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CONTRIBUTIONS TO OBTAINING BIODIESEL FROM BIOMASS WASTES

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Abstract: Vegetable oils and their derivatives (especially methyl esters), commonly referred to as biodiesel, are important candidates as alternative diesel fuels. They are technically competitive and offer technical advantages compared to conventional diesel fuel. Besides being a renewable and domestic resource, biodiesel reduces most emissions while engine performance and fuel economy are nearly identical compared to conventional fuels. The paper presents contributions on synthesis and characterization of biodiesel from vegetable waste of sunflower, maize and soybean oils and used oil (cooking oil).

Keywords: biodiesel, sunflower, maize, soybean, used oil.

1. INTRODUCTION

The use of biofuels, as a renewable source of energy has become increasingly important in the last few years. More in particular, biofuels for transport have the potential to displace a substantial amount of petroleum around the world.

The continuous depletion of global fossil fuel energy has generated an increasing need for alternative sources of energy. Biomass can be considered as a renewable energy source, and can be converted into either direct energy or energy-carrier compounds by direct combustion, anaerobic digestion systems, destructive distillation, gasification, chemical and biochemical hydrolysis.

The estimated resources of today, while we concentrate on a liquid energy carrier like mineral oil, have a world-wide distribution which implies possible difficulties in future besides the fact that they are limited, while yearly consumption still rises. In this case the principal liquid energy sources are the vegetable oil product especially the rapeseed oil methyl ester known under biodiesel name, which was the first type of biodiesel fuel produced commercially.

Biodiesel, actually an alcohol ester of vegetable oil, can be made from most any plant-derived oil. Research has involved the following types of oils: rapeseed oil, canola oil, soybean oil, hydrogenated soybean oil and tallow oil.

Rapeseed oil was the first type of vegetable oil used for transesterification and rather by chance this oil is highly suitable production of quality biodiesel. Rapeseed oil has a content of approx. 60% monosaturated oleic fatty acid and approx 6% saturated fatty acids and shows both good stability and winter operability. New developed varieties (like LZ 7632) have higher levels of up to 87 % oleic fatty acid, this type of rapeseed is still by far the biggest source of feedstock for biodiesel production and has become more interesting as rapeseed breeders have succeeded in improving yield levels of up to 2.9 to oil./ ha [1, 2, 4].

Biodiesel has several distinct advantages [8, 10] compared with petrodiesel: (a) derivation from a renewable source, thus reducing the dependence on and preserving petroleum; (b) reduction of most exhaust emissions; (c) biodegradability; (d) higher flash point, leading to safer handling and storage; (e) excellent lubricity, a fact that is steadily gaining importance with the advent of low-sulphur petrodiesel fuels, which have greatly reduced lubricity. In addition to ignition quality as expressed by the cetane scale, several other properties are important for determining the suitability of biodiesel as a fuel. Heat of combustion, cloud point, (kinematic) viscosity, oxidative stability are among the most important of these properties [2, 5].

The principal problems with using unmodified oils in diesel are that residuals, such as waxes and gums, clog the fuel lines, high viscosity causes poor atomization and therefore combustion, and polymerization of unsaturated components in the combustion chamber causes deposits on the cylinders. Therefore, unless degummed filtered oils are used, some form of oil modification is required.

Four methods to reduce the high viscosity of vegetable oils to enable their use in common diesel engines without operational problems such as engine deposits have been investigated:

- (a) blending with petrodiesel

- (b) pyrolysis
- (c) microemulsification or cosolvent blending
- (d) transesterification.

Among these four methods only the transesterification leads to the products commonly known as biodiesel [1].

The most commonly prepared esters are methyl esters, largely because methanol is the least expensive alcohol, although there are some exceptions in some countries, for example, in Brasil where ethanol is less expensive, ethyl esters are used as fuel. In addition to methanol and ethanol, esters of vegetable oils and animal fats with other low molecular weight alcohols were investigated for production and their biodiesel properties [4, 6, 11].

