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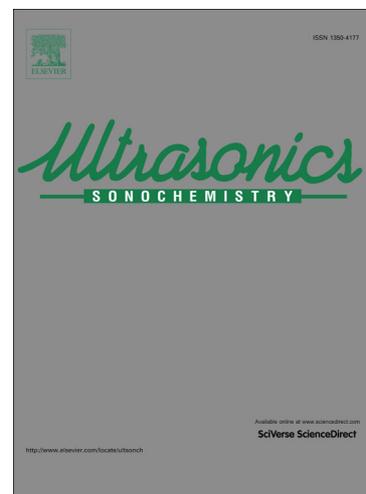
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Effect of Ultrasonic Irradiation on the Properties and Performance of Biodiesel Produced from Date Seed Oil Used in the Diesel Engine

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Abstract

In the present study, the effect of ultrasound irradiation on the transesterification parameters, biodiesel properties, and its combustion profiles in the diesel engine was investigated. Moreover, Date Seed Oil (DSO) was firstly utilized in the ultrasound-assisted transesterification reaction. DSO was extracted from Zahidi type date (*Phoenix dactylifera*) and was esterified to reduce its Free Fatty Acid (FFA) content. Biodiesel yield was optimized in both heating methods, so that the yield of 96.4% (containing 93.5% ester) at 60 °C, with 6 molar ratio of methanol/oil, 1 wt. % of catalyst (NaOH) and at 90 min of reaction time was reported. The ultrasound irradiation did not influence the reaction conditions except reaction time, reduced to 5 min (96.9% yield and 91.9% ester). The ultrasonic irradiation also influenced on the physicochemical properties of DSO biodiesel and improved its combustion in the diesel engine. The analysis results related to the engine and gas emission confirmed that the ultrasound-assisted produced biodiesel has lower density and viscosity, and higher oxygen content facilitating injection of fuel in the engine chamber and its combustion, respectively. Although, B40 (biodiesel blend consisting of 40.% biodiesel and 60 % net diesel fuel) as a blend of both fuels presented higher CO₂ and lower CO and HC in the emissions, the DSO biodiesel produced by ultrasound irradiation presented better specifications (caused about 2-fold improvement in emissions than that of conventional method). The findings of the study confirmed the positive effect of the ultrasound irradiation on the properties of the produced biodiesel along with its combustion properties in the diesel engine, consequently reducing air pollution problems.

Keywords: Date seed oil (DSO); Ultrasonic irradiation; Optimization; Biodiesel; Engine Performance, Exhaust emissions.

1. Introduction

Fatty Acid Methyl Ester (FAME) named as biodiesel is one of the renewable energies usually produced by transesterification of triglycerides in the vegetable oils using an alcohol (methanol) and a catalyst (usually NaOH or KOH). Due to the environmental problems caused by petroleum fuels consumption and advantages of biodiesel, it is widely studied to find suitable ways for using in the current diesel engines [1], [2]. Moreover, this fuel has an appropriate cetane number and higher oxygen content compared to the net diesel fuel presenting similar engine performances, better combustion, and lower engine emissions [3], [4]. Nowadays, soybean, rapeseed, and palm oils are respectively used for biodiesel production in the US, Europe, and Asia. However, feedstock cost accounts for 80% of biodiesel production cost; therefore, finding the raw materials with low price for biodiesel production is a challenge [5]. Although the use of some inedible oils such as waste cooking oil and *Jatropha* has been discussed previously, the research in this area is continued. Middle East countries such as Iran and Iraq have an appropriate climate for cultivating date palm trees (*Phoenix dactylifera*) making them as the top ten date producing countries with a production rate about 2 M ton/year [6], [7]. Most types of *Phoenix* have a slow to medium rate of growth and start bearing fruits from 3-5 years of age and surviving for long years. One matured and productive date tree can have a production rate of approximately 70-140 kg per year depending on the type, age and conditions, which increases annually [8]. In addition to the pulpy layer, which can be directly consumed by human or used for the production of palm oil, it can be said that Date seed accounts for about 10-15% of the fruit's weight. Date seed, which is usually used as animal foods, contains around 5-12% of the oil that can be used as a feedstock for the production of biodiesel [9]. Zahedi is one of the high-yield types of date palm cultivated in Iran and Iraq. Zahedi's dates are elliptical with quite thin and sharp ends. Its seed is oval, brown in color, with medium adhesion to pulp (see Figure S1).

