

Link sito dell'editore: <https://www.elsevier.com/books-and-journals/elsevier>

Link codice DOI: 10.1016/j.fuel.2018.02.145

Citazione bibliografica dell'articolo:

F. Jaliliantabar, B. Ghobadian, A.P. Carlucci, G. Najafi, A. Ficarella, L. Strafella, A. Santino, S. de Domenico "Comparative evaluation of performance, emission and combustion characteristics of brassica, cardoon and coffee based biodiesels as fuel in a compression-ignition engine", pubblicato in Fuel, 2018, vol. 222, pagg. 156-174

Comparative evaluation of physical and chemical properties, emission and combustion characteristics of
brassica, cardoon and coffee based biodiesels as fuel in a compression-ignition engine

Farzad Jaliliantabar¹, Barat Ghobadian², Antonio Paolo Carlucci³, Gholamhassan Najafi⁴,
Antonio Ficarella⁵, Luciano Strafella⁶, Angelo Santino⁷, Stefania De Domenico⁸

¹PhD student, Department of Mechanical and Biosystems Engineering, Tarbiat Modares
University, Tehran, Iran

²Full Professor, Department of Mechanical and Biosystems Engineering, Tarbiat Modares
University, Tehran, Iran

³Associate professor Department of Engineering for Innovation, University of Salento, Lecce,
Italy

⁴Associate professor, Department of Mechanical and Biosystems Engineering, Tarbiat Modares
University, Tehran, Iran

⁵Full Professor – University of Salento, Dept. Engineering for Innovation

⁶PhD– University of Salento, Dept. Engineering for Innovation

⁷Senior Researcher - Institute of Sciences of Food Production, National Research Council, Lecce

⁸Research Fellow - Institute of Sciences of Food Production, National Research Council, Lecce

(Correspondent author's E-mail: Ghobadib@modares.ac.ir)

Abstract

This study have been considered the effects of the three type of biodiesel (brassica, cardoon and coffee) on the performance, tailpipe emissions and combustion characteristics of a single cylinder

direct injection compression ignition engine operated in four different speeds (1200, 1700, 2200, 2700 rpm) and three different engine loads (15, 30 and 45 %). The differences in combustion and performance parameters and exhaust emissions of engine fueled by these fuels have been compared. The free fatty acid profile of the biodiesels has been considered. The properties of the biodiesels according to the ASTM D6751 have been analyzed. Highest degree of unsaturation is achieved for biodiesel produced from brassica (94.64%) compared to biofuels derived from cardoon and coffee, 79.81% and 57.65%, respectively. The high value of the erucic acid (C22:1) in the brassica biodiesel (48.7 wt, %) is the reason of higher unsaturation degree than the other biodiesels. The components of the free fatty acid profile of the considered biodiesels mostly include long chain free fatty acids (C18 and higher). The physical properties of the biodiesel fuel is influenced by the fatty acid profile. The CN of the brassica, cardoon and coffee is 56.44, 56.11 and 57.44, respectively. The surface tension of the brassica, cardoon and coffee biodiesel fuel is 42.05, 40.99 and 37.62 mN/m. The oxygen content of the brassica, cardoon and coffee is 13.44, 10.91 and 7.77%, accordingly. Dynamic viscosity of the brassica, cardoon and coffee was 6, 5.7 and 9.5 cSt, respectively. The ignition delay of the brassica, cardoon and coffee biodiesel diesel fuel blends at 15% engine load is 9.52, 11.05, 5.07% and at 30% engine load is 12.88, 13.85, 15.78% lower than diesel fuel on average, respectively. The additional oxygen have decreased the CO and THC emissions. The highest reduction of the THC emission than standard diesel fuel was 41.19%. The maximum BTE (brake thermal efficiency) obtained for different biodiesel diesel blends fuels was lower than that of standard diesel fuel. The CA50 of the biodiesel diesel fuels was lower than diesel fuel due to their lower ignition delay.

Keywords: Biodiesel, Brassica, Cardoon, Coffee, Diesel engine, FFA.

1 Introduction

Nowadays, increasing the oil prices, insufficiency of its reserves and greater restrictions on 45 emissions of pollutants imposed on automakers, led to the scientific research to play a n 46 increasingly active role in assessing the use of biofuels as an alternative to petroleum products. In 47 this context, the biodiesel is applicable solution immediately. The biodiesel is a biofuel obtained from oil by a transesterification process, consisting of a mixture of methyl esters of long chain 49 fatty acids with similar chemical and physical characteristics to those of the diesel fuel [1]. The 50 term biofuels includes all those substances, of vegetable or animal origin, able to produce energy. 51 In this category fall biofuels, obtained from biomass, which can be used for the feeding of internal 52 combustion engines [2]. The main reason that prompted the research in this direction is 53 renewability of biodiesel. In fact, the balance of CO₂ emitted during the entire cycle of biodiesel 54 (i.e. cultivation, production and use) is more beneficial than traditional diesel fuel [3]. As reported 55 in the literature, the regulated emissions of biodiesel appeared to be generally lower than those 56 affecting traditional fuel engines. However the amount of nitrogen oxides emissions is strongly 57 dependent on the amount of oxygen present in biodiesel molecule [4, 5]. From an energy point of 58 view, the use of biodiesel entails a slight decrease in power and an increase of specific fuel 59 consumption which is attributable to a lower calorific value of biodiesel compared to diesel fuel 60 [5].

The researches on finding new suitable sources to production of the biodiesel is ongoing. Sajjadi 62 et al., [6] introduced 29 edible sources (such as sunflower [7], corn [8] and canola [9]) and 43 63 nonedible sources (such as castor [10], kranja [11] and jatropa [12]) which have been studied to 64 biodiesel production.

Xue et al., [13] considered different researches on engine emission and performance (Table 1) and 66 summarized that 70.4% researchers have agreed that engine power can be dropped with biodiesel 67 as fuel due to the lower LHV of biodiesel, 87.7% agreed on decrease in PM, 65.2% agreed on 68 increase in NO_x, 84.4% agreed on decrease in CO, 89.5% agreed on decrease in HC and 46.2% 69 agreed on increase in CO₂.

Table 1: Bio-fuel statistics effects on engine emission and performances [13].

Total number of references		Increase		Similar		Decrease	
		Number	%	Number	%	Number	%
Power	77	2	7.4	6	22.2	19	70.4
PM emissions	73	7	9.6	2	2.7	64	87.7
NO _x emissions	69	45	65.2	4	5.8	20	29.0
CO emissions	66	7	10.6	2	3	57	84.4
HC emissions	57	3	5.3	3	5.3	51	89.5
CO ₂ emissions	13	6	46.2	2	15.4	5	38.5

The most important properties of the biodiesel fuel which are effective on the engine performance, 73 combustion and engine emission are kinematics viscosity, lower heating value, cetane number and 74 oxygen content. Lower heating value of the biodiesel is lower than diesel fuel and kinematics 75 viscosity, cetane number and in other hand oxygen content of biodiesel is higher than diesel fuel 76 [14]. High viscosity will increase the soot formation and engine deposit due to insufficient 77 atomization. It is observed that this parameter is higher for biodiesel compared to diesel and it is 78 increases as the content of saturated fatty acids increases. Furthermore, the viscosity of the

biodiesel is proportional to the length of the fatty acid chains, so the reaction of transesterification 80 is configured as a critical factor, as such reaction breaks the triglyceride molecule to form three 81 molecules of methyl esters, smaller and, as is said, less viscous [15]. The dynamic viscosity has 82 been the most effective parameter on the fuel injection properties such as SMD. The SMD of the 83 injected fuel increased by increasing in the fuel viscosity [16]. The energy density (i.e. the lower 84 calorific value, LHV) of biodiesel is lower than diesel fuel because its molecule contains on 85 average about 10% (wt, %) oxygen. This oxygen content of biodiesel makes possible complete 86 combustion. It shows that in terms of combustion efficiency biodiesel offers a better performance 87 than which is offered by the diesel fuel [17].

Filling a gap of the relevant literature, this study presents a research on the effect of three different 89 type of biofuels on emission, performance and combustion characteristics of a single cylinder 90 engine. Biodiesel derived from waste coffee, brassica and cardoon are used in blends with diesel 91 fuel in the various engine speed and load in a DI (direct injection) diesel engine, under the same 92 operating conditions. To the authors' knowledge this is the first time that such a comparison is 93 reported for these bio-fuels diesel fuel blends. Specifically, the comparative evaluation is carried 94 out on a common solid basis (engine and operating conditions) concerning combustion, 95 performance (specific fuel consumption, brake thermal efficiency) and all regulated emissions 96 (smoke, NO_x , CO (carbon monoxide), THC (hydrocarbons)) characteristics of blends in diesel fuel 97 of coffee, cardoon and brassica biodiesel.

2 **Materials and methods**

2.1 Biodiesel production

In this research three biofuels derived from three oleaginous species of great interest, brassica and cardoon seed and waste coffee have been characterized in order to assess the potential of them for

the production of biodiesel. The biodiesels were provided by the Institute of Food Production (ISPA-CNR Sciences) and method which is described in [18].

2.2 Engine and dynamometer

The experimental set up has been realized on a four stroke and common rail AVL single cylinder 106 research engine 5402. The technical features of the engine are reported in Table 2. The motor shaft 107 is coupled to an eddy current dynamometer (SYSTEM ANTRIEBSTECHNIK), which acts as 108 necessary by the electric motor in the execution of motored cycles. The control unit and the 109 dynamometer are interfaced with the test bench (AVL EMCON series 300). By using of this test 110 bench the values for the rotation speed, the driving /braking torque and the load can be monitored.

Table 2. Engine Specifications of AVL Single Cylinder Research Engine 5402

Engine type	4-stroke water cooled Diesel
Manufacturer	AVL
Model	5402
Number of cylinders	1
Maximum power	18 kW
Bore	85 mm
Stroke	90 mm
Connecting rod	138 mm
Displacement	510 cm ³
Compression ratio	17.1:1
Combustion chamber	Bowl with valve pockets and flat head
Injection system	Common rail

Max. injection pressure	1300 bar
Number of nozzles	5
Nozzle diameter	170 μm
Spray angle	142°

2.3 Instrumentation

Figure 1 shows a schematic diagram of engine setup and its instrumentation. The fuel injection 115 system is a common rail type, which feeds an injector to five holes of a diameter equal to 170 116 microns. ETK interface manages, through a dedicated PC, the engine control unit (BOSCH 117 EDC15C7) and therefore it is possible to monitor the fuel injection parameters, in particular the 118 pressure, the injection advance with respect to TDC and the scope introduced into the combustion 119 chamber in a cycle.

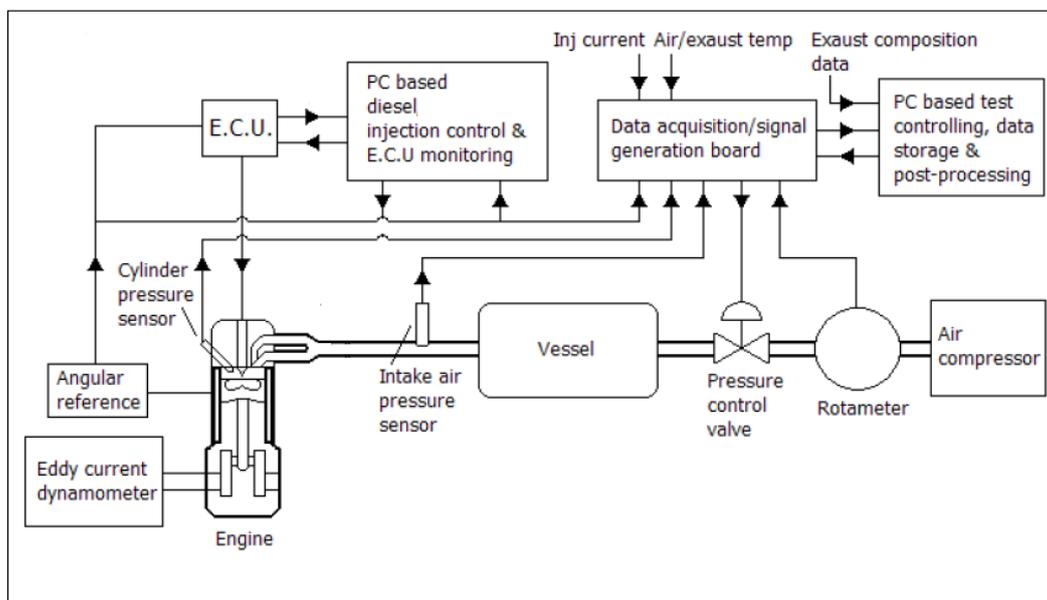


Figure 1. Schematic of the experimental layout.

A piezoelectric sensor (AVL QC33C), equipped with a charge amplifier (AVL 3066A01), was used to measure the pressure inside the combustion chamber. Two piezo resistive sensors allow the estimation of the absolute pressure of the fuel injection (KISTLER 4067A2000) and the pressure upstream of the cylinder (KISTLER 4045A2). Both sensors mentioned above are connected to a voltage amplifier (respectively, KISTLER 4618A2 and 4643). The sampling of the pressure signals takes place on an angular basis, provided by an encoder AVL 364C, which determines the acquisition of the signals in term of the time intervals corresponding to 0.2° CA. The data acquisition card PCI 6251 LABVIEW characterized by a sampling frequency of 300 kHz was used to sampling.

The measurements of the temperatures of the coolant and exhaust gas which took place by means of thermocouples, have allowed to ascertain the correct operation of the engine. Thermocouples of the same type have been used for the purpose of measuring the temperature of the intake and the lubricating oil temperature. The test set up was conducted by LabVIEW software, a development environment for applications oriented to the acquisition of data, the management of electronic devices and signal processing. This allows real-time display and generation of a report of the variables values. The consumption of the engine have been recorded with the aid of the balance AVL Fuel Balance 733S, which enables the sampling of the signal corresponding to the fuel consumption at intervals of a tenth of a second, with an accuracy of 0.12%.

Combustion of the fuel is most effective process on the engine performance and emission. Among all combustion parameters the in cylinder pressure, combustion temperature, ignition delay, heat release and cumulative heat release rate are of the most important. The in cylinder pressure can be measured directly by the sensors and the other combustion parameters can be calculated by the data of the in cylinder pressure [19]. In order to calculation of the heat release rate the Heywood

method has been used. In this method heat release rate can be calculated by the in cylinder pressure 146 data and other combustion characteristics can be concluded from heat release data. In this method, 147 the heat release rate is calculated by using the in cylinder pressure data. According to the first law 148 of the thermodynamic:

$$\frac{du}{dt} = \dot{Q} - \dot{W} \quad \text{Eq. 1}$$

$$mC_v \frac{dT}{dt} = \dot{Q} - P \frac{dv}{dt} \quad \text{Eq. 2}$$

Which \dot{Q} is the combination of the heat release rate and heat transfer across the cylinder wall. \dot{W} is 150 the rate of work done due to the boundary movement. The ideal gas law can be used to 151 simplification of the eq. 2:

$$PV = mRT \quad \text{Eq. 2}$$

By derivation of the above equation (assume mass is constant):

$$\frac{dT}{dt} = \frac{1}{mR} \left[P \frac{dV}{dt} + V \frac{dP}{dt} \right] \quad \text{Eq. 3}$$

By combination of these two equations:

$$\dot{Q} = \left[\frac{C_v}{R} + 1 \right] P \frac{dV}{dt} + \frac{C_v}{R} V \frac{dP}{dt} \quad \text{Eq. 4}$$

By replacing the time (t) by the crank angle degree (θ):

$$\dot{Q} = \frac{\gamma-1}{\gamma} p \frac{dV}{d\theta} + \frac{1}{\gamma-1} V \frac{dp}{d\theta} \quad \text{Eq. 5}$$

In this equation, θ is the crank angle degree and γ is the specific heat ratio of the in cylinder mixture gases and its value is 1.35 for diesel engine [20].

2.4 Experimental technology for performance and emission test

The analysis of CO, CO₂, NO_x and THC exhaust was measured by AVL system DiCom 4000, 159 while the device AVL Smoke Meter 415S provided for the measurement of particulate 160 concentration.

2.5 Tested parameters and experimental procedure

Tests were conducted by fueling the engine with B20 (20% biodiesel and 80% standard diesel) 163 mixtures obtained from the three biodiesels. The tests were conducted at four different engine 164 speeds between 1200 rpm and 2700 rpm, with intervals of 500 rpm. For each engine speed, the 165 behavior of the engine was assessed in three different load conditions (15%, 30% and 45%). For 166 each test were considered ten engine cycles. In summary, the test is planned for each fuel as shown 167 in Table 3.

