Determination of Physicochemical Properties and Emissions for Different Blends of Biodiesel from Watermelon (*Citrullus lanatus* L.) Seeds and Diesel Fuel

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Across the world the fossil fuels are depleting and countries are forced to find an alternative source to reduce green house gases and replace petroleum fuels. Depending of the raw material sources, vegetable oils, animal fats or algae, biodiesel offers a solution for a clean-burning diesel fuel. Watermelon (Citrullus lanatus L.*) seed were collected and the oil was extracted. The oil was transformed into fatty acid methyl esters through a transesterification process and blended in various proportions with diesel fuel. The physico-chemical properties of fuels were determined. Results obtained showed that the biodiesel has a density (0.870 g/cm^3), kinematic viscosity 40°C (3.1 mm^2/s), flash point (128°C), saponification index (150 mgKOH/g), iodine index (108 mgI$_2$/100g), peroxide index (3.7 mEqO$_2$/Kg) and oxidation stability (6 hours) in the range of UE specifications. The engine tests were conducted on a Deutz F4L912 diesel engine, 51 kW, 4-stroke, air cooled, direct injection diesel engine. From the test performed was observed that the CO and HC emissions were reduced due to high content of oxygen in biodiesel blends.*

Keywords: Citrullus lanatus L., seeds, biodiesel, emissions

During last decades the environmental impacts of fossil fuels on climate change have led to increase usage of alternative fuels. Numerous studies are undergoing to find a potential replacement for petroleum fuels either using biodiesel or bioethanol [1,2]. Biodiesel is defined as a fuel composed of mixture of fatty acid alkyl esters obtained by a transesterification process from vegetable oils or animal fats [3]. In July 2017 the biodiesel production in U.S. was 149 million gallons with an increase of 9 million gallons higher than June 2017 with 63 million gallons sold as B100 and 87 million gallons sold as blends with petrodiesel fuels [4]. Researchers are focused in obtaining the biofuel from various vegetable oils like soybean, palm, jatropha, sunûower, linseed, cotton, rape, mustard, neem, peanut, etc. The main drawback of biodiesel production is the high cost of the raw material and limited availability especially of the alimentary oils [5]. Using biodiesel in internal combustion engines can reduce considerably hydrocarbons (HC), carbon monoxide (CO) and smoke and increase NOx emission due to the higher content of oxygen. Another drawback of biodiesel is higher viscosity, lower volatility and higher molecular weight which can cause poor atomization and incomplete combustion [6]. Watermelon (*Citrullus lanatus*) is a member of the Cucurbitaceae family, known as gourd family (include cucumbers, pumpkins and other melons). *Citrullus lanatus* is a popular species cultivated in the summer in S-V region of Romania [7]. The seeds are often discarded or in others countries used as animal feed or snack food [8]. The seeds have a high percent of oil predominant in lenoleic, oleic, palmitic, and stearic acids and minor constituents as palmitoleic, myristic and linolenic acids [9]. Praveen A. [10] studied the effects of adding blends of watermelon biodiesel on the performance and emission characteristics on a kirloskar single cylinder diesel engine 5.2 kW, 4-stroke with eddy current dynamometer. The results showed a reduction in the Brake Thermal Efficiency and in the total fuel consumption for all biodiesel blends compared with petrodiesel fuel. B20 blend gave the best performance in the emissions of Hydrocarbons and Carbon Monoxide. The emissions of Nitrogen Oxide were higher for all biodiesel blends (B20, B40, B60, B80 and B100). Soundarrajan et al. [11] used a single cylinder water cooled diesel engine to investigate the emissions and performance of watermelon biodiesel blends (B25, B50, B75, and B100) as alternative fuel. The emissions of CO, HC and smoke opacity of biodiesel blends were less than petrodiesel. The NOx emissions for B75 blend were slightly more than normal diesel fuel. Panneerselvam et al. [12] reported for various watermelon biodiesel blends an increase in the brake-specific fuel consumption and a decrease in the brake thermal efficiency. Emissions were reduced for carbon monoxide and hydrocarbons with slight increase in the while the oxides of nitrogen and smoke. Also the cylinder pressure and heat release rate decreased at higher biodiesel blends. In this present work watermelon seeds which normally are discarded were used to produce biodiesel and to investigate emissions for various blends of biodiesel/petrodiesel.