In addition to vegetable oils and animal fats, other materials such as used frying oils can be also suitable for biodiesel production. Generally, transesterification can proceed by base or acid catalysis. However, in homogeneous catalysis, alkali catalysis (sodium or potassium hydroxide, or the corresponding alkoxide) is a much rapid process than acid catalysis. For the transesterification to give maximum yield, the alcohol should be free of moisture and the free fatty acids content of the oil should be <0.5% [10]. The absence of moisture in the transesterification reaction is important because hydrolysis of the formed alkyl esters to free fatty acids can occur.

Similarly, because triacylglycerols are also esters, the reaction of the triacylglycerol with water can form free fatty acids. At 32°C, transesterification was 99% complete in 4 hours when using an alkaline catalyst (NaOH, NaOMe) [7, 10]. At temperature over 60°C, using an alcohol:oil molar ratio of at least 6:1 and fully refined oils, the reaction was complete in 1 h, yielding methyl, ethyl, or butyl esters.

Although the crude oil could be transesterified, ester yields were reduced because of gums and extraneous material present in the crude oils.

These parameters (60°C reaction temperature and 6:1 methanol:oil molar ratio) have become a standard for methanol-based transesterification. Other alcohols (ethanol and butanol) require higher temperatures (75°C and 114°C, respectively) for optimum conversion.

Alkoxides in solution with the corresponding alcohols (made either by reacting the metal directly with alcohol or by electrolysis of salts and subsequent reaction with alcohol) have the advantage over hydrolysis than the water-forming reaction cannot occur in the reaction and system remains as water free as possible. This reaction, however, is the one forming the transesterification-causing alkoxide when using NaOH or KOH as catalysts.

In principle, transesterification is a reversible reaction, although in the production of vegetable oil alkyl esters, i.e. biodiesel, the back reaction does not occur or is negligible because the glycerol formed is not miscible with the product, leading to a two-phase system.

A reaction in which all three positions of the triacylglycerol react virtually simultaneously to give three alkyl ester molecules and glycerol originally proposed [6] as part of the forward reaction was shown to be unlikely, that second-order kinetics are not followed, and that miscibility phenomena play a significant role. The reason is that the vegetable oil starting material and methanol are not well miscible.

The addition of cosolvents such as tetrahydrofuran or methyl tert-butyl ether to the methanolysis reaction was reported to significantly accelerate the methanolysis of vegetable oils as a result of solubilizing methanol in the oil to a rate comparable to that of the faster butanolysis [6, 7]. This is to overcome the limited miscibility of alcohol and oil at the early stage, creating a single phase.

Other possibilities for accelerating the transesterification are microwave, or ultrasonic irradiation. The main aim of the transesterification is to get a lower viscosity (from 70 for plant oils to 4,5 mm²/sec at 40 °C for their methyl esters), and thus gets a diesel fuel with the following properties: cetane number 58; no sulphur, no aromatics; best emissions with oxidation catalysts; biodegradable, non-toxic; high oxygen content (11%); winter operability -22 °C [5].

Biodiesel is a clean burning fuel, which runs in any unmodified diesel engine. This fuel is an environmentally friendly alternative to the higher emission petroleum diesel used in large transport vehicles. In addition, biodiesel can be made from renewable resources such as vegetable oil or animal fat and from used cooking oil, an abundant waste product.

2. EXPERIMENTAL

Our research was focused on establishing a laboratory method for obtaining biodiesel from maize oil, sunflower oil, soybean oil and used oil (cooking oil). The synthesis of biodiesel was performed by transesterification reaction of triacylglycerols from the above mentioned oils with methanol in basic catalysis (sodium methoxide).

As, both characterization methods of raw materials and monitoring the synthesis process, the following parameters have been investigated: (a) the acidity index; (b) the iodine number; (c) the peroxide number; (d) the saponification number.