Table 3. Design of experimental tests for each fuel.

Number of experiment	Speed (rpm)	Load (%)
1	1200	15
2		30
3		45
4	1700	15
5		30

6		45
7	2200	15
8		30
9		45
10	2700	15
11		30
12		45

3 Results and discussion

3.1 Results of laboratory tests

In the following paragraphs the behavior of tested fuels will be analyzed.

3.1.1 Fatty acid profile

The data relating to the fatty acids percentage composition and the corresponding degree of unsaturation of each biodiesel were analyzed with a gas chromatography analyzer and are shown in Figure 2. The presence of palmitic acid influences unsaturation degree in the three biodiesel. Highest degree of unsaturation is in biodiesel produced from Brassica (94.64%) compared to biofuels derived from Cardoon and from coffee waste, 79.81% and 57.65%, respectively.

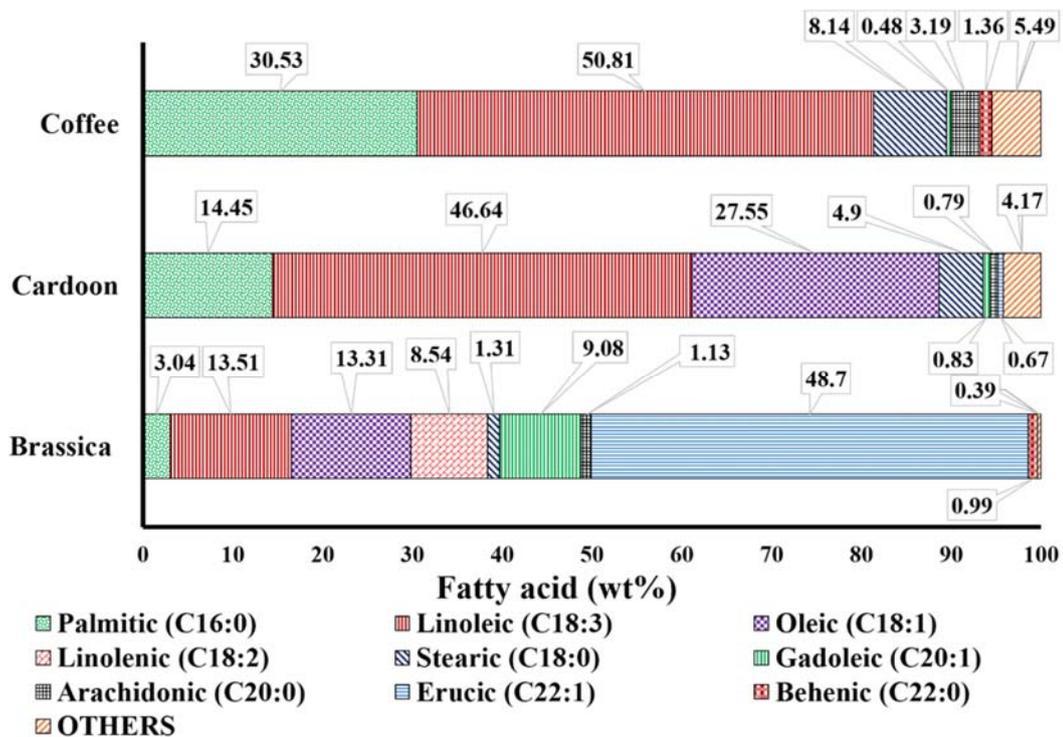


Figure 2: Fatty acids composition of brassica, cardoon and coffee biodiesels.

The fatty acids in the coffee biodiesel primarily comprised of 50.81 (wt, %) linoleic acid (C18:3), 30.53 (wt, %) palmitic acid (C16:0), and 8.14 (wt, %) stearic acid (C18:0), as shown in Figure 2. This shows the coffee biodiesel is mainly include shorter carbon chain fatty acid methyl esters. By comparison, the fatty acids in the cardoon biodiesel were mainly, including 40.04 wt % linoleic acid (C18:2), 27.55 (wt, %) oleic acid (C18:1) and 14.45 (wt, %) palmitic acid (C16:0). But the most of the fatty acids profile of brassica biodiesel is consist of erucic acid (48.7 wt,%). The unsaturated fatty acid content of brassica is significantly higher than coffee. This is due to presence of the higher value of the erucic acid (48.7 wt, %) in brassica biodiesel. Generally the differences between the saturation degrees of the different biodiesel are effective on the physical and chemical properties of them. The high value of the erucic acid (C22:1) in the brassica biodiesel (48.7 wt, %) has increased its degree of unsaturation than the other biodiesels. The erucic acids are not a

common fatty acid in biodiesels. The higher value of biodiesel is also reported for the jojoba (11.15 wt, %) [21], mustard (44.10 wt, %) [22], crambe abyssinica (57.06 wt, %) [23, 24]. But in the most 194 of the biodiesels such as safflower, sunflower, palm [25], cotton seed, rape seed, corn and castor 195 biodiesel [26] the value of the erucic acid in the fatty acid profile is very low or zero. The physical 196 properties of the biodiesel fuel is influenced by the fatty acid profile [27]. So, in following sections 197 the physical properties of biodiesels are discussed according to their fatty acids profile.

3.1.2 Test fuel standardization

The properties of biodiesels and their blends are compared to ASTM biodiesel standards. The tested properties of methyl esters of brassica, cardoon and coffee oil are found to be reasonable 201 agreement with ASTM 6751. It is observed from

Table 4 that the typical characteristics of brassica, cardoon and coffee biodiesels are in the range of the requirement of the engine.

Table 4. Characteristics of produced biodiesels

Parameter	Standard	Unit	Limits	Cardoon	Coffee	Brassica	Diesel
Flash point	ASTM D93	°C	93 min	309	292	296	78
Calcium	EN14538	mg/g	-	4.83	21.75	9.8	-
Magnesium	EN14538	mg/g	-	0.1	0.98	0.1	-
Calcium+ Magnesium	EN14538	mg/g	0.005 max	4.93	22.73	9.9	-
Sodium	EN14538	mg/g	-	1.86	1.77	1.08	-
Potassium	EN14538	mg/g	-	1.54	0.58	0.84	-
Sodium+ Potassium	EN14538	mg/g	0.005 max	3.4	2.35	1.92	-
Monoglycerides	ASTM D6584	% m/m	0.4 max	0.04	0.06	0.05	-
Methanol content	EN14110	% m/m	0.2 max	<0.01	<0.01	<0.01	-
Water and sediment content	ASTMD2709	% v/v	0.05 max	<0.01	<0.01	<0.01	-

Dynamic viscosity at 40 C	ASTM D445	cSt	1.9-6.0	9.5	5.7	6	3.5
Sulfated Ash	ASTM D874	% m/m	0.02 max	<0.02	<0.02	<0.02	-
Total sulfur	ASTM D5453	% m/m	0.015 max	<0.001	<0.001	<0.001	-
Copper Strip Corrosion	D130	--	No. 3 max	Exceeded	Exceeded	Exceeded	-
Carbon Residue 100% sample*	D4530	% m/m	0.05 max	<0.001	<0.001	<0.001	-
Acidity number	D664	mgKOH/g	0.5 max	0.3	0.7	0.6	-
Phosphorus Content	D4591	mg/g	0.001 max	1.58	4.93	0.86	-
Distillation	D1160	°C	360 max	>300	>300	>300	-
Cetane number	ASTM D 613		47 min	57.44	56.11	56.44	48
oxidation stability	EN 15751	h	3 min	>12	9	>12	-
Visual aspect	ASTM D 4176	-	-	Clear yellow	Clear yellow	Clear yellow	-
Lower heating value	-	MJ/kg	-	40.69	39.18	40.10	-
Oxygen content	-	%	-	10.91	7.77	13.44	0
Surface tension	Drop shape method	mN/m	-	40.99	37.62	42.05	34.1

3.2 Biodiesel fuels characteristics comparison

3.2.1 Oxygen content

The fuel oxygen content has a strong impact on combustion characteristics of biodiesels [28]. The 209 inherent oxygen content of the biodiesel helps the more complete combustion of fuel in the engine 210 [29]. The more saturated molecules have a slightly lower oxygen content than those with more 211 double bonds [30]. This is due to reduction in the molecular weight related with the displacement 212 of two hydrogen atoms by each double bond [31]. This can be concluded by comparing the 213 unsaturation percent of the different biodiesels with their oxygen content. The oxygen content of 214 the brassica, cardoon and coffee is 13.44, 10.41 and 7.77 (wt,%) which is in accordance with their 215 unsaturation degree (96.64, 79.81 and 57.65%, respectively). The reported oxygen content of the 216 biodiesel fuels is 10 to 12 (wt,%) [27].

3.2.2 LHV

Capability of the fuel to produce energy is measured by its lower heating value (LHV). The LHV increases with chain length (carbon number) in the molecular structure. In addition, LHV increases

with increase in the unsaturation degree (double bond carbon) of the fuel. Biodiesel has lower energy content. However, the increase is more meaningful at lower molecular weight length (from C8 to C14) than in longer carbon chains (from C20 to C22). Verduzco et al., proposed that the higher calorific values should decrease 0.21 MJ/kg for each increase in the degree of unsaturation of FAMEs. Unsaturation level demonstrated stronger effect upon heating values than carbon chain length [3].

The LHV of the brassica, cardoon and coffee biodiesels are 40.10, 40.69 and 39.18 MJ/kg. These values are close to each other. These observed values of the LHV can be explained by comparing the chain length and unsaturation degree of the considered biodiesels. The unsaturation percent of the coffee biodiesel is lower than brassica biodiesel (57.65 and 94.64%, respectively). But the chain length of the coffee is lower than brassica biodiesel. Coffee biodiesel is mainly consist of C16:0 (30.53 wt, %) and C18:0 (50.81 wt, %) but in brassica biodiesel fatty acids profile the C22:1 (48.7 wt, %) is the main fatty acid. However the high unsaturation degree of the brassica biodiesel has prevented to more increase of the brassica biodiesel than coffee biodiesel. Unsaturation degree of the cardoon biodiesel is lower than brassica and higher than coffee biodiesel. Additionally the carbon chain length of main fatty acids of cardoon (C18:1 (27.55 wt, %)) is longer than coffee and shorter than brassica biodiesels (79.81%). This is the reason of the higher value of cardoon LHV than brassica and coffee biodiesel fuel. The value of the LHV of the brassica, cardoon and coffee biodiesel is a high value of the LHV among biodiesels fuel. The LHV of the peanut (33.6 MJ/kg), soya bean (33.5 MJ/kg) [53], palm (33.5 MJ/kg) and sunflower (33.6 MJ/kg) [54].

3.2.3 Surface tension

Surface tension is a physical property of a liquid caused by the cohesive forces between liquid molecules [32]. Surface tension is not specified in ASTM D6751 but it is nevertheless an important

fuel property that affects atomization in combustion chambers in compression–ignition (diesel) 244 engines [16]. Allen et al. [33] have predicted the surface tension of pure biodiesel fuels at 40 °C 245 from their respective fatty acid compositions. Their results showed that the surface tension of 246 biodiesels could be up to 22% higher than that of diesel no. 2 (D2). Higher fuel surface tension 247 opposes the formation of the droplets from the liquid fuel and atomization [34]. In addition, SMD 248 of the biodiesel is larger than diesel fuel due to its higher surface tension [16, 34]. The surface 249 tension of saturated fatty acid esters increased with increasing in carbon number [33]. Increasing 250 levels of unsaturation were reported to increase surface tension [35]. Additionally, longer chain 251 lengths among similar molecules are reported to increase surface tension [33].

There is not any information about the surface tension of the brassica, cardoon and coffee biodiesel 253 in the literature. The surface tension of the brassica, cardoon and coffee biodiesels is 40.99, 37.62 254 and 42.05 Nm/m, respectively. The surface tension of these biodiesels is approximately close to 255 mahua (37 Nm/m) and castor (39 Nm/m) surface tensions [36]. But it is higher than most of the reported surface tension for other biodiesels such as soybean (30.56 Nm/m), rape seed (31.17 257 Nm/m), palm (30.55 Nm/m), sunflower (31.15 Nm/m), jatropha (30.10 Nm/m) and canola (30.56 258 Nm/m) [37].

3.2.4 Dynamic viscosity

The dynamic viscosity of the biodiesels were analyzed. The dynamic viscosity of the cardoon 261 biodiesel (9.5 cSt) is considerably higher than that in brassica and coffee biodiesels (5.7 and 6 cSt, 262 respectively). It was found that the increasing chain length increases kinematic viscosity. However, 263 increasing the unsaturation degree causes a decreasing in viscosity. The brassica has highest 264 amount of unsaturated fatty acids (94.64%) but its fatty acids composition is mostly include long 265 chain fatty acids (48.7 %wt erucic acid (C22:1)). So the unsaturated fatty acid of the brassica has

decreased and the length of the carbon chain has increased viscosity of brassica biodiesel. The lowest value of unsaturated fatty acid is for coffee (57.56 (wt,%)). But its dynamic viscosity is 268 lower than brassica and cardoon biodiesel due to higher length of the fatty acids in coffee biodiesel 269 fatty acids profile than other two biodiesels (8.14% arachidonic). The unsaturation degree percent 270 of cardoon (57.56%) biodiesel is lower than brassica but higher than coffee biodiesel and the 271 amount of long chain fatty acids of cardoon (some value of the palmitic acid (C16:0) in coffee has 272 been replaced by oleic acid (C18:1)) is lower than brassica and higher than coffee biodiesel. So 273 the dynamic viscosity of the cardoon (9.5cSt) is higher than brassica and coffee biodiesel. This is 274 in agreement with the other reported researches [38, 39].

3.2.5 Cetane number

The cetane index of a fuel shows its ignition quality in diesel engines. A higher cetane index means a shorter ignition delay. Shorter ignition delay causes faster engine cold start and better combustion 278 efficiency. The fatty acids composition of a fuel is responsible to cetane index. A fuel with longer 279 carbon chain and saturated fatty acid content has higher cetane index [40, 41]. Previous studies have shown that CN increases with length of chain and decreases with unsaturation degree. Besides 281 increasing number of double bonds causing lower CN [42]. According to [64] low cetane number 282 have been associated with more highly unsaturated components such as the linoleic acid (C18:2) 283 and linolenic (C18:3) acids while high cetane numbers were observed for palmitic acid (C16:0) 284 and stearic acid (C18:0).

The cetane number of the cardoon biodiesel (57.44) is higher than that in brassica and coffee 286 biodiesels (56.44 and 56.11, accordingly). The brassica has highest amount of unsaturated fatty 287 acids (94.64%) but its fatty composition is mostly include long chain fatty acids (48.7 (wt,%)) erucic acid (C22:1)). So the unsaturated fatty acid of the brassica has decreased and the length of

the carbon chain has increased CN of brassica biodiesel. The lowest value of unsaturated fatty acid 290 is for coffee (57.56 (wt,%)). But its CN is lower than brassica and cardoon biodiesel due to its 291 higher length of the fatty acids in coffee biodiesel fatty acid profile than the other two biodiesels 292 (8.14% arachidonic). The unsaturation percent of cardoon (57.56%) biodiesel is lower than 293 brassica but higher than coffee biodiesel and the amount of long chain fatty acids of cardoon (some 294 value of the palmitic acid (C16:0) in coffee has been replaced by oleic acid (C18:1)) is lower than 295 brassica and higher than coffee biodiesel. So the CN of the cardoon (57.44) is higher than brassica 296 and coffee biodiesel. This is in accordance to the results of other researches [39, 43]. The CN of 297 the considered biodiesel (brassica, cardoon and coffee) is higher than most of the biodiesels such 298 as corn (37.6), cotton seed (41.8), peanut (41.8), soya bean (37.9), sunflower (37.1), palm (42) and 299 babsu (38) biodiesels [44].

3.2.6 The acid number (AN)

The acid number is an analytical parameter to evaluate the quality and stability of the biodiesel. 302 This parameter can be used to determine the corrosive degree of the biodiesel which is a critical 303 factor effective of on the fuel tank and vehicle engine [45]. This parameter, generally stated as the 304 weight of potassium hydroxide (in mg) per weight of sample (in g), is related to the fuel's overall 305 content of the titratable acids, which is derived from the oxidation of the fuel or from the oil or fat 306 used for its production [46].

