

New Technology for Bio-Diesel Production

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Abstract: The increased demand for liquid petrol fuels, as well as their higher and higher price, the non-uniform allocation of petroleum reserves on the globe, corroborated with the restrictions imposed by environment conservation, have an impulse to the scientific researches regarding new unconventional energy sources and alternative fuels such as bio-diesel. Bio-diesel has been gaining worldwide popularity as an alternative energy source because it is non toxic, biodegradable and non flammable. The classic ways of producing bio-diesel have certain difficulties and disadvantages that determined researches for finding alternative technologies for its production. Thus, a new technology for second generation bio-diesel production has been proposed, that starts with the catalytic treatment of triglycerides contained in vegetable oils and animal fats with hydrogen enriched gas, obtaining fatty acids and glycerin. The hydrogen enriched gas is a gas obtained by the electrolysis of water. For obtaining the final product - "reformulated bio-diesel", the catalytic hydrogenation is continued until reaching fat alcohols and superior alkanes. The enriched bio-diesel thus obtained will be tested with regard to the physical and chemical characteristics, the caloric power and cetane number and will be also tested on an engine, on a specialized stand.

Keywords: Bio-diesel, hydrogenation, acids, fat alcohols, alkanes

1. Introduction

The more and more present concern regarding the planet's pollution level lead, among others, to the elaboration and implementation of the standards on the pollution emissions and the norms on the protocol for the report of gas emission with greenhouse effect. The ratification of the Kyoto Protocol by Romania, along with the adhesion of our country to the EU, imposes, among other, the re-dimensioning of the energy production and consumption field strategy. Therefore, the development strategy of the different systems for the use of energy sources is established taking into consideration the conservation/improvement of the environment quality, as well as their social and economic impact.

The increased demand for liquid petrol fuels, as well as their higher and higher price, the non-uniform allocation of petroleum reserves on the globe, corroborated with the restrictions imposed by environment conservation, have an impulse to the scientific researches regarding new unconventional energy sources and alternative fuels such as bio-diesel. The bio-diesel became very popular in the last decade as an ecological fuel obtained from recyclable sources, the so-called "domestic" such as vegetable oil and animal fat. In the present, bio-diesel is used on a large scale

in road and water transport, as well as for construction equipment and even for home heating devices.

2. General aspects regarding bio-diesel

In present, bio-diesel is obtained by the chemical conversion of agricultural lipids and a primary alcohol in alkyl esters of the fat acids. Glycerin is obtained as sub-product in the classical process used in present on a large scale that is the catalytic methyl-transesterification in the presence of a base or of an acid, of triglycerides constituent of vegetable oils or of animal fats [3]. From the chemical point of view, bio-diesel is an oxygenated organic compound which can be used in pure state, known as B100, or in compound with diesel, B_n as mixture of B100 and diesel (B₂₀ for example contains 20% pure bio-diesel and the rest diesel). In these mixtures, bio-diesel is considered as "oxygenated compound" which "releases" oxygen in fuel injected dense areas in the burning chamber, so as "soot pyrolysis distillation" is considerably reduced and oxidation burning of fuel molecules start earlier. It has to be mentioned that even since 1998 the experimental researches on a Cummins engine emphasized that when the mass content of Oxygen in fuels is at 30%, particle emission at exhaust gas evacuation practically disappear.

Bio-diesel burning in Diesel engine, has real benefits [1] such as: it can be used in any unmodified conventional engine in pure state, or in a mixture with diesel; has better lubricating properties than diesel, its use increase the operating life of the engines, it is recommended the use on a large scale in mixture with new "dry" diesels such as Euro 5, etc which have low lubricating properties due to the absence of sulfur; has a higher ignition temperature than diesel, and therefore is safer to transport; specific consumption, nominal power and maximum couple are almost not affected by the use of bio-diesel, the only "inconvenience" is the characteristic smell "fried potatoes oil"; the oxygen content has an important role in the transformation of oils and fats in clean diesel fuels; the constituent esters of bio-diesel, with more reduced viscosity than vegetal oils and fats, offer "non-altered" injection quality compared to the diesel. One can say that they improve the injection process ensuring a better atomization of fuel in the burning chamber; bio-diesel reduce with 90% the risk of cancer, according to Ames Mutagenicity Test; bio-diesel is a "domestic", renewable energy source; is biodegradable. Also, bio-diesel deriving from domestic renewable sources, the petroleum dependency is reduced, thus contributing to the preservation of petroleum reserves. The properties of classical bio-diesel obtained from rapeseed oil are presented in Table 1, together with those of classic diesel fuel.

