



Sustainable City Transport Development and Reduction of Greenhouse Gas Emissions through the Introduction of Biodiesel Fuel

Kakha Karchkhadze^{1*} and Natela Khetsuriani²

¹*Ilia State University, Tbilisi, Georgia*

²*TSU, Institute of Physical and Organic Chemistry, Tbilisi, Georgia*

Abstract. Biodiesel, as one of the most effective, alternative, environmentally friendly, and carbon-neutral alternative biofuel, can be especially useful in urban areas, where concentration of vehicles is high and the air is polluted with the harmful emissions from internal combustion engines. The present work is focused on the analysis of the most important characteristics of both biodiesel and conventional (oil-based) diesel fuels; based on its research and findings, the article gives the recommendations how to improve the nano-composition of biodiesel so that it could be more widely used in diesel engines. The oil and acid compositions of biodiesel fuel have been studied and identified through liquid chromatography and the functional groups of the fuel were analyzed using the Fourier IR spectrometer. Based on the results of the research, an improved composition of biodiesel has been identified, which, while meeting the demands of EN 14105, ASTM D 6751, and EN 590 standards, can significantly reduce greenhouse gases (GHGs) and harmful emissions.

Keywords. *biodiesel, sustainable transportation, GHG emissions, nano-composition*

*Correspondence:
kakhak@iliauni.edu.ge

Introduction

Biodiesel is mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats through the process of etherification. 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; therefore, biodiesel can be used in any segment of industry where petro-diesel is used, including internal combustion engines.

The greatest advantage of biodiesel, however, is that it is an eco-friendly fuel. Biodiesel is renewable and sustainable and can significantly reduce the danger of an environmental disaster. Biodegradability in both soil and water is another important advantage of biodiesel, some 89% of the carbon contained in biodiesel will be biodegraded in just 28 days. Biodiesel can sharply re-

duce - up to 85% - emissions of Polycyclic Aromatic Hydrocarbons, which are identified as carcinogenic compounds.

The physical and chemical characteristics of biodiesel are quite close to those of petroleum-based diesel fuel, but at the same time, biodiesel is eco-friendly and carbon-neutral. In addition, since biodiesel has a closed carbon cycle, biodiesel, unlike petroleum-based products, does not add greenhouse gases (GHGs) to the atmosphere (Antolin et al., 2002; Khan et al., 2007; Sheehan et al., 1998; Vicente et al., 2004). Biodiesel is especially effective in urban areas, where the concentration of vehicles is high and the air is more polluted with harmful emissions from internal combustion engines

Biodiesel can be blended with petroleum diesel. 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. B20 can be used in almost every type of vehicle, including the municipality buses, i.e. public transport in the cities, thus contributing toward eco-friendly and sustainable development of urban transportation.

The present work is focused on analysis of the most important characteristics of both biodiesel and conventional (petroleum-based) diesel fuels; based on its research and findings, the article gives the recommendations how to improve the nano-composition of biodiesel so that it could be more widely used in diesel engines without any modification of the engines.

Materials and Research Methodology

The well-adopted method for producing biodiesel is the biochemical process named etherification of triglycerides (TGs), usually those of plant oils. TGs react with alcohol in the presence of the acid or base catalysts and the outcome is alkyl esters of fat acids and glycerin (Freedman et al., 1986; Wright et al., 1944). Reactions are consecutive and reversible. From the pure chemical point of view, biodiesel is methyl ester if methanol is used in the process of etherification, and consequently, ethyl ester, if ethanol is applied.

The whole process is comprised of three reversible reaction when di- and monoglycerides are created as intermediate products (Freedman et al., 1986). The reaction needs 1 mol of triglycerides and 3 mol of alcohol, and after the reaction, alongside the esters, glycerin as a by-product is obtained.

It has been proved that methyl ester and ethyl esters are almost similar from the point of view of thermal content. Therefore, while receiving esters, using ethanol can bring extra advantages related to the extra carbon atom of the molecule of ethanol, which increases thermal content and cetane number. And in addition, ethanol, as the alcohol of organic origin, can make the production of biodiesel completely based on bio resources (Tyson, 2001; Vicente et al., 2007).

The reaction can be run by acid or a base catalyst as well as a ferment catalyst; the chemical catalysts, however, proved to be more practical, rational, and the process of etherification goes faster and it is cost-effective as well, comparing the reaction in the presence of ferment catalysts. The process of etherification in the presence of base catalysts such as NaOH or KOH, implies the removal of glycerin from fatty acids and replacing it with alcohol, usually methanol. The by-product, glycerin, is used in the industry for the production of soap, and after refining, the cosmetic and perfumery industry (Knothe et al., 2005).

