BIO-FUELS EMPLOYABLE AT ALL SEASONS OBTAINED BY VEGETABLE OILS PROCESSING

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Rezumat. *Ca şi combustibilii pe bază de petrol, bio-combustibilii sedimentează când vremea se răceşte, umplându-se de cristale fine de ceară ce pot bloca filtrul de combustibil. Noi propunem o soluţie de a obţine bio-combustibili, soluţie ce poate fi utilizată în oricare anotimp. Multe tipuri de uleiuri vegetale au fost utilizate în experimentele noastre: ulei de rapiţă, de floarea soarelui, de soia şi diverse combinaţii ale acestora. Au fost amestecate la o anumită temperatură şi la presiune normală în diverse proporţii cu alcool/ester/hidrocarburi lichide. Toate amestecurile au o foarte bună stabilitate în timp (stabile pentru mai mult de 3 luni, la 20°C), o bună viscozitate cinematică la 20°C (cam 25 cSt), densitatea între 0,87 – 0,92 g/cm^3 şi puterea calorică de 45400 J/g. Valoarea acidităţii a fost în toate cazurile mai mică de 0.75 mgKOH/g. Dar numai o parte dintre aceste amestecuri sunt în stare lichidă la 18 °C sub zero. Două participaţii de hidrocarburi au fost utilizate pentru amestecuile de uleiuri vegetale pe care le propunem şi au densitatea de aproximativ 0,827 g/cm3 şi 0,92 g/cm3, viscozitatea cinematică la 20°C aproximativ 8,75 cSt şi respectiv, 6,41 cSt, iar puterea calorică de aproximativ 47440 J/g pentru prima participaţie şi 50000 J/g pentru cea de a doua.*

Cuvine-cheie: *bio-combustibili, uleiuri vegetale, punct de îngheţ.*

Abstract. *Like petroleum diesel fuels, bio-fuels clouds when the weather gets cold, filling with little crystals of wax that can clog the fuel filter. We propose a solution for bio-fuels obtaining, which can be used at all year seasons. Many types of vegetable oils were used in our experiments: rapeseed oil, sunflower oil, soybean oil and different mixture of them. They were mixed at a specific temperature and normal pressure with different mass ratio of alcohol/ester/liquid hydrocarbons mixture. All the mixtures have a very good stability in time (stabile for more than 3 month, kept at 20°C), good cinematic viscosity at 20°C (about 25 cSt), their density is between 0.87 – 0.92 g/cm^3 and the heat value is about 45400 J/g. The acid value was in all cases less than 0.75 mgKOH/g. But only some of these mixtures are in the liquid state at 18 °C below zero. Two hydrocarbons fractions have been used for our vegetable oils mixtures and they have the density about 0.827 g/cm^3 and 0.92 g/cm^3, the cinematic viscosity at 20°C about 8.75 cSt and respectively, 6.41 cSt and the heat value were about 47440 J/g for the first fraction and 50000 J/g for the second one.*

Keywords: *bio-fuel, vegetable oil, and freezing point.*

1. INTRODUCTION

For engines designed to burn diesel fuel, the viscosity of vegetable oil must be lowered to allow for proper atomisation of fuel, otherwise incomplete combustion and carbon build up will ultimately damage the engine. Many enthusiasts refer to vegetable oil used as fuel as **waste vegetable oil** if it is oil that was discarded from a restaurant or **straight vegetable oil** (SVO) to distinguish it from biodiesel.

Periodic petroleum shortages spurred research into vegetable oil as a diesel substitute during the 30s and 40s, and again in the 70s and early 80s when straight vegetable oil enjoyed its highest level of scientific interest. The 1970s also saw the formation of the first commercial enterprise to allow consumers to run SVO in their automobiles.

Academic research into straight vegetable oil fell off sharply in the 80s with falling petroleum prices and greater interest in biodiesel as an option that did not require extensive vehicle modifications.

The basic choices for running diesels on biofuels are:

- ✓ make biodiesel and just use it, no need to convert the engine, or
- ✓ convert the engine so it can be run on SVO - no need to process the fuel.

