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STUDY ON THE TRIBOLOGICAL PERFORMANCE OF VEGETABLE OILS

Abstract
Field experiment with nine different oilseed crops was conducted. The seeds are cleaned, pressed in an oil mill, and then the oil is extracted. Yield of grain, yield of oil and physical-chemical parameters were determined. Tribological properties were investigated on ball-on-disc test device using steel specimens in boundary lubricated conditions. Wear results indicate that trygliceride structure of sample oils is effective enough to prevent wear at contact pressure of 1 GPa. Some oil samples retain their wear resistance at 2 GPa, however only at 50 °C initial substrate temperature. Investigation is focused in the direction of detecting of suitable crops and improving yields of common ones.

Introduction

Vegetable oils and animal fats have been used as lubricants for over 5,000 years [1]. However, since the discovery that mineral oil could be refined to produce high quality lubricants, the transition from widespread use of vegetable and animal products to mineral oils was effected in a few decades. The change was promoted by several factors: growing industrial demand and the requirements of the railways was forcing up the cost of vegetable oils and animal fats, many of existing lubricants were unstable and systematic evaluations of the relative performance of oils from different sources were showing the readily available mineral oils to be entirely satisfactory for most applications. All these factors contributed to the ready acceptance of mineral oil in industry and creation of strong market for another product of the rapidly expanding petroleum industry [1]. Nevertheless, seed oils derived from renewable agricultural sources have always been attractive. The benefits of vegetable oils include lower pollution (air, water and soil), minimal health and safety risks and easier disposal due to their facile biodegradability [2].

In Slovenia, the main sugar company has been closed recently and 6,000 – 8,000 ha of fields that were planted by sugar beet annually became available for alternative crops. Recently, the total production of vegetable oils around the world is growing at a rapid pace of approximately doubling the volume for every 25 years. Four oil crops clearly dominate the feedstock sources used for world-wide vegetable-oil production: palm, soybean, rapeseed and sunflower. Together, these four crops account approximately 77% of worldwide vegetable-oil production [2,3]. In central Europe, rapeseed and sunflower are species being cultivated on a sizable scale, while other oil seed crops are less important. The aim of the study was to investigate which other oilseed crops would be appropriate for vegetable oil production in the prevailing weather conditions. There are almost 40% fields planted by maize, which is row plant, therefore alternative crops are desired to be included in the field crop rotations. Oilseed crops contain higher content of oil in seeds and could be raw material for lubricants and biodiesel production, but are rarely sown. Monocultures, which have negatively impact on the soil characteristics, accelerate pests and diseases increasing, so higher doses of chemical agents to suppress them are needed, would be broken by including these crops in present field crop rotations. Additionally, some hectares that are planted by maize will be loosen because of the Western Corn Rootworm is spreading in Slovenia.

Experimental

Materials and methods

Field experiment was conducted as a block trial in three replications with plot size of 36 m^2 in 2008. Different oilseed crops were cultivated for the purpose of the research, Table 1.

Table 1: Oil samples

Oil seed crop	**Latin name**	**Type**	**Code**
Hemp	*Cannabis Sativa*	Bialobrzeska	HP
Common flax	*Linnum usitatissium*	Rengeo	CF
Oilseed rape	*Brassica napus*	PR46W31	OR
Soy bean	*Glycine max*	Borostyan	SB
Sunflower	*Helianthus annuus*	NK Maldini	SF
False flax	*Camelina Sativa*	Rengeo	FF
White mustard	*Sinapsis alb*	Rengeo	WM
Maize*	*Zea mays*	NS 6012	OM
Castor bean	*Ricinus communis*	Duan	CB

* … with high content of oil in seeds

Experiment was taken care of according to good agricultural practice for each included field crop. Each oilseed crop was harvested at the time of technological maturity. Yields per plot were weighed; samples for oil content, moisture content, fatty acids composition, determination of iodine value and oil viscosity. For determination of previously mentioned physical-chemical parameters following ISO standardized methods were used; oil content – ISO 659:1998, moisture content –

ISO 665:2000 and ISO 662:1998, fatty acid composition – ISO 5509:2000 and ISO 5508:1990, iodine value – ISO 3961:1996, and viscosity ISO 3104:2002. Results were statistically processed.