The acid number of the coffee and brassica (0.7 and 0.6 mgKOH/g, respectively) is approximately 308 two times more than cardoon acid number (0.3 mgKOH/g). So it can be stated that the coffee and 309 brassica biodiesel is more corrosive than cardoon biodiesel. The acid value (AV) of biodiesel 310 samples also increased by increasing storage time [47]. The value of the acid number for coffee is 311 approximately same as palm (0.65 mgKOH/g) and castor (0.65 mgKOH/g) biodiesels. The value

of the acid number for cardoon is approximately same as canola (0.26 mgKOH/g). The value of 313 the acid number for cardoon is approximately same as soybean (0.71 mgKOH/g) [46]. In addition 314 acid number can be used to estimate the biodiesel quantity of free fatty acids. Higher acid number 315 means higher content of the free fatty acid [48]. The higher acid number of the coffee biodiesel 316 indicates its higher free fatty acid content than brassica and cardoon biodiesels.

3.2.7 Flash point

The flash point is the minimum temperature which will give off enough vapors to prepare a 319 combustible gas above the fuel surface [49]. The flash point is in the contrary to the explosiveness 320 [50]. The flash point might be given by chemical structures of biodiesel such as the fatty acids 321 chain as well as the unsaturation degree [51]. The flash point of the brassica, cardoon and coffee 322 is 296, 292 and 309°C. The higher flash point of biodiesel than diesel fuel ensures greater safety 323 in storage and transportation [8, 52]. According to the review of the literature, it seems that the 324 flash point of brassica, cardoon and coffee are highest value of the flash point among all of the 325 biodiesels. The high carbon chain length in the brassica, cardoon and coffee is the main reason of 326 their high flash point. About 69.47, 85.55 and 96.96 wt,% of the main fatty acid component of the 327 cardoon biodiesel is long or very long chain fatty acids (C18 and higher). Most of the fatty acids 328 profile components of the brassica, cardoon and coffee biodiesel is (46.64 wt,% linoleic (C18:3) 329 and 27.55 wt,% oleic acid (C18:1)).

Effect of the unsaturation degree and chain length on flash point to compare it among the brassica, 331 cardoon and coffee is same as CN. The brassica has highest amount of unsaturated fatty acids 332 (94.64%) but its fatty composition is mostly include long chain fatty acids (48.7 (wt,%) erucic acid 333 (C22:1)). So the unsaturated fatty acid of the brassica has decreased and the length of the carbon 334 chain has increased flash point of brassica biodiesel. The lowest value of unsaturated fatty acid is

for coffee (57.56 (wt,%)). But its flash point is lower than brassica and cardoon biodiesel due to its higher length of the fatty acids than the other two biodiesels (8.14% arachidonic). The unsaturation degree percent of cardoon (57.56%) biodiesel is lower than brassica but higher than coffee biodiesel and the amount of long chain fatty acids of cardoon (some value of the palmitic acid (C16:0) in coffee has been replaced by oleic acid (C18:1)) is lower than brassica and higher than coffee biodiesel. So the flash point of the cardoon (309°C) is higher than the other two biodiesels.

3.2.8 Calcium, magnesium, sodium and potassium

In order to produce the biodiesel some catalysts such as potassium and sodium hydroxides in alcoholic solution may be used. Incomplete purification of the prepared biodiesel leads to presence of the catalyst residues as impurities in the biodiesel. Presence of the calcium and magnesium in the biodiesel is due to washing with hard water or by adding the drying agents such as $MgSO_4$ and CaO in the purification process. Additionally these products may be inherently present in the source oil [53]. The specifications from ASTM D6751 state that calcium and magnesium content in biodiesel combined must be less than 5 ppm. The combine calcium and magnesium of the brassica, cardoon and coffee biodiesel is 9.9, 4.93 and 22.73 mg/g, respectively. The value of the combine sodium and potassium is 1.92, 3.4 and 2.35 for brassica, cardoon and coffee biodiesel, respectively. The high value of these elements are due to bad purification process.

3.2.9 Monoglycerides

Monoglycerides are introduced as the most effective components on the lubricity of the biodiesel fuel [52, 54]. But high concentration of the monoglycerides in the biodiesel lead to low temperature operability [52]. The ATM D6571 specifies that the monoglycerides of the biodiesel should be less than 0.4 %m/m. The monoglycerides of the brassica, cardoon and coffee biodiesel is 0.05, 0.04

and 0.06 %m/m, accordingly. It seems to be a good idea to add some monoglycerides to the 359 considered biodiesel up to allowable limit (0.4 %m/m) in order to have a good lubricity of the 360 biodiesel.

3.2.10 Methanol and water and sediment content

The water content in the biodiesel can be corrosive in the engine or reacts with the glyceride to 363 produce soap and glycerin. In addition water may freeze in 0°C and creates ice crystal particle in 364 the fuel. This will change the fuel properties [55]. The ASTM D6751 imposes, therefore, a 365 maximum content of 0.05% (m/m) of water in fuels [56]. In addition it can cause the microbial 366 growth in the fuel and water boundary [57]. Water can be as dissolved water or suspended droplet 367 in the biodiesel. The water content of the brassica, cardoon and coffee is in acceptable range (lower 368 than 0.01% %v/v).

Methanol can cause corrosion in the metal specially aluminum. In addition it can decrease the flash point of the fuel. So, according to ASTM D6751 the methanol content in the fuel should be lower 371 than 0.2% (m/m)[6] . The methanol content of the brassica, cardoon and coffee is in allowable 372 range (lower than 0.01% m/m).

3.2.11 Total sulfur

In order to protect the after treatment systems of the diesel engine the sulfur content of the fuel should be reduced. The lubricant additive of the diesel fuel contains sulfur which is harmful for 376 after treatment system. So sulfur reduction is required to protect these after treatments system 377 especially catalytic convertor. But the sulfur can serve as a lubricant and reduction of the sulfur of 378 the diesel fuel causes a great reduction of the fuel lubricity and increase in engine component 379 wearing. One solution to this problem is using of the biodiesel fuel which has low or no sulfur 380 content [58]. Low or no sulfur content of the biodiesel fuel is one of its advantages [8]. The lower

sulfur content of biodiesel reduces production of the sulfuric acid and engine wearing. In addition, it can enhance the lubricity of the biodiesel [59]. Total sulfur content of the brassica, cardoon and coffee biodiesel fuel is lower than 0.001 % m/m. This is in agreement with the observed sulfur content for other biodiesels [52]. According to the ASTM6751 the maximum total sulfur in biodiesel fuel should be 0.05% m/m.

3.2.12 Copper strip corrosion

The copper strip corrosion measurement is used to measure the level of copper corrosion that would occur if biodiesel were used in any application where metals such as copper are present. Knothe and Dunn had considered the effects of the three metals (copper, nickel and iron) on the stability of the biodiesel fuel. They found that the copper is the most powerful catalyst of oxidation processes in biodiesel [60]. So the measurement and control of the copper to prevent of the any changes in the physical properties of the biodiesel due to presence of the high copper is necessary. The copper strip corrosion property of all the investigated biodiesels was found to be within the specifications of ASTM D 6751. This is in agreement with the other researches [61].

3.2.13 Carbon residue

Presence of the carbon residue in the fuel is an indication of its carbon depositing tendencies. The carbon residue is more important in biodiesel than diesel fuel due to its high correlation with FFA, glycerides, soap, higher unsaturated fatty acids and in organic contents [62]. High carbon residue may possibly cause higher carbon deposits in combustion chamber of the engine [63]. According to the ASTM D6571 the value of the carbon residue in biodiesel fuel should be lower than 0.05% m/m. The carbon residue of the brassica, cardoon and coffee is lower than 0.001 %m/m. Carbon residue value of the brassica, cardoon and coffee biodiesel is lower than its value in corn

(0.24%*m/m*), Cotton seed (0.24%*m/m*), peanut (0.24%*m/m*), sunflower (0.27%*m/m*) and palm (0.23%*m/m*) [80].

3.2.14 Phosphorus content

According to the ASTM D6751 the phosphorous content in biodiesel must be less than 0.001 mg/g. 408 The value of the phosphorous content of the brassica, cardoon and coffee biodiesel is higher than 409 the limitation which I determined by the ASTM D6751 (0.86, 1.58 and 4.93 mg/g, respectively). 410 The phosphorous content of the brassica, cardoon and coffee biodiesel can be reduced by 411 degumming of their oil to meet the ASTM D6751 standard. This is in agreement with the result of 412 the Foidl et al., [64]. High value of the phosphorus content in the fuel may cause the increase in 413 particulate emission of the engine. This high value of the particulate emission may lead to problems 414 in the operation of the catalytic convertor. The amount of the phosphorus content in the biodiesel 415 is correlated with the purification of its base oil [65].

3.3 Performance analysis

In this section, performance of each parameter for the neat diesel fuel and its blends with 20% (by vol.) brassica, cardoon and coffee, at the three loads have been considered. Brake specific fuel consumption (BSFC (g/kWh)), brake thermal efficiency (BTE (%)) and exhaust gas temperature 420 (ET (°C)) measurements results are presented and discussed here.

3.3.1 BSFC

The brake specific fuel consumption of (BSFC) variation with engine speed in different engine 423 load is shown in the Figure 3. As it can be seen in this figure, BSFC has been increased by 424 increasing in the engine load. The trend of the BSFC variation in the 15% engine load is different 425 than 30 and 45% engine loads. This can be explained by consideration of the BSFC formula:

$$\text{BSFC} = \frac{\text{Fuel consumption (kg/h)}}{\text{Brake power (kWh)}} \quad \text{Eq.6}$$

Notice that BSFC will increase by increasing the fuel consumption or decreasing the engine power. The produced power of the engine can be divided into brake power and frictional power.

$$\text{Engine power} = \text{Brake power} + \text{Frictional power} \quad \text{Eq.7}$$

Most of the engine power is used to overcome frictional resistance of the engine parts in lower engine load or idle condition. So, the BSFC decreases by increasing the engine load [66]. As it can be seen in the Figure 3, in the higher engine load (45%) BSFC of the biodiesel-diesel blends are lower than the diesel fuels. Maximum increase in BSFC for cardoon, coffee and brassica is 12.03, 7.54 and 9.09%. This increasing in the BSFC comes from lower heating value of the biodiesel fuel [67]. Lower heating value of the biodiesel means consuming the higher value of the biodiesel in order to produce same value of the brake engine power [68]. Also it can be concluded by comparing the lower heating value of the different biodiesels. The lowest LHV is for coffee (39.18g/kWh) and as it can be seen in the Figure 3 the BSFC value of this fuel is higher than brassica and coffee biodiesel which have higher LHV (40.10 and 40.69 for brassica and cardoon, respectively). The result of biodiesel fuels on the BSFC is in accordance to the result of the other BSFC reported for other biodiesels [68, 69].

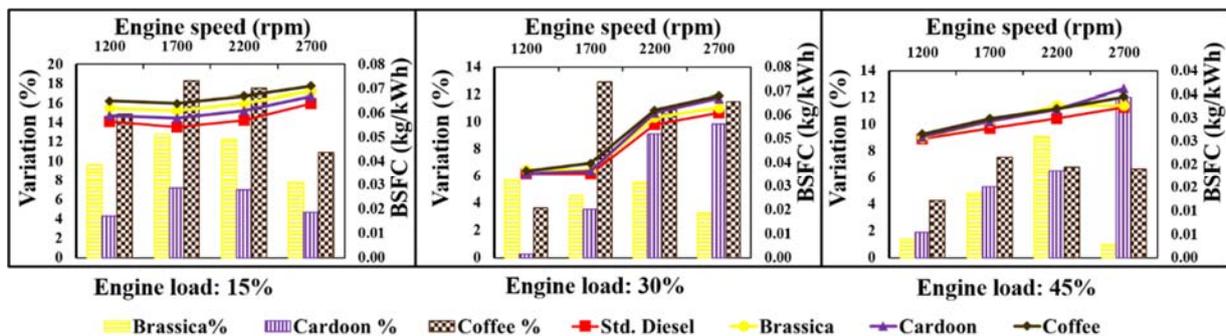


Figure 3. The variation of BSFC (kg/kWh) for the biodiesel blend and diesel fuels with engine speed in different engine loads.

3.3.2 Brake thermal efficiency

Brake thermal efficiency (BTE) is the ratio of the power output to the energy supplied through fuel injection. BTE increased by increasing the percent load for all the fuels tested as it is evident from Figure 4. In Figure 4 brake thermal efficiency (BTE) of the engine for different biodiesel diesel blends in different engine load and engine speed is shown. As it can be seen in this figure, BTE has been increased by increasing the engine load and decreased by increasing the engine speed. This is in accordance to the result of [70]. The improved BTE at higher engine load was due to the reduction in the friction loss and increase in brake power by increasing the percent load [70]. In lower engine load (15 and 30%) the value of the BTE for biodiesel blends are higher than the standard diesel but in 45% engine load ME of the biodiesel blends is lower than the standard diesel.

The reduction of the BTE in the higher engine load is in accordance to the result of the [66]. Though the existence of inherent oxygen improved the combustion of diesel-biodiesel blends, the BTE in general decreased as compared to standard diesel in the higher engine load. This might be due to combine effect of lower calorific value of fuel and higher fuel consumption [70]. The maximum BTE obtained for different fuels as well as standard diesel was around 38%. At 45% load BTE for the coffee, cardoon, and brassica was found to be only 4.63%, 7.73% and 4.63% lower than the standard diesel. This might be due to combined effect of higher BSFC and early combustion [66].

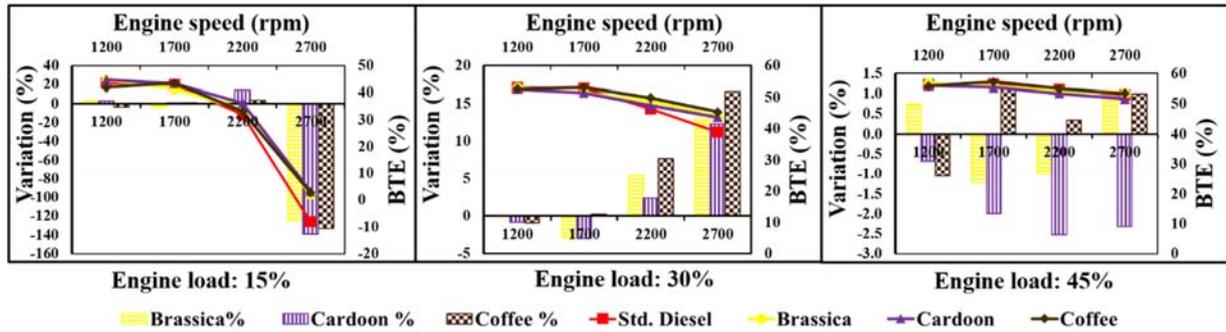


Figure 4. The variation of brake thermal efficiency (%) for the biodiesel blend and diesel fuels with engine speed in different engine loads.

3.3.3 Exhaust gas temperature

Variation of the exhaust gas temperature (ET) for different fuels in different test condition is shown 468 in the Figure 5. ET has been increased by increasing in an engine load. Increasing the engine speed 469 has not very effective on the ET but ET has been increased by increasing the engine speed and 470 then decreased by further increasing the engine speed. Same trend has been reported by the Orkun 471 Özener, *et al.* [71] stated the higher values of ET of biodiesel than standard diesel in full load condition and he stated this is an indication of lower heating loss and higher engine performance 473 of the engine for diesel fuel. In addition lower heating value and earlier combustion has may be 474 the reason of the lower ET of biodiesel diesel fuel blends [72]. The earlier combustion allows more 475 time and crank angle for the expansion process [71]. In other words the ignition delay is an 476 effective parameter on the exhaust gas temperature. Longer ignition delay results in a delayed 477 combustion and higher exhaust gas temperature [73]. In addition, it can be concluded by 478 considering the heat release graphs (Figure 15). The ET of the biodiesel fuel blends in 15% engine 479 load is higher than diesel fuel except coffee biodiesel, in 30% engine load the ET of the diesel fuel 480 and in 45% engine load the ET of the all biodiesel-diesel blend fuels is lower than the diesel fuel.

The maximum reduction in ET for brassica, cardoon and coffee biodiesels diesel fuel blends in 45% engine load is 27.51, 27.87 and 17.61%, respectively.