Figure S1

The conventional heating system is usually utilized for conversion of oil to biodiesel, while new technologies such as supercritical fluid, microwave, and ultrasonic irradiation have been suggested for the acceleration of the reaction and less energy consumption [10]. Some of these energy sources can modify the materials' properties. Moreover, it has been mentioned that modification of physical properties of biodiesel can be achieved under the influence of these energies on the micro molecular level of the chemical structure in the biodiesel [11].

To accelerate the transesterification processes, ultrasound technology has been intensively studied, so that the reaction yield can shortly reach over the standard level (> 96.5%) by forming bubbles and the collapse of those bubbles (cavitation) through which high pressure and temperature is produced [12], [13], [14]. Previous studies showed that the temperature and pressure could respectively reach to almost 5000 K and 1000 bar during this collapse [15]. Ultrasound is defined as any sound in the range of 20-100 KHz (low frequency) [16]. When sound passes through the liquid, it creates both negative (expansion) and positive pressure waves (compression). The bubbles are produced by these waves, consequently dissolving the gases. Finally, implosive bubble collapse allows the formation of microstreaming or mild swirls, creating intense local heating, high pressures, and very short lifetimes [17], [18].

Samani et al. [19] evaluated the ultrasonic-assisted biodiesel production conditions from *Pistacia atlantica Desf.* Oil, and reported that the yield under ultrasonic irradiation was 7.5 times greater than that of the conventional method along with the reduced reaction time. Mostafaei et al. [20] studied biodiesel production from waste cooking oil through sonication. They presented higher efficiency, less time, and energy consumption in favor of ultrasonically-produced biodiesel compared to those produced through conventional

mechanical stirring. Yadav et al. [21] have also assessed the ability of biodiesel production from Karabi oil under ultrasound irradiation. They reported an improvement in the physiochemical characteristics of the biodiesel produced under sonication. Although some studies have been performed on the conversion of palm oil through sonication method [22], [23], [24] or DSO through conventional method [25], [26], [27], no study was found on utilizing the date seed oil as raw material under ultrasonic irradiation. Moreover, the performance of biodiesel produced by ultrasonic irradiation in the diesel engine has not been compared with that of the conventional method, and there is only limited evidence about the engine performance fueled by DSO biodiesel [28], [29].

The present study was designed and carried out due to the lack of research on the DSO for biodiesel production, especially through ultrasound irradiation, along with insufficient information about utilizing DSO biodiesel in diesel engine, either produced by the conventional method or ultrasonic method. In this study, the effect of ultrasonic irradiation on the transesterification reaction conditions, increasing the rate of reaction temperature, properties, and performance of biodiesel in the diesel engine, and exhaust gas emissions were deeply evaluated while using DSO as raw material. Then, for the first time in this study, all the variables related to the DSO biodiesel produced by ultrasonic irradiation were compared with the DSO biodiesel produced by the conventional method.

For this purpose, DSO obtained from Zahidi type seeds was converted to the biodiesel via both heating methods (conventional and microwave). In both heating methods, the transesterification reaction conditions such as reaction temperature, methanol amount, catalyst concentration, reaction time, and ultrasonic power were assessed. Then, the biodiesel produced through both heating methods was analyzed to investigate the effect of ultrasound on the properties of DSO biodiesel. Finally, both fuels were blended with net diesel to test in the single cylinder engine to assess the engine performance and exhaust emissions.

2. Materials and Methods

2.1. Date seed oil extraction

The oil content of date seed oil was extracted using Soxhlet extraction system. At first, the seeds of Zahidi type date were separated from date pulp and washed with warm distilled water. Then, they were dried in an oven overnight and crushed for simple oil extraction. The crushed seeds were subjected to the hexane (99% purity, Merck co.) to extract their oil. Finally, the oil-solvent mixture was heated for vaporizing the solvent and obtaining the pure oil. The physicochemical properties of DSO are shown in Table 1.

