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BIOLUBRICANTS FROM NATURAL WASTE OILS AND FATS

Abstract

The increase of ecological concern inspires research of raw materials from renewable sources in lubricant industry. Growing consumption of different lubricant types which are mostly mineral based or synthetic, leads to accidental but unavoidable inflow of considerable lubricants quantity into the environment. Therefore biodegradable lubricants produced from natural oils and fats become important if application is possible. Biodegradable lubricants produced by classical procedure from high quality natural oils and fats can be several times more expensive compared to conventional lubricants. Lower prices of waste natural oils and fats makes biodegradable lubricants much more competitive on the market. In this work the procedure of chemical synthesis, in which biodiesel (mixture of fatty acid methyl esters) is the raw material for TMP lubricants preparation will be presented as well.

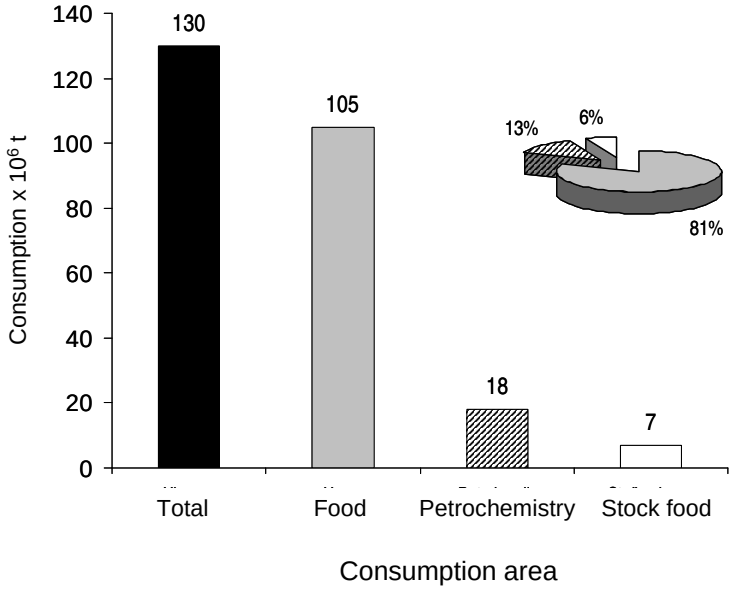
1. Introduction

Modern society is supplied with energy and general use of products based on the fossil raw materials. Resources of fossil origin are limited, but we are still not familiar with alternative energy and raw material. Research teams from the area of natural, technological, economic and social sciences are facing the challenges of the future sustainable development [1].

Biolubricants (bio base oil + additives) are a partial alternative to petrochemical products. The higher price of biolubricants restricts their use even in the ecologically endangered areas with soil and water inevitably polluted by petrochemical lubricants. On the European lubricant market the annual consumption of biolubricants is reaching 172000 tons, Germany and the Scandinavian countries being the biggest consumers of biolubricants [2].

For the time being, the insecurity of raw material availability (vegetable oil and animal fat) is the main obstacle for the development of new technologies in the production of bio base oils. It is probably just a matter of time, depending on the number of population on our planet, when neat oil and fat (coming from those

species that do not participate in the human nutrition chain) will be allowed in the production of non-food products. The Figure 1 shows the evaluation of oils and fats distribution in the world today [3]. Already used oils and fats (˝waste˝) from the human nutrition chain present an interesting raw material basis [4].