The alternative method is to use heterogenic (solid) catalysts for the process of etherification. The heterogenic (solid) catalysts have the advantage that they could be removed from the area of reaction and used again. Process of etherification with solid catalysts is considered as the most “green” process of etherification. That process does not require neither recovery of the catalyst, nor the phase of water treatment (washing), thus ensuring the high outcome of the methyl esters, which are very close to the theoretical values (Cao et al., 2008), as per the glycerin, it will be produced with the higher purity, with 98% and more not containing impurities (Bournay et al., 2005; Melero et al., 2009).

As per the method of supercritical area of alcohol, it has only one phase for etherification, which provides many advantages for the industry (Dermidas, 2002; Kusidiana and Saka, 2001; Madras et al., 2004; Warabi et al., 2004).

Results and Discussions

The present work is focused on analysis of the most important characteristics of both biodiesel and conventional (petroleum-based) diesel fuels and based on its research and findings, the article gives the recommendations how to improve the nano-composition of biodiesel so that it could be more widely used in diesel engines.

We have studied and analyzed biodiesel obtained from the fresh oil of rapeseeds (*Brassica napus*), as well as secondary (cooking) oil from the food industry, which served as raw materials

for biodiesel production. From these bio resources, through the process of etherification of with methanol, we have received pure biodiesel fuel, i.e. B100 and free glycerin. Alongside, we have received several composites of biodiesel (B10 and B20) and analyzed their physical and chemical characteristics.

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, received 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. B20 can be used in almost every type of vehicle, including 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.

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 were carefully analyzed and compared to those of a conventional petroleum diesel fuel. Each character was analyzed according to the existing standards (Table 1).

The physical and chemical parameters of biodiesel were analyzed using *SPECTRUM Version 10.4.2.PerkinElmer*. Figure 1 shows the spectrum of B100, where the functional groups of the compounds have been identified.

The compositions of fatty acids in biodiesel 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 (Li et al., 2008).

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°C, kg/m ³	884,0	848,0	834,0
Density °API	28,56	35,36	38,16
Viscosity, mm ² /s at 40°C	5,2	3,3	2, 0
Flash point, °C	120	64	56
Acid number, mg KOH/g	0,015	0,0069	0,0048
Cetane Number	51	50	48
Sulfur content, mg/kg	-	4,5	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°C)	№2	№1,5	№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°C	260°C	240°C
96%	300°C	305°C	295°C