It's not quite that simple. For instance, if someone wants to use waste vegetable oil, which is often free, it should be processed anyway, though less so than to make biodiesel. And it still might not be very good fuel. The best option is made always in connection with the chemical aspects.

SVO used as diesel fuel represents usually new oil, fresh, uncooked. SVO-systems can be a clean, effective and economical option.

Unlike biodiesel, with SVO you have to modify the engine. The best way is to fit a professional with replacement injectors and glow plugs optimised for vegetable oil, as well as fuel heating. There are some German single-tank SVO systems that use petroleum-diesel, biodiesel or SVO, in any combination. Just start up and go, stop and switch off, like any other car. There are also two-tank SVO systems, which pre-heat the oil to make it thinner. It has to start the engine on ordinary petroleum diesel or biodiesel in one tank and then switch to SVO in the other tank when the vegetable oil is hot enough, and switch back to petroleum- or bio-diesel before stop the engine, or coke up the injectors.

Related to choose the best way for petroleum diesel replacing, a question will be always in actuality: bio-diesel or SVO?

Biodiesel has some clear advantages over SVO: it works in any diesel-engine, without any conversion or modifications to the engine or the fuel system - just put it in and go. It also has better cold-weather properties than SVO (but not as good as petroleum-diesel). Unlike SVO, it's backed by many long-term tests in many countries, including millions of miles on the road.

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Biodiesel is a clean, safe, ready-to-use, alternative fuel, whereas it's fair to say that many SVO systems are still experimental and need further development.

On the other hand, biodiesel can be more expensive, depending how much you make, what you make it from and whether you're comparing it with new oil or used oil (and depending on where you live). And unlike SVO, it has to be processed first.

Anyway many SVO has to process too, especially waste vegetable oil, used, cooked, which many people with SVO systems use because it's cheap or free for the taking. With waste vegetable oil food particles and impurities and water must be removed, and it probably should be de-acidified too. Regularly, during the using processes many chemical and physical transformations lead to many changes in intimate structure of normal triglycerides and their arrangement.

2. EXPERIMENTAL WORK

The interest is to obtain a fuel with good viscosity and low temperature of crystals formation, comparable or better with those of petroleum-diesel.

Like petroleum diesel fuels, bio-fuels clouds when the weather gets cold, filling with little crystals of wax that can clog the fuel filter.

A solution for bio-fuels obtaining, which can be used at all year seasons is proposed. Three types of vegetable oils were used in the experiments: rapeseed oil, sunflower oil, soybean oil and different mixture of them. They were mixed at a specific temperature and normal pressure with different mass ratio of alcohol/ ester/liquid hydrocarbons mixture.

Our option for SVO using in bio-fuel making employable at all seasons involves in fact a blending of compatible compounds. Each chemical compound used plays a specific role in general behaviours of the mixtures.

Experimental Observations. Four alcohol's with small chain of carbons were used: methanol, ethanol, 1-propanol and 1-butanol. Butanol seems to be the best as miscibility with vegetable oil. Ethanol and methanol (in more than 10%(wt) proportion) are completely non-miscible with vegetable oils, even if the temperature was reached next to their boiling point, and a very good agitation was kept. It is possible that changing the proportion (90% alcohol and 10% oil) they are miscible, but this wasn't our interest.

Table I

The main characteristics of used chemical compounds

Compound	Molar mass, [g/mole]	Density, [g/cm^3]	Freezing Point, [°C]	Boiling point, [°C]
Methanol	32	0.792	- 97.0	65.0
Ethanol	46	0.789	- 114.3	78.4
Propanol	60	0.840	- 126.5	97.0
Butanol	74	0.810	- 89.5	117.7
Ethyl acetate	88	0.900	- 83.6	76.0

The distilled products (MOd and HFd) have a large proportion of heavy hydrocarbons (with more than 18 atoms of carbon) with a low cloud point (around 10°C). As a consequence, in the mixtures prepared, the content in distilled should be kept at the most 25%(wt). At higher value, it induces a gelification process.