Experimental part

Materials and methods

Watermelon (Citrullus lanatus) sedes

The seeds were obtained from twelve batches of certified watermelon (*Citrullus lanatus*) purchased from Craiova market during summer in 2017. The selecting process was done randomly. The watermelons (*Citrullus lanatus*) were cut and the seeds were collected and washed with water.

Oil from watermelon (Citrullus lanatus) sedes

The extraction of oil from watermelon seeds was carried out in a Soxhlet-type device using light petroleum solvent. The extraction time was 6 h. After oil extraction, the excess

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solvent was distilled off reduced vacuum using a rotary evaporator [13-15].

Biodiesel

The biodiesel was produced by alkali catalyzed transesterification process, (fig. 1,2). in biochemistry lab of Chemistry Department of University of Craiova.

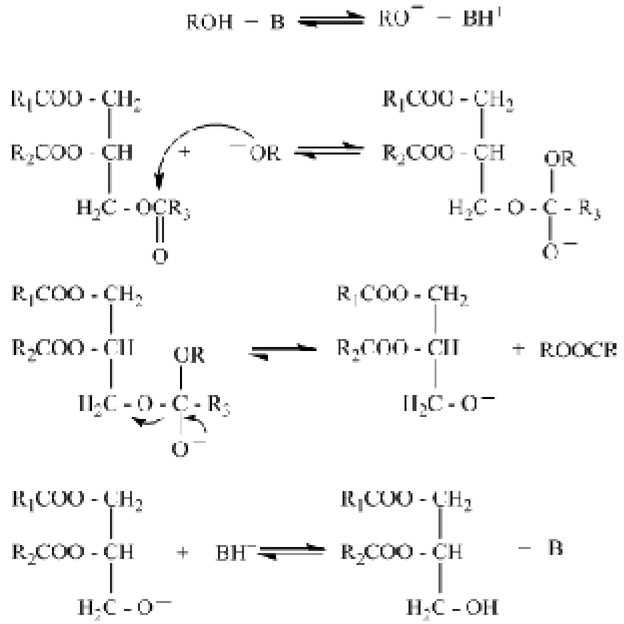

Fig. 1. Mechanism of the base catalyzed transesterification of vegetable oils (from Ogunwole, 2015)