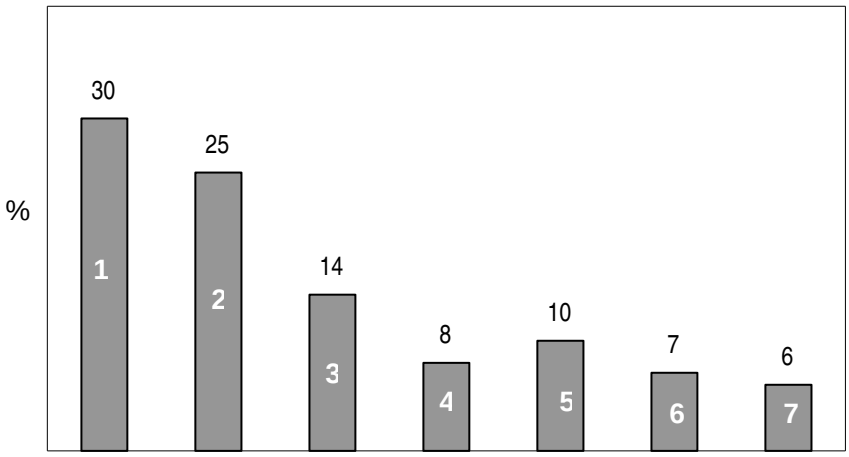


Picture 1: Global distribution evaluation of oils and fats consumption today

2. Oils and fats – the raw material basis of oleochemistry

Oil and fat are natural compounds with the dominant triglyceride chemical structure (compounds with three ester functional groups –CO-O-). The processing of oil and fat started with the invention of soap (by treating the raw fatty material with leach) which is ascribed to the Arabs. Today oils and fats are raw materials used in oleochemistry which is an important segment of chemical industry. The Figure 2 shows the distribution of the most abundant natural oils and fats in the global production. Physical and chemical properties of fats and oils sum up the properties of particular triglyceride structures. High proportion of some triglyceride has a great influence on the final properties of fats and oils. Complex oleochemical processes are adjusted to heterogeneous content of a raw material. The most significant process is chemical fat and oil splitting, the result of which is fatty acid blend, whose content can be optimized for the further treatment by separation processes.

The preparation processes for fatty esters and amides which serve as base oils include these reactions: esterification, preesterification and amidation.



Oil/fat: 1 - soybean oil, 2 - palm oil, 3 - rapeseed oil, 4 - sunflower oil, 5 - tallow, 6 - butter, 7- laurin (C_{12}-C_{14})

Figure 2: Mass portion of natural oil/fat in total mass of their global production

2.1. Esterification reactions

fatty acids	+	primary alcohol (petrochemicals or bioalcohol)	------> fatty acid esters
fatty acids	+	secondary alcohol (petrochemicals)	------> fatty acid esters

2.2. Preesterification reactions

2.2.1. ester **A** + alcohol **B** --------> ester **B** + alcohol **A**

2.2.2. fatty acid **A** + ester **B** -------> ester **A** + fatty acid **B**

2.2.3. ester **A** + ester **B** --------> ester **C** + ester **D**

2.3. Amidation reaction

fatty acids	+	ammonia (petrochemical)	------> fatty acid amides
fatty acids	+	amines (petrochemicals)	------> fatty acid amides

3. Base oils based on natural triglycerides and synthetic fatty esters

For the production of lubricants of shorter biodegradation, mineral base oils can be substituted by bio base oils which are, by their chemical content, natural esters (triglycerides in oils and fats) and synthetic fatty esters.

Diversity of biolubricants is based on the mutual solubility of oils and fats (which are dominated by the triglyceride structure) and synthetic fatty esters as base oils.

Synthetic fatty esters are an important raw material basis in chemical and processing industry. During the last decade the production capacities of fatty acid methyl esters (known as biodiesel fuel) have been growing in many EU countries [5]. The Figure 3 shows the processing of oil and fat scheme in Germany in the period between 2000-2005. The 2003/30/EU directive of the European parliament and council promotes the use of biofuels and other renewable energy-generating products in transportation. Biodiesel fuel is included in these biofuels [6]. Fatty acid methyl esters (biodiesel) globaly tend to be implemented in production of biodegradable lubricating oils [7].

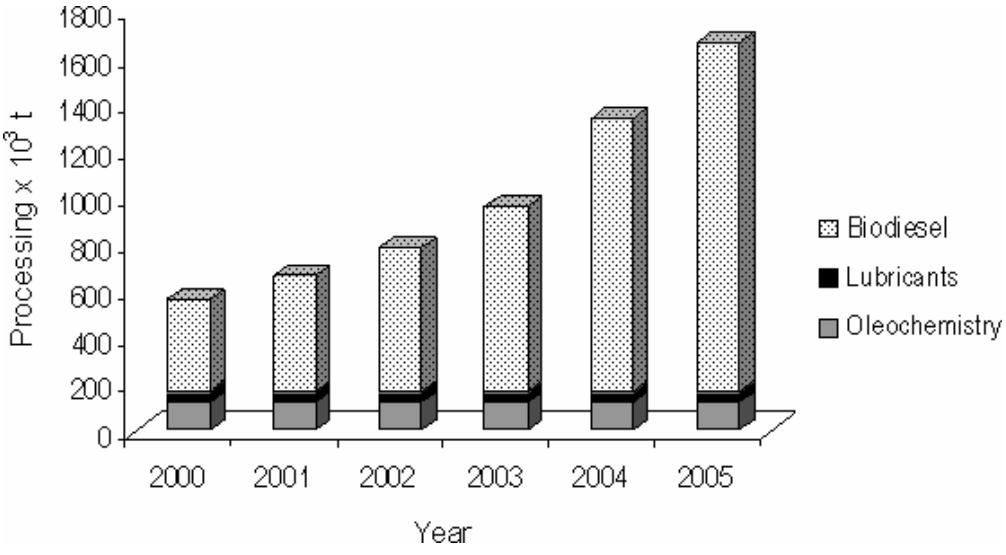


Figure 3: Oil/fat processing in Germany (2000-2005)

Important synthetic fatty esters as base oils are: monoglycerides and diglycerides. They are prepared by strictly controlled reactions of esterification and preesterification.