In these mixtures, the alcohol or the hydrocarbons don't play a solvent role, because they aren't in a proper quantity. These are special mixtures, where the molecules are distributed far enough from each other as much as there are no conditions for crystals formation at low temperature, lower than their own solidification point.

3. RESULTS. DISCUSSIONS

As no all compounds are fully miscible in each other all the mixtures are in fact micro-emulsions; the procedure is not new and it is known that they can improve spray characteristics by explosive vaporisation of a low boiling point constituents in the micelles (Pryde, 1984). Novelty is the blending with combustion improving compounds and the using of distilled mixtures instead of petroleum-diesel.

We've start our researches considering the physical characteristics of tested oils and their methyl esters; in tables II and III are presented these characteristics.

As not all the mixtures were stable in time, at room temperature, in the table IV are shown only those compositions with good results related to phases miscibility, stability in time and good viscosity at low temperature.

The components behaviours observed during preparation induced our own analysis for physical characteristics of involved materials. In the table V the measured physical properties are presented.

The first observation is referring on cinematic viscosity values; at 40°C, the measurements show that the mixtures have a viscosity of 7 – 9 cSt, which is bigger with 2 – 3 unites related to those requested by standard for biodiesel (1.9 – 6 cSt). By the other way, the values are significantly lower then those measured for pure oils. In the figure 1 the variation of mixtures viscosity with temperature can be shown.

For some mixtures the density is slightly reduced related with pure vegetable oil end evidently closer to Diesel value.

All mixtures present a good low heat value, higher than for pure oils but still lower than Diesel.

The cloud point was the characteristic that we've tried to improve in order to obtain by simple processing, bio-fuels employable at all season.

The intention being to develop a technical methodology for bio-fuels making, before blending the established components, the evolution of cloud point for different compositions with were calculated.

Using the thermal transfer and cryoscopy theoretical equations (1) and (2), and MathLAB program for calculations, the evolution of temperature inside the bio-fuel recipients for different thermal conditions and the freezing temperature for different oils mixtures, depending on chemical composition of the blended compounds can be predicted.

For a right interpretation of components influence on cloud point evolution, the same proportion of pure oil has kept, respectively 50% (wt).

In the figures 2 – 4 the curves of cloud point evolution with temperature are shown, for the case of rapeseed oil using. The same curves were obtained for all involved vegetables oils in this research work.

In the case of using butanol, all experimental observations are verified by the estimation values.

Our problems in managing the differences on theoretical aspects and practical facts were principally connected with the oils – alcohol's miscibility. As a matter of fact, the oils are not miscible with methanol and butanol, neither at room temperature, nor at alcohol's boiling point.

Table II

Physical characteristics of vegetable oils [1]

Oil	Cinematic viscosity at 20°C, [cSt]	Cinematic viscosity at 40°C, [cSt]	Density, [kg/m^3]	Acid Value, [mg_{KOH} / g]	Low Heat Value, [kJ/kg]	Cloud Point, [°C]
Rapeseed	96.1	26.8	993	0.022	39700	-5.0
Sunflower	78.9	45.6	953	2.124	39600	-8.0
Soya bean	74.1	35.8	950	0.669	39600	-3.0
Diesel	4 - 5	2.5 – 2.7	840	-	42000 - 44000	-2.2

Table III

Physical characteristics of methyl esters obtained from vegetable oils [2]

Methyl ester from:	Cinematic viscosity at 20°C, [cSt]	Cinematic viscosity at 40°C, [cSt]	Density, [kg/m^3]	Acid Value, [mg_{KOH} / g]	Low Heat Value, [kJ/kg]	Cloud Point, [°C]
Rapeseed	4.06	1.94	956	0.006	40150	-8.0
Sunflower	1.89	1.32	909	0.003		-12.0
Soya bean	1.88	1.11	915	0.001		-7.0
Biodiesel ASTM	-	1.9 – 6.0	-	0.8 max	-	-