Table 1

2.2. Biodiesel Production Process

Due to high FFA content of DSO, it was firstly esterified using a homogeneous acid catalyst (H_2SO_4 , 98%, Shimi Pajouhesh Sanat co.) to meet the standard limitation for transesterification of oil using homogeneous alkali catalyst ($\text{FFA} < 3\%$). The esterification reaction was carried out at $60\text{ }^\circ\text{C}$ using 1 wt% of catalyst, and a molar ratio methanol/oil of 9:1 (99% purity, Merck co.) for 1 h. After settling for 2 h, the main reaction products (biodiesel and triglycerides) were separated from by-products (methanol, catalyst, and water).

After reducing the FFA value of oil (0.35 wt.%), the transesterification reaction was performed under conventional and ultrasonic heating methods, and the set-up of each process is depicted in Figure S2.

The transesterification reaction was carried out under ultrasonic irradiation in a 150-mL double-wall vessel in which water circulated between two walls that the reactor was poured by 50 g DSO for each run. The ultrasonic processor (UP400-S, Hielscher, Germany) was a

horn-type transducer generating low-frequency ultrasound waves of 24 kHz, consisted of a power adjusting key to control the power of ultrasonic irradiation along with a key to adjust the amplitude, as set on 1 (non-stop irradiation). The effective parameters such as ultrasound power (100, 200, 300 and 400 W), circulated water temperature (40, 50, 60 and 70 °C), methanol/oil molar ratio (3, 6, 9 and 12), NaOH amount as catalyst (0.5, 0.75, 1 and 1.25 wt.%) and reaction time (2.5, 5, 7.5 and 10 min) were evaluated [19].

The conventional transesterification reaction was carried out in a 150-mL two-neck round bottom flask connected to a condenser to reflux the evaporated methanol. The flask was poured by 50 g DSO for each run. In this process, reaction temperature (40, 50, 60 and 70 °C), methanol/oil molar ratio (3, 6, 9 and 12), NaOH amount as catalyst (0.5, 0.75, 1 and 1.25 wt.%) and reaction time (60, 75, 90, 105 and 120 min) were assessed.

After each reaction, the top layer containing DSO biodiesel was separated by centrifuging the product mixture and was heated to eliminate the excess methanol. Finally, the yield of the reaction and Fatty Acid Methyl Ester (FAME) content of the produced biodiesel were measured by weighting and gas chromatography (Perkin Elmer Claus 580; equipped with a Flame Ionization Detector (FID) and capillary column Select Biodiesel CP9080 (30 m × 0.32 mm × 0.25 μm)) methods, respectively. The formulas were presented as follow:

$$\text{Yield (\%)} = (\text{Weight of produced DSO biodiesel} / \text{Weight of DSO}) \times 100 \quad \text{Eq.1}$$

$$\text{FAME content (\%)} = \frac{\text{area of all FAME} \times \text{weight of internal standard}}{\text{area of internal standard} \times \text{weight of biodiesel sample}} \times 100 \quad \text{Eq.2}$$

Where methyl nonadecanoate (C19:0) was used as internal standard.

2.3. Fuel characterization

Density, kinematic viscosity at 40 °C, flash point, cloud point and pour point of DSO biodiesel were determined according to the ASTM D1298, ASTM D445, ASTM D93, ASTM D2500, and ASTM D97, respectively. Chemical components of DSO biodiesel containing fatty acids were also measured by a GC chromatograph (Perkin Elmer Claus 580) equipped with a Flame Ionization Detector (FID) and capillary column Select Biodiesel CP9080 (30 m × 0.32 mm × 0.25 μm). The methyl nonadecanoate (C19:0) was used as an internal standard [30].

