UDC 541.121:621.391.

PRODUCTION OF BIODIESEL USING SUPERCRITICAL FLUIDS TECHNOLOGY

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The use of renewable energy sources contributes to the development of mechanisms of technology to save traditional energy carriers. Research into present-day method, particularly, the use of technology of supercritical fluids for production of biodiesel fuel gains an offing for large-scale development of industrial production of biodiesel. Introduction of biodiesel production may have a positive effect on economic and ecological development of the country.
Keywords: *biodiesel, Rapeseed oil, cooking oils, supercritical fluids technology.*

INTRODUCTION

Biodiesel is mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats though the process of esterification. The name "Biodiesel" has been given since it is a clean burning alternative fuel, made from natural vegetable oils, and/or animal fats, i.e. bio resources. Biodiesel is a high quality fuel which can be used in any segment of industry where petro-diesel is used, including the internal combustion engines.

Development of biodiesel industry can contribute to the growing national GDP and significantly improve the country's negative export import balance; it will create new businesses and new jobs. Since biodiesel is based on local bio resources, biodiesel can give a new impulse to agribusiness development as well. As locally made and based on local renewable resources, biodiesel reduces dependence on imported (foreign) petroleum and thus strengthens the country's energy and economic independence.

The greatest advantage of biodiesel is that it is an eco-friendly fuel. Biodiesel is renewable and sustainable and can significantly reduce danger of an environmental disaster. Biodegradability in both soil and water is another important advantage of biodiesel, some 89 % of the carbon containing in biodiesel will be biodegraded in just 28 days. Biodiesel can sharply reduce - up to 85% - emissions of Polycyclic Aromatic Hydrocarbons, which are identified as carcinogenic compounds.

The best raw materials for manufacturing biodiesel is oil obtained from Rapeseeds (Latin: *Brassica napus*), the seeds of which contain 32-34% of oil. Alongside with oil crops, such as rapeseeds, soybeans etc., biodiesel can be derived from the used cooking oil as well, thus bringing double ecological benefit: the used cooking oil, which actually is a sort of liquid waste, will not contaminate any more the environment, but will be collected and turned into the alternative, eco-friendly fuel – biodiesel.

In 2015, Georgia has submitted its Intended National Determined Contribution (INDC) to the UN Climate Change Conference and committed to reduce GHG emissions by 15% below the Business as Usual (BAU) by 2030, Georgia also signed the Paris Climate Agreement in 2016, therefore the country has taken obligations to reduce GHG emissions and develop renewable, eco-friendly energies and by launching and developing biodiesel Georgia will meet these obligations and responsibilities.

In 2012-2015, a pilot project titled "Biodiesel in Georgia" started at Ilia State University [1]. A new lab for producing biodiesel was launched and today it is fully operational. The lab can produce up to 0.5 tons of biodiesel daily. Having produced biofuel from Rapeseeds, Ilia State University also developed agro-economical calculations and recommendations for Georgian agriculture sector to create Rapeseed plantations in eastern

Georgia for receiving oil and ultimately producing biodiesel. The project of Ilia State University has theoretically proven and practically demonstrated that Georgia can start production of its alternative, renewable eco-friendly fuel – biodiesel and bring economic and ecological benefits.

The first batch of biodiesel at Ilia State University was obtained from the used cooking oil which was collected from the local fast-foods. The oil was cleaned from mechanical mixtures, filtered and then through the process of esterification turned into biodiesel. The newly received fuel was tested in both vehicles and the labs. Chromatographic analysis of the B100 fuel revealed the following substances: the acids of hexane, octane, nonane, decane, and the mono methyl esters. The test showed that biodiesel B100 produced in the lab of Ilia State University met the existed standards defined as ASTM D 6751. The analysis of biodiesel obtained from both plant oil and the secondary cooking oil, have shown that the characteristics of biodiesel are quite similar to those of the conventional, petroleum based diesel fuel.

Biodiesel can be blended. The blend **B20** (i.e. mixture of 20% biodiesel with 80% petro-diesel) improves the parameters of the fuel and meets better the demands in terms of emissions control and what is most important, B20 does not require any engine modification and can be used in almost every type of vehicles, including the municipality buses, i.e. public transport. As per B100, which is a pure biodiesel, it can be successfully used in any tracks and tractors and other farming machinery with diesel engines.

RESULTS AND THEIR DISCUSSIONS

Since biodiesel is intended to be used in internal combustion engines, the physical and chemical parameters and characteristics of the blend B20 and pure biodiesel B100 have carefully been analyzed and compared to those of a conventional petroleum diesel fuel. Each character has been studied according to existing standards. The results are presented in the Table 1.

Table 1. Chemical and physical characteristics of biodiesel fuels B100, B20 and petroleum diesel.