Table IV

Composition of mixtures

Mixture		Oil, %(wt)	Alcohol, %(wt)		Ester, %(wt)	MOd, %(wt)	HFd, %(wt)
Rapeseed Oil	ROb1	50	Butanol	15	10	25	-
	ROb2	50		15	10	-	25
	ROp1	50	Propanol	15	10	25	-
	ROp2	50		15	10	-	25
Sunflower Oil	SFO1	50	Butanol	15	10	25	-
	SFO2	50	Propanol	15	10	-	25
Soybean Oil	SO1	50	Butanol	15	10	25	-
	SO2	50	Propanol	15	10	-	25

Table V

Physical characteristics of used vegetable oils and obtained mixture

Vegetable oil / Mixture	Cinematic viscosity at 20°C, [cSt]	Cinematic viscosity at 40°C, [cSt]	Density, [kg/m^3]	Low Heat Value, [kJ/kg]	Cloud Point, [°C]
Rapeseed Oil	73.91	37.00	920	33112	-4.2
Sunflower Oil	73.55	32.6	900	38180	-6.7
Soybean Oil	79.25	28.86	940	37000	-4.5
ROb1	14.47	6.98	857	41322	-18
ROb2	13.37	8.07	875	39356	-16
ROp1	11.45	7.69	943	38213	-12
ROp2	11.90	8.13	873	39643	-12
SFO1	12.51	8.27	943	40195	-16
SFO2	10.57	7.54	965	38988	-16
SO1	13.43	9.26	864	40336	-17
SO2	11.62	7.85	878	40098	-17

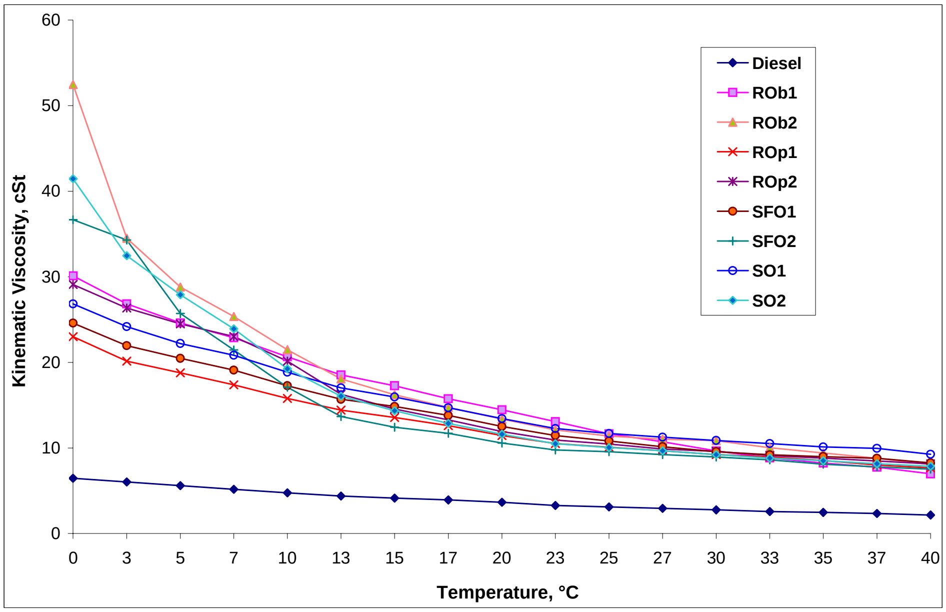

Fig. 1. Viscosity variation with temperature.