2.4. Test of Engine Performance and Exhaust Emissions

The experimental setup (engine test bed) consisted of a single-cylinder, four-stroke diesel engines, an eddy current dynamometer (WE400), and a gas analyzer. The scheme of the engine test and its specifications are depicted in Figure 1. An AVL gas analyzer model DIGAS 1000 was used to measure CO₂, CO, HC, and NO_x emissions [31], [32]. The diesel engine was fuelled with blends of net diesel fuel and produced DSO biodiesel based on volume and production process as Bx-Conv., Bx-Ultra., in which x (0, 10, 20, 40), Conv. and Ultra, respectively are related to the volume of biodiesel, conventional heating, and ultrasonic heating. The performance and exhaust emissions from the engine were evaluated at speeds of 1800, 2150, and 2500 rpm at full load.

Figure 1

3. Results and Discussion

3.1. Properties of date seed oil

The Zahidis' date seed contained around 10 wt.% oil with a density of 916 kg/m³ and kinematic viscosity of 28 mm²/s. Moreover, the high-amount FFA of DSO (8.5 mg KOH/g)

makes it insufficient for biodiesel production using homogeneous alkali catalyst. Therefore, the esterification reaction was performed to reduce the acid value (FFA content) to the limit (< 3%) [33].

Chemical characterization of the DSO showed that, it contains 21.08, 13.85, 12.38, 2.73, 43.23 and 5.94% of Lauric acid, Mysteric Acid, Palmitic acid, Stearic acid, Oleic acid, Linoleic acid, respectively.

3.2. Ultrasonic-Assisted Transesterification Reaction

3.2.1. Optimization of the transesterification reaction parameters

The parameters influencing on the yield and conversion of the transesterification reaction of DSO to biodiesel under ultrasonic irradiation were evaluated, the results of which are presented in Figure 2. First of all, the effect of methanol amount was assessed (Figure 2 (a)), and it observes the amount of methanol has a positive effect on increasing the reaction yield and conversion. It is well known that the transesterification reaction is reversible, and increasing the methanol can move the reaction on the forward direction [34]. However, a high amount of methanol can negatively influence on the yield and conversion due to decreasing the concentration of catalyst in the reaction medium and increasing the separation problem [35]. It also can be attributed to the change in reaction temperature that will be discussed in the following.

The effect of reaction time is illustrated in Figure 2 (b), in which the reaction reached to equilibrium point after 5 min. So, with the increase in the reaction time, an insignificant change was observed in the conversion and yield.

As mentioned, water with a constant temperature circulated outside the reactor vessel to prevent remarkably increase in the reaction temperature. The temperature of the circulated water changed between 40 and 70 °C, and its influence on the conversion and yield is shown

in Figure 2 (c). The reaction yield and conversion increased by raising the temperature from 40 to 50 °C, related to reaching the reaction temperature to near methanol boiling point that caused to enhance the solubility of methanol in the other phase [21]. However, 6.3 (11.6%) and 12.8% (17.7%) reduction was respectively found in the yield (conversion) as a result of increasing the circulated water temperature at 50 and 60 °C corresponding to the insufficient increase in the reaction temperature and/or dampening the cavitation effects at higher operating temperature [11].

The effect of ultrasonic irradiation power on the transesterification reaction yield and FAME content is depicted in Figure 2 (d). Increasing the ultrasonic power enhances the formation of bubble inside the reaction medium, and their explosion has two major influences: (1) sufficient mixing and emulsification of two immiscible reaction layers at higher levels of power dissipation, and (2) sharply increasing the local and bulk temperature of transesterification reaction [36]. Therefore, the yield and conversion intensively increased by raising the ultrasonic power from 100 to 300 W. Lower conversion and yield were obtained at 400 W of ultrasonic power which may be attributed to the insufficient increase in reaction temperature over the boiling point of methanol and cushioning effect[37].

The effect of catalyst amount on the transesterification of DSO was investigated in different concentrations varying from 0.5 to 1.25 wt.%. The conversion of oil to ester increased as a result of loading more amount of NaOH as a catalyst due to increased formation of the catalyst-reactant complex. However, loading more amount of catalyst (over than 1 wt.%) leads to the occurrence of the side reactions like saponification reaction and reducing the conversion and yield of ultrasonic-assisted transesterification reaction [38].

Therefore, the transesterification reaction conditions of 300 W of ultrasonic power, 50 °C of circulated water, 6 molar ratio of methanol to oil, 1 wt.% of catalyst and 10 min of reaction time was obtained as optimum.