3.1. Esterification reactions

RCO_2H + $C_3H_8O_3$ $\rightleftharpoons$ $RCO_2C_3H_7O_2$ + H_2O

fatty acid glycerol monoglyceride water

$RCO_2C_3H_7O_2$ + RCO_2H $\rightleftharpoons$ $(RCO_2)_2C_3H_6O$ + H_2O

monoglyceride fatty acid diglyceride water

3.2. Preesterification reactions (triglycerides = oil or fat)

$(RCO_2)_3C_3H_5$ + $C_3H_8O_3$ $\rightleftharpoons$ $RCO_2C_3H_7O_2$ + $(RCO_2)_2C_3H_6O$

triglyceride glycerol monoglyceride diglyceride

$(RCO_2)_2C_3H_6O$ + $C_3H_8O_3$ $\rightleftharpoons$ 2 $RCO_2C_3H_7O_2$

diglyceride glycerol monoglyceride

Glycerol can be of natural or synthetic origin. Natural glycerol is a by-product of the fatty acid production from natural oil and fat, as well as a by-product of synthesis of biodiesel fuel from plant oil and methyl alcohol. Synthetic glycerol is prepared in the hydrolysis reaction of epichlorhydrine (also a synthetic petrochemical).

4. Biodiesel fuel – raw material for preparation of TMP base oils

Synthesis of biodiesel fuel (a blend of fatty acid methyl esters) is the first stage of synthesis of trimethylolpropane (TMP) base oils. Prepared fatty acid methyl esters are transformed in the second level by preesterification with trimethylolpropane (1,1,1 tri – hydroximethyl propane) in the new ester structures which proved to be excellent base oils (TMP – base oils).

Vegetable oils with high content of oleic acid in triglyceride structure show suitable properties as the raw material for TMP-base oils. High content of oleic triglycerides in some oleaginous plants is achieved by genetic engineering.

I stage

glycerol – trioleate + 3 CH_3OH --------> 3 $CH_3C_{16}H_{30}CO_2CH_3$ + $C_3H_8O_3$

methyl alcohol oleic acid methyl ester or methyl oleate glycerol

II stage

3 $CH_3C_{16}H_{30}$ CO_2CH_3 + $(HOCH_2)_3CC_2H_5$ ---> $(CH_3C_{16}H_{30}CO_2CH_2)_3CC_2H_5$ + 3 CH_3OH

oleic acid methyl ester trimethylolpropane trimethylolpropane trioleate methyl alcohol

Regardless of chemical composition of triglycerides (oils and fats) the first stage of synthesis can be conducted under very convenient conditions: with the temperature up to 100 ^{0}C, atmospheric pressure; the separation techniques (by which the optimal

cut into fraction can be achieved: fractional distillation, fractional crystallization); the second stage synthesis does not require a significant energy input. Splitting of oils and fats, in order to produce fatty acids (the raw material for the preparation of fatty esters) require much greater energy input (Fig.4). Synthesis of fatty acid methyl esters can also be conducted from ”waste” oils and fats from the nutrition chain [8].

Plant oil derivatives with high content of oleic acid in a ester form (isopropyl oleate, TMP trioleate, pentaerythritol tetraoleate) as one of the components which gives some of the lubricant properties, are the best stimulation for the chemical synthesis researchers who are looking for new structures, and some of them will certainly be applied in lubricants.

