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INCREASING THE OXIDATION STABILITY OF VEGETABLE OIL BY CATALYTIC HYDROGENATION FOR APPLICATION IN LUBRICATION

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Abstract

The vegetable oils as soybean, canola and sunflower oils provide new alternatives for environmental friendly lubricants.

This paper presents investigations on increasing the oxidation stability of soybean oil by catalytic hydrogenation over catalysts with Cu, Cr and Ba. These investigations allow choosing parameters for hydrogenation and emphasize the oxidation stability of the hydrogenate oil treated with different antioxidants additives.

Keywords*: catalytic hydrogenation of the vegetable oils, oxidation stability of vegetable oil*

Introduction

The lubricating oils and their decomposition products are pollutants that reach circumambience in a greater or smaller proportion. The pollution is smaller for the biodegradable lubricating oils.

The lubricating oils contain base lube oils and additives. Among base lube oils, mineral oils and some synthetic oils categories have a low biodegradability. In contrast, the vegetable oils and some synthetic oils have an acceptable biodegradability and represent, from this point of view, lube base oils very convenient for lubricating oils formulation.

Numerous studies have lead to achieve of some biodegradable lubricants starting from vegetable oils [1-10].

Chemically, the vegetable oils are esters of glycerin and long- chain fatty acids. The disadvantage of these oils is the low oxidation stability that depends on the degree of the fatty acid unsaturation. Due to the critical points presented in the figure 1, the oxidation stability of these oils is much lower than the other base lube oils.

A refined soybean oil contains the following fatty acids: palmitic acid (C16:0) – 10,1%; stearic acid (C18:0) – 4,1%; oleic acid (C18:1) – 23,2%; linoleic acid (C18:2) – 52,8%; linolenic acid (C18:3) – 7,2% [3]. The major fatty acid constituents of sunflower oil are: palmitic acid 3,0 – 10,0%; stearic acid 1,0 – 10,0%; oleic acid 14,0 – 65,0%; linoleic acid 20,0 – 75,0 [4].

The oxidation stability improvement of vegetable oils can be achieved by genetic or chemical structure modification [3, 6, 8, 10].

Chemical modification refers to the modifications of the carboxyl group (esterification), the modifications of the fatty acid chain (selective hydrogenation, dimerization, formation of C-C and C-O bonds).

This paper presents the characteristics of some vegetable oils and a catalytic hydrogenation survey of some soybean oil for decreasing its unsaturation degree and increasing its oxidation stability.

Vegetable oils oxidation stability

Three base oils were analysed for selection of vegetable oil with the purpose of biodegradable lubricating oils preparation: soybean oil, sunflower oil and, for comparison, mineral oil SAE 10. The main physical-chemical characteristics of these base oils are presented in table 1. In order to determine the oxidation stability of these oils, two methods were used:
the method of Rotary Bomb Oxidation (RBOT) and a method, much less severe, which consist in keeping the oil at 140 ^{0}C for 160 hours. This method was chosen in order to compare base oils with lower oxidation stability.
The data presented in the table 1 show that the vegetable oils have a low variation with temperature of viscosity (IVE>200), low volatility (flash point>250^{0}C), but as it is, well known from literature, a low oxidation stability.

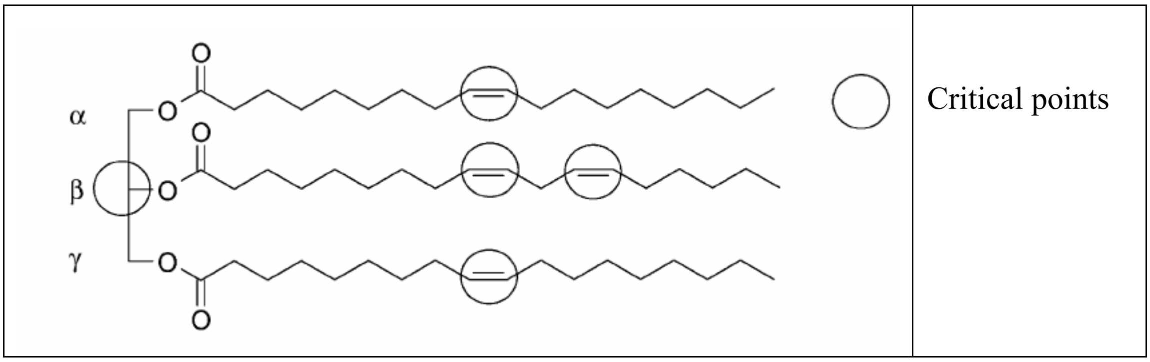

Fig. 1 Critical points of tryglicerides: β-CH-group and unsaturated double bonds.

Table 1. The lube base oils characteristics

Characteristics	Vegetable Oils		Mineral Oils
	Soybean	Sunflower	SAE 10
Relative density	0.9245	0.9066	0.8954
Kinematics Viscosity at 40^{o}C, mm^2/s at 100^{o}C, mm^2/s	 31.04 7.61	 31.32 7.61	 29.50 4.93
Viscosity Index	212	226	92
Pour Point ^{o}C	-10	-16	-12
Flash Point, ^{o}C	300	264	210
Organic Acidity, mgKOH/g	0.57	9.23	0.05
Copper Corrosion	1b	1b	1a
Oxidation stability by RBOT, min	20	15	70
Viscosity Increasing after 160h at 140 ^{o}C at 40^{o}C, % at 100^{o}C, %	 23.2 15.4	 95.3 74.1	 7.0 2.0