Figure 2

3.2.2. Temperature monitoring of transesterification reaction

Due to lack of study on evaluating the rate of transesterification reaction temperature under ultrasonic irradiation, the effect of each parameter evaluated in the previous section on the temperature of transesterification reaction was precisely investigated, the results of which are illustrated in Figure 3. The reaction temperature increased by increasing methanol/oil molar ratio, which is due to a decrease in the viscosity of the mixture at a high amount of methanol and simple explosion of the bubble inside the reaction. However, by loading more amount of methanol, the reaction temperature sharply increased to its evaporation temperature. After that, due to the high proportion of methanol in the reaction medium, the temperature increased over the boiling point of methanol and led to its evaporation from the reaction medium. Therefore, the proportion of methanol in the liquid phase reduced, and the yield and conversion decreased [39].

The same behavior was observed by increasing the water circulation temperature such that, the rate of increasing the temperature and maximum temperature of the reaction medium was raised. As the reaction temperature reached the boiling point of methanol, the yield and conversion sharply decreased due to the reduction in methanol amount in the reaction medium.

The same phenomenon was observed for ultrasonic irradiation, in which the reaction temperature increased followed by an increase in the conversion and yield. However, the high power of ultrasound irradiation resulted in high reaction temperature over methanol boiling

point. For the catalyst concentration, the formation of soap in a high level of catalyst amount is attributed to a decrease in the heat transfer between reaction materials and circulated liquid [36]. Moreover, the soap increases the viscosity of the mixture, leading to reaching the reaction temperature over the boiling point of methanol that is not suitable. In terms of the temperature monitoring, the reaction temperature must be lower than boiling point of the used alcohol (around 58 °C for this study).

Figure 3

3.3. Optimization of Conventional Transesterification Reaction Parameters

The conventional transesterification reaction was also performed to compare the reaction conditions under conventional heating and stirring method with those of the ultrasonic irradiation method. The methanol/oil molar ratio (3-12), reaction temperature (30-70 °C), reaction time (60-120 min) and catalyst concentration (0.5-1.5 wt.%) were evaluated in the conventional method, the results of which are shown in Figure S3.

As mentioned in the ultrasonic-assisted transesterification reaction section, the higher reaction temperature accelerates the reaction rate and increases the conversion and yield. The conversion and yield reached to the highest values by raising the temperature from 30 to 60 °C while they reduced due to evaporation of methanol and reduction its proportion in the liquid medium, as mentioned above [39]. The methanol amount had a positive effect on moving the reaction to forward direction until 6 molar ratio of methanol/oil, and then the yield reduced due to dilution of reaction medium and difficulty in separation of product from by-product [10], [40]. The effect of catalyst concentration on the reaction yield and conversion proved that loading more amount of catalyst (over 1 wt.%) leads to the formation of soap limiting the conversion of triglycerides to esters [41]. After selecting 60 °C of

temperature, 6 molar ratio of methanol/oil and 1 wt.% of catalyst amount as optimum conditions, the reaction time varied between 60-120 min and the highest conversion (93.5%) was obtained after 90 min, and then was maintained constant. Therefore, the transesterification reaction conditions of 60 °C, 6 molar ratio of methanol to oil, 1 wt.% of catalyst and 90 min of reaction time was obtained as optimum.

The results of the study showed that the ultrasonic irradiation has an insignificant effect on the optimum methanol and catalyst amount for esterification reaction, whereas the reaction time significantly decreased from 90 to 5 min. Regardless of energy consumed in the separation and purification steps, the ultrasonic irradiation meaningfully reduced the energy consumption.

Figure S3

3.4. Biodiesel Fuel

The biodiesel produced by conventional and ultrasonic methods was characterized to evaluate the effect of ultrasonic irradiation on the physicochemical properties of DSO biodiesel (see Table 1). Ultrasonic irradiation sharply reduced the density and viscosity of DSO compared to the conventional method. Although these fuels showed similar flash point (around 110 °C), however, DSO biodiesel produced by conventional method showed better cold flow properties (cloud point and pour point), attributing to lower amount of triglycerides in this fuel (the FAME content of biodiesel produced by conventional method is 93.5% while it is 91.9 for biodiesel produced via ultrasonic irradiation. Probably around 6.5 and 8.1% triglycerides respectively contained in these structures.) Cetane number, higher heating value and saponification value of both produced biodiesel almost are same and met the standards.