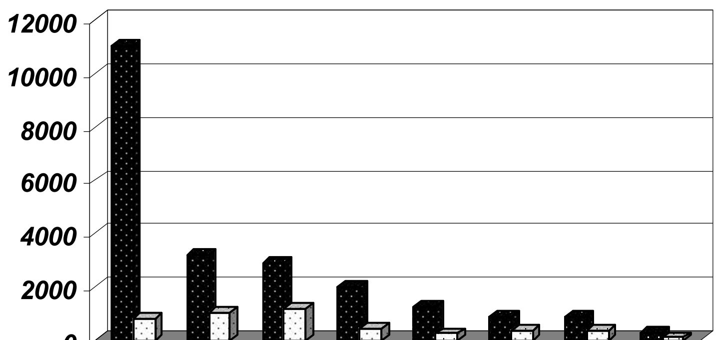
Friction and wear tests

Tests were performed using a reciprocating ball-on-disc test device. The upper 10 mm diameter 100Cr6 bearing steel test specimen is rubbed against a lower steel specimen, on which a few milligrams of test oil is placed. The physical observation of wear scar was performed using optical microscope. A load of 10, 80 and 300 N and was used that gave an initial Hertzian contact pressure of approximately 1, 2 and 3 GPa, respectively. The tests were conducted at average linear speed of 0.1 m/s and initial temperature of the disc specimen of 50 °C and 100 °C. Total sliding distance was 600 m that corresponding to 300,000 load cycles. The tests were repeated at least two times.

Results

Field experiment

In 2008 the yield of grain was the highest at maize, followed by sunflower and oilseed rape, and then by soy bean, Fig. 1.



	OM	SF	OR	SB	CB	FF	CF	HP
■ *Yield (kg DM seed/ha)*	*11061*	*3169*	*2870*	*2018*	*1263*	*889*	*886*	*288*
□ *Yield of oil (kg/ha)*	*792*	*1038*	*1191*	*432*	*246*	*339*	*345*	*99*

Figure 1: Yield of grain (kg DM/ha) and yield of oil (kg/ha) with regard to different oilseed crops

The rest of the included oilseed crops (castor bean, common flax, false flax, and white mustard) gave rather low yield of grain in the soil and weather conditions in Slovenia in 2008, there were not significant differences in their grain yields according to Duncan multiple range test ($p < 0.05$). The highest yield of oil per area unit was produced by oilseed rape, closely followed by sunflower and then by oilseed maize. Just approximately one third of that yield of oil was reached by soy bean and much lower by the rest of the included oilseed crops (castor bean, common flax and white mustard), Fig. 1. In energetic and financial view, oilseed rape is still the most convenient oilseed crop in central Europe for environmentally adapted lubricants production.

Physical and chemical parameters

Most vegetable oils are tryglicerides constituting a complex mixture of fatty acids with different chain length and unsaturation content [2,3]. From the fatty acid composition of the oils, it is observed that chain length C18 is dominating, Table 2. The content of polyunsaturated fatty acids (C18:2 and C18:3) is rather high for HP, SB, SF and OM. Under thermal conditions the double bonds in polyunsaturated fatty acids polymerize much faster than monounsaturated (C18:1 and C22:1) or saturated (C16:0 and C18:0) fatty acids. Unfortunately, the saturation of fatty acid degenerate the low temperature behavior or pour point of the oil. Monounsaturated fatty acids can be called “a convincing compromise” between having high stability and low pour point. Castor oil is distinguished by its high content (over 80%) of ricinoleic acid ($C_{18}H_{34}O_3$). No other vegetable oil contains so high a proportion of fatty hydroxyacids.

Table 2: Particular fatty acid content [%] in test oils

Fatty acid	HP	CF	OR	SB	SF	FF	WM	OM	CB
C16:0	6.5	5.5	4.9	9.9	7.0	6.1	3.2	11.3	1.8
C18:0	2.6	3.6	1.6	3.2	2.5	2.4	1.1	2.4	2.4
C18:1 n9	11.1	19.7	56.7	18.5	25.8	15.8	22.3	30.6	4.8
C18:1 n7	1.1		4.6	1.6	1.3	1.3	1.5	1.2	
C18:2	56.4	16.9	20.8	57.4	62.0	22.7	11.3	51.2	6.8
C18:3	16.2	49.4	8.7	8.3		31.7	9.7	2.1	1.0
C20:1	1.3	1.2	1.0			12.1	9.5		
C22:1						2.8	33.5		
$C_{18}H_{34}O_3$									81.6
other	4.8	3.7	1.7	1.1	1.4	5.1	7.9	1.2	1.6

As can be seen from Table 3, viscosities of vegetable oils produced from oil seeds fall between 26 and 46 mm^2/s measured at 40 °C, except for castor oil (CB). Kinematic viscosity of CB is more than five times higher compared to other vegetable oils mainly due to a high content of ricinoleic acid, see Table 2.

Table 3: Viscosity data and measured iodine value for oil samples.