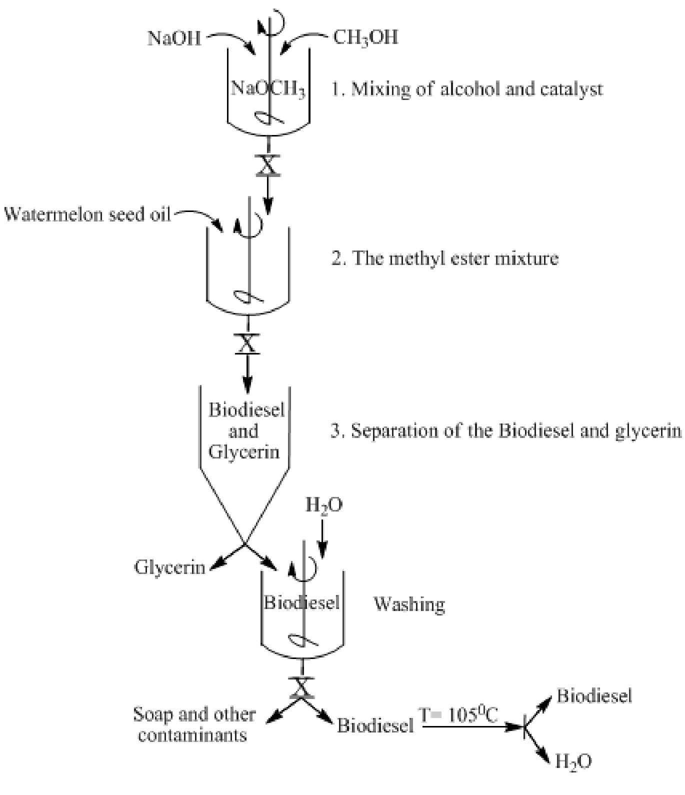

Fig. 2. Transesterification process

Among these methods, alkali catalyzed process including an alkali catalyst (usally NaOH, KOH, or sodium methoxide) has been accepted industrially due to its high conversion of triglycerides to methyl esters in a short reaction time and high reaction rates.

Biodiesel characterization

Density measurement

The density of biodiesel were determined by means of pycnometer in accordance with ISO 4787 standard [18].

Determination of Viscosity

The test is relatively simple and follows a basic procedure. The oil is placed into a calibrated glass viscosity tube. It is allowed to settle overnight and is submerged in a warm bath at 40°C. Then the fluid is suced up a portion of the tube to the highest line on the right side of the tube seen. Once the oil's meniscus touches this line a timer is started and continues until the oil's meniscus touches the lower line. The time intervals are then converted into seconds and multiplied by a constant that is specific for the glass viscosity tube used. This number is then the kinematic viscosity of the fluid [18].

Flash point

Flash point is defined as the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test. The ûash point measurements were done according to method ASTM D6751 [19]. A closed cup Pensky-Martens device was used.

Determination of saponification index

The saponification index (Is) represents the quantity of potassium hydroxide expressed in miligrams, necessary for the saponification of fatty acids from a gram of fat. The saponification index is calculated with the aid of the formula [20]:

$$I_s = \frac{(V_m - V_p) \times t_{KOH}}{m_p} \text{ mgKOH/g}$$

where:

t_{KOH} - titre of the solution of KOH = 28.055 mg KOH/mL;

m_p - mass of sample submitted to the saponification, g;

V_m -volume of the solution of KOH used in the titration of sample control, mL;

V_p - volume of the solution of KOH used in the titration of analysed sample, mL.

The iodine index

The iodine value represents the quantity of iodine, expressed into grams, which is added by 100 g of lipids. It is a measure of the unsaturated fatty acids grade which enters in the structure of animal and vegetal lipids.

The iodine value was calculated using the Hanus method. The iodine value was calculated according to the formula [20]:

$$I_i = \frac{(V_m - V_p) \times t \times f \times 100}{m_p} \text{ g I/100g}$$

where:

V_m - volume of the solution of sodium thiosulphate 0.1 N used in the titration of sample control, mL;

V_p - volume of the solution of sodium thiosulphate 0.1 N used in the titration of analysed sample, mL.

t - titre of the solution of sodium thiosulphate 0.1 N in relation with the iodine (0.01269 mg/mL);

f - factor of the solution of sodium thiosulphate 0.1 N;

m_p - mass of the analysed sample.

Determination of peroxide value level by Hara-Totani method

Peroxide of biodiesel samples was determined at the beginning and after determining oxidation stability. In a 250 mL conical bottle was weighed on analytical balance a fixed quantity of biodiesel (20 mg) and were dissolved in 10 mL chloroform. Add 15 mL glacial acetic acid and mix. After replacing air with nitrogen or CO_2, add 0.3 mL saturated KI solution and shake for 1 min, followed by cooling in ice water bath in the dark. Add 100 mL cold distilled water and shake and then titrated potentiometrically with sodium thiosulfate solution 0.001 N keeping the vial in ice bath. During titration, there is a change in potential that in the equivalence moment shows a sudden drop. Parallel running a blank solution without oil where volume 0.001 N sodium thiosulphate used in titration until the equivalence point should not exceed 0.15 mL. If this amount is exceeded then another will prepare a saturated solution of KI. Index value is calculated in milliequivalents peroxide oxygen/kg biodiesel using formula [15, 21- 23]:

$$IP = \frac{(V - V_m) \times F \times N \times 1000}{m} \ \mathrm{mEqO_2/Kg}$$

where: V - number ml 0.001 N sodium thiosulphate solution used for titration of sample to be analyzed;

V_m - number ml 0.001 N sodium thiosulphate solution used in blank titration;

m - mass of biodiesel sample (g);

F - factor solution 0.001 N sodium thiosulphate;

N - normality of 0.001 N sodium thiosulphate.