The analysis results related to the chemical compositions of two fuels illustrated that biodiesel produced by ultrasonic irradiation contains a higher amount of saturated

components compared to those produced by conventional method causing an increase in its oxidation stability. In both fuels, oleic acid ester was found to be the most FFA.

3.5. Engine Performance

The effect of heating system used for biodiesel production from DSO on its combustion properties and performance in a diesel engine is illustrated in Figure 4. The torque and power of the engine had reverse behavior, such that the value of torque against power reduced by increasing the engine speed for all kinds of fuel. The torque decreases with the increase in the engine speed as a result of a decrease in the force on the piston and crankshaft [1].

However, different behavior was observed by loading biodiesel in net diesel fuel, such that the DSO biodiesel produced by conventional presents more uniform trend, according to the increasing the biodiesel content in the fuel) compared with the net diesel fuel blended with DSO biodiesel produced by ultrasonic irradiation.

The blend fuel containing DSO produced by conventional method (unlike those produced by ultrasonic irradiation) showed a reduction in torque and power in low engine speed (except B40). The decrease in these parameters is related to the lower heating value of biodiesel compared to the net diesel fuel. On the other hand, enhancement of the torque and power of the engine has been reported to result from high oxygen content and flammability of biodiesel [2]. The appropriate results obtained from blending net diesel fuel with DSO biodiesel produced by the ultrasonic method can be attributed to the explosion of bubbles inside the reaction medium, increasing the dissolution of oxygen from the air into the reaction medium. This higher oxygen content provides better fuel combustion in the engine chamber resulting in higher torque and power.

The Specific Fuel Consumption (SFC) as shown in Figure 4 (c) decreased by loading the DSO biodiesel. It can correspond to the increase in the oxygen content of the net diesel fuel

by blending with biodiesel and its better combustion. Lower SFC was observed in DSO biodiesel produced by ultrasonic irradiation, due to higher oxygen content, compared to DSO biodiesel produced by a conventional method. Moreover, B40 presented the lowest SFC and almost higher power and torque for both fuels in all engine speeds.

Figure 4

3.6. Engine emissions

The CO₂ emission of exhaust gas from a diesel engine fueled by various blends of DSO biodiesel and net diesel fuel is shown in Figure 5. Due to higher oxygen content of biodiesel compared to the net diesel fuel, the amount of CO₂ is expected to be increased [31]. The results proved better combustion of fuel as a result of blending with biodiesel. A decrease in the CO₂ emission was observed while utilizing B40-Ultra. compared to B20-Ultra., attributing to the increase in the density of fuel and insufficient spraying the fuel in the engine chamber [42].

For all emissions, the proportion of released emission was compared with the net diesel fuel according to the following equation:

Eq. 1

$$\frac{\text{Increasement (reduction)}}{=} \frac{\text{Released gas emission from blend fuel} - \text{released gas emission from net diesel fuel}}{\text{released gas emission from net diesel fuel}}$$

B20-Ultra. fuel exhibited the highest increase in CO₂ emissions in all engine speeds and B40-Conv. also presented the highest amount of CO₂ emissions among other blended fuels produced by mixing the net diesel fuel and DSO biodiesel produced by a conventional method. Moreover, better combustion can be obtained in lower engine speed.

Figure 5

The blends of net diesel fuel and biodiesel produced through conventional and ultrasonic methods significantly reduced the CO emission, as shown in Figure 6. Due to the higher oxygen content of biodiesel, the combustion of blended fuels completely occurred, and the carbon atoms of fuel converted to CO₂ against of CO, as presented in CO₂ emission analysis [43]. By increasing the portion of biodiesel in the blended fuel, the amount of CO further reduced such that B40 presented the lowest CO emissions. Among the two heating systems, ultrasonically-produced DSO biodiesel exhibited appropriate combustion in the engine such that all the blends of this fuel released the lower amount of CO compared to those produced by a conventional method, attributing to the high dissolved oxygen content in ultrasonically-produced DSO biodiesel [44]. Moreover, B40-Ultra. fuel showed the maximum reduction of CO emission in all volumes of its blends, especially at an engine speed of 2150 rpm (31%).