TABLE 1. Comparative properties of diesel / classical bio-diesel obtained from rapeseed oil.

Properties	Measure unit	Diesel	Classical bio-diesel from rapeseed oil (RME)
Density at 15°C	g/ml	0,820...0,845	0,880
Viscosity at 40 °C	mm ² /s	2,0...4,5	8,5 la 15 °C
Flammability	°C	Over 55 °C	140 °C
Filterability	°C	Max. -20 °C	- 8 °C
Carbon residuum	mg/kg	<0.03	-
Soot	%	Max 0,01	Slight traces
Sulfur	ppm	<50	<25
Cetane number		48,51	>53
Inferior caloric power	MJ/kg	42,5	37,5
Carbon	%	86,7	77,5
Oxygen	%	0	10,7
Minimum air	kg/kg	14,5	12,5
Boiling range	°C	180 -330	350-360

The main drawbacks are: the slight increase of NO_x emissions; the light increase in consumption (calculated on the basis of 10% lower caloric power for B100); during the winter time the bio-diesel fuel engine start with difficulty, the use of fuel antifreeze is necessary; bio-diesel is more expensive than diesel.

As detailed presented in the specialty literature on NO_x emissions, the oxygenated fuels have an inferior caloric power compared to non-oxygenated petroleum fuels, and therefore in the burning chamber there are developed lower temperatures of the stoichiometric adiabatic flame [6]. This should lead to the decrease of NO_x emissions. But, the research on the engine stand, on constructive and adjustment unmodified diesel engines supplied with oxygenated fuels demonstrated that, rarely, the NO_x emissions are reduced and that most times they increase. This is explained by that the testes are carried out on an injection system unmodified at the same setting of the advance at injection. It is a known fact that by increasing the oxygen content in the fuel molecular chain is reduced the delay in self-ignition and therefore the advance at ignition should be placed later, as close as possible to the inferior dead point. The burning start earlier and this leads to an increased maximum burning pressure and maximum temperature, which finally is reflected in an increase of NO_x emission level.

3. New technology for bio-diesel production – brief description

The classic ways of producing bio-diesel have certain difficulties, mainly because they require the initial preparation of the raw materials (the biomass made from oily seeds or from oily and animal waste from the meat industry and/or burned oils resulted in the food industry or from restaurant chains), they require the removal of the catalyst by neutralization and the eventual preparation of the salts from the esters, which has a high level of difficulty and the recovery of the glycerin as a sub-product is a difficult process especially when result large quantities of inorganic materials that have to be eliminated. Furthermore, transesterification can be complicated when the raw materials contain high quantities of free acids, so that unwanted secondary chemical reactions can be obtained.

This is why several European institutions having independent approaches have developed and are developing research activities in the field of second generation bio-fuels and their obtaining technologies. Complex research programs for the production of second generation bio-diesel, using a hydrogen enriched gas treatment of the fat acids contained in seed oil and in animal fat have began. Vegetable oils and animal fats are mainly converted into n-alkane type hydrocarbons, C_nH_{2n+2}, with an increased caloric power, and superior cetane numbers both to diesel as well as to classic bio-diesel (first generation). The process is schematically represented in Fig. 1.

The proposed technology for producing a "reformulated bio-diesel" starts with the catalytic treatment of triglycerides contained in vegetable oils and animal fats with hydrogen enriched gas, obtaining fatty acids and glycerin.

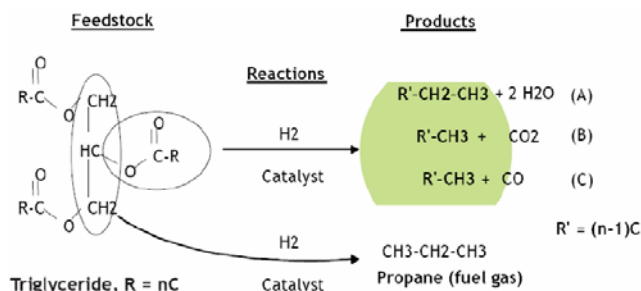


Figure 1. Schematic diagram for catalytic hydrogenation of vegetable oils and fats.