Oxidation stability through the Hadorn-Zürcher method (Rancimat)

This method consists in the biodiesel oxidation in accelerate conditions. The method permits the establishment of the induction period, which corresponds, with the initiation step of the biodiesel auto-oxidation. To determine the stability in oxidation it was used an installation, which used oxidized biodiesel samples (10 g) at a temperature of 110°C. Through the oil samples, it was bubbled air with a debit of 8 L per hour. Because of the oxidation reactions, which take place in a reactor, the formed volatile acids are trained by the air current and absorbed in the measurement cell where there is bidistilled water. The measurement of the solution conductibility is done with a conductometer of Radelkis type. In the beginning, we notice a slow increasing of the solution conductibility, after that it appears a sudden increasing of this because of the formation of volatile acids. The induction period is considered the interval until the moment of the suddenly curve's change [15, 22, 24].

Experimental setup. A 4 cylinders, direct injection, four stroke, air cooled, naturally aspirated Compression Ignition (CI) engine was used in experiments. All the engine specifications and technical data are presented in table 1.

Table 1

SPECIFICATIONS OF DEUTZ F4L912 DIESEL ENGINE

Number of cylinders	4
Bore/stroke (mm)	100/120
Displacement (l)	3.770
Compression ratio	19
Maximum rated speed (rpm)	2500
Mean piston speed (m/s)	10
Power (kW) @ 2350rpm	51
Mean effective pressure (bar)	6.9
Maximum torque (Nm) @ 1450rpm	238
Minimum idle speed (rpm)	650

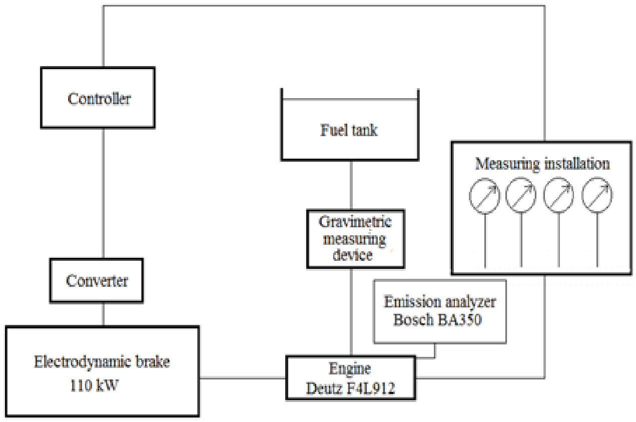

Fig. 3. Schematic diagram of experimental setup (INCESA, Craiova)

Table 2

PRECISION OF PARAMETERS BY MEASURING SYSTEM

Parameter	Precision value
Speed (rpm)	0…6000±2%
Torque (Nm)	0…1000±2%
Fuel consumption (kg/h)	0…50±2%
Intake air temperature (°C)	0...50 ±5%
Inlet pressure (kPa)	-50…300±5%
Exhaust temperature (°C)	0…800±5

The engine setup; schematic diagram are presented in figure 3 BEA350 gas smoke analyzer & smoke meter was used to measure engine emissions. The engine and different instruments are interfaced to a control panel which receives data, process and display on the monitor. The engine was tested with various blends under five discrete part load conditions (20, 40, 60, 80 and 100%). The precision of measuring system is given in table 2. Four blends of biodiesel and diesel were used in the experiments to measure the gas emissions. The blends were mixed by volume basis.