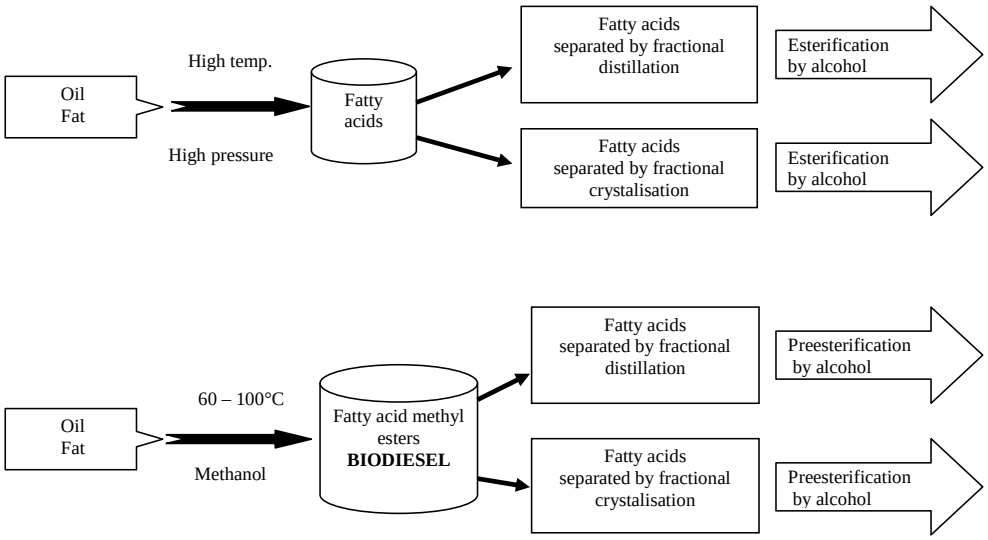


Figure 4: Scheme of preparation processes for fatty acid esters

5. Properties of base oils based on natural triglycerides and synthetic fatty esters

Fatty acid methyl ester (biodiesel fuel) has been synthesized in the process developed at the Company INA d.d. Zagreb [8] in semi-industrial scale, whose properties comply with the stringent requirements of the international standards. Nevertheless, these products have a poor oxidation stability influenced by not only the production processes, but also storage and handling conditions and the autooxidation process. Free radicals produced by autooxidation make long-chained and network structures, and all these structures produce undesirable sludge. Oxidation stability is improved by adding additives, so called antioxidants [9]. By

adding different types of additives to a lubricant based on esters desirable properties can be provided [10].

The comparison of base oil properties of mineral and natural origin is shown in the Table 1. Apart from faster biodegradation, some of the applicational properties of natural and synthetic fatty esters are better than mineral base oil properties. These products are advertised as "renewable, bio, green, ecological, naturally biodegradable" since they are more human- and environmentally friendly than those products of specifically petrochemical origin.

Table 1: Comparison of lubricant properties related to the base oil origin

Lubricant	Base oil of mineral origin		Base oil of natural origin	
	Mineral oil	Synthetic oil	Synthetic oil based on natural oil and fat	Natural oil and fat
Wear protection	+	++	++	++
Lubrication	+	++	++	++
Stability	+	++	++	-
Toxicity	-	+	+	++
Biodegradation	- -	+	+	++
Saving fossil resources	- -	- -	+	++
Price, Euro / L	1	5	5	3

Marks: + = good, ++ = excellent, - = lack of, - - = lack of-bad

Synthetic base oils based on natural oil and fat have some advantages when compared to natural triglycerides (oils and fats), they are of the equal quality and they do not tend to produce sludge, deposits and resin. Synthetic oil based on natural oil and fat have good lubrication properties, good viscosity index, less need for lubrication additives and they are less toxic. Their disadvantages are doubtful compatibility with mineral oils and seal materials. Stabilizers need to be added due to their tendency to oxidation and hydrolysis; they are 3-5 times more expensive than mineral oils.

6. Conclusion

Natural oil, natural fat and synthetic oil based on the natural oil and fat are applied in lubricants. It has been estimated that today's portion of these oils which serve as lubricants is: 1 % in motor oils, 10 % in hydraulic oils and 10 – 20 % in oils in material treatment. These numbers also tend to grow.

Market surplus management of hygienically and sanitary clean oil and fat (butchery waste, oil and fats from restaurants and households) provides a lower price of raw materials.

Some of the possible chemical synthesis processes of synthetic oils (biodiesel interphase), from natural oil and fat, especially waste oil and fat, are promising from the techno-economical and ecological standpoint.

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UDK	ključne riječi	key words
621.892.31/.32	bazno mazivo ulje, organskog polusintetskog porijekla	semisynthetic organic base lubricating oil
621.899	bazno mazivo ulje, iz otpadnih organskih sirovina	lubricating oil of organic waste origin
665.7.032.52	naftni i slični produkti dobiveni preradom biljnih ulja	petroleum and related products worked-up from vegetable oil
.001.18	gledište predvidivog razvoja	viewpoint of predictable develoment
66.094.942	transesterifikacija	transesterification
547.295.8 ' 26	esteri masnih kiseline	fatty acid, esters
547.426	trimetilolpropan (TMP)	trimethylolpropane (TMP)
.001.37	gledište evaluacije	evaluation viewpoint

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