By a very good agitation, emulsions non-stable in time have been obtained.

$$\Delta T_{cr} = K_{1cr} \cdot \sum_{i=2}^{k} m_i \qquad (1)$$

$$K_{1cr} = \frac{R T_{0_1}^2 M_1}{1000 \cdot \Delta H_1} \qquad (2)$$

$$m_i = \frac{n_i}{n_1 M_1} \qquad (3)$$

where: K_{1cr} = cryoscopic constant of solvent [K·kg/mole]; m_i = molal concentration of components (no solvent) [mole/kg solvent]; R = universal gas constant [J/kmole/K]; T_{0_1} = solvent cloud point [K]; M_1 = molar mass of solvent [kg/kmole]; ΔH_1 = latent heat of fusion of solvent [J/kg]; n = number of moles; i = number of components; "1" = index for solvent

Any other intervention, as changing the order of components or increasing the temperature of blending process did not improve the stability of these samples.

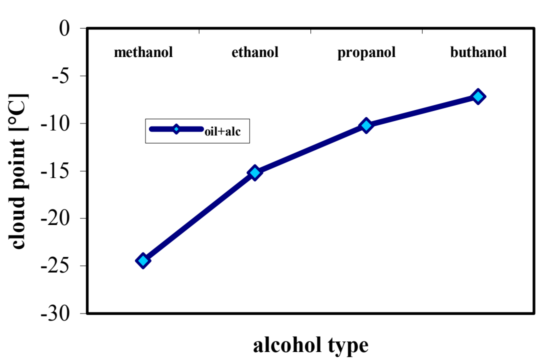

Fig. 2. Cloud point variation with alcohol type, estimated in mixture rapeseed oil + alcohol.

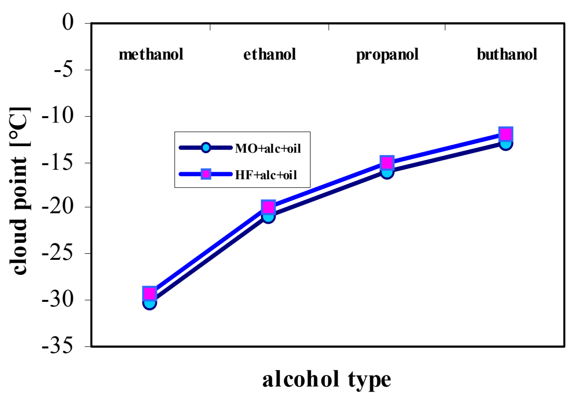

Fig. 3. Cloud point variation with alcohol type, estimated in mixture rapeseed oil + alcohol + + hydrocarbons.

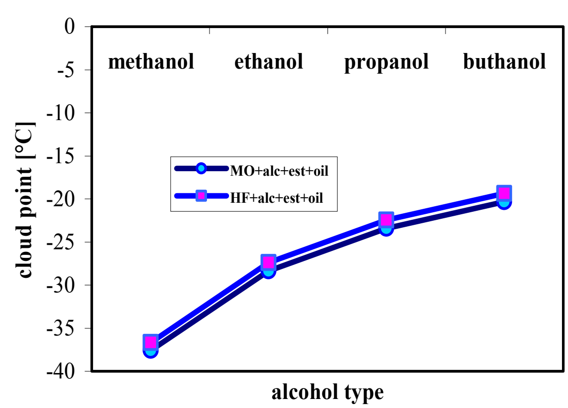

Fig. 4. Cloud point variation with alcohol type, estimated for final mixtures of rapeseed oil.

4. CONCLUSIONS

The presented experimental work was oriented on bio-fuel making, starting on different types of vegetable oils, largely used for biodiesel making. Our aims for initiate this study are given by the experimental data already achieved by engine running with bio-fuels obtained from animal fats, which were presented in another publication, [3].

For the situations when other processing ways are not preferred or are not possible, a liquid fuel with good physical characteristics and employable also at low temperatures can be obtained.

The benefice of proposed method is that the process is in fact just a mixing of some components in a right proportion, at a specific temperature depending directly on components characteristics. Part of these components are products obtained by some wastes materials processing (i.g. used motor oil, heavy fuel).

It was found that the esters are playing an important role, not as a solvent but as reducing viscosity agent and evidently it have a good influence on cloud point value.

The engine test will be performed in the next future in order to describe the combustion characteristics and emissions level and eventually to adapt the chemical composition of bio-fuels prepared.

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