Results and discussions

Physical chemical properties

In the case of biodiesel the specific gravity depends of the fatty acid composition and purity of mixed esters and in petroleum based diesel fuel of the refinery feedstock and of variability of the blending streams. Viscosity and density are the main physical properties which are responsible for the engine performance. The combustion process is dependent of the quality of atomization which in turn is dependent of the fuel properties as density, viscosity and surface tension. Higher viscosity and specific gravity of biodiesel may lead to lower volatility and poor atomization causing incomplete combustion and carbon deposits. Biodiesel exhibits a higher flash point comparative with diesel fuel as a result of the increased molecular weight. The biodiesel sample has no residual methanol after biodiesel processing. Iodine value (IV) is useful for determining the overall degree of saturation of the oil. The biodiesel with high number of iodine value contains high amounts of unsaturates and will have a low cetane number. IV is greater than 50 may lead to the decrease of the engine life but in turn give better viscosity characteristics in cooler periods of the year. Although the peroxide value is not regulate in biodiesel standards measure the presence of oxidative moieties in the sample and signalize the hydroperoxides formed when oxygen reacts with fatty esters. The oxidation stability is used to predict the fuel's stability for longer-term storage. The

Table 3
BIODIESEL AND DIESEL PROPERTIES

Properties	Unit of measurement	Value (Biodiesel)
Specific gravity	-	0.87
Kinematic viscosity, 40°C	mm^2/s	3.1
Flash point	°C	128
Saponification value	mgKOH/g	150
Iodine value	$gI_2/100g$	108
Peroxide value	$mEqO_2/Kg$	3.7
Oxidation stability	h	6

biodiesel oxidizes and organic acids or polymers are created which are responsible for corrosion or filter plugging.

Emission characteristics

Carbon Monoxide (CO) emissions

The variation of Carbon Monoxide emissions with Load of the engine for different blends of biodiesel is shown in figure 4. All the blends of exhibits lower amount of CO emissions compared with diesel fuel. This is mainly due at lower loads to the presence of oxygen in biodiesel which enhance combustion at higher temperatures. Similar results were found by other researchers; Nabi et al. [25]

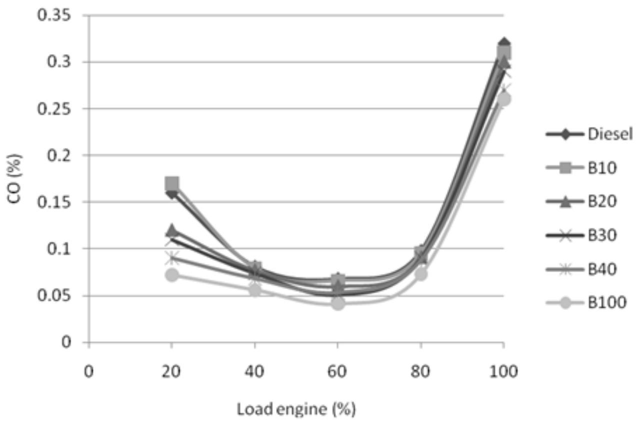

Fig. 4. Variation of Carbon Monoxide emissions with Engine Load

with a reduction of 24% for cotton biodiesel, Çelikten et al. [26] with 28% for soybean biodiesel and Anand et al. [27] with 46.5% for karanja biodiesel compared to petrodiesel fuel.

Carbon Dioxide (CO_2) emissions

The effect of Engine load on Carbon Dioxide is shown in figure 5. Carbon dioxide (CO_2) emissions are produced by complete combustion. All biodiesel blends are higher than diesel fuel for each engine load. This is due mainly to the high viscosity of biodiesel which worsens the atomization