Materials and methods

The solvents (commercial products, Chimopar) used to solve the oils were: ethanol, ethyl ether, chloroform and acetic acid. The solutions of: KOH (in ethanol) 0.1n, KI 10%, Na₂S₂O₃ 0.01n, starch, phenolphthalein were prepared in laboratory. The reagents used: NaOH, Hanus solution (IBr), KJ, Na₂S₂O₃ were commercial products (Chimopar).

a) Determination of the acidity index (I_a). A sample containing 1 g of oil (lipid) was dissolved into 10 mL mixture of ethanol and ethyl ether. The solution was titrated, in presence of phenolphthalein [4].

b) Determination of the iodine number (I_i). A sample containing 1 g of oil (lipid) was dissolved into 10 mL of chloroform. 15 mL of Hanus solution were added. In parallel a blank sample was prepared. Each Erlenmeyer containing the

two samples was gently mixed and let stand in dark, at room temperature for 30 minutes. After 30 minutes, in both Erlenmeyer, 15 mL of KI solution 10% and 25 mL of distilled water were added and the reaction mixture was titrated with $\text{Na}_2\text{S}_2\text{O}_3$ 0.01N, in presence of chemical indicator starch [4].

c) *Determination of peroxide number (I_p)*. A sample containing 1 g of oil (lipid) was dissolved into 20 mL of mixture of acetic acid and chloroform 1:2 and 1 mL of saturated KI solution was added. In parallel a blank sample was prepared. Each Erlenmeyer containing the two samples was let to stand in dark, for 3 minutes at room temperature. After that, both samples were titrated with $\text{Na}_2\text{S}_2\text{O}_3$ 0.01N, in presence of chemical indicator starch [4].

d) *Determination of the saponification number (I_s)*. A sample containing 1 g of oil (lipid) treated with 25 mL of KOH 0.5 N solution was submitted to boil for 30 minutes. In parallel a blank sample was prepared and boiled the same period of time. The two samples were titrated with HCl 0.5 N solution in presence of phenolphthalein chemical indicator [4].

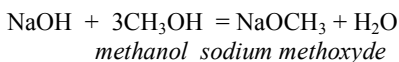
e) *Determination of the viscosity* was performed with Oswald viscosimeter. The determination consists on measuring (with the stop-watch) the flowing time for a liquid situated into an established volume [7, 10].

f) *The superficial tension* was determined by stalagmometric method [9].

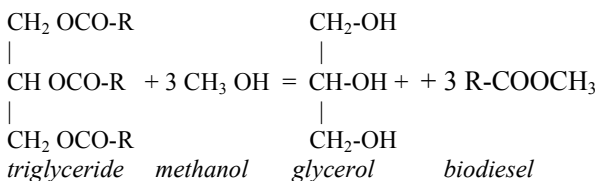
g) *The Flash Point* was determined by Pensky-Martens apparatus [10, 11].

The synthesis of biodiesel

The biodiesel synthesis was performed into a 250 mL glass reactor, equipped with a mechanical agitation system and control temperature system. As preliminary stage, the synthesis of a basic catalyst by mixing methanol with NaOH solution (reaction time 10-20 minutes) was performed, conforming with the following reaction:



The transesterification reaction of maize, sunflower and soybean oils with sodium methoxyde performed under continuous stirring, at 50°C , for 50-70 minutes, as following:



The reaction mixture was poured in a separating funnel, when two layers were separated. The bottom layer, containing glycerol, unreacted methanol, water traces and salts, the residual methanol was distilled. The glycerin, obtained as a secondary product, can be utilized as raw material in cosmetics industry (as hydratation agent) or for obtaining the glycerin soap. The separated residual methanol can be recycled as raw material for the next processes.

3. RESULTS AND DISCUSSIONS

The characteristics of the oils submitted to the transesterification reaction with methanol are presented in Table 1.

Table 1. The characteristics of the oils used for transesterification

Oil	Acidity index	Iodine number	Peroxide number	Saponification number
Sunflower	1.1017	12.5631	0.0085	123.4288
Maize	1.6075	12.0550	0.0086	161.2990
Soybean	1.1017	11.1672	0.0098	140.2600
Used oil	0.9590	10.1520	0.0172	110.8721

It can be observed that the maize oil presents a greater saponification number and a higher iodine number, which can be correlated with the presence of monosaturated oleic fatty acid in his chemical structure.

The saponification number was also used for monitoring the transesterification process. The decreasing of the saponification number in time can be correlated with the progress of transesterification reaction.

It can be observed that higher saponification number was obtained for the biodiesel synthesised from the used oil due to the higher level of transesterification reaction of the used oil (cooking oil) with methanol.

