30	20:40:40
RO/ME/T MPE	% (w/w)	80:10:10	60:20:20	40:30:30	20:40:40	80:10:10	60:20:20	40:30:30	20:40:40
Viscosity	mm ² /s	42.34	37.61	35.91	33.54	42.67	39.52	36.17	34.05
Density	g/cm ³	0.945	0.929	0.905	0.893	0.946	0.931	0.907	0.894
Colour	ball	1.5	2.0	3.5	4.5	1.5	2.5	3.0	3.5
Emulsion stability	(hour)	38	47	59	60	37	46	58	59
Copper plate corrosion	(level)	Class 2	Class 2	Class 3	Class 3	Class 1	Class 2	Class 3	Class 3
Thermo-oxidative stability	Change in viscosity %	+3.24	+2.65	+1.53	+0.42	+2.89	+2.47	+1.69	+0.98
	Change in acid value (mg KOH/g)	+8.06	+7.45	+6.17	+4.26	+8.25	+7.54	+6.47	+5.01

From this follows the conclusion that the most stable are the emulsions obtained from RO with higher acidity (possibly the highest), in their mixtures with ME and TMPE, presented in a higher weight percentage composition. Each component influences the characteristics of the obtained emulsions. In this way, by combining the different components, an optimal ratio between them is achieved, thus favoring the stabilization of

the emulsion for a longer period of time, which would allow its application for various purposes and specifically as an MWF/CFL.

4 Conclusion

Suitable emulsions based on modified vegetable fatty acids have been obtained, and their technical and physicochemical parameters have been determined.

Based on the comparison of the technical parameters of emulsions of modified vegetable fatty acids with those of paraffin emulsions, it was found that the former can be used in preference to the latter, although they have a number of disadvantages.

The physicochemical parameters of vegetable oils with increased acidity were studied: density, viscosity, emulsion stability, and corrosion resistance. It was found that vegetable oils with increased acidity, after appropriate processing, could be used as a starting base for the production of MWF/CFLs.

The influence of the obtained mixtures of vegetable oil with ME, as well as mixtures of vegetable oil with TMP esters in different percentages, on the studied physicochemical indicators was studied. Based on this, it was established that increasing the percentage of ME and TMP esters separately in the mixture with vegetable oil has a positive, but diverse influence by improving the different characteristics. For example, increasing the percentage of ME improves some indicators, and TMP esters – others.

The influence of vegetable oil mixtures with ME and TMP esters in different percentages on the studied physicochemical parameters was studied, and based on this, it was found that combining ME with TMP esters in different percentages also has a mixed effect. Increasing the % content of ME compared to TMP esters has a positive effect on viscosity and density, and increasing the % content of TMP esters compared to ME increases the stability of the emulsion and corrosion resistance.

It has been found that emulsions obtained with vegetable oils with higher acidity are more stable. For this reason, further studies on the influence of vegetable oil mixtures with ME and TMP esters in different percentages on the studied physicochemical parameters were carried out with vegetable oils with the highest acidity.

A synergistic effect is also observed regarding the influence of mixtures of ME with TMP esters when they are in an equal percentage ratio.

Based on the comparison of the technical parameters of emulsions of modified vegetable fatty acids with those of paraffin emulsions, it was found that the former can be used in preference to the latter, although they have a number of disadvantages.

It was found that the obtained modified vegetable fatty acids (ME and TMP esters) could be successfully used as a starting component included in the composition of various types of MWF/CFLs.

This study is financed by the European Union-NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria, project № BG-RRP-2.013- 0001.

This research was funded by Research Science Fund of the University of Ruse (Project 2025-AIF-02).

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