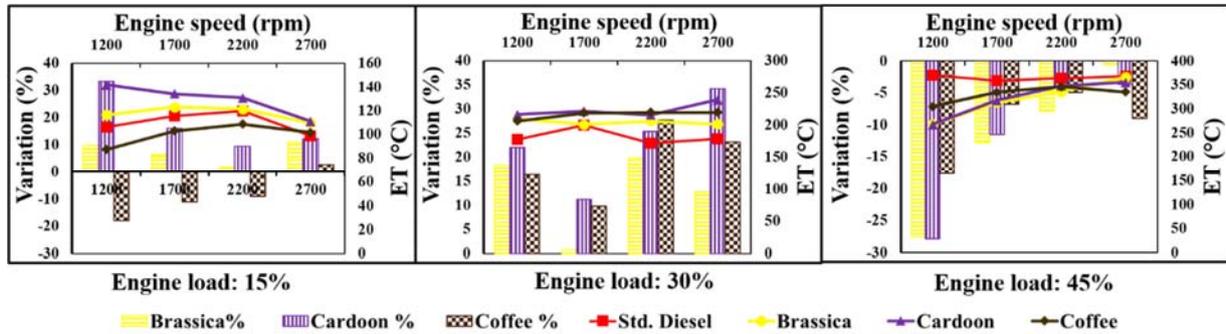


Figure 5. The variation of exhaust temperature (ET (°C)) for the biodiesel blend and diesel fuels with engine speed in different engine loads.

3.4 Engine exhaust emissions

In the following sections the results of the engine exhaust emission measurement have been 488 reported and evaluated. These emissions includes THC (unburned hydrocarbons (ppm)), 489 NO_x (nitrogen oxides (ppm)), CO (carbon monoxide (ppm)), CO_2 (Carbon dioxide (ppm)) and soot 490 concentration (mg/m^3).

3.4.1 THC

Figure 6 shows the corresponding diagram for the emitted total unburned THC (hydrocarbons) in 493 ppm. The THC emission which is one of the organic compounds is formed as the result of 494 incomplete combustion [74]. The unburned hydrocarbons emission for all type of fuels decrease 495 by increasing the engine load [74-76]. The lower equivalence ratio at higher engine loads and less 496 oxygen available for the reaction when more fuel is injected into the engine cylinder can be the 497 reason for THC increasing load [73-77]. Another reason for reduction in THC emissions is the

delay in combustion which increases the quantity of mixture at the perimeter of the reaction zone, being too lean to burn by increasing the engine load [75].

As it can be observed the unburned THC emitted by the all type of biodiesel diesel fuel blends and 501 in all engine load are lower than the standard diesel, this tendency is stronger in the higher engine 502 speed [78]. Differences are small among the three blends, especially in low engine speed. The 503 maximum reduction in THC for brassica, cardoon and coffee biodiesel-diesel blend fuels in 15% 504 engine load is 58.43, 61.67 and 42.35%, respectively. In 30% engine load the values of maximum 505 reduction of THC for brassica, cardoon and coffee biodiesel-diesel blend fuels is 62.23, 73.46 and 506 77.69%, respectively. This values in 45% engine load for reduction of the brassica, cardoon and 507 coffee biodiesel-diesel blend fuels is 48.38, 42.06 and 50.05, accordingly. When THC emissions 508 are compared to diesel, a noticeable improvement is observed for all the test fuel blends of 509 biodiesel. The most reduction of total THC is 77.69% for coffee (2700 rpm and 30% engine load) 510 and the lowest reduction of THC is for cardoon (1200 rpm and 45% engine load). The reduction 511 in THC is mainly due to the result of improved combustion of biodiesel blends within the 512 combustion period due to the presence of excess oxygen and lower the carbon and hydrogen 513 content atom in biodiesel when compared to the diesel fuel [11, 71, 79, 80]. This improved 514 combustion due to using biodiesel can be followed in increasing of CO_2 (Figure 9) [75]. In addition 515 the higher temperature and cetane number of biodiesel can be the reason for this improvement. 516 The heaviest hydrocarbons may be prevented to condense due to high temperature. The lower 517 combustion delay of biodiesel (Figure 18), which come from its higher cetane number (

Table 4), decreases THC emission [72, 81].

There is different report on the effect of the unsaturation degree and fatty acid chain length on the THC. Less unsaturated fatty acids can reduce THC. As it can be seen in the Figure 6 coffee

biodiesel which has lowest value of unsaturation (57.65%) has lowest value of THC. This is in agreement with [38] and in contrast with [82, 83]. In addition THC increase with increase in chain length of fatty acid methyl esters. The oxygen content of the shorter fatty acids is higher and this improve combustion quality [5].

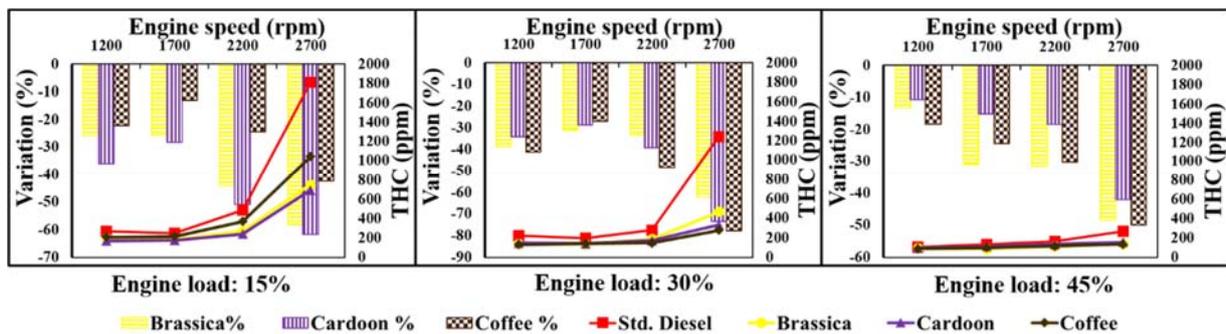


Figure 6. The variation of THC emission for the biodiesel blend and diesel fuels with engine speed in different engine loads.

3.4.2 NO_x

NO_x emissions of the engine for diesel and biodiesel – diesel blends fuels in various load and engine speed are shown in Figure 7. It is well known that NO_x formation is highly dependent upon volumetric efficiency (oxygen availability), combustion duration and especially combustion temperature [71, 72]. As it can be seen in this figure, the NO_x emissions increase due to increasing the engine load. This is due to increase in engine temperature by increasing the engine load (Figure 11). In all engine load the NO_x emissions decrease by increasing the engine speed. This is primarily due to decrease in the exhaust gas temperatures (Figure 11). In addition, by increasing the engine speed the volumetric efficiency and gas flow motion inside the cylinder has been increased. This will improve air fuel mixing and also shorten the ignition delay. So the residence time of the gas

inside the cylinder decreased and the required time to NO_x formation reaction is not provided. 540 These will reduce the NO_x formation in the higher engine speed. The NO_x emission for diesel- 541 biodiesels blends are lower than that of the standard diesel fuel in the 15% engine load and lower 542 engine speeds (1200-1700). In the 45% engine load and all engine speeds the NO_x emissions for 543 biodiesel are lower than the standard diesel.

The most increasing in NO_x emission is 265.09% and for cardoon (15% engine load and 2700 545 engine speed). Also, the highest NO_x emission reduction due to using diesel-biodiesel blends is 546 30.78% for cardoon (45% engine load and 1700 engine speed). Thus, there should be 547 characteristics in cardoon biodiesel which are very effective on engine NO_x . The availability of 548 oxygen in biodiesel can explain the increasing in the NO_x emission, since additional oxygen for 549 NO_x formation may be provided by the fuel oxygen [79]. The reduction of NO_x emission using 550 biodiesel is also reported by Dorado et al. [84] which found a decrease in NO_x emissions while 551 using waste olive oil methyl ester.

Although, it seems that the increasing in NO_x in the high engine speed and 15 and 30% engine 553 load, were high, due to the higher temperatures of the combustion chamber and the presence of 554 oxygen in the fuel. The difference between NO_x emissions of the blends and diesel fuel was lesser 555 at lower engine speed. In the lower engine speed more external oxygen is available, the external 556 oxygen supplied by the air is more effective than the fuel borne oxygen in the production of NO_x 557 [85]. According to comparison between PCT and NO_x graphs, it can be stated that there is high 558 dependency between these two parameters. With increasing in PCT the NO_x value has been increased and the fuel with higher PCT has produced higher NO_x emission. So, the most important 560 parameters in amount of NO_x formation has been PCT.

Longer chain fatty acids would increase the CN and reduce ID [30]. Reduction of the ID will increase the residual time of the mixture in the cylinder and in consequence increase formation of thermal NO_x . In addition, with increase in length of the fatty acids chain the adiabatic temperature will increase and formation of thermal NO_x . However it is found that the effect of the CN is more than adiabatic temperature on thermal NO_x formation [30]. Increasing in unsaturation degree of the biodiesel will increase the NO_x emission. This is due to the increasing of CN and reduction of ID is due to increasing in unsaturation degree [5].

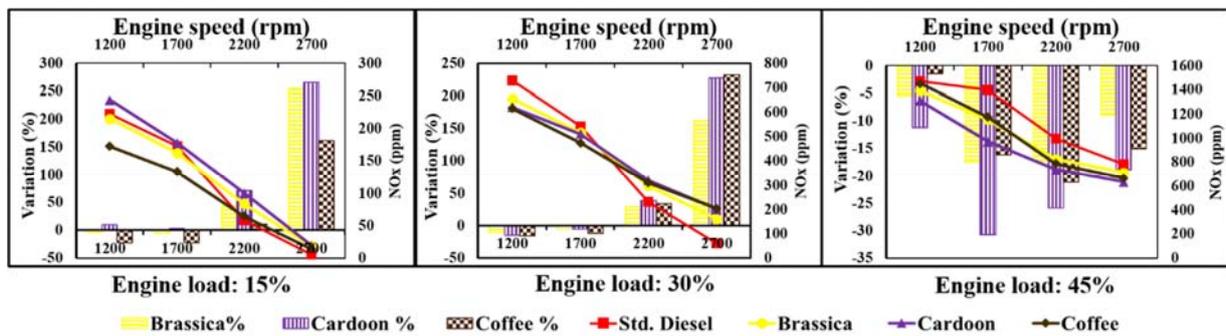


Figure 7. The variation of NO_x emission for the biodiesel blend and diesel fuels with engine speed in different engine loads.

3.4.3 CO

One of the product of incomplete combustion is CO (Carbon monoxide). The common effective parameters on the production of CO emission are the air–fuel equivalence ratio, fuel type, combustion chamber design, atomization rate, start of injection timing, injection pressure, engine load and speed. Figure 8 shows the variation of CO emissions of the standard diesel fuel and three types of diesel-biodiesel fuel blends operation at the different engine speed and various load conditions. It was observed that the CO emission increased by the increasing the engine speed. At

low engine load (15%), the CO emissions of the brassica and cardoon is 24.47 and 25.36%, 580 respectively, and for coffee is 4.22% which is higher than diesel fuel. In 30% engine load the CO 581 emission of the brassica, cardoon and coffee biodiesel is 31.3, 33.87 and 41.19% which is lower 582 than that of diesel fuel, respectively. The CO emission in brassica and coffee is 1.23 and 13.86% 583 which is lower than diesel fuel, respectively and it is 9.94% higher than the diesel engine. The 584 decreasing in CO emission of biodiesel fuel may be due to the oxygen content of the biodiesel. 585 The highest CO emission of 2765.11ppm was measured for diesel fuel at 2700 rpm and 30% engine 586 load. The behavior of this emission in various engine load is not same and in some loads are equal 587 or higher than standard diesel fuel. The gas temperature inside the cylinder in lower engine load is 588 lower and it prevents the CO converted to CO_2 emission [75].

The CO emissions of the blends were higher than those of the diesel fuel at the higher load and 590 speed settings but were lower at the lower speed and load settings. The adding of the biodiesel in 591 the fuel blends reduces the CO at the low load setting but the reverse is the case with the higher 592 load settings. There are several variables acting on the combustion process that has an impact on 593 CO formation. The additional Oxygen present in the biodiesel will assist in making the combustion 594 more complete in the combustion zone but at the high load condition the higher viscosity of the 595 biodiesel could affect the fuel injection and atomization characteristics could adversely impact on 596 the CO emission value as the injector was optimized for diesel fuel. The increasing in-cylinder 597 temperatures at high load would have a greater impact on the CO production of diesel fuel due to 598 the enhanced atomization and mixing. Modifications to the fuel injection system may improve the 599 atomization characteristics of the biodiesel and hence improve the combustion at high load [78]. 600 The most improvement in CO emissions regard to standard diesel is 57.27% for diesel-coffee 601 biodiesel blends. The CO emissions are shown the increase for all the fuels from 1700 rpm to 2700

rpm. Reduction in CO emissions were maintained, probably, thanks to the oxygen inherently 603 present in the biofuel, which makes it easier to be burnt at higher temperature in the cylinder, 604 Similar results can be found in other studies [72, 77, 86, 87]. In addition, this reduction of CO may 605 be due to the C/H ratio of biodiesel which is less than for diesel fuel [76]. The other reason for this 606 improvement can be attributed to the higher cetane number of biodiesel fuel that puts the fuel-rich 607 mixture zone away and improves combustion thus reducing CO emissions. Ignition delay is an 608 important parameter on the combustion quality and thereupon CO emission value. By 609 consideration of the ID of the combustion in different test condition and comparing it with the CO 610 emission values a dependency between these two parameters can be concluded. In 30% engine 611 load and different engine speed the value of the CO emission for coffee biodiesel is lower than the 612 other fuels. In addition the values of the ID for coffee in these test conditions is lower than the 613 other fuels. The longer ID for STD, brassica and cardoon biodiesel cause a retardation and lower 614 value rate of heat release. Totally it can be stated that the ID has been the most effective parameters 615 on CO emission values. Finally, the advanced injection time of biodiesel use due to molecular 616 structure of biodiesel may also explain the reduction in CO emissions [74]. The viscosity of 617 biodiesel diesel blends which is higher than diesel caused the poor atomization, less homogenous 618 mixtures and uneven distribution small portions of fuel across the combustion chamber. These can 619 be the reason of higher CO of the cardoon biodiesel than the other fuels. The viscosity of the 620 cardoon is 9.7 cSt while for brassica and coffee is 6 and 5.7 cSt [80, 87]. Same results has been 621 reported in the literature [88]. Effect of the fatty acids compositions on CO is similar to THC [38].

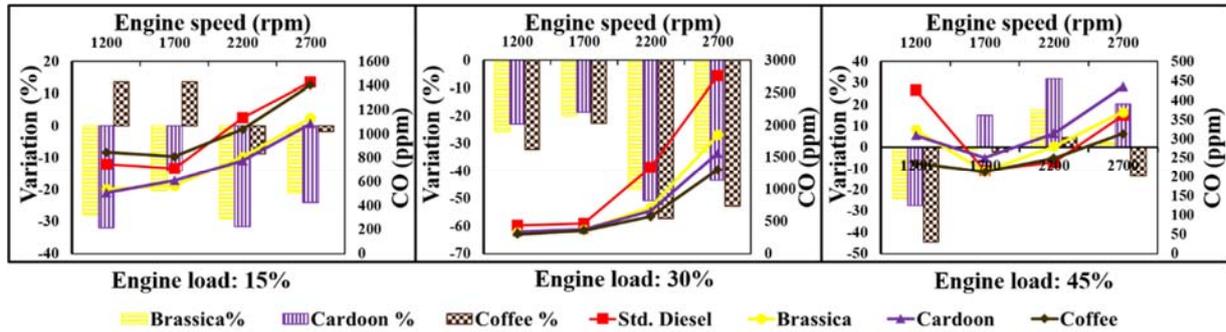


Figure 8. The variation of CO for the biodiesel blend and diesel fuels with engine speed in different engine loads.

3.4.4 CO₂

Figure 9 shows the corresponding diagram for the emitted CO₂ in ppm. These emissions can contribute to serious public health problems [89] and also is one of the greenhouse gases which contributes in ozone formation and global warming [90]. In other hand, the increasing in this emission is a signal of the complete combustion. Thus, in the literature the CO₂ rarely have been considered as a harmful emission. In this study, the value of this emission has been considered only to understand effect of using different diesel biodiesel blend fuels on it.