The characteristics (the acidity index, iodine number, peroxide number, saponification number) of the biodiesel obtained by transesterification reaction with methanol of sunflower oil, maize oil, soybean oil and used oil are presented in Figures 1- 4 together with the same parameters determined for oils.

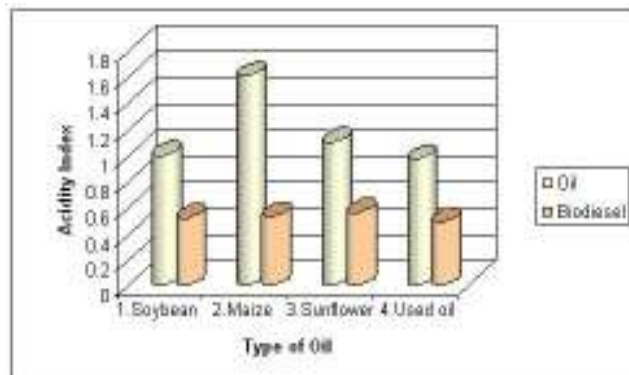


Figure 1. The acidity index of oils and biodiesel

The acidity index gives information related to the intensity of lipids biodegradation process. In the chart above, there are presented the experimental values for different oils and biodiesel obtained by transesterification reaction of these oils. We can see that the acidity index is lower for the biodiesel compared with its corresponding oils, because after during the transesterification free carboxylic groups from oils disappeared and ethyl esters of fatty acid (biodiesel) are formed.

Biodiesel can be also characterized by iodine number. Iodine reacts quantitatively with double bonds and the degree of unsaturation (double bonds which react with iodine compounds) can be estimated by the iodine number. A high level of unsaturation gives the oil a high iodine number and low oxidative stability. The higher the iodine number, the more unsaturated fatty acid bonds are present in a fat.

The decreasing of iodine number for biodiesel comparing with iodine number for oils can be correlated to some oxidation reactions during the synthesis of biodiesel by transesterification reaction, generating more double bonds which added larger quantities of iodine solution.

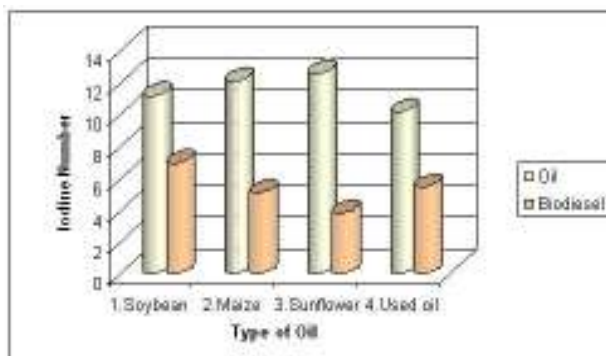


Figure 2. The iodine number of oils and biodiesel

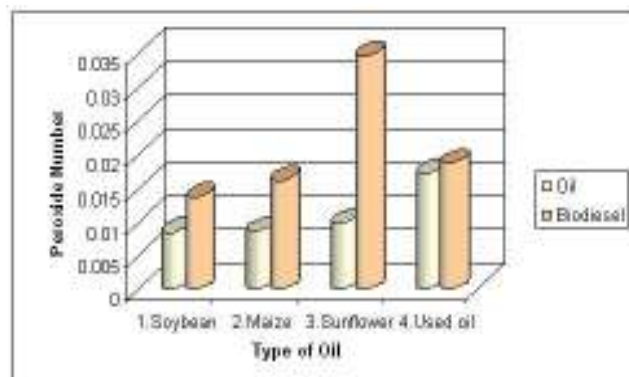


Figure 3. The peroxide number of oils and biodiesel

The increasing of peroxide number for biodiesel comparing with peroxide number for oils can be also correlated with some oxidation reactions during the synthesis of biodiesel by transesterification reaction, generating more carbon-carbon double bonds very sensitive to peroxide compounds formation, evidenced by peroxide number analysis.