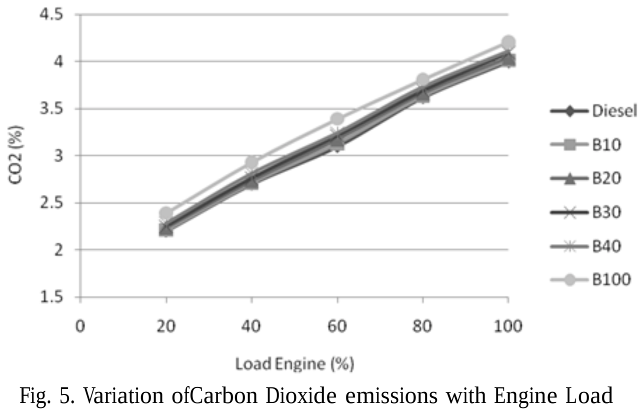

Fig. 5. Variation ofCarbon Dioxide emissions with Engine Load

and vaporization in the combustion chamber. Fontaras et al. [28] found a reduction by 14% for soybean biodiesel and 9% for B50 blend.

Hydrocarbon (HC) emissions

The variation of Hydrocarbon emissions with Engine Load for different blends of biodiesel is shown in figure 6. Because of the high content of oxygen in the biodiesel it is expected that HC emission will decrease for biodiesel blends [29]. Other researchers found reduction in HC emissions by 20.64, 20.73 and 6.75% using biodiesel from karanja, jathropa and polanga and 50% for rapeseed biodiesel [30, 31].

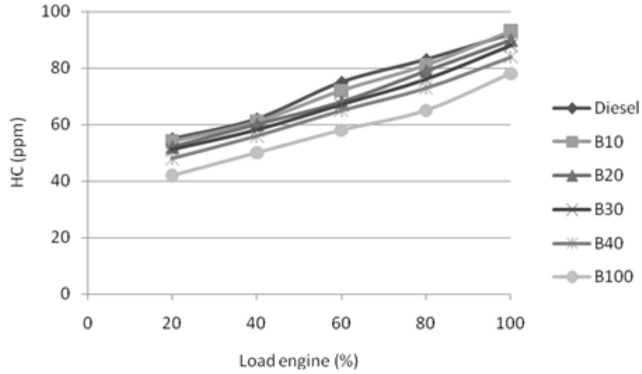

Fig. 6. Variation of hydrocarbon emissions with Engine Load

Nitrogen Oxide (NOx) emissions

Figure 7 shows that, the relation between Engine Load and Nitrogen Oxide increased by increasing the load for each blend. All the Blends give higher NOx emissions than diesel. It was found higher for watermelon biodiesel due to the high oxygen content which cause a high combustion temperature. Aydin and Ýlkiliç [32] found an increase of NOx emissions by 16.7% with B20 blend and 11.8% with B100 for biodiesel of rapeseed.

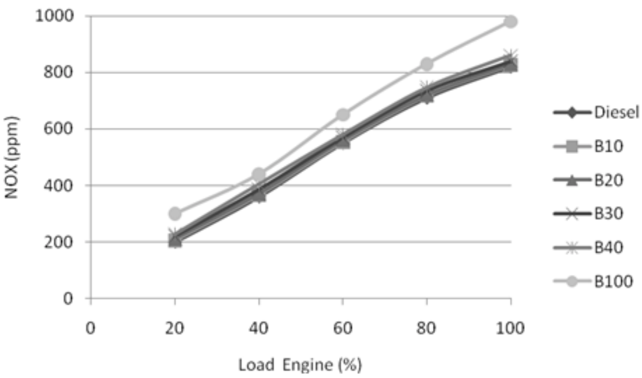

Fig. 7. Variation of nitrogen oxide emissions with Engine Load

Conclusions

Seeds of watermelon which normally were discarded were used to produce biodiesel by chemical transesterification. The biodiesel was evaluated and the physical chemical properties were measured in the laboratory. The biodiesel properties are dependent of the fatty acid structure and to some extent on the production process. A 4 cylinder diesel engine, air cooled was used during tests to measure gas emissions of various blends of biodiesel and diesel. The emissions of CO, HC are reduced but the maximum temperature during combustion increases especially to the high content of oxygen of biodiesel blends. All the blends of biodiesel present high values of CO_2 and NO_x compared with diesel fuel. The engine could run with biodiesel blends without major modifications in the injection system and combustion chamber.

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