ELEMENTAL ANALYSES FOR DIFFERENT TYPES OF BIODIESEL AND DIESEL

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Rezumat. Introducerea biodieselului pe piaţă ca o alternativă viabilă la combustibilul diesel fosil pentru aplicaţii în motoarele cu aprindere prin compresie (CI) a dus la o cercetare intensivă în acest domeniu în ultimile două decenii. Acest lucru se datorează epuizării resurselor de petrol şi a creşterii gradului de conştientizare al impactului asupra mediului şi a sănătăţii din arderea dieselului fosil. Pe măsură ce utilizarea biodieselului devine mai răspândită, producătorii de motoare motoare şi-au exprimat îngrijorarea cu privire la performanţele acestuia în motoarele diesel. În această lucrare este deteminată compoziţia elementară pentru diferite tipuri de biodiesel din uleiuri (grăsimi animale) şi motorină. Datele experimentale obţinute indică conţinutul de carbon, hidrogen şi azot prezent în fiecare probă. Procesul de combustie în motoarele diesel este analizat în funcţie de compoziţia elementară a fiecărui combustibil.
Cuvinte cheie: compoziţie elementară, combustie, biodiesel, petrodiesel.

Abstract. The biodiesel introduction on the market as economically viable alternative to fossil diesel for applications in compression ignition (CI) engines has led to intense research in the field over the last two decades. This is predominantly due to the depletion of petroleum resources and increasing awareness of environmental and health impacts from the combustion of fossil diesel. As the use of biodiesel becomes more widespread, engine manufacturers have expressed concern about his performance in diesel engines. In this paper is determined the elemental composition for different type of biodiesel from oils (animal fat) and petrodiesel. The experimental data obtained indicate the content of carbon, hydrogen and nitrogen present on each probe. The combustion process in diesel engines is analyzed function of elemental composition of each fuel.
Keywords: elemental composition, combustion, biodiesel, petrodiesel.

1. INTRODUCTION

The search for an alternative fuel for diesel engins has intensified in recent years with the imminent depletion of fossil fuel in the next four decades, based on present consumption rate of the proven reserves [2]. Plant oils are usually converted into biodiesel by transesterification with short chain alcohols, such as methanol or ethanol, to bring their combustion properties closer to those of conventional fuel. Biodiesel is currently being produced from grease, vegetable oils or animal fats.

The use of edible plant oils for biodiesel production is under discussion as they compete with food crops for scarce agricultural land and water [8]. Other key factors contributing to this include growing environmental concerns and volatile crude oil prices. Among alternative fuels touted, biodiesel is currently favored in the ground transportation sector due to the availability of current production technology, and compatibility with existing infrastructure of conventional diesel fuel. Owing to a combination of these factors and encouraging measures adopted by policy makers in the form of fiscal policies, mandatory blending, trading laws, biodiesel standards and emission legislations, biodiesel has since seen a rapid annual increment in its worldwide production [7]. Despite the many apparent benefits from the usage of biodiesel in diesel engines, widespread adoption of the fuel within the automotive sector is hindered mainly by the high cost and associated operational problems. At present, biodiesel is still not as cost-competitive as fossil diesel due to the high price of the feedstock oil [5]. Positive governmental policies and subsidies have proven to encourage the initial uptake of biodiesel. Nevertheless, the eventual cost competitiveness of biodiesel in the long term future is expected to be governed by maturing production technology, utilization of cheaper non-edible oil as feedstock and the rising trend in global crude oil prices. Outstanding technical challenges in areas involving low temperature operation, storage, carbon deposition and corrosion have been addressed, with varying degrees of success, through simple measures, such as fuel preheating, biocide application, proper filter maintenance and drainage of retained water [3], [6].

Quality and usability of biodiesel can be further improved upon through the use of fuel additives in the form of antioxidants, cetane enhancer, corrosion inhibitor and cold flow improver. However, production of effective biodiesel fuel additives proves to be more challenging as fuel additives are effective for specific compounds in fuels. Biodiesel must be satisfactory according to accepted fuel standards such as ASTM D6751 in the United States or the Committee for Standardization (CEN) standard EN 14214 in Europe before it can be used in compression–ignition (diesel) engines. The fatty acid methyl esters (FAME) composition, along with the presence of contaminants and minor components, determines fuel properties of biodiesel fuel.