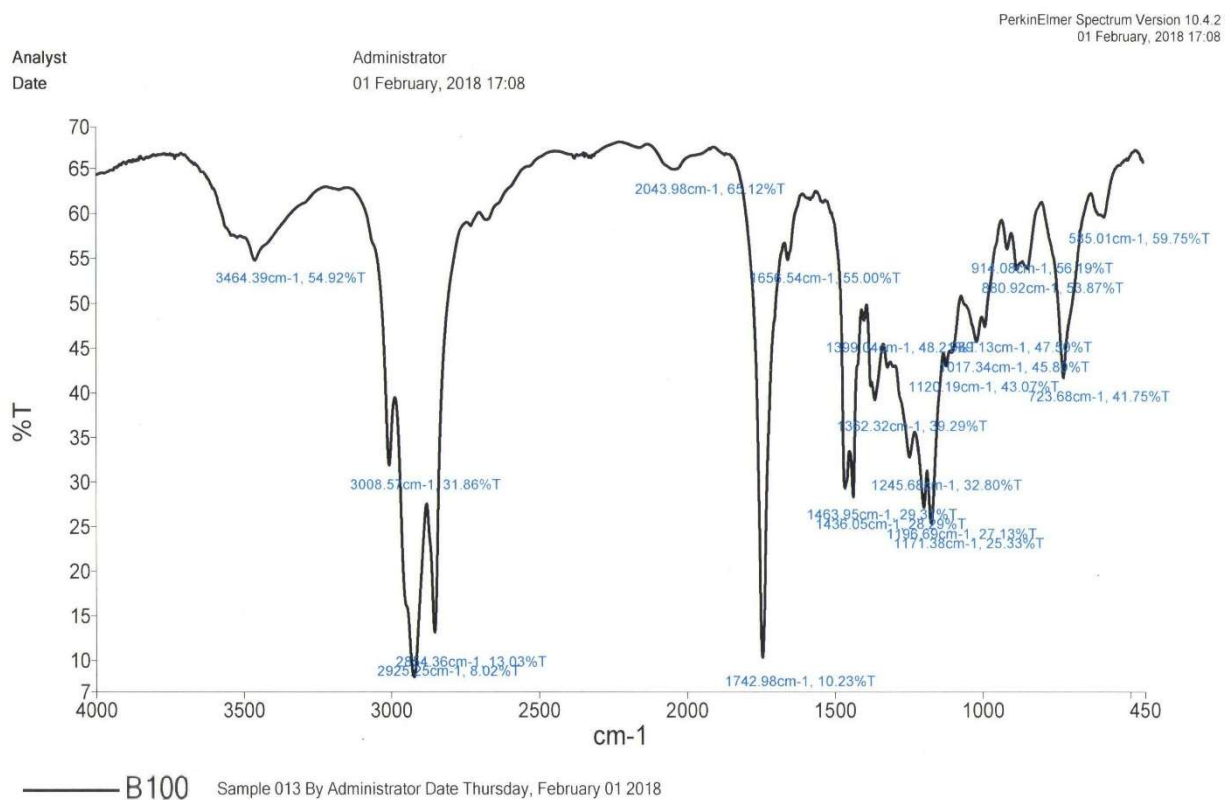


Figure 1: Biodiesel B100 spectrum

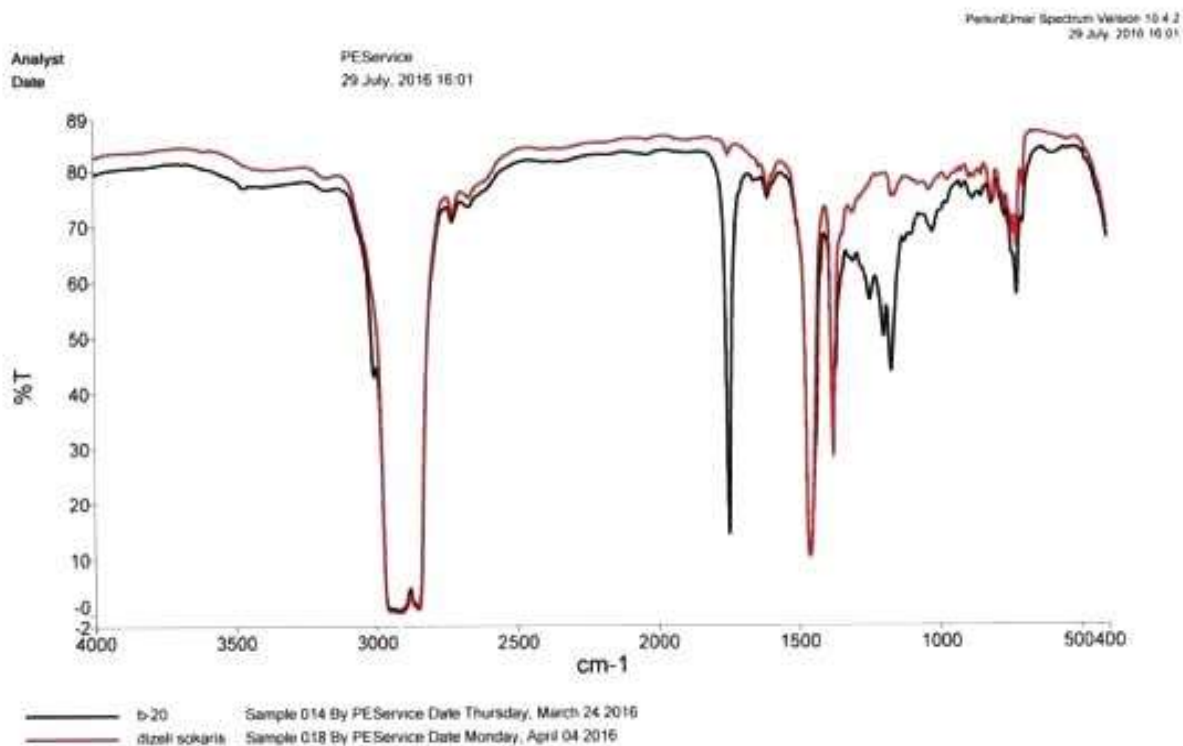


Figure 2: Petroleum diesel fuel and B20 biodiesel spectrums

Figure 2 shows the spectrums of B20 and conventional (petroleum-based) diesel fuels. While comparing these two spectrums, we can see that B20 characteristics are similar to those of the conventional diesel fuel, however, biodiesel and its blends are much more eco-friendly, reducing harmful emissions (Khetsuriani et al., 2017).