	HP	CF	OR	SB	SF	FF	WM	OM	CB
Kinematic viscosity at 40 °C [mm^2/s]	27.4	26.5	34.6	29.6	31.0	31.3	46.5	33.5	148.0
at 100 °C [mm^2/s]	6.9	7.0	8.0	7.4	7.5	7.7	10.0	7.7	19.5
Viscosity Index	230	247	210	230	223	232	209	211	89
Iodine value	170	131	121	143	131	157	103	102	65

Higher viscosity of castor oil is very desirable when formulating viscous lubricants, such as environmentally adapted gear oils or greases. Castor neat oil falls into ISO VG 220 viscosity grade and further increase by using traditional polymeric thickeners is possible. However, thickeners reduce biodegradability and impose shear stress problems. Viscosity index of CB is significantly lower compared to other vegetable oils and is in the range of typical mineral oil formulation. Significantly higher viscosity index of other vegetable oils indicate that their viscosity does not vary with temperature as much as mineral oil. This can be an advantage when designing lubricants for use over a wide temperature range.

Iodine value characterizes particular oil on the base of unsaturated fatty acids. Oils with high iodine values are more problematic for oxidation processes, however values fewer than 100 are not recommended since such oils are more problematic for changing the characteristics at lower temperatures. From Table 3 it could be seen that iodine values for hemp and false flax oils are higher than 150, indicating low oxidation stability.

Friction and wear study

Boundary lubrication phenomena are often associated with adsorption and tribochemical reaction occurring on the metal surface [5]. The adsorption occurs mainly through the polar functional groups of the trygliceride molecule, while tribochemical reactions resulting out of chemical reactions of the lubricants themselves or with other materials in the contact area [6,7].

Fig. 2 is a plot of the wear scar diameter, for low initial contact pressure (1 GPa), moderate initial contact pressure (2 GPa) and high initial contact pressure (3GPa), determined at 50 and 100 °C substrate temperatures. For low contact pressure, similar wear scars between 0.18 and 0.23 mm are observed for both substrate temperatures. The only exception is CB that exhibits two times higher wear at 100 °C. At moderate contact pressure and 50 °C (Fig. 2a), high distribution of measured wear scars is observed, remarkably higher than at the highest contact pressure.

At 100 °C and moderate contact pressure (Fig. 2b), significantly higher wear is found and lower distribution of measurements. The diameters of wear scars are again quite similar at the high contact pressure. A little bit higher wear at 100 °C is observed, however the difference is much lower than at moderate load. The exception is HP with the high content of linoleic C18:2 fatty acid (Table 1) and the highest iodine value (Table 2) that exhibits the highest wear at both temperatures. Results from Fig. 2 indicate that trygliceride structure of sample oils is effective enough to prevent wear at contact pressure of 1 GPa. Especially oil samples HP, OR, SF, WM and CB, retain their wear resistance at more severe load condition of 2 GPa, however only at 50 °C initial substrate temperature.

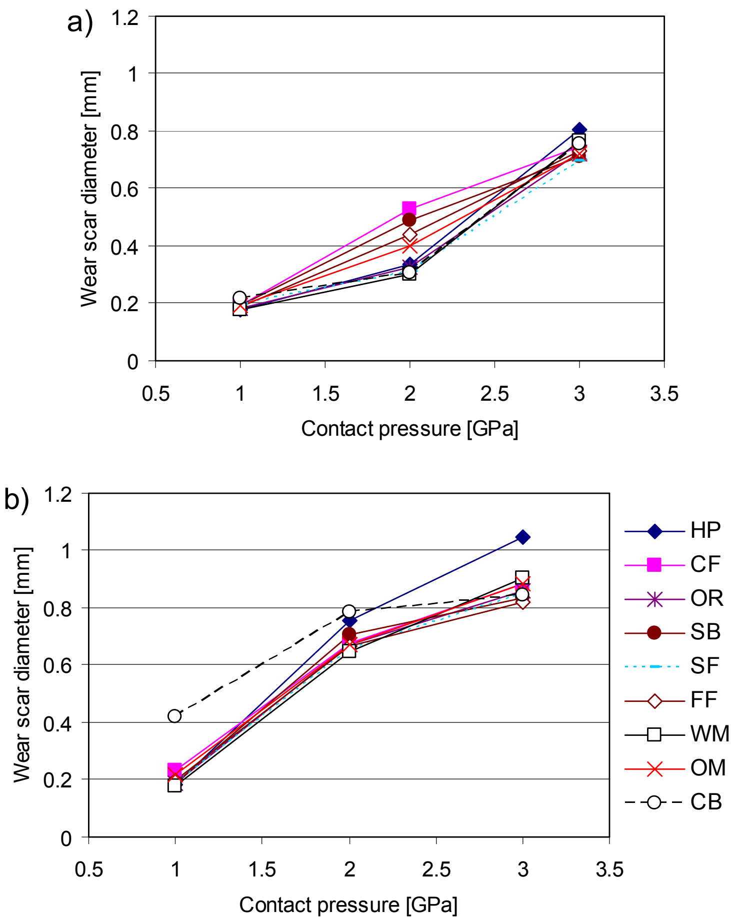


Figure 3: Wear results a) initial substrate temperature of 50 °C
b) initial substrate temperature of 100 °C