Because each feedstock has a unique chemical composition, biodiesel produced from different feedstocks will in turn have different fuel properties. Important properties of biodiesel that are directly influenced by FAME composition include low temperature operability, oxidative and storage stability, kinematic viscosity (KV), exhaust emissions, cetane number, and energy content [1].

The objective of this study is to investigate the elemental composition of biodiesel fuels in order to estabilsh the energy combustion in diesel engines.

2. CHEMICAL STRUCTURE

Figure 1 shows the chemical structures of vegetable oil methyl ester, vegetable oil and hydrocarbon-based fossil diesel.

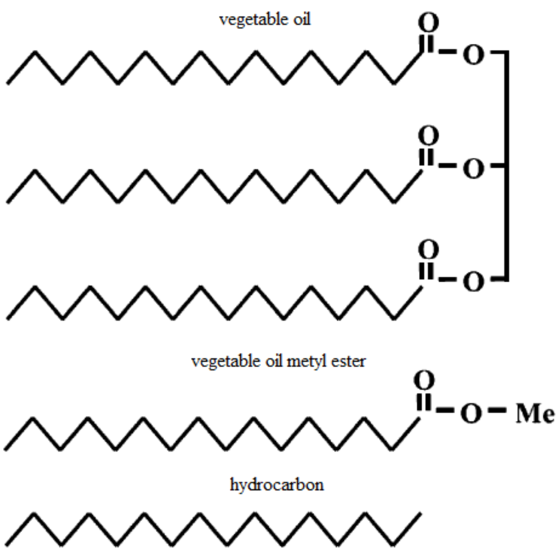

Fig. 1. Molecular structure for vegetable oil, metyl ester and hydrocarbon [4]

Vegetable oil, with three hydrocarbon chains attached to a common group, has greater intermolecular association that results in even higher density and viscosity values. As summarised in Table 1, fatty acid compositions of naturally occurring vegetable oils varies with feedstock. These fatty acids also vary in chain length and number of double bonds. Most vegetable oils and their methyl ester derivatives contain a significant portion of unsaturated fats, which possess at least one reactive double bond.

These features are contrary to fossil diesel which contains mainly saturated hydrocarbons with only single bonds. Hydrogen atoms can be added to an unsaturated fat for each degree of unsaturation, as opposed to a saturated fat due to the absence of double bonds. For this reason, unsaturated fatty acids such as palmitoleic and oleic acids are more reactive than saturated fatty acids such as palmitic and stearic acids. Fats and oils contain a distribution of carbon chains of varying lengths, typically ranging from 10 to 22 carbons (referred to as C10 to C22 chains).

Table 1

Structural formula for common fatty acids and methyl esters [4]

Acid chain	No. of carbon	Structure
Saturated		
Caprylic	8	$CH_3(CH_2)_6COOH$
Capric	10	$CH_3(CH_2)_8COOH$
Lauric	12	$CH_3(CH_2)_{10}COOH$
Myristic	14	$CH_3(CH_2)_{12}COOH$
Palmitic	16	$CH_3(CH_2)_{14}COOH$
Stearic	18	$CH_3(CH_2)_{16}COOH$
Arachidic	20	$CH_3(CH_2)_{18}COOH$
Behenic	22	$CH_3(CH_2)_{20}COOH$
Monounsaturated		
Palmitoleic	16	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
Oleic	18	$CH_3(CH_2)$7CH=CH(CH2)7COOH
Eicosenoic	20	$CH_3(CH_2)_7CH=CH(CH_2)_9COOH$
Erucic	22	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$
Polyunsaturated		
Linoleic	18	$CH_3(CH_2)_4CH=CHCH2CH=CH(CH_2)_7COOH$
Linolenic	18	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$

The differences in length and degree of unsaturation in the fatty acid alkyl chains found in biodiesel produced from different feedstocks (animal or vegetal) give each a unique set of fuel properties. The physical properties of biodiesel can be grouped and compared in terms of their impacts on combustion, flow and storage behaviours.