The CO₂ emission of all fuels has the tendency to decrease by increasing the engine speed and increase by increasing the engine load for all fuels. In all engine loads, the CO₂ is lower when engine fueled by diesel – biodiesel blends than fueling by standard diesel in 1200-1700 engine speed, except cardoon. The CO₂ emission has been increased in 15 and 30% engine load for all diesel biodiesel blends fuel and 2200 -2700 rpm. In the higher engine speed (e.g. 2700 rpm) volumetric efficiency of the engine has been decreased and CO₂ emission of the engine will decreased due to lack of sufficient oxygen to combustion. But the inherent oxygen content of the biodiesel fuel has been compensated some of this reduction of the oxygen inside the cylinder

mixture. Increasing of CO_2 in exhaust emission is an indication of the complete combustion of fuel [641] and this is due to oxygen content of biodiesel [77, 79]. The brassica biodiesel-diesel blend causes [642] highest increase in CO_2 emission (highest increase in CO_2 43.80% in 15% engine load and 2700 [643] rpm). This can be related to the higher oxygen content of the brassica biodiesel (13.44%) than [644] cardoon (10.91%) and coffee (7.77%) biodiesels. In 45% engine load and all engine speeds the [645] CO_2 is lower when using diesel biodiesel fuel instead of standard diesel in engine. The higher [646] cylinder pressure in 45% engine load may be the reason of the reduction of the quality of the [647] atomization of the sprayed fuel into cylinder and hence combustion and CO_2 value. In addition the [648] lambda and oxygen content in 45% has been decreased drastically. Although the CO_2 emission of [649] cardoon and coffee is lower than brassica. This can be due to lower oxygen content of the coffee [650] than the other biodiesels and the reason for cardoon higher viscosity (9.5 cSt) is a negative [651] parameter which decrease the quality of the combustion and decreases the CO_2 emission. The [652] highest reduction in CO_2 emission is for cardoon (13.15% in 45% engine load and 1700 rpm). It [653] should be noticed that cardoon biodiesel has highest dynamic viscosity (9.5 cSt) and medium [654] oxygen content (10.91%) among all three considered biodiesels [80].

Considering the CO_2 emission regard to other emission such as THC and CO is more useful. There [656] are some different reports in various study about effect of biodiesel on engine CO_2 emission. Some [657] researchers stated that the biodiesel cause increasing in CO_2 emission [71] and the other reported [658] a decreasing in CO_2 emission when using diesel biodiesel blends instead of standard diesel in [659] engine [79]. According to the result of this study it can be stated that using of biodiesel instead of [660] standard diesel fuel will decrease CO_2 emission in lower engine speed and higher loads because [661] of its higher viscosity than diesel fuel and it will increase the CO_2 emission in higher engine speeds

which comes from its inherent oxygen content. In addition, the emitted CO_2 of the engine can be 663 captured by the plant during the process of photosynthesis, while preparing seed for biodiesel [75].

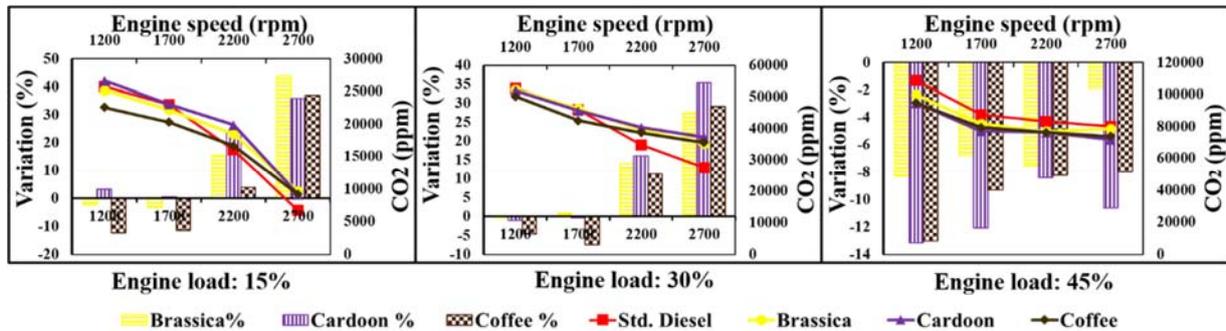


Figure 9. The variation of CO_2 for the biodiesel blend and diesel fuels with engine speed in different engine loads.

3.4.5 Soot

Figure 10 depicts the soot of biodiesel diesel blends compared to the diesel fuel. Soot emission 669 increases by the increasing load for the whole fuels due to incomplete fuel combustion [76, 79]. 670 As the load increases, more fuel is injected, causing an increasing of diffusion combustion 671 duration. In addition in higher engine load (45%) the volumetric efficiency has been decreased and 672 the mixture inside the cylinder is richer than 15 and 30% engine loads. This reduces the oxidation 673 of soot during the expansion stroke because there is less time after the end of diffusion combustion 674 and there is also less oxygen [75]. This trend is because particles are mainly formed during the 675 diffusion combustion, and most of the combustion is diffusive at high load, which means that the 676 oxygen content of biodiesel is more effective in soot formation reduction [13].

The emitted soot decreased by increasing in engine speed for all engine loads and diesel biodiesel 678 blends. There is a different behavior in engine soot emission for different engine load, especially 679 in lower engine speed. The emitted soot for 15% engine load in 1200-1700 engine speeds are

approximately constant but in higher engine load (30 and 45%) there is a remarkable percent of 681 reduction in soot value with engine speeds. In higher engine speeds (1700-2700) rate of reduction 682 is lower than that in lower engine speeds. This can be attributed to an increase in turbulence effects 683 by an increase in the engine speed, which enhances the extent of complete combustion [13].

The soot emitted by all bio-fuels blends, is higher than that for the corresponding standard diesel 685 fuel case in low (15%) and medium (30%) engine load, so that the highest value of increase in this 686 emission is 435.30% (Cardoon, 2200 rpm) and 169.40% for 15 and 30% (Brassica, 2200 rpm) 687 engine loads, respectively. On the contrary, using of biodiesel diesel blends has decreased the soot 688 emission in 45% engine load and all engine speed. Although the lowest value of this emission is 1 689 mg/m³ (cardoon, 2700 rpm) but the highest percent reduction is 67.24% and the other engine 690 speeds (Cardoon, 2200 rpm). Reduction in soot emission indicates better combustion and oxidation 691 of already formed soot assisted by the presence of the fuel-bound oxygen of fuel even in locally 692 rich zones and its higher cetane index [74, 77]. There is lesser amount of unburned hydrocarbons 693 present in the engine exhausts gases [71] (Figure 6). So, lower soot emission values are achieved 694 by biodiesel blends as compared to the diesel fuel [72, 76, 79].

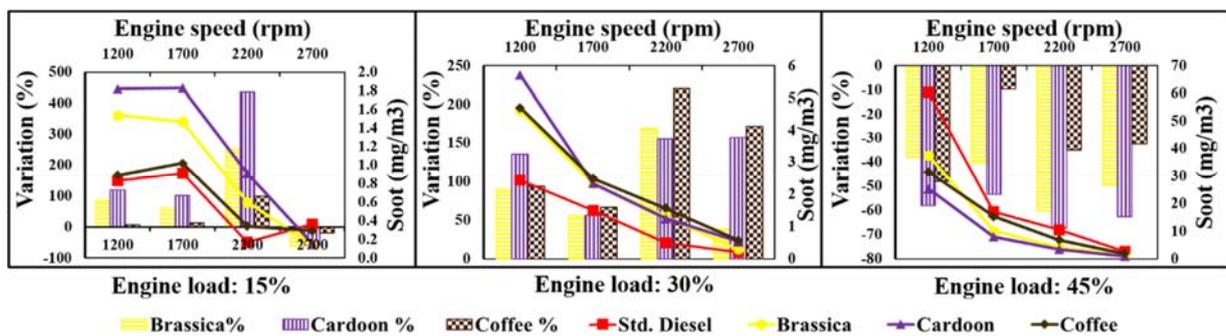


Figure 10. The variation of soot for the biodiesel blend and diesel fuels with engine speed in different engine loads.

3.5 Combustion

In the following section the results for different combustion characteristics of diesel biodiesel blend fuels and diesel fuel burning in the engine are presented.

3.5.1 Combustion peak temperature

Figure 11 shows the variation of peak combustion temperature of diesel fuel and diesel and diesel- 703 biodiesel blends. It is clear that the peak combustion temperature decreases by increasing the 704 engine speed and increases by increasing the engine load for all the test fuels. The maximum 705 combustion temperature of all the biodiesel fuels is lower than diesel in 45% load. It can be 706 observed that the peak combustion temperature for the brassica, cardoon and coffee biodiesel, 707 diesel fuel blends are a little higher than diesel fuel in low engine speed (1200-1700) and engine 708 load (15%) than the corresponding ones for the diesel fuel case, it increases in the higher engine 709 speeds (2200-2700). This trend is repeated for 30% engine load with a little changes in the 710 percentage of variations. But in 45% engine load the peak combustion temperature for all diesel- 711 biodiesel blends is lower than that for diesel fuel. The most increase and decrease in peak 712 combustion temperature are 14.13% (2700 rpm and 30% engine load) and 6.97% (2700 rpm and 713 45% engine load) for Cardoon, respectively. Generally, it can be stated that the biodiesel diesel 714 blends fuel have decreased the peak temperature of combustion. This is due to availability of 715 oxygen in biodiesel which enhanced the air fuel ratio and decreased combustion temperature. In 716 addition lower carbon-hydrogen ratio of the biodiesel decreases the combustion temperature. At 717 lower engine speeds and load operating points, inadequate mixing of fuel and air results in lower 718 in-cylinder temperatures for biodiesel fueled engines [91].

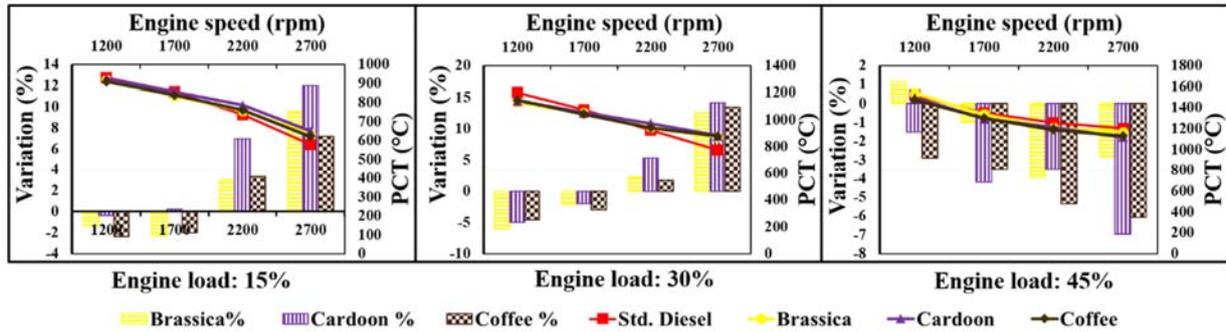


Figure 11. The variation of PCT for the biodiesel blend and diesel fuels with engine speed in different engine loads.

3.5.2 Engine cylinder pressure (CP)

The engine cylinder pressure (CP) characterizes the ability of the fuel to mix well with air and burn. After starting of combustion, pressure rose rapidly due to the expansion of the cylinder contents and reached to a peak few degrees before TDC (top dead center). Then it decreased gradually during the expansion stroke [66]. It can be seen that the peak pressure occurred earlier for biodiesel-diesel blends than STD especially in higher engine speed (Figure 12). The combustion phenomenon for different fuel occurred very late and this is due to late ignition time and so, the combustion occurred very late and in the middle of the expansion course. In such a condition PCP (peak combustion pressure) is lower than maximum cylinder pressure in TDC. This problem is worse for standard diesel. This also has decreased the engine power and mechanical efficiency. The highest acceptable advance in PCP CA° is for 30% engine load. The PCT CA° for brassica, cardoon and coffee were 2.8, 3, and 3.20 CA° before that for STD and this is in accordance to oxygen content of the biodiesel fuels (13.44, 10.91 and 7.77% for brassica, cardoon and coffee, respectively).

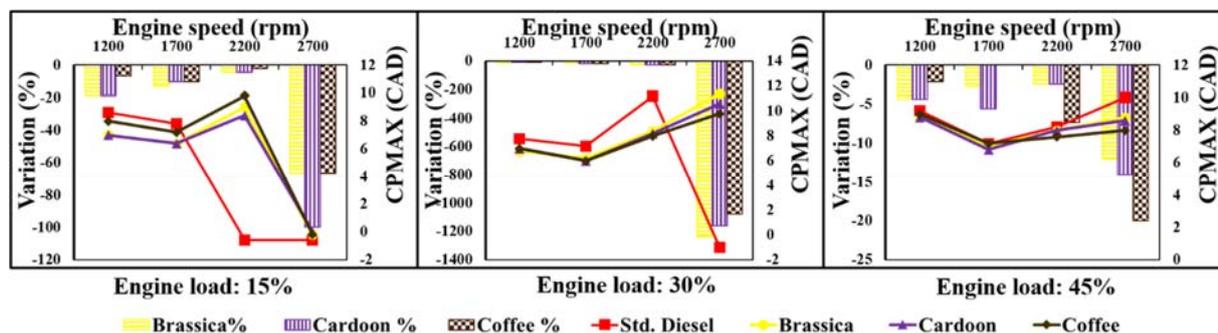


Figure 12: The variation of CPMAX (peak pressure crank angle) for the biodiesel blend and diesel fuels with engine speed in different engine loads.

The variation of the cylinder pressure in different crank angle for all 12 experiments are shown in 740 the Figure 14. As it can be seen in this figure, the peak engine cylinder pressure decreased by 741 increasing the engine speed. This is a common trend for all engine loads and fuels. The trend of 742 the engine cylinder pressure for different biodiesel-diesel fuels is similar especially in lower engine 743 loads. In lower cylinder pressure especially for 15% engine load, the value of peak engine cylinder 744 pressure for standard diesel is lower than that in all different type of diesel-biodiesel blend fuels. 745 So, as it can be seen in all engine speed the highest peak engine cylinder pressure is for cardoon 746 biodiesel blends and the lowest was for standard diesel fuel. In the higher cylinder pressure, the 747 amount of peak cylinder pressure of diesel fuel is higher than other fuels and in some cases it is 748 approximately same as the other fuels. The highest increase in cylinder peak pressure is 31.63% 749 for coffee in 30% engine load and 2700rpm.

As it can be seen in the cylinder pressure curves the ignition process has improved by presence of 751 oxygen in biofuels and reduction in the ignition delay. The low quality of the combustion at low 752 loads (15 and 30%) at 2200 and 2700 rpm with standard diesel have been improved while using 753 biofuels. In all graphs for all fuels and experiments the cylinder pressure graph is shifted slightly

to the left. Totally it can be stated that the trend of cylinder pressure of diesel biodiesel blends is 755 similar to standard diesel fuel. Same result is reported by Özener et al., [71] and Zhu et al., [92]. 756 The start of rise in cylinder pressure for biodiesel-diesel blends is started before diesel fuel. This 757 may be due to the higher viscosity of biodiesel and increase in start of injection [71].

The increase in peak cylinder pressure of diesel-biodiesel blends than standard diesel may be due 759 to their lower ignition delay. The sooner start of combustion of biodiesel diesel blends cause 760 increase in cylinder peak pressure. The other reason for increasing in cylinder peak pressure comes 761 from its oxygen content. On the other hand, the lower LHV of biodiesel than diesel fuel increases 762 the required fuels in premixed combustion phase [93]. In addition, the higher viscosity and 763 volatility of biodiesel increases the cylinder pressure. These two parameter decrease the ignition 764 delay of biodiesel combustion and increase the cylinder engine pressure [72].

According to the result of the cylinder pressure curve consideration, it can be stated that the 766 biodiesel fuel has some special characteristics (e.g. their inherent oxygen content) which make 767 them suitable fuels in the higher engine load and engine speed. Differences among the brassica, 768 cardoon and coffee biodiesel-diesel fuels blends cylinder pressure is lower than that between these 769 fuels and STD fuel.

It is found that peak pressure increases in line with the increased number of double bounds or 771 unsaturation degree [38]. This is a signal that an increased premixed (close to TDC) combustion 772 has occurred, as it is confirmed in the ROHR plots (Figure 15). Additionally initial pressure rise 773 increases slightly as the chain length increases.