PROPERTY	Biodiesel **B100**	Biodiesel **B 20**	Diesel fuel from "SOCAR"
Density at 15^{0}C, kg/m^3	884,0	848,0	834,0
Density ^{0}API	28,56	35,36	38,16
Viscosity, mm^2/s at 40^{0}C	5,2	3,3	2, 0
Flash point, ^{0}C	120	64	56
Acid number, mg KOH/g	0,015	0,0069	0,0048
Cetane Number	51		48
Sulfur content, mg/kg	-	5	10
Ash content , %	0,021	0,0091	0,0155
Polycyclic aromatic hydrocarbons , %	-	5	6
Carbon residue (on 10% residue), %	0,4	0,28	0,3
Copper strip Corrosion, (3 hours 50^{0}C)	№3	№2	№1,5
Corrosion resistance, g/m^3	6	6	6
Content of fatty acids and methyl ester, %	5	5	5
Total contamination, mg/kg	-	-	20,5
Distillation			
50%	270^{0}C	260^{0}C	240^{0}C
96%	300^{0}C	305^{0}C	295^{0}C

The physical and chemical parameters of biodiesel have been analyzed using SPECTRUM Version 10.4.2.PerkinElmer. Fig. 1 and 2 show the spectrum of B100, B20 and petroleum diesel, where the functional groups of the compounds have been identified.

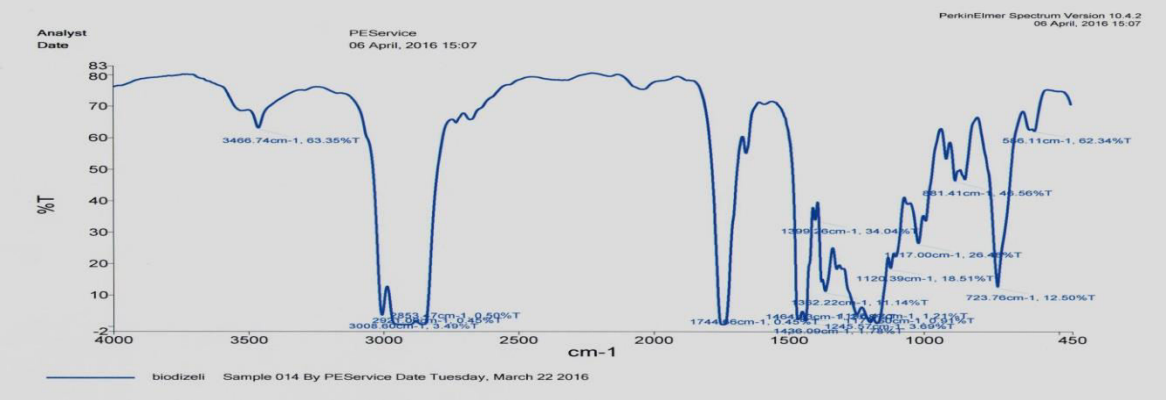

Fig 1. Biodiesel B100 spectrum

The composition of fatty acids in **B100** and **B20** were defined by using a liquid chromatographer and the functional groups by Spectrum Two spectrometer. The conducted analyses have clearly demonstrated that the physical and chemical parameters of both B100 and B20 were within the standards of EN 14214, ASTM D6751 and EN 590 [2].