3. EXPERIMENTAL DATA

Vegetable oil and animal fat was converted to biodiesel using alkaline transesterification [9]. In the reaction a catalyst (sodium hydroxide) was dissolved in alcohol (methanol routes), with a rapport of 1:6 oil:alcohol molar ratio and this mixture were added to the oil.

The reaction of transesterification involves the reaction of methanol with the triglycerides of the sunflower oil to form the corresponding methyl esters and glycerin as indicated on the following reaction scheme (Fig.2):

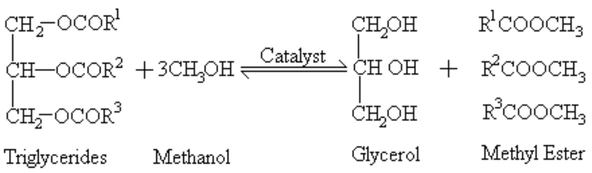

Fig. 2. The general equation for transesterification of triglycerides

For the biodiesel production was used an experimental insatllation build in the laboratory of Thermodynamics and Thermal Machine of Faculty of Mechanics of Craiova. The installation can produce biodiesel from both vegetable oil and animal fat.

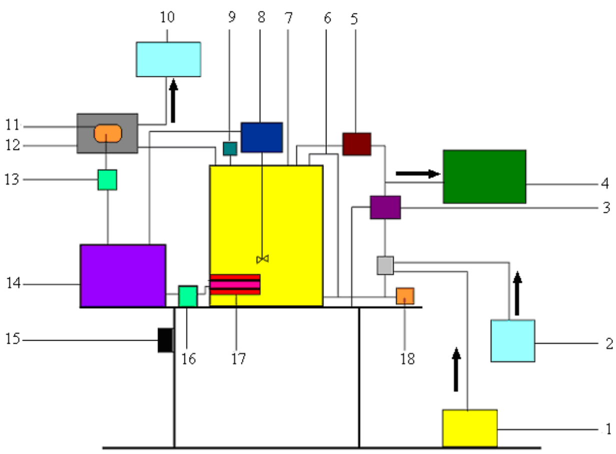

Fig. 3. Scheme of principle for biodiesel installation
1- tank of vegetable oil; 2- methoxid barrel; 3- pump; 4- tank of biodiesel; 5- meter; 6- level pipe; 7- reactor; 8- electric mixer; 9- manometer; 10- methanol tank; 11- fan; 12- heat exchanger; 13- variable voltage control; 14- command panel; 15- meter electric power; 16- variable voltage control; 17- 2000W electrical resistance; 18- thermometer;

The installation presented in Fig.3. is composed by a reactor (were the reaction take place), a command panel to establish the reaction condition, an electrical resistance to heat the blend, a system for methanol recovery and different barrels for the reactants.

The reactant mixing is done in three different ways: by the electric mixer, through the recirculation of the blend with the pump and to the use in the same time of the electric mixer and the pump.

The reaction mass was stirred at room temperature for 60 min and heated at a temperature of 60^0C. After the decantation process, the glycerin was removed and the biodiesel was purified with the addition of water, then the biodiesel was dried and characterized.

The biodiesel obtained respect the ASTM and EN standards.