The plot in Fig. 3 shows the average value of coefficient of friction (COF) for test samples. COF reduction is evident from Fig. 3a at contact pressure of 2 GPa, especially for oils that exhibit the lower wear (Fig. 2a). COF at 3 GPa is higher than at 2 GPa, but generally lower compared to the initial value at 1 GPa. Friction behavior at 100 °C (Fig. 3b) is strictly oil type dependent. With the increased contact pressure COF is reduced for OR, SF and WM.

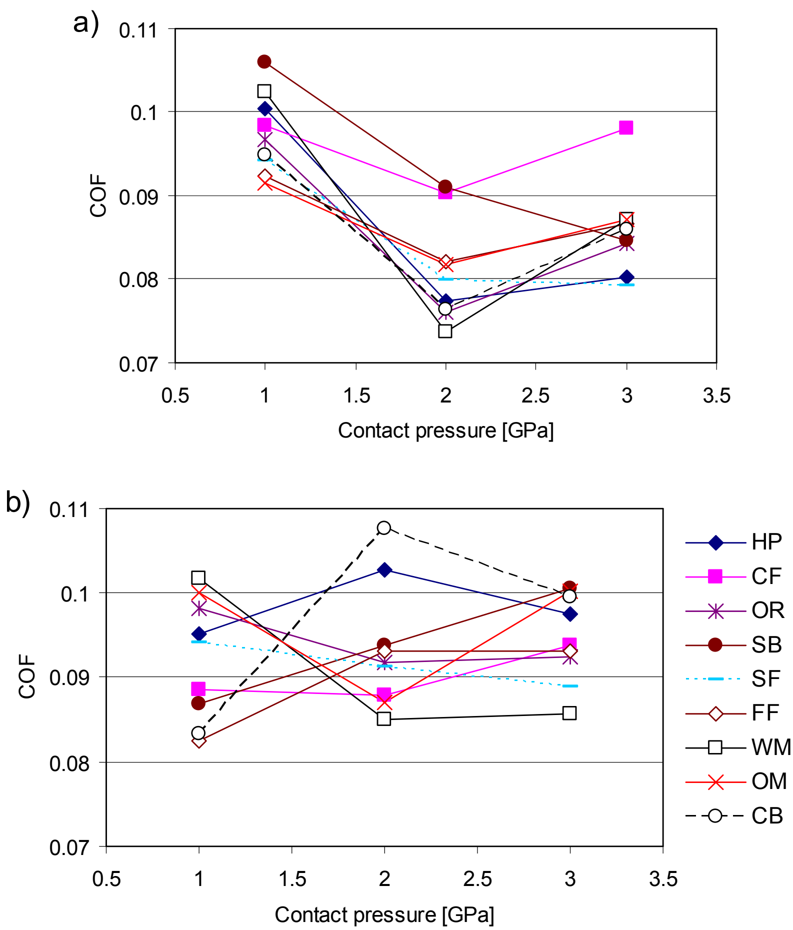


Figure 3: Friction results a) initial substrate temperature of 50 °C
b) initial substrate temperature of 100 °C

Conclusions

The main purpose of this work was to investigate which oilseed crops would be appropriate for both, lubricant and biodisel production in the prevailing weather conditions. The highest yield of oil per area unit was produced by oilseed rape, followed by sunflower and oilseed maize with the high content of oil in seed.

Friction and wear tests together with the fatty acid profile of the oil samples reveal that vegetable oils cannot be treated as a group where all has the same behaviour. Good rapeseed oil and sunflower oil lubrication properties at moderate loads and low temperatures are well known, while white mustard potential has yet to be reported. For some applications, castor oil could be very useful, especially because of its inherently five times higher viscosity compared to other seed oils.

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UDK	ključne riječi	key words
665.32.014	biljna ulja, ispitivanje sastava i svojstava	vegetable oils, content and properties testing
621.891.2	svojstva maziva	lubricant properties
621.892.31	mazivo ulje, biljnog porijekla	vegetable lubricating oil
.004.14	gledište podobnosti za upotrebu	application value viewpoint
.002.33	gledište podobnosti sirovine za obradu	process capability of feedstock
.001.37	gledište komparativne evaluacije	comparative evaluation viewpoint
631.165	procjena poljoprivednih prinosa	agricutural yield estimation

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