Figure 6

The results of the effect of blending the biodiesel produced by different heating systems with the net diesel fuel on the HC emissions are illustrated in Figure 7. Through better combustion of the net diesel fuel in the engine resulting from mixing with biodiesel, the amount of HC is expected to be decreased as well as CO. As mentioned, ultrasonically-produced DSO biodiesel has higher oxygen content consequently leading to better combustion in the engine. Therefore, blends of this fuel produced lower HC, so that B40-Ultra. showed the lowest HC emission and the maximum reduction was obtained at an engine speed of 1800 rpm (Figure 7 (b)). It must be mentioned that conventionally- produced biodiesel released higher HC at low engine speed, which can be explained as a result of the

lower heating value of the pure biodiesel indicating probably higher fuel consumptions (see Figure 4 (c)). Therefore it could produce high local fuel-to-air ratios causing an increase in HC emissions [29], [45].

Figure 7

Biodiesel fuels are well known to have higher NO_x emissions compared to the net diesel fuel due to the higher oxygen content of the pure DSO biodiesel (B100) and higher gas temperature in the combustion chamber [46]. The results of NO_x emission are illustrated in Figure 8, upon which B40-Conv. and B20-Ultra. produced the highest amount. Due to the higher oxygen content of biodiesel produced by the ultrasonic method, the NO_x of this fuel is higher than those produced by the conventional method. On the other hand, B40-Ultra. and B10-Conv. produced an almost low amount of NO_x . B40-Ultra. is expected to produce the highest NO_x attributing to the minimization of the ignition delay and heating value of fuel while mixing with biodiesel [47], [48]. By increasing the proportion of biodiesel in the fuel, less mass is ignited during the ignition period, resulting to lower ignition rate than in the net diesel fuel. This phenomenon reduces maximum ignition pressure inside the chamber and subsequently reduces NO_x emissions [49].

The results showed a decrease in NO_x amount by raising the engine speed due to the shorter residence time available for NO_x formation, resulting from an increase both in the volumetric efficiency and flow velocity of the reactant mixture at higher engine speeds (Figure 8 (a)) [50].

Figure 8

4. Conclusion

This study was the first attempt to investigate the ability of DSO to convert into biodiesel and being used in the diesel engine. Moreover, for the first time, the effect of ultrasonic irradiation on the transesterification reaction conditions, properties of final product and produced biodiesel performance in the diesel engine was compared with those performed and produced under conventional heating method. The temperature monitoring of ultrasonic-assisted transesterification reaction showed that the reaction temperature must be lower than the boiling point of the methanol to obtain the highest yield and FAME content. This behavior was also observed in the conventional method, such that 60 °C of temperature was the optimum temperature for both heating systems. The optimization of the reaction conditions exhibited that the ultrasonic irradiation has an insignificant effect on the reaction conditions (reaction temperature, methanol/oil molar ratio, and catalyst concentration) except reaction time. The reaction time significantly decreased from 90 min for the conventional method to 5 min for ultrasound irradiation method. Ultrasonic irradiation also influenced on the molecular properties of biodiesel, causing a decrease in the viscosity of biodiesel, which in turn, had a positive effect on spraying the fuel in the engine chamber. According to the result of combustion the produced biodiesel blended with the net diesel fuel, the ultrasonic irradiation not only decreases the reaction time and energy consumption during transesterification reaction but also improves the combustion of the net diesel fuel in the engine. As DSO biodiesel was blended with the net diesel fuel, the engine performance was improved as well as emissions gases. In these cases, ultrasonically-produced DSO biodiesel presented better characteristics to blend with the net diesel fuel. Moreover, the same results were observed on the SFC reduction.