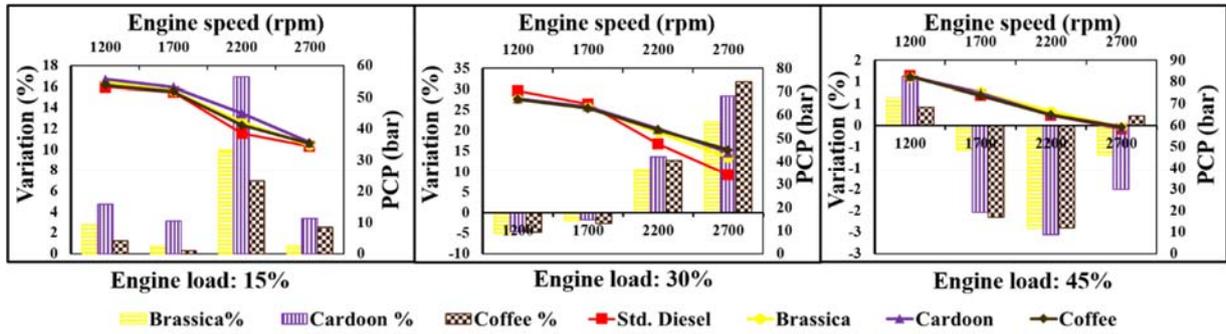


Figure 13. The variation of peak cylinder pressure for the biodiesel blend and diesel fuels with engine speed in different engine loads.

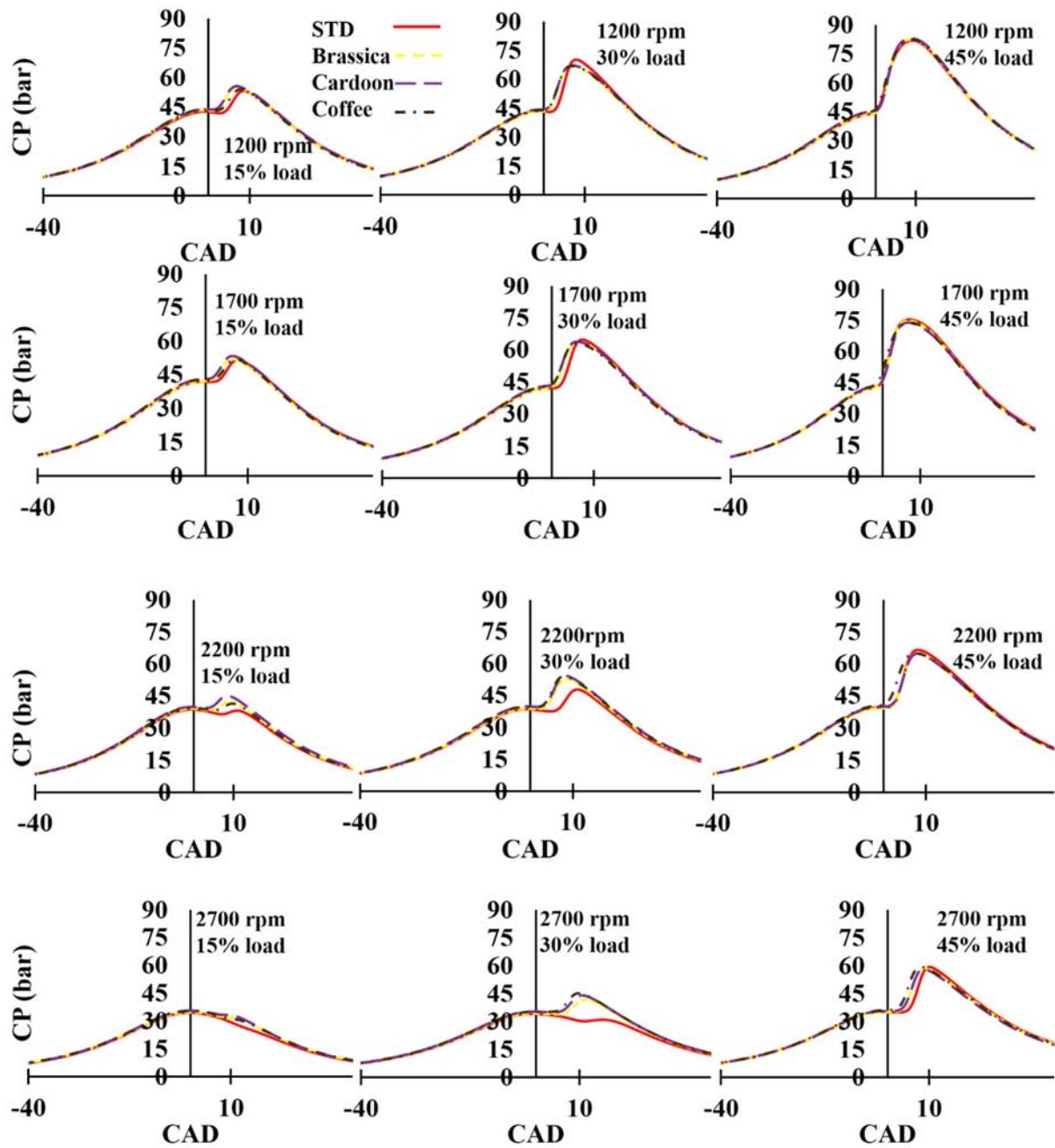


Figure 14. Cylinder pressure against crank angle diagrams, at the different load and speed conditions for the neat diesel fuel and its blends with Brassica, Cardoon and Coffee biodiesel.

3.5.3 Net heat release rate (NHRR) (J/CAD)

The heat release rate for all 12 experiments are shown in Figure 15. As it can be seen in this figure 785 and graphs, the ignition delay for all biodiesel-diesel fuels blends is shorter than standard diesel. 786 In addition the net heat release decreases by increasing the engine speed and it increased by 787 increasing the engine load. In lower engine speed (1200-1700 rpm) and all engine loads the net 788 heat release of biodiesel-diesel blends were lower than that in standard diesel. But in the higher 789 engine speed (2200-2700 rpm), the value of diesel-biodiesel blend flues net heat release were 790 higher than that in standard diesel fuel. This is due to oxygenate content of biodiesel which 791 improves combustion quality especially in higher engine load. In the higher engine load the intake 792 oxygen decreased and the effect of oxygen content in biodiesel fuels shows itself more clearly. As 793 stated about cylinder pressure graphs, the heat release graphs of biodiesel-diesel blends are similar 794 to diesel fuel but they are slightly shifted to the left. So, the rise in heat release is started sooner in 795 biodiesel diesel fuels than standard diesel fuel.

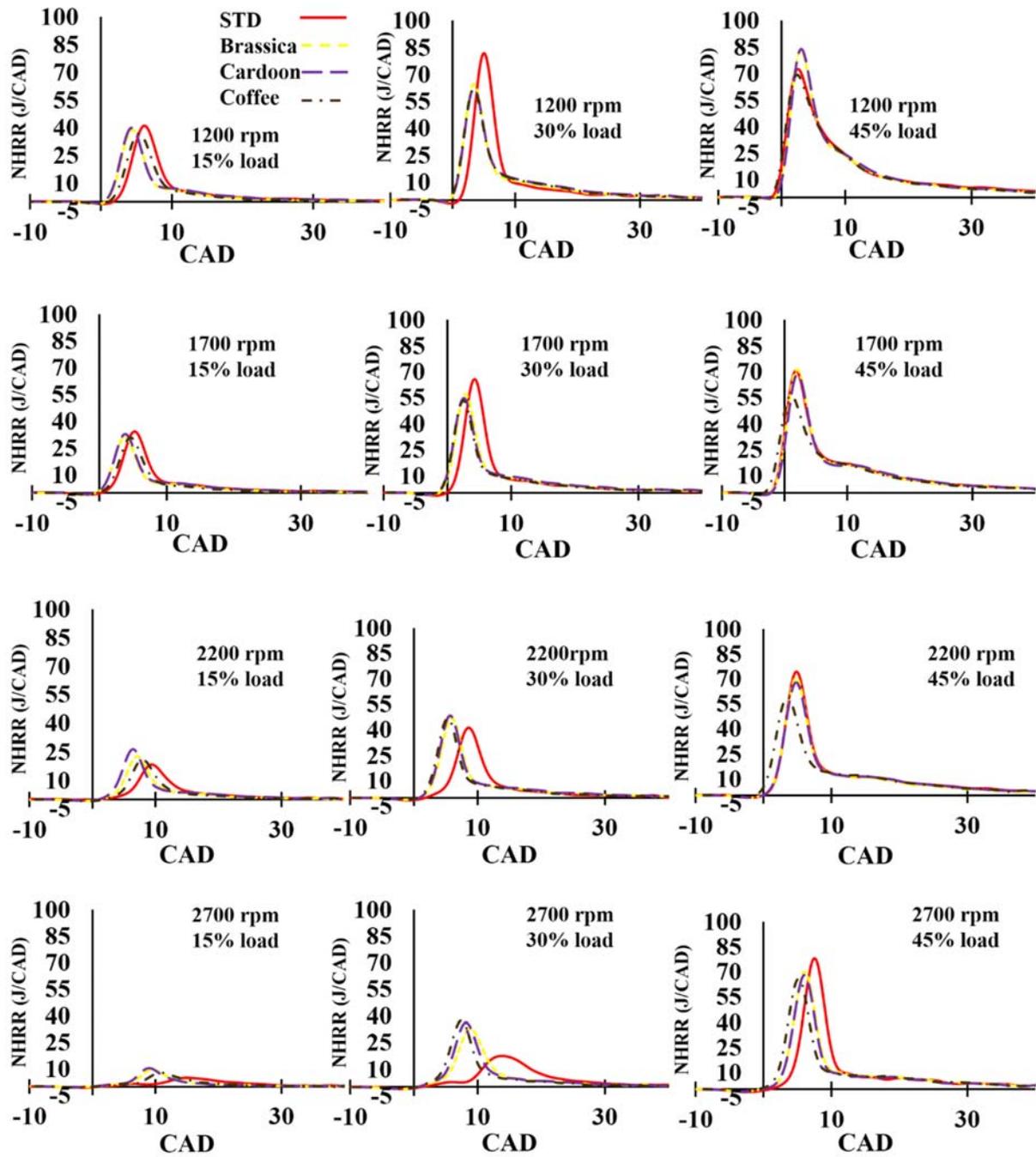


Figure 15. Heat release rate against crank angle diagrams, at the different engine load and speed conditions for the neat diesel fuel and its blends with Brassica, Cardoon and Coffee biodiesel

Two important parameters of the biodiesel are effective on the NHR (net heat release) (J/cycle). 801 The first is the LHV which increases the NHR and the other one is the oxygen of the biodiesel 802 which enhances the combustion quality and NHR. Presence of the oxygen in the biodiesel fuel is 803 effective on NHR especially in the higher engine speed and lower stoichiometric ratio. As it can 804 be seen in the Figure 16, in 45% engine load the NHR in different engine speeds for biodiesels is 805 lower than that in diesel fuel. The NHR of the coffee biodiesel is lowest among all the fuels and it 806 is because of its value of LHV (39.18 MJ/kg) which is lowest among all the fuels. The NHR of the 807 brassica and cardoon is in accordance to their LHV. The LHV of the cardoon (40.69 MJ/kg) is 808 higher than brassica (40.10 MJ/kg). In 2700 rpm the NHR of brassica is higher than cardoon 809 because of the low stoichiometric ratio and higher oxygen content of the brassica (13.44%) than 810 cardoon (10.91%). The NHR of the biodiesels fuels in the in 15 and 30% engine load and 1200 811 and 1700 rpm engine speed is lower than diesel fuel due to their lower LHV. The value of the 812 NHR is in accordance to their value of LHV. In higher engine speeds (2200 and 2700 rpm) due to 813 the decreasing of stoichiometric ratio, the value of NHR of biodiesel fuel is higher than diesel fuel. 814 The inherent oxygen content in biodiesel has compensated the oxygen reduction inside the 815 cylinder. But the increasing in the NHR of the different biodiesels is influenced by the value of 816 their LHV. The fuel with higher LHV has higher NHR.

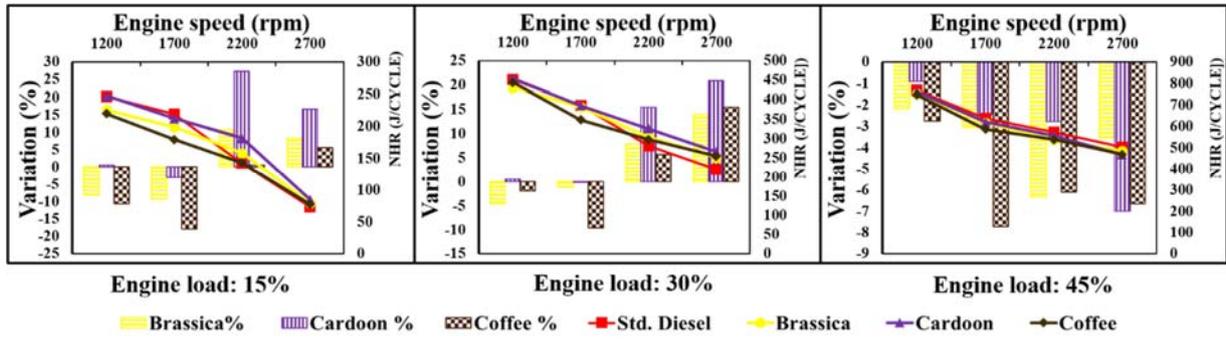


Figure 16: The NHR for the biodiesel blend and diesel fuels with engine speed in different engine loads.

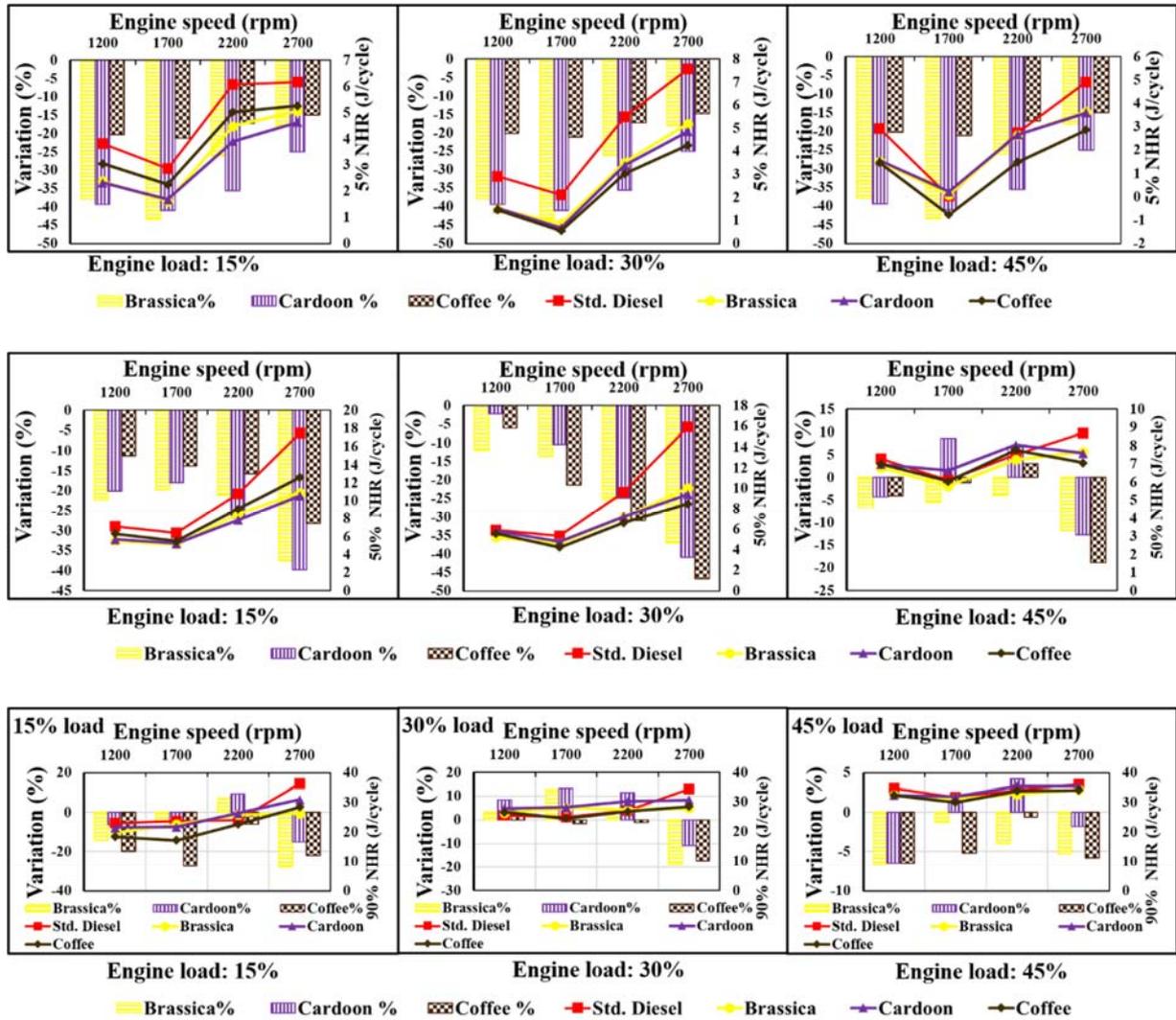


Figure 17: The 5%, 50% and 90% cumulative net heat release (Cum NHR) for the biodiesel blend and diesel fuels with engine speed in different engine loads.