With the aim to improve the parameters of biodiesel and make it suitable for a wider spectrum of engines without any modification, we identified a new nano-composition of Biodiesel. Having defined a new composition of biodiesel, we have compared the physical and chemical characteristics of this new composition with the

standards of B100 ASTM D6751-07a. We have analyzed the structural groups using an infrared spectrometer. We have compared the spectrum of B100 and that of newly defined nano-composition of biodiesel.

Figure 3 shows the spectrum of both B100 and the newly defined nano-composition of biodiesel. When comparing the physical and chemical parameters of conventional biodiesel and nano-diesel, and their spectrums, it becomes obvious that several major parameters of biodiesel have been improved and what is important, the structural compositions remained stable.

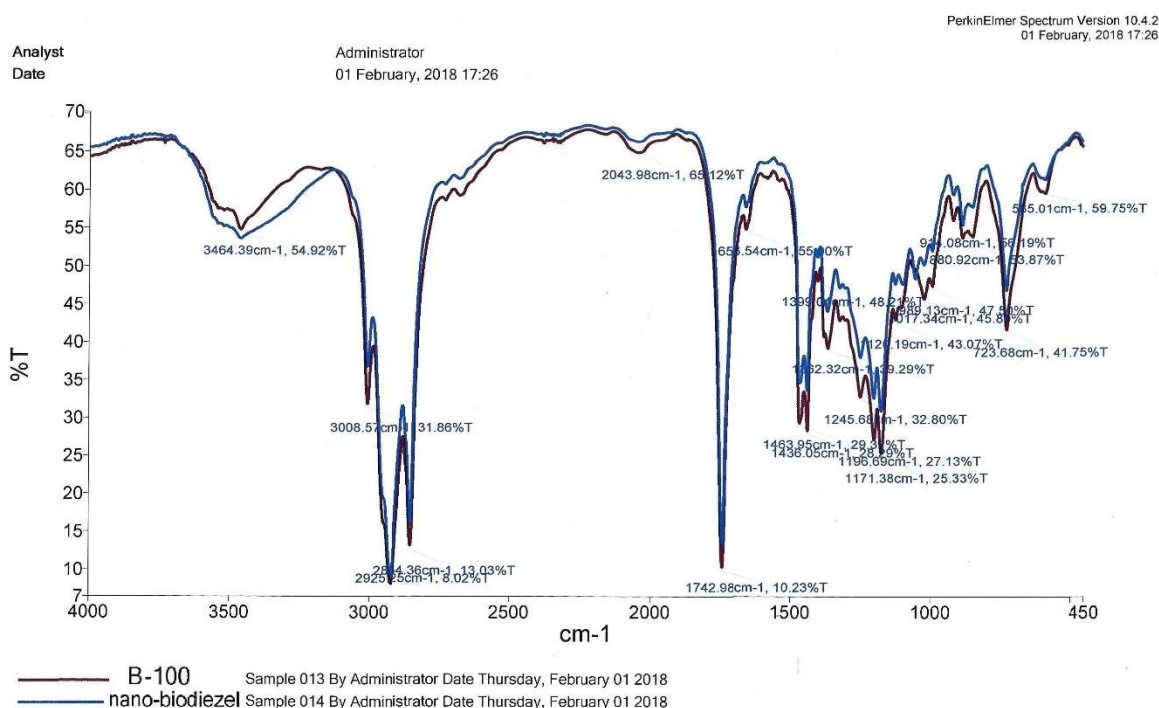


Figure 3: B-100 biodiesel and nano-biodiesel spectrums

Conclusions

We have found that acid number was reduced 3 times, which means that the corrosion resistance index has been significantly improved. The other main parameters also were improved, namely the flash point became closer to the optimal point, as defined by the standards; density at 15°C, kg/m³, as well as ash content and carbon residue characteristics have been also improved.

All these improvements give biodiesel fuel the possibility to be used in a wider range of engines, and the improved nano-composition allows biodiesel to be used both in pure, i.e. B100, and/or blended with petroleum diesel fuel forms. Based on the parameters of the newly defined nano-composition of biodiesel, the performance of the engine powered by this type of biofuel will be improved.