In literature there are many studies for the catalytic hydrogenation of vegetable oils and fats [2, 4, 5]. Within the technology for obtaining the "reformulated bio-diesel" the catalytic hydrogenation of the previously obtained fat acids is continued until reaching fat alcohols and superior alkanes. The hydrogen enriched gas is a gas obtained by the electrolysis of water, through a special technological process. It is known that in a diesel fuel the increase of the ratio between the number of hydrogen and carbon atoms, H/C from the molecular chain, by the increase of the C_nH_{2n+2} content leads to the increase of the cetane number only with a slight reduction of the smoke intensity. An ideal diesel fuel would be that has the atomic H/C ratio around a value of 2,5 and O/C around a value of 0,5. A reformulated second generation diesel bio-fuel should be situated in the area marked in Fig. 2.

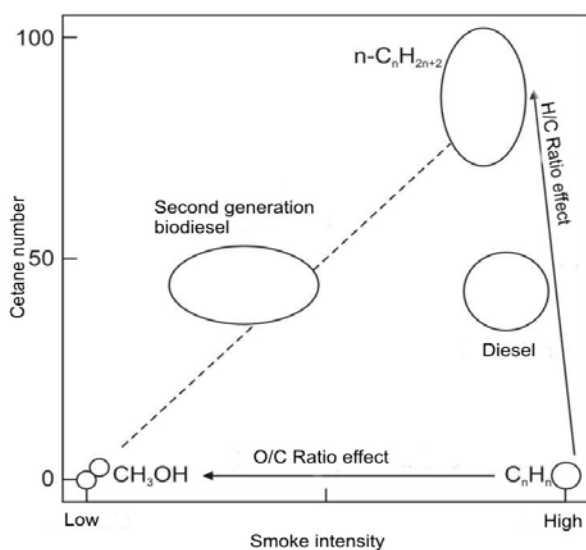


Figure 2. Distribution area for main properties of reformulated second generation bio-diesel

First experiments showed that special attention must be paid for the energetic consumptions optimization of the stabilized continuous production process of the hydrogen enriched gas at flows over $10m^3$ per hour. At this time the hydrogen rich has producing generators work in "batches" of 1,5-2 m^3 /hour, while for the proposed technological processes, the continuous production of the hydrogen enriched gas at flows over $10 m^3$ /hour is necessary. Several

catalytic agent types shall be tested, and each time, there shall be defined the parameters to be monitored in view of automatically managing the technological processes at the pilot level and at the industrial scale level. The generator shall be continuously supplied with water, and it shall be provided with a system to measure/filter water in the electrolyte in view of maintaining the electrolyte concentration and quality in quasi – constant ratios. The energetic consumption triggered by the electrolysis and the heat discharge out of the system shall be optimized depending on the operational requests (flow, pressure, humidity, etc.) set during the lab phase both for the hydro-cracking process and for the catalytic hydrogenation process, as well.

The enriched bio-diesel thus obtained will be tested with regard to the physical and chemical characteristics, the caloric power and cetane number and will be also tested on an engine, on a specialized stand. Once the optimal technological solution is established, a testing program regarding the performances of the poly-cylindrical engine will be carried out.

4. Conclusions

The development of the proposed technology and the obtaining of second generation enriched bio-fuel will represent the transformation of researches into products with market demand, taking into consideration the efforts of EU to align to the requests of the Kyoto Agreement regarding the reduction with 8% of the gaseous emissions that contribute to the production of the greenhouse effect until 2008-2012 and with 1% annually until 2020.

To achieve a new technology to obtain a second generation bio-fuel by using an enriching catalytic treatment with hydrogen enriched gas obtained, by electrolysis, from water, also corresponds to the pre-competitive and application research policies in Romania, regarding the increase of the use level of non-polluting, oxygenated fuels, corroborated with the use of hydrogen at a significant level.

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