The heat release rate diagram has been drawn by using the cylinder pressure data (Figure 15). This 826 diagrams can be used to determine the start of the combustion (SOC), rate of the fuel burning and 827 ignition delay values. As it can be seen in these diagram the ID of the biodiesel diesel blends fuel 828 is shorter than the ID of the diesel fuel. The peak of the heat release rate for brassica, cardoon and 829 coffee biodiesel diesel blend fuels is lower than that in diesel fuel in most of the test conditions.

Due to shorter ignition delay of the biodiesel diesel fuel blends, the SOC of these fuel is earlier 831 than the diesel fuel. In higher engine speeds and lower engine loads (15 and 30%) the combustion 832 of the diesel fuel starts very late and close to the end of the combustion stroke due to its long ID. 833 But the ID of the biodiesel diesel blends is shorter than diesel fuel and the combustion start earlier, 834 the energy of combustion is released more close to the start of the combustion stroke. For example 835 in the test condition number 11, the CA50 cumulative heat release (which is the angle in which 836 50% of the total fuel has been burned [94]) of the brassica, cardoon, coffee biodiesel diesel blends 837 and diesel fuel is 10.05, 9.42, 8.50 and 15.95 °CA. But in test condition number 3, the CA50 for 838 the brassica, cardoon, coffee biodiesel diesel blends and diesel fuel is 6.81, 6.97, 6.99 and 6.99 839 °CA. These is a good behavior of the biodiesel diesel fuel which increases the efficiency and 840 decreases the THC and CO emission of the engine. The thermal efficiency of brassica, cardoon, 841 coffee biodiesel diesel blends and diesel fuel in test number 11 is 21.27, 22.45, 22.07 and 16.22 842 %, respectively and in test number 3 is 36.65, 36.57, 35.82 and 36.55%. The THC emission of the 843 brassica, cardoon, coffee biodiesel diesel blends and diesel fuel in test number 11 is 468.84, 844 329.41, 276.92 and 1241.26 ppm, respectively and in test number 3 is 108.18, 93.80, 96.7088.22 845 and 108.18 ppm. This is also repeated for CO emission. A longer ignition delay allowed for more 846 time for the fuel/air mixture to homogenize, which is ready to auto ignite and results a higher 847 premixed peak [71]. This can be seen in the Figure 15. Same results has been reported by Ozsezen 848 et al. [95] and Buyukkaya [72].

3.5.4 Ignition delay (ID)

The ignition delay is one of the most important parameter in combustion phenomenon [72] because of its direct effect on the engine heat release and engine emission [96]. This parameter is the time 852 between the start of injection (SOI) and the start of combustion (SOC). ID is heavily affected by

fuel type and especially its CN [97]. The ignition delay of diesel-biodiesel blends is lower than 854 that in diesel fuel in most of engine speeds and engine loads (Figure 18). ID of the all the fuels has 855 been decreased by increasing the engine load due to higher combustion temperature in higher 856 engine load which decreases the physical ID [98]. The most decreasing in the ignition delay is for 857 coffee biodiesel and in 45% engine load (29%). Higher cetane number of the biodiesel makes auto 858 ignition easily and in the consequence it would shorten ID [99]. It can be observed that the delay 859 is longer at lighter loads and shortens as the load increases. This behavior may be due to lower 860 volatility and higher viscosity of biodiesel which causes poor fuel atomization and mixing at light 861 loads and lower cylinder pressure [69, 96]. The ignition delay of the brassica, cardoon and coffee 862 biodiesel diesel fuel blends in 15% engine load is 9.52, 11.05, 5.07% and in 30% engine load is 863 12.88, 13.85, 15.78% lower than diesel fuel on average, respectively. The ignition delay of the 864 brassica and cardoon biodiesel diesel fuel blends in 45% engine load is 0.11 and 1.21% higher and 865 for coffee biodiesel diesel fuel blends is 12.35% lower than diesel fuel on average, respectively.

The ID is affected by some parameters. Any parameters which change the quality of atomization, 867 air fuel mixing and temperature of the inside the cylinder may change the ID. By increasing the 868 viscosity, the quality of the injection and atomization will change. High viscosity of the biodiesel 869 cause the poor atomization, slower mixing, increased penetration and reduced cone index and in 870 consequence reduced ID. [100]. The dynamic viscosity of the brassica, cardoon and coffee is 6, 871 5.7 and 9.5 cSt, respectively. These values are higher than viscosity of diesel fuel (1.9-4.1 cSt). In 872 other hand increasing in the CN of the fuel will decrease the ID [38, 101]. The CN of the brassica, 873 cardoon, coffee and diesel fuel is 56.44, 56.11, 57.44 and 48, respectively. So, the CN of the 874 biodiesels is approximately same and is higher than the CN of the diesel fuel. As it can be seen in 875 the Figure 18, ID of the biodiesel diesel blend fuels is lower than the diesel fuel. The ID of the

coffee biodiesel in 30 and 45% engine load and all engine speeds are shortest among all fuels because of its lower CN.

In 15% engine load, the ID is more influenced by the CN of the fuel and the ID of cardoon biodiesel is lowest which has the highest value of the CN. In 30% engine load the cylinder pressure and 880 temperature is higher than 15% engine load. So the effect of the viscosity and surface tension 881 (generally effect of atomization and evaporation of the fuel) is more significant than 15% engine 882 load but not as much as 45% engine load. In 30% engine load the values of the ID for brassica, 883 cardoon and coffee is approximately same. In fact the low dynamic viscosity and surface tension 884 of the coffee biodiesel and high CN of the cardoon and brassica has shortened the ID similarly. In 885 45% engine load effect of the viscosity and surface tension on the atomization and evaporation of 886 the fuel inside the cylinder in consequence, the ID is more than CN of the fuels. So, the coffee 887 biodiesel with lowest viscosity and surface tension has the lowest ID. A shorter ID of biodiesel 888 than diesel fuel has been reported in most of researches which has been carried out on the 889 combustion characteristics of the biodiesel. Jaichandar et al., [102] stated that the higher cetane 890 number, higher cylinder pressure and temperature are the reason of the shorter ID delay of the 891 palm biodiesel. Sahoo and Das the complex and rapid pre-flame chemical reaction in high cylinder 892 temperature as the reason of the biodiesel shorter ID [93].

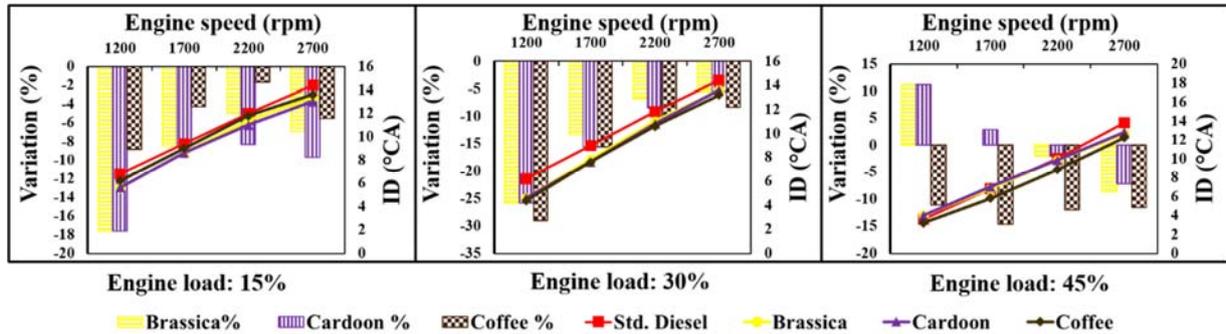


Figure 18. The variation of ignition delay for biodiesel blend and diesel fuels with engine speed in different engine loads.

4 Conclusions

This study are presented the results of a series of experimental tests which have affected a 898 compression-ignition engines fueled with mixtures of three different biofuels: brassica, cardoon 899 and coffee biodiesels. The aim of experimental investigations was to evaluate the effects of the 900 burning of B20 blends and compare them to those obtained from traditional diesel. It is evinced 901 as, maintaining fixed the injection parameters in each test condition, and the performance in terms 902 of power are almost unaltered between the various fuels. The exhaust emissions recorded a 903 substantial decrease, except for nitrogen oxides: in this context, it must be concluded that the 904 increase in these emissions is a critical aspect, which will require in the near future to further 905 investigations, especially in light of the possibility to employ effective methods of reducing 906 emissions in question. In addition:

1. The CN of the brassica, cardoon and coffee is 56.44, 56.11 and 57.44, respectively, which is higher than CN of the standard diesel fuel (44) and this have shorten the ID for the combustion of the biodiesels diesel fuels.

2. The oxygen content of the brassica, cardoon and coffee is 13.44, 10.91 and 7.77% respectively. The additional oxygen have decreased the CO and THC emissions.
3. The surface tension of the brassica, cardoon, coffee and diesel is 42.05, 40.99 and 37.62 mN/m. The higher value of the surface tension for biodiesel fuels was effective on injection and atomization of the fuel.
4. The result of the experiment shows that different characteristics of biodiesel are effective on the performance, emissions and combustion parameters of the engine. In order to talk about the effect of these parameters all of these characteristics should be taken account.
5. In lower engine load (15 and 30%) and engine speed (1200-1700) and also in 45% engine load (all engine speed) amount of the NO_x emission has been decreased. This comes from the lower peak combustion temperature of the different biodiesel due to their lower LHV. When the peak combustion temperature is sufficiently high to formation of the NO_x , the inherent oxygen content of the biodiesel fuels have increased the NO_x emission.
6. The soot of the brassica, cardoon and coffee biodiesel diesel blends is higher than the diesel fuel for lower engine load (15 and 30% engine load) and it is higher than diesel fuel in higher engine load (45% engine load). The reduction of the soot of the biodiesel diesel blend fuels is mainly due to oxygen content of the biodiesel and improve in combustion quality.
7. The maximum BTE obtained for different fuels as well as standard diesel was lower than that of standard diesel. This might be due to combined effect of higher BSFC and early combustion (shorter ignition delay).
8. The start of combustion of biodiesel diesel blends was earlier than diesel fuel due to their shorter ID. In addition, this increases the CA50 of the diesel fuel especially for higher

engine speeds and lower engine load. This phenomenon (higher CA50 of diesel fuel) has increased the engine THC and decreased the engine efficiency rather than biodiesel diesel fuels.

9. The most effective parameters on combustion and emission is the ID.
10. The dynamic viscosity of the cardoon biodiesel (9.5 cSt) is considerably higher than brassica and coffee biodiesels (5.7 and 6 cSt, respectively).
11. The surface tension of the brassica, cardoon and coffee biodiesels is 40.99, 37.62 and 42.05 Nm/m, respectively.
12. The LHV of the brassica, cardoon and coffee biodiesels is 40.10, 40.69 and 39.18 MJ/kg.

Further studies will be conducted by respect to the spray formation of bio-fuel in the combustion chamber and the optimization of the relative process of introduction into the cylinder, in order to evaluate how the injection parameters of the biodiesel blends effect on the performance and emissions of the engine.

5 Acknowledgment

The authors thank d'Amico Leone, technician - Institute of Sciences of Food Production, National Research Council of Lecce for biofuels production and Antonio Tricarico, research fellow of University of Salento, Dept. Engineering for Innovation, for conducting the experiments.

6 References

- [1] Demirbas A. Importance of biodiesel as transportation fuel. *Energy Policy* 2007;35(9):4661-70.

- [2] Suganya T, Varman M, Masjuki HH, Renganathan S. Macroalgae and microalgae as a potential source for commercial applications along with biofuels production: A biorefinery approach. *Renewable and Sustainable Energy Reviews* 2016;55:909-41.
- [3] Ramírez-Verduzco LF, Rodríguez-Rodríguez JE, Jaramillo-Jacob AdR. Predicting cetane number, kinematic viscosity, density and higher heating value of biodiesel from its fatty acid methyl ester composition. *Fuel* 2012;91(1):102-11.
- [4] Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science* 2007;33(3):233-71.
- [5] Lapuerta M, Armas O, Rodríguezfernandez J. Effect of biodiesel fuels on diesel engine emissions. *Progress in Energy and Combustion Science* 2008;34(2):198-223.
- [6] Sajjadi B, Raman AAA, Arandiyan H. A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models. *Renewable and Sustainable Energy Reviews* 2016;63:62-92.
- [7] Rakopoulos CD, Rakopoulos DC, Hountalas DT, Giakoumis EG, Andritsakis EC. Performance and emissions of bus engine using blends of diesel fuel with bio-diesel of sunflower or cottonseed oils derived from Greek feedstock. *Fuel* 2008;87(2):147-57.
- [8] Gülüm M, Bilgin A. Density, flash point and heating value variations of corn oil biodiesel–diesel fuel blends. *Fuel Processing Technology* 2015;134:456-64.
- [9] Yang J, Astatkie T, He QS. A comparative study on the effect of unsaturation degree of camelina and canola oils on the optimization of bio-diesel production. *Energy Reports* 2016;2:211-7.

- [10] Rahimi A, Ghobadian B, Najafi G, Jaliliantabar F, Mamat R. Performance and emission parameters of single cylinder diesel engine using castor oil bio-diesel blended fuels. IOP Conference Series: Materials Science and Engineering 2015;100(1):012012.
- [11] Sahoo PK, Das LM, Babu MKG, Arora P, Singh VP, Kumar NR, et al. Comparative evaluation of performance and emission characteristics of jatropha, karanja and polanga based biodiesel as fuel in a tractor engine. Fuel 2009;88(9):1698-707.
- [12] Kaisan MU, Anafi FO, Nuzzkowski J, Kulla DM, Umaru S. Exhaust emissions of biodiesel binary and multi-blends from Cotton, Jatropha and Neem oil from stationary multi cylinder CI engine. Transportation Research Part D: Transport and Environment 2017;53:403-14.
- [13] Xue J, Grift TE, Hansen AC. Effect of biodiesel on engine performances and emissions. Renewable and Sustainable Energy Reviews 2011;15(2):1098-116.
- [14] Shahir VK, Jawahar CP, Suresh PR. Comparative study of diesel and biodiesel on CI engine with emphasis to emissions—A review. Renewable and Sustainable Energy Reviews 2015;45:686-97.
- [15] Silitonga AS, Masjuki HH, Mahlia TMI, Ong HC, Chong WT, Boosroh MH. Overview properties of biodiesel diesel blends from edible and non-edible feedstock. Renewable and Sustainable Energy Reviews 2013;22:346-60.
- [16] Ejim CE, Fleck BA, Amirfazli A. Analytical study for atomization of biodiesels and their blends in a typical injector: Surface tension and viscosity effects. Fuel 2007;86(10-11):1534-44.
- [17] Agarwal AK, Das L. Biodiesel development and characterization for use as a fuel in compression ignition engines. Journal of engineering for gas turbines and power 2001;123(2):440-7.

- [18] De Domenico S, Strafella L, D'Amico L, Mastroilli M, Ficarella A, Carlucci P, et al. Biodiesel production from *Cynara cardunculus* L. and *Brassica carinata* A. Braun seeds and their suitability as fuels in compression ignition engines. *Italian Journal of Agronomy* 2016;10(1s):47.
- [19] Rajasekar E, Selvi S. Review of combustion characteristics of CI engines fueled with biodiesel. *Renewable and Sustainable Energy Reviews* 2014;35:390-9.
- [20] Heywood JB. *Internal combustion engine fundamentals*. McGraw-hill New York; 1988.
- [21] Canoira L, Alcántara R, Jesús García-Martínez M, Carrasco J. Biodiesel from Jojoba oil-wax: Transesterification with methanol and properties as a fuel. *Biomass and Bioenergy* 2006;30(1):76-81.
- [22] Azad A, Uddin SA, Alam M. Mustard oil, an alternative Fuel: An experimental investigation of Bio-diesel properties with and without Trans-esterification reaction. *Global advanced research journal of engineering, technology and innovation* 2012;1(3):075-84.
- [23] Rosa HA, Wazilewski WT, Secco D, Chaves LI, Veloso G, de Souza SNM, et al. Biodiesel produced from crambe oil in Brazil—A study of performance and emissions in a diesel cycle engine generator. *Renewable and Sustainable Energy Reviews* 2014;38:651-5.
- [24] Wazilewski WT, Bariccatti RA, Martins GI, Secco D, Souza SNMd, Rosa HA, et al. Study of the methyl crambe (*Crambe abyssinica* Hochst) and soybean biodiesel oxidative stability. *Industrial Crops and Products* 2013;43:207-12.
- [25] Demirbaş A. Fuel properties and calculation of higher heating values of vegetable oils. *Fuel* 1998;77(9-10):1117-20.