Due to the improvement of the fuel combustion in the engine chamber caused by using DSO biodiesel, the CO₂ amount increased whereas the amounts of CO and HC significantly decreased. The results related to the efficacy of DSO biodiesel exhibited that, it can be used

in the high proportion to be blended with the net diesel fuel (B40). As mentioned, among the DSO biodiesel produced through two different heating systems, ultrasonically-produced DSO biodiesel presented suitable properties and performance, such that higher power and torque were obtained using the blended fuel with a high volume of biodiesel (40 vol.%). B40-Ultra. also produced less emission compared to the net diesel fuel, and B40-Conv. in which CO₂, CO, and HC reduced more than 1.5, 2 and 3 times compared to B40-Conv., respectively. DSO biodiesel can be utilized as a high potential fuel in the diesel engine at high volume ratio and ultrasonic irradiation must be studied further as a significant parameter that can improve the properties of the final biodiesel.

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Declarations of interest

None

Reference

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Table 1. Physicochemical properties of date seed oil and produced biodiesel by conventional and ultrasonic methods

Properties	Unit	DSO ^b	DSO biodiesel	
			Conv. ^c	Ultra. ^d
Physical properties				
Density at 25 °C	Kg/m ³	916	878	865
Kinematic viscosity at 40 °C	mm ² /s	28	4.85	3.06

Flash point-closed cup	°C	-	107	111
Cloud point	°C	-	6	10
Pour point	°C	-	0	2
Cetane Number ^e	-	-	57.1	57.2
Higher heating value ^f	MJ/kg	-	39.7	39.6
Saponification value	mg KOH/g	-	210	212
Acid value	mg KOH/g	8.5	0.25	0.25
Iodine value	gI ₂ /100g	49	63	62
Chemical properties				
Lauric acid (C12:0) ^a	wt.%	21.08	14.8	15.6
Mysteric Acid (C14:0) ^a	wt.%	13.85	9.9	9.9
Palmitic acid (C16:0) ^a	wt.%	12.38	10.8	10.6
Palmitoleic acid (C16:1) ^a	wt.%	-	1.0	1.2
Stearic acid (C18:0) ^a	wt.%	2.73	3.1	3
Oleic acid (C18:1) ^a	wt.%	43.23	45.6	44.7
Linoleic acid (C18:2) ^a	wt.%	5.94	11.4	11.9
Other component	wt.%	0.79	3.2	3.1

^a Carbon atoms number: double bond number

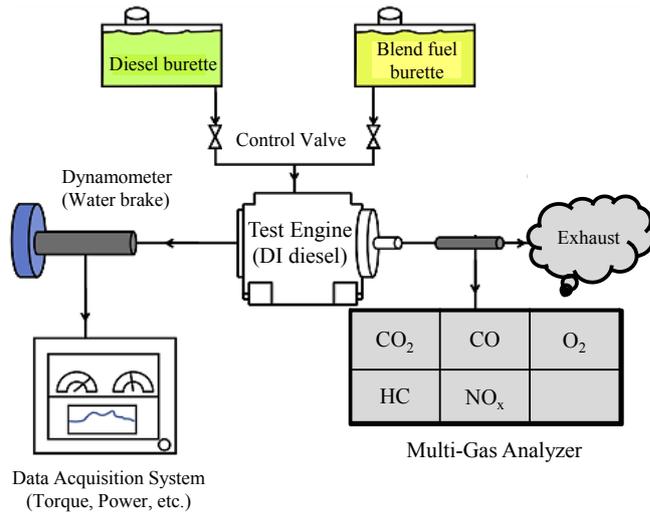
^b DSO: Date seed oil

^c Conv.: Conventional heating system

^d Ultra.: Ultrasonic heating system

^e Cetane number calculated by the formula suggested by Gopinath et al. [51] according to biodiesel composition

^f Calorific value calculated by the formula suggested by Demirbas [52]



Spec.	
Engine Model	3LD 510, Lombardini, Italy
Number of cylinder	Single
Cooling system	Air-cooled
Bore×Stroke	90×85
Displacement volume (cc)	510
Compression ratio	17.5:1
Max. power (kW)@3000 rpm	7.1
Max. Torque (Nm)@1800 rpm	22.8

Figure 1. Schematic diagram of engine experiment and its specification