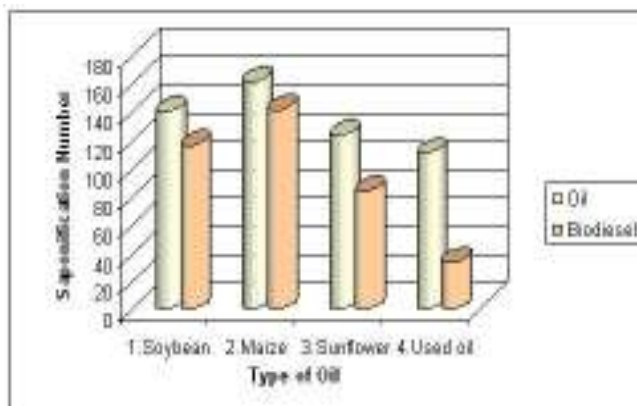


Figure 4. The saponification number of the oils and biodiesel

The determination of unsaponifiable matter must not be confused with the saponification number of a fat. The saponification number represents the number of milligrams of potassium hydroxide required to convert one gram of the fat completely into glycerin and potassium soap. It gives information concerning the character of the fatty acids of the fat and in particular concerning the solubility of their soaps in water. The higher the saponification number of a fat free from moisture and unsaponifiable matter, the more soluble the soap that can be made from it.

Table 2. The physical-chemical characteristics of the biodiesel obtained

Characteristic	Biodiesel STAS EN 14214	Biodiesel (sunflower oil)	Biodiesel (maize oil)	Biodiesel (soybean oil)	Biodiesel (used oil)
Density, g/cm ³	0.875-0,900	0.820	0.835	0.840	0.830
Viscosity, cP	4-6	4.98	5.47	5.55	5.50
Superficial Tension, cP	0.028	0.020	0.025	0.030	0.025
Flash Point, Pensky-Martens, °C	Limit (min) 100	168	165	175	180

Saponification number gives us the information regarding the fat molecular mass: the higher the saponification number, the smaller the molecular mass of the fat, and vice versa.

The saponification number of the synthesized biodiesel decrease during advancing the biodiesel synthesis, in order: used oil biodiesel > sunflower oil biodiesel > maize oil biodiesel > soybean oil biodiesel.

The physical-chemical characteristics of the biodiesel obtained by transesterification with methanol of sunflower oil, maize oil, soybean oil and used oil (cooking oil) are presented in the table 2.

4. CONCLUSION

The scarcity of known petroleum reserves will make renewable energy resources more attractive. The most feasible way to meet this growing demand is by utilizing alternative fuels. The biggest advantage that biodiesel has over gasoline and petroleum diesel is its environmental friendliness. Biodiesel burns similar to petroleum diesel as it concerns regulated pollutants. On the other hand, biodiesel probably has better efficiency than gasoline. One such fuel for compression-ignition engines that exhibit great potential is biodiesel. Diesel fuel can also be replaced by biodiesel made from vegetable oils. Biodiesel is now mainly being produced from soybean, rapeseed and palm oils.

Economic benefits of a biodiesel industry would include value added to the feedstock, an increased number of rural manufacturing jobs, an increased income taxes and investments in plant and equipment. The production and utilization of biodiesel is facilitated firstly through the agricultural policy of subsidizing the cultivation of non-food crops.

The European Union accounted for nearly 89% of all biodiesel production worldwide in 2005. By 2010, the United States [9] is expected to become the world's largest single biodiesel market, accounting for roughly 18% of world biodiesel consumption, followed by Germany.

Our research aimed to establish simple methods, both for monitoring the synthesis of biodiesel by transesterification of sunflower, maize, soybean and cooking oils with methanol, and for characterization of oils and biodiesel obtained. The characteristics of the four types of biodiesel obtained are comparable with those of the STAS values, as can be seen from the data presented in Table 2. It is also encouraging that biodiesel obtained from used oil (cooking oil) presents good physical-chemical properties enlarging the possibilities for better recycling the vegetable wastes as biofuels.

The EU Commission intends [2, 3] to develop a 5% market share for biofuels up to the year 2010 and recommends time-limited exemptions or reductions of taxes on biofuels to 0-10% of normal amounts for the first 10 years, then to increase stepwise.

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