- [26] Demirbaş A. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. *Energy Conversion and Management* 2003;44(13):2093-109.
- [27] Lanjekar RD, Deshmukh D. A review of the effect of the composition of biodiesel on NO_x emission, oxidative stability and cold flow properties. *Renewable and Sustainable Energy Reviews* 2016;54:1401-11.
- [28] Sendzikiene E, Makareviciene V, Janulis P. Influence of fuel oxygen content on diesel engine exhaust emissions. *Renewable Energy* 2006;31(15):2505-12.
- [29] Ramadhas A, Jayaraj S, Muraleedharan C. Biodiesel production from high FFA rubber seed oil. *Fuel* 2005;84(4):335-40.
- [30] Schönborn A, Ladommatos N, Williams J, Allan R, Rogerson J. The influence of molecular structure of fatty acid monoalkyl esters on diesel combustion. *Combustion and flame* 2009;156(7):1396-412.
- [31] McCormick RL, Graboski MS, Alleman TL, Herring AM, Tyson KS. Impact of biodiesel source material and chemical structure on emissions of criteria pollutants from a heavy-duty engine. *Environmental science & technology* 2001;35(9):1742-7.
- [32] Esteban B, Riba J-R, Baquero G, Puig R, Rius A. Characterization of the surface tension of vegetable oils to be used as fuel in diesel engines. *Fuel* 2012;102:231-8.
- [33] Allen CA, Watts KC, Ackman RG. Predicting the surface tension of biodiesel fuels from their fatty acid composition. *Journal of the American Oil Chemists' Society* 1999;76(3):317-23.

- [34] Wang X, Huang Z, Kuti OA, Zhang W, Nishida K. Experimental and analytical study on biodiesel and diesel spray characteristics under ultra-high injection pressure. *International Journal of Heat and Fluid Flow* 2010;31(4):659-66.
- [35] Doll KM, Moser BR, Erhan SZ. Surface tension studies of alkyl esters and epoxidized alkyl esters relevant to oleochemically based fuel additives. *Energy & fuels* 2007;21(5):3044-8.
- [36] Melo-Espinosa EA, Sánchez-Borroto Y, Errasti M, Piloto-Rodríguez R, Sierens R, Roger-Riba J, et al. Surface Tension Prediction of Vegetable Oils Using Artificial Neural Networks and Multiple Linear Regression. *Energy Procedia* 2014;57:886-95.
- [37] Chhetri AB, Watts KC. Surface tensions of petro-diesel, canola, jatropha and soapnut biodiesel fuels at elevated temperatures and pressures. *Fuel* 2013;104:704-10.
- [38] Pinzi S, Rounce P, Herreros JM, Tsolakis A, Pilar Dorado M. The effect of biodiesel fatty acid composition on combustion and diesel engine exhaust emissions. *Fuel* 2013;104:170-82.
- [39] Lin C-Y, Lin Y-W. Fuel Characteristics of Biodiesel Produced from a High-Acid Oil from Soybean Soapstock by Supercritical-Methanol Transesterification. *Energies* 2012;5(12):2370-80.
- [40] Ramadhas AS, Jayaraj S, Muraleedharan C, Padmakumari K. Artificial neural networks used for the prediction of the cetane number of biodiesel. *Renewable Energy* 2006;31(15):2524-33.
- [41] Bello E, Out F, Osasona A. Cetane number of three vegetable oils, their biodiesels and blends with diesel fuel. *Journal of Petroleum Technology and Alternative Fuels* 2012;3(5):52-7.

- [42] Knothe G, Matheus AC, Ryan TW. Cetane numbers of branched and straight-chain fatty esters determined in an ignition quality tester☆. *Fuel* 2003;82(8):971-5.
- [43] Sokoto M, Hassan L, Dangoggo S, Ahmad H, Uba A. Influence of fatty acid methyl esters on fuel properties of biodiesel produced from the seeds oil of *Curcubita pepo*. *Nigerian Journal of Basic and Applied Sciences* 2011;19(1).
- [44] Singh SP, Singh D. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renewable and Sustainable Energy Reviews* 2010;14(1):200-16.
- [45] Aricetti JA, Tubino M. A green and simple visual method for the determination of the acid-number of biodiesel. *Fuel* 2012;95:659-61.
- [46] Barbieri Gonzaga F, Pereira Sobral S. A new method for determining the acid number of biodiesel based on coulometric titration. *Talanta* 2012;97:199-203.
- [47] Bouaid A, Martinez M, Aracil J. Long storage stability of biodiesel from vegetable and used frying oils. *Fuel* 2007;86(16):2596-602.
- [48] Lin C, Lin H, Hung L. Fuel structure and properties of biodiesel produced by the peroxidation process. *Fuel* 2006;85(12-13):1743-9.
- [49] Khajeh A, Modarress H. QSPR prediction of flash point of esters by means of GFA and ANFIS. *Journal of hazardous materials* 2010;179(1-3):715-20.
- [50] Mejía JD, Salgado N, Orrego CE. Effect of blends of Diesel and Palm-Castor biodiesels on viscosity, cloud point and flash point. *Industrial Crops and Products* 2013;43:791-7.
- [51] Carareto NDD, Kimura CYCS, Oliveira EC, Costa MC, Meirelles AJA. Flash points of mixtures containing ethyl esters or ethylic biodiesel and ethanol. *Fuel* 2012;96:319-26.

- [52] Hoekman SK, Broch A, Robbins C, Cenicerros E, Natarajan M. Review of biodiesel composition, properties, and specifications. *Renewable and Sustainable Energy Reviews* 2012;16(1):143-69.
- [53] de Caland LB, Silveira EL, Tubino M. Determination of sodium, potassium, calcium and magnesium cations in biodiesel by ion chromatography. *Analytica chimica acta* 2012;718:116-20.
- [54] Hu J, Du Z, Li C, Min E. Study on the lubrication properties of biodiesel as fuel lubricity enhancers. *Fuel* 2005.
- [55] Demirbas A. Progress and recent trends in biodiesel fuels. *Energy Conversion and Management* 2009;50(1):14-34.
- [56] Felizardo P, Baptista P, Menezes JC, Correia MJ. Multivariate near infrared spectroscopy models for predicting methanol and water content in biodiesel. *Analytica chimica acta* 2007;595(1-2):107-13.
- [57] Von Wallbrunn A, Richnow HH, Neumann G, Meinhardt F, Heipieper HJ. Mechanism of cis-trans isomerization of unsaturated fatty acids in *Pseudomonas putida*. *Journal of bacteriology* 2003;185(5):1730-3.
- [58] Wain KS, Perez JM, Chapman E, Boehman AL. Alternative and low sulfur fuel options: boundary lubrication performance and potential problems. *Tribology International* 2005;38(3):313-9.
- [59] Datta A, Mandal BK. A comprehensive review of biodiesel as an alternative fuel for compression ignition engine. *Renewable and Sustainable Energy Reviews* 2016;57:799-821.

- [60] Knothe G, Dunn RO. Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals. *Journal of the American Oil Chemists' Society* 2003;80(10):1021-6.
- [61] Mahmudul HM, Hagos FY, Mamat R, Adam AA, Ishak WFW, Alenezi R. Production, characterization and performance of biodiesel as an alternative fuel in diesel engines – A review. *Renewable and Sustainable Energy Reviews* 2017;72:497-509.
- [62] Meher L, Vidyasagar D, Naik S. Technical aspects of biodiesel production by transesterification—a review. *Renewable and Sustainable Energy Reviews* 2006;10(3):248-68.
- [63] Balat M. Potential alternatives to edible oils for biodiesel production – A review of current work. *Energy Conversion and Management* 2011;52(2):1479-92.
- [64] Foidl N, Foidl G, Sanchez M, Mittelbach M, Hackel S. *Jatropha curcas* L. as a source for the production of biofuel in Nicaragua. *Bioresource technology* 1996;58(1):77-82.
- [65] Mittelbach M. Diesel fuel derived from vegetable oils, VI: Specifications and quality control of biodiesel. *Bioresource technology* 1996;56(1):7-11.
- [66] Pradhan P, Raheman H, Padhee D. Combustion and performance of a diesel engine with preheated *Jatropha curcas* oil using waste heat from exhaust gas. *Fuel* 2014;115:527-33.
- [67] Srinivasa Rao M, Anand RB. Performance and emission characteristics improvement studies on a biodiesel fuelled DICI engine using water and AlO(OH) nanoparticles. *Applied Thermal Engineering* 2016;98:636-45.
- [68] Žaglinskis J, Lukács K, Bereczky Á. Comparison of properties of a compression ignition engine operating on diesel–biodiesel blend with methanol additive. *Fuel* 2016;170:245-53.

- [69] Sakthivel G. Prediction of CI engine performance, emission and combustion characteristics using fish oil as a biodiesel at different injection timing using fuzzy logic. *Fuel* 2016;183:214-29.
- [70] Raheman H, Phadatare AG. Diesel engine emissions and performance from blends of karanja methyl ester and diesel. *Biomass and Bioenergy* 2004;27(4):393-7.
- [71] Özener O, Yüksek L, Ergenç AT, Özkan M. Effects of soybean biodiesel on a DI diesel engine performance, emission and combustion characteristics. *Fuel* 2014;115:875-83.
- [72] Buyukkaya E. Effects of biodiesel on a DI diesel engine performance, emission and combustion characteristics. *Fuel* 2010;89(10):3099-105.
- [73] Chauhan BS, Kumar N, Cho HM, Lim HC. A study on the performance and emission of a diesel engine fueled with Karanja biodiesel and its blends. *Energy* 2013;56:1-7.
- [74] İlkılıç C, Aydın S, Behcet R, Aydın H. Biodiesel from safflower oil and its application in a diesel engine. *Fuel Processing Technology* 2011;92(3):356-62.
- [75] Li S, Wang Y, Dong S, Chen Y, Cao F, Chai F, et al. Biodiesel production from *Eruca Sativa* Gars vegetable oil and motor, emissions properties. *Renewable Energy* 2009;34(7):1871-6.
- [76] Buyukkaya E, Benli S, Karaaslan S, Guru M. Effects of trout-oil methyl ester on a diesel engine performance and emission characteristics. *Energy Conversion and Management* 2013;69:41-8.
- [77] Chauhan BS, Kumar N, Cho HM. A study on the performance and emission of a diesel engine fueled with *Jatropha* biodiesel oil and its blends. *Energy* 2012;37(1):616-22.

- [78] Aliyu B, Shitanda D, Walker S, Agnew B, Masheiti S, Atan R. Performance and exhaust emissions of a diesel engine fuelled with Croton megalocarpus (musine) methyl ester. *Applied Thermal Engineering* 2011;31(1):36-41.
- [79] Gumus M, Kasifoglu S. Performance and emission evaluation of a compression ignition engine using a biodiesel (apricot seed kernel oil methyl ester) and its blends with diesel fuel. *Biomass and Bioenergy* 2010;34(1):134-9.
- [80] Silitonga AS, Masjuki HH, Mahlia TMI, Ong HC, Chong WT. Experimental study on performance and exhaust emissions of a diesel engine fuelled with Ceiba pentandra biodiesel blends. *Energy Conversion and Management* 2013;76:828-36.
- [81] Monyem A, Van Gerpen J, Canakci M. The effect of timing and oxidation on emissions from biodiesel-fueled engines. *Transactions of the ASAE* 2001;44(1):35.
- [82] Knothe G, Sharp CA, Ryan TW. Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine. *Energy & Fuels* 2006;20(1):403-8.
- [83] Graboski M, McCormick R, Alleman T, Herring A. The effect of biodiesel composition on engine emissions from a DDC series 60 diesel engine. *National Renewable Energy Laboratory (Report No: NREL/SR-510-31461)* 2003.
- [84] Dorado M. Exhaust emissions from a Diesel engine fueled with transesterified waste olive oil*. *Fuel* 2003;82(11):1311-5.
- [85] Usta N. An experimental study on performance and exhaust emissions of a diesel engine fuelled with tobacco seed oil methyl ester. *Energy Conversion and Management* 2005;46(15-16):2373-86.

- [86] Gumus M, Sayin C, Canakci M. The impact of fuel injection pressure on the exhaust emissions of a direct injection diesel engine fueled with biodiesel–diesel fuel blends. *Fuel* 2012;95:486-94.
- [87] Gokalp B, Buyukkaya E, Soyhan HS. Performance and emissions of a diesel tractor engine fueled with marine diesel and soybean methyl ester. *Biomass and Bioenergy* 2011;35(8):3575-83.
- [88] Nabi MN, Rahman MM, Akhter MS. Biodiesel from cotton seed oil and its effect on engine performance and exhaust emissions. *Applied Thermal Engineering* 2009;29(11-12):2265-70.
- [89] Rice SA. Human health risk assessment of CO₂: survivors of acute high-level exposure and populations sensitive to prolonged low-level exposure. *environments* 2014;3(5):7-15.
- [90] Gillett NP, Arora VK, Matthews D, Allen MR. Constraining the ratio of global warming to cumulative CO₂ emissions using CMIP5 simulations*. *Journal of Climate* 2013;26(18):6844-58.
- [91] Dhar A, Agarwal AK. Performance, emissions and combustion characteristics of Karanja biodiesel in a transportation engine. *Fuel* 2014;119:70-80.
- [92] Zhu L, Cheung CS, Zhang WG, Huang Z. Combustion, performance and emission characteristics of a DI diesel engine fueled with ethanol–biodiesel blends. *Fuel* 2011;90(5):1743-50.
- [93] Sahoo PK, Das LM. Combustion analysis of Jatropha, Karanja and Polanga based biodiesel as fuel in a diesel engine. *Fuel* 2009;88(6):994-9.

- [94] de O. Carvalho L, de Melo TCC, de Azevedo Cruz Neto RM. Investigation on the Fuel and Engine Parameters that Affect the Half Mass Fraction Burned (CA50) Optimum Crank Angle. SAE International; 2012.
- [95] Ozsezen AN, Canakci M, Turkcan A, Sayin C. Performance and combustion characteristics of a DI diesel engine fueled with waste palm oil and canola oil methyl esters. *Fuel* 2009;88(4):629-36.
- [96] Rodríguez RP, Sierens R, Verhelst S. Ignition delay in a palm oil and rapeseed oil biodiesel fuelled engine and predictive correlations for the ignition delay period. *Fuel* 2011;90(2):766-72.
- [97] Xing-cai L, Jian-guang Y, Wu-gao Z, Zhen H. Effect of cetane number improver on heat release rate and emissions of high speed diesel engine fueled with ethanol–diesel blend fuel. *Fuel* 2004;83(14-15):2013-20.
- [98] Qi DH, Chen H, Geng LM, Bian YZ. Experimental studies on the combustion characteristics and performance of a direct injection engine fueled with biodiesel/diesel blends. *Energy Conversion and Management* 2010;51(12):2985-92.
- [99] Gumus M. A comprehensive experimental investigation of combustion and heat release characteristics of a biodiesel (hazelnut kernel oil methyl ester) fueled direct injection compression ignition engine. *Fuel* 2010;89(10):2802-14.
- [100] Lee CS, Park SW, Kwon SI. An experimental study on the atomization and combustion characteristics of biodiesel-blended fuels. *Energy & fuels* 2005;19(5):2201-8.
- [101] Song H, Jacobs TJ. The influence of soot radiation on NO emission in practical biodiesel combustion. *Fuel* 2014;128:281-7.

- [102] Jaichandar S, Annamalai K. Influences of re-entrant combustion chamber geometry on the performance of Pongamia biodiesel in a DI diesel engine. *Energy* 2012;44(1):633-40.