Catalytic hydrogenation of vegetable oils

Soybean oil was hydrogenated in a micro pilot laboratory plant (figure 2) endowed with a fixed bed reactor. The hydrogenation was made on a hydrogenation catalyst with Cu, Cr and Ba with the following composition: Cu= 14.2wt%, Cr_2O_3 = 8.3 wt%, BaO = 1.7wt %

Operating parameters of the laboratory plant are:
Temperature = 60…..200^{0}C
Pressure = 5………..10 bar
Oil flow = 2………..50 ml/h
H_2 flow = 20……….1000 ml/h

The operating conditions were chosen therefore to achieve a selective hydrogenation of acids with two or three double bonds, avoiding as possible, double bond hydrogenation of the oleic acid which can lead to the obtaining of a hydrogenated soybean oil with high pour point . The temperature and the space velocity influence on the hydrogenated oil characteristics were investigated. The experimental data have shown that the influence of space velocity is insignificant.

The influence of the reaction temperature on the oxidation stability is presented in table 2. The hydrogenated vegetable oils used in process contain two antioxidants additives A1 and A2. Afterwards, there are presented some indications regarding the additive composition: A1 is a combination of antioxidants, corrosion inhibitors, non ferrous metal deactivator (alkylphenol 25-35 wt%; alkyl diaryl amine 25-35 wt%, tri-n-butyl phosphate 5-10 wt%). A2 is a antioxidant, antiwear , anticorrosion and antirust additive (sulfur 5wt%, phosphorous 3 wt%, zinc 3.5 wt%).

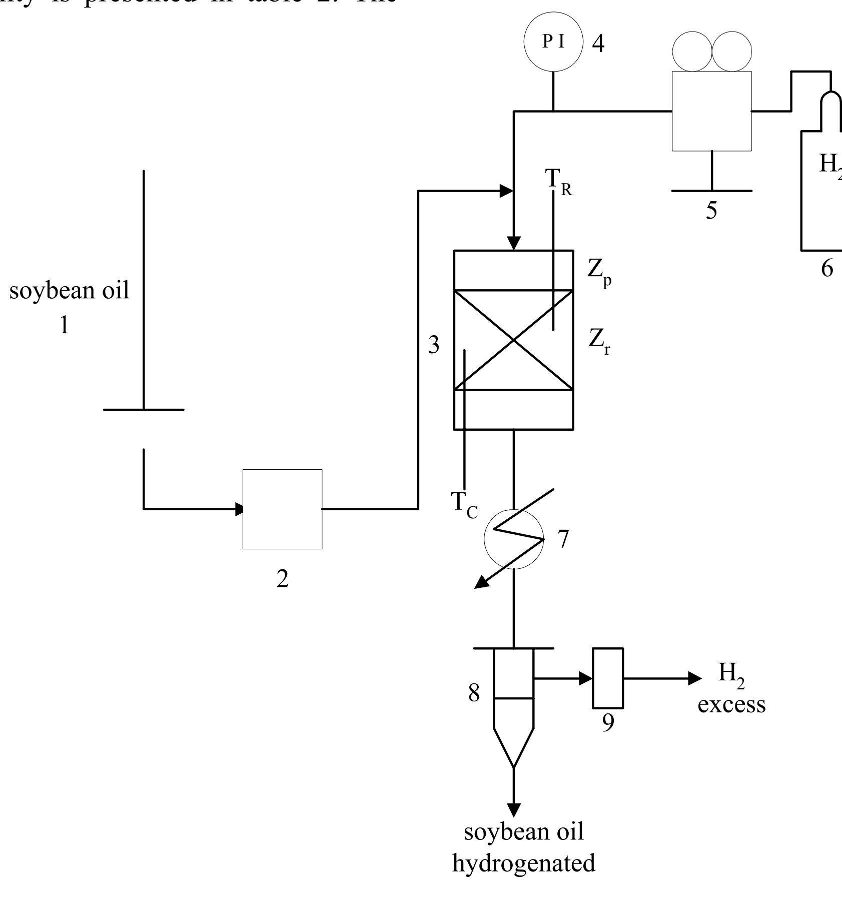

Fig. 2 Scheme of the micro pilot laboratory plant (1-biuret, 2- pump, 3- isothermal reactor, 4- manometer, 5- pressure reducer, 6-hidrogen bottle, 7- cooler, 8- phases separator, 9- flow meter, T_R- thermal resistance, T_C- thermocouple, Z_P-preheating zone, Z_R- reaction zone.

Conclusions

- The vegetable oils have convenient reological properties but inconvenient oxidation stability;
- The hydrogenation of vegetable oils increases the oxidation resistance of vegetable oils;
- The reological properties of the hydrogenated oil are insignificant modified;
- The rising of the hydrogenation temperature decreases the selectivity of the catalyst (the pour point rises);
- It is important to increase the stability of the catalyst in order to avoid the transfer of the metal into the oil, which favours the poly condensation reactions.

Table 2. Physical-chemical characteristics of hydrogenated vegetable oils

	Hydrogenated vegetable oils			
	SH1		SH2	
Operating parameters Temperature, ^{0}C Space velocity, h^{-1}	 150 1.2		 200 1.2	
Characteristics				
Kinematics Viscosity at 40^{o}C, mm^2/s at 100^{o}C, mm^2/s	 32.86 7.70		 33.85 7.88	
Pour point, ^{0}C	-4		-2	
Antioxidant additives	A1	A2	A1	A2
Viscosity Increasing after 160h at 140 ^{o}C at 40^{o}C, % at 100^{o}C, %	 16.2 10.25	 17.3 11.2	 19.8 12.5	 20.3 14.1

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