The new composition of the biodiesel has been tested in the vehicles of Ilia State University fleet,

as well as in the selected municipality buses of the city of Tbilisi, Georgia. We are planning to vigorously test the new nano-composition of biodiesel in the city buses and then gradually switch the petroleum diesel fuel with biodiesel fuel for the municipality vehicles.

On the basis of our research, a new biodiesel production plant is under construction in Tbilisi, Georgia, and it will be fully operational in April 2018. The plant will provide the city transport with clean, eco-friendly fuel—biodiesel—thus improving air quality and ensuring sustainable development of the city transport.

The improved physical and chemical parameters of biodiesel will allow the usage of this eco-friendly fuel and its blends in almost all kind of internal combustion diesel type engines, without any modification, thus serving as a reliable, alternative fuel for sustainable city transport and reducing GHG emissions.

References

- Antolin G., F. Tinaut, Y. Briceno, V. Castano, C. Perez, A. Ramirez (2002), "Optimization of biodiesel production by sunflower oil transesterification", *Bioresource Technology*, 83, pp. 111-114
- Bournay L., D. Casanave, B. Delfort, G. Hillion, J.A. Chodorg (2005), "New heterogeneous process for biodiesel production: a way to improve the quality and the value of the crude glycerin produced by biodiesel plants", *Catalyst Today*, 106, pp. 190-192
- Cao F., Y. Chen, F. Zhai, J. Li, J. Wang, X. Wang, S. Wang, W. Zhu. (2008), "Biodiesel production from high acid value waste frying oil catalyzed by superacid heteropolyacid", *Biotechnology and Bioengineering*, 101, pp. 93-100
- Dermidas (2002), "Biodiesel from vegetable oils via transesterification in supercritical methanol", *Energy Conversion and Management*, 43, pp. 2349-2356
- Freedman B., R.O. Butterfield, E.H. Pryde (1986), "Transesterification kinetics of soybean oil", *Journal American Oil Chemists' Society*, 63, pp. 1375-1380
- Khan N., M.A. Warith, G. Luk (2007), "A comparison of acute toxicity of biodiesel, biodiesel blends, and diesel on aquatic organisms", *Journal of the Air & Waste Management Association*, 57, pp. 286-296
- Khetsuriani N., K. Karchkhadze, V. Tsitsishvili, K. Goderdishvili (2017), "Production of Biodiesel using Supercritical Fluids Production", *Chemical Problems Journal*, 1, pp.21-25
- Knothe G., J. van Gerpen, J. Krah. (2005). *The Biodiesel Handbook*. AOCS Press, Champaign, IL, USA
- Kusidiana D., S. Saka (2001), "Biodiesel fuel from rapeseed oil as prepared in supercritical methanol", *Fuel*, 80, pp. 225-231
- Li Y., Garcia-Gonzalez D.L., Yu X., van de Voort F.R. (2008), "Determination of free fatty acids in edible oils with the use of a variable filter array IR spectrometer", *JAOCs*, vol.85, no 7, p.599-604
- Madras G., C. Kolluru, R. Kumar (2004), "Synthesis of biodiesel in supercritical fluids Fuel", *Fuel*, 83, pp. 2029-2033

- Melero J.A., J. Iglesias, G. Morales (2009), "Heterogeneous acid catalysts for biodiesel production: current status and future challenges", *Green Chemistry*, 11, pp. 1285-1308
- Sheehan J., V. Cambresco, J. Duffield, M. Garboski, H.H. Shapouri (1998), An overview of biodiesel and petroleum diesel life cycles. A report by US Department of Agriculture and Energy, pp. 1-35
- Tyson K.S. (2001), Biodiesel Handling and Use Guidelines, National Renewable Energy Laboratory, NREL/TP-580-30004. Golden (September)
- Vicente G., M. Martinez, J. Aracil (2004), "Integrated biodiesel production: a comparison of different homogeneous catalysts systems", *Journal of Bioresource Technology*, 92, pp. 297-305
- Vicente G., M. Martinez, J. Aracil (2007), "Optimisation of integrated biodiesel production. Part I. A study of the biodiesel purity and yield", *Bioresource Technology*, 98, pp. 1724-1733
- Warabi Y., D. Kusadiana, S. Saka (2004), "Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols", *Bioresource Technology*, 91, pp. 283-287
- Wright H.J., J.B. Segur, H.V. Clark, S.K. Coburn, E.E. Langdon, E.N. DuPuis. (1944), "A report on ester interchange", *Oil Soap*, 21, pp. 145-148