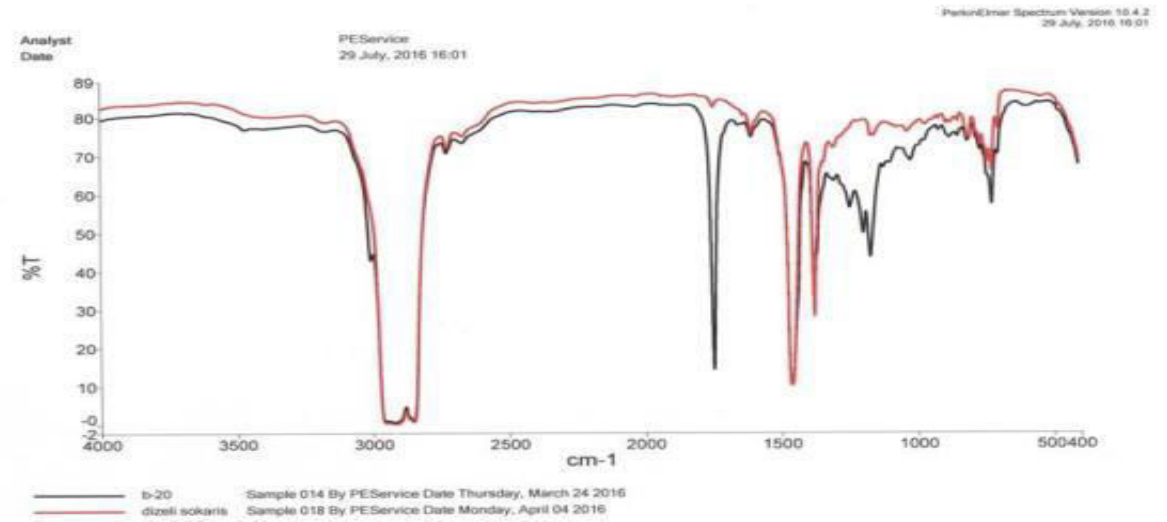

Fig 2. Petroleum diesel fuel and B20 biofuel spectrums

Biodiesel fuel B100 is not toxic and easily biodegradable, it is a good lubricant too. Regarding reduction of harmful emissions, biodiesel is way cleaner comparing to the petroleum diesel. When biodiesel is used the emission of soot is reduced by 50%, CH4 by 20%. The content of sulphur in biodiesel is practically insignificant 0,005- 0,05%.

The oils from the renewable sources, i.e. plant oils, have many useful features such as high lubricity, biodegradability, non-toxicity, so they can be used for production of various lubricants by adding them to anti-corrosion, transmission and other industrial oils; friction mechanical parameters of the plant based oils are also higher than those of petroleum based oils, and in addition, while producing biodiesel

a by-product – glycerin is obtained, which is also very valuable product for technical washing and after the further cleaning, glycerin can be used in perfumery industry as well.

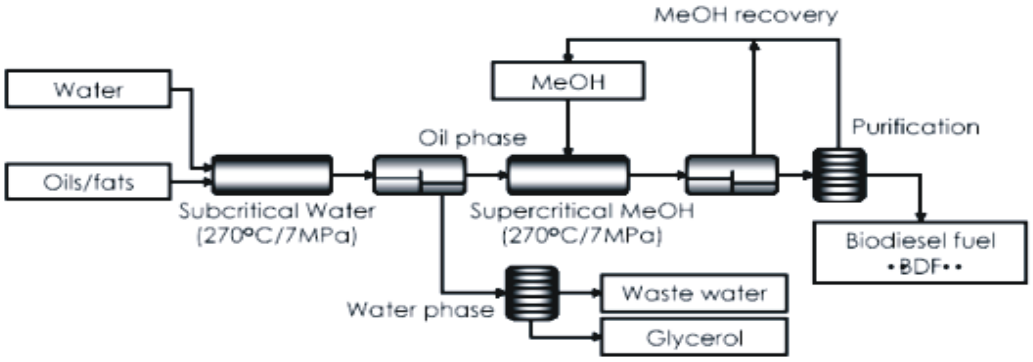

Fig.3. Scheme of the two-step supercritical methanol method (Saka-Dadan Process)

Fig.3 shows the technology of Saka-Dadan for receiving biodiesel through the process of supercritical methanol i.e. without using catalyzers. The scheme shows one step technology for producing biodiesel from plant oil using supercritical methanol [3]. This method ensures quick esterification of the fatty acids of the oil in the area of supercritical methanol, where the reactions of transesterification and esterification run successfully and quickly, without catalyzers, in addition the content of water and the quality of the raw material do not affect the process of the chemical reaction and the outcome of the final product – i.e. biodiesel.

It has been proven that the acids are almost totally processed without any catalyzers by trans-esterification of sunflower oil in supercritical methanol and supercritical ethanol areas at various temperature (200-400 °C) and under 200 bar pressure. The traditional method with catalyst implies two necessary steps – cleaning and washing, whilst for the supercritical method these two steps are no more needed and the total time is reduced to 4-10 minutes. All that can significantly reduce production expenses and the final price of biofuel too.

The method of supercritical methanol is relatively easily adoptable for industry from technological and economical points of view, it allows to use both fresh oils and those with high content of water and free fatty acids for production of biodiesel, therefore this new method – esterification of the fatty acids in supercritical fluids, has great potential to be used in the industry for biodiesel production.

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ПРОИЗВОДСТВО БИОДИЗЕЛЬНОГО ТОПЛИВА С ИСПОЛЬЗОВАНИЕМ ТЕХНОЛОГИИ СВЕРХКРИТИЧЕСКИХ ФЛЮИДОВ

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Использование возобновляемых источников энергии способствует развитию механизмов технологии по сбережению традиционных энергоносителей. Изучение современных методов, в частности использование технологии сверхкритических флюидов для производства биодизеля, дает возможность для масштабного развития индустриального производства биодизеля. Внедрение производства биодизеля окажет позитивное влияние на экономическое и экологическое развитие страны.

Ключевые слова: *биодизель, рапсовое масло, масло для жарки, технологии сверхкритических флюидов.*

Поступила в редакцию 10.11.2016.