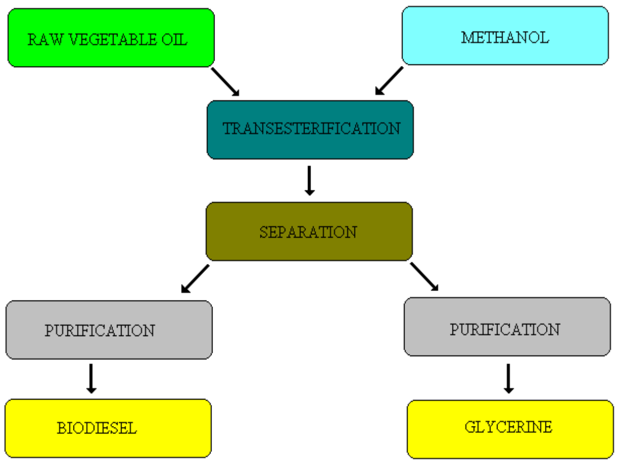

Fig. 4. Basic scheme of base-base process for biodiesel production

4. RESULTS AND DISCUSSION

Biodiesel samples were analyzed using an apparatus COSTECH ECS 4010 – CHNS-O of Department of Equipment and Nuclear Classic and Thermomechanics in the Polytechnics of Bucharest to determine elemental composition of different fuels. It is based on an automatic analytical unit whose operation - from sampling up to signal detection - is microprocessor controlled.

It represents an evolution in the technique of elemental analysis by flash combustion/chromatographic separation and multi-detector techniques. The value of each element is measured through his corresponding area on the diagram.

For the analyses was used two types of biodiesel from vegetable oil (palm and rapeseed) and one type of animal fat (fish oil). The samples was measured with an analytical balance Sartorius to determine the weight of each fuel.

As diesel fuel was used a Euro L Diesel purchased form a local gas station from Craiova.

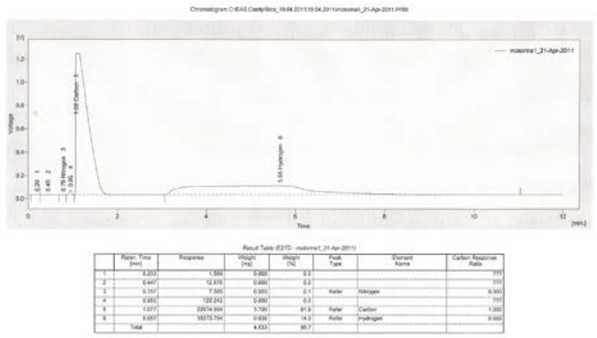

Fig. 5. Elemental analysis for petrodiesel

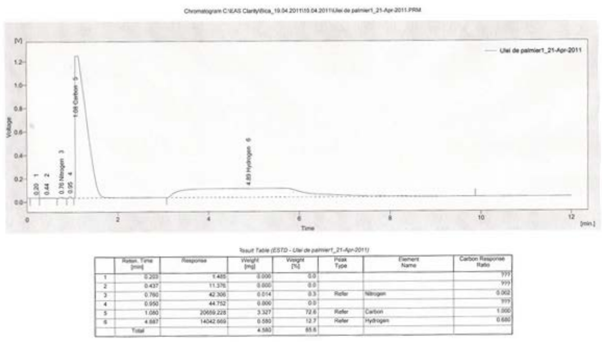

Fig. 6. Elemental analysis for biodiesel of palm oil

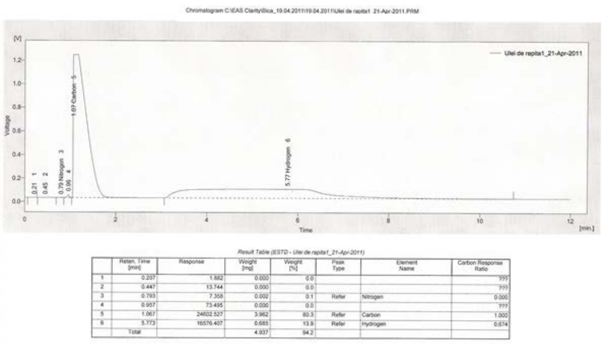

Fig. 7. Elemental analysis for biodiesel of rapeseed oil

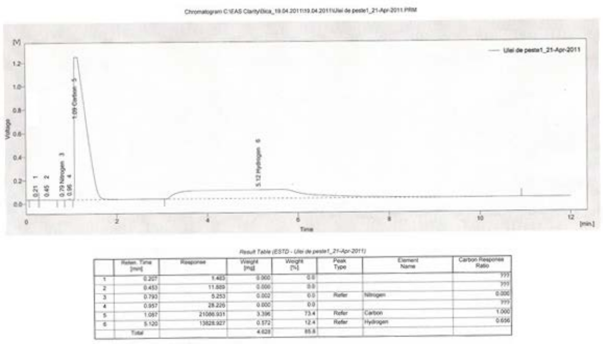

Fig. 8. Elemental analysis for biodiesel of fish oil

The higher heating value (HHV) is an important property defining the energy content and thereby efficiency of fuels, such as vegetable oils and biodiesels. The HHV of biodiesel is approximately 10 % less than that of petrodiesel.

The higher heating value of a fuel increases with increasing carbon number in fuel molecules and also increases as the ratio of carbon and hydrogen to oxygen and nitrogen increases studied the correlation between viscosity and higher heating value.

Higher heating value (HHV) and composition of biomass, are important properties which define the energy content and determine the clean and efficient use of these fuels.

There exists a variety of correlations for predicting HHV from ultimate analysis of fuels. Energy content is an important indication of the suitability of a fuel.

Heat of combustion is found to increase with carbon chain length. As CH_2 unit increases for every additional carbon, higher number of carbon–carbon and carbon–hydrogen bonds which can be broken to release the energy contained within them increases.

Table 2

Higher (HHV) and Lower (LHV) Heating values [4]

Fuel	HHV [MJ/kg]	LHV [MJ/kg]
Hydrogen	141.80	121
Carbon	32.8	-

Hydrogen is the most energetic component. It is a pollution-free and ash less fuel. Hydrogen, as one of the important constituents of fuels, plays a very important role in the combustion.

The higher the percentage of hydrogen content in the fuels, the better it is for their ignition/combustion.

Also the carbon present in the fuel composition with high heating value improves the engine combustion processes. A fuel with high content of hydrogen and carbon represent the best solution for diesel engines.

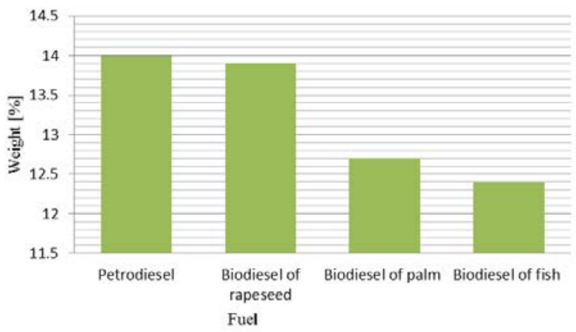

Fig. 9. Hydrogen content of fuel sample

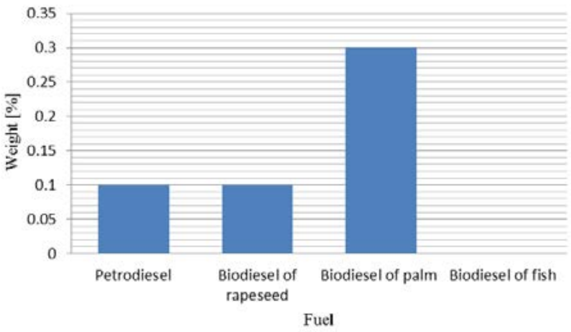

Fig. 10. Nitrogen content of fuel sample

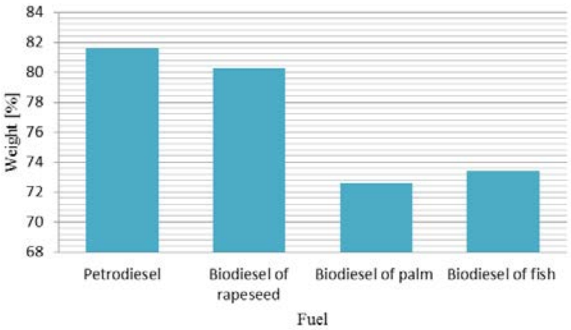

Fig. 11. Carbon content of fuel sample

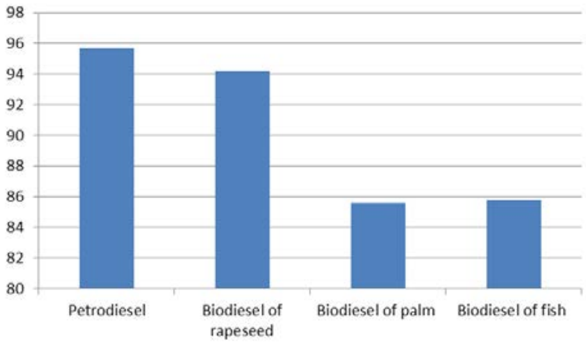

Fig. 12. Total content Nitrogen, Hydrogen and Carbon of fuel sample

According to the data obtained petrodiesel have higher hydrogen content than biodiesel samples.

Biodiesel of rapeseed has a value of hydrogen closed to diesel with good combustion in the engine. Biodiesel of rapeseed and palm oil have values higher than petrodiesel corresponding with higher emission of NO_X reported in specialty literature. Biodiesel of fish oil has no nitrogen in composition and therefore will not have emission of NO_X.

Petrodiesel have a higher content of carbon than all the biodiesel samples. In a diesel engine that completely combusts the carbon in the fuel, all the carbon will result in CO and CO_2.

A percentage of the total carbon content of the biodiesel is actually recycled biomass carbon and should not be considered in the net emissions of CO2. On average, pure biodiesel is 77% carbon.

In the biodiesel, the carbon contained in the fatty acids reacted with methanol is considered non-biomass carbon while the carbon in the fatty acid portion of the methyl ester is considered biomass carbon.

5. CONCLUSION

Biodiesel represents an alternative fuel for diesel engines that is produced from renewable agricular sources and animal fat.

Elemental analyses of four types of fuels indicate the content of carbon, hydrogen and nitrogen present in the samples. Petrodiesel have the highest content of carbon and hydrogen fallowed by the biodiesel of rapeseed oil.

The biodiesel of fish oil have no nitrogen in composition and therefore will not have NO_X emission. Neat biodiesel can be used in current configuration of diesel engines with little to no hardware modifications, although regular engine maintenance and servicing are recommended by the entire engine manufacturer.

Biodiesel is a viable substitute to fossil diesel due to its renewable biomass origins, which can satisfy mid-term global energy demands while forming part of the solution to arrest further environmental deterioration from human activities linked to technological advancements.

ACKNOWLEDGEMENT

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Situated in the South-South-West of Romania, the county of Dolj is located between 44 00' and 44 30' latitude North and 22 00' and 23 00' longitude East and is traversed from North to South by the Jiu river, whose name it bears - Doljiu, meaning Lower Jiu. Its total surface of 7.717 km2 accounts for 3.1 % of the country's surface. Dolj county neighbors the counties of Mehedinti to the West, Gorj and Valcea to the North, Olt to the East and the Danube to the South, over a length of 150 km, which also represents a part of the natural border between Romania and Bulgaria.

Its climate is mild with an annual, average temperature of 11.5 Celsius degrees and its relief is made up of plains, hill areas and the banks of the Danube. From South to North, the county's terrain soars from 30 meters to 350 meters, creating the impression of a wide amphitheater facing the Sun. This beautiful land is the home of approximately 770.000 people grouped in 2 cities, 3 municipalities and 94 communes, with the cities accounting for 51 % of the total population.

Short history...

The land of Dolj has been blessed with the spiritual and material wealth created by its inhabitants over the course of time. The ancient cultures of Cârna, Verbicioara, Salcuta, Cîrcea and Coţofeni, dating from the Paleolithic and the Neolithic stand testament to this claim, as well as its numerous Dacian and Roman archeological sites.

These sites give testimony to the existence of a prosperous life in the cities and villages in the land of the Jiu, Getodacian society having reached its zenith here during the reign of kings Burebista and Decebal. Such a site is the Pelendava castrum, whose name was adopted by the Romans and recorded in the Tabula Peutingeriana, which is cartograpically atested circa 225 A.D. The county`s teritory was defended by fortifications, the most important of which, "Brazda lui Novac" (or Novac`s Wall), was created in the IVth century A.D. and runs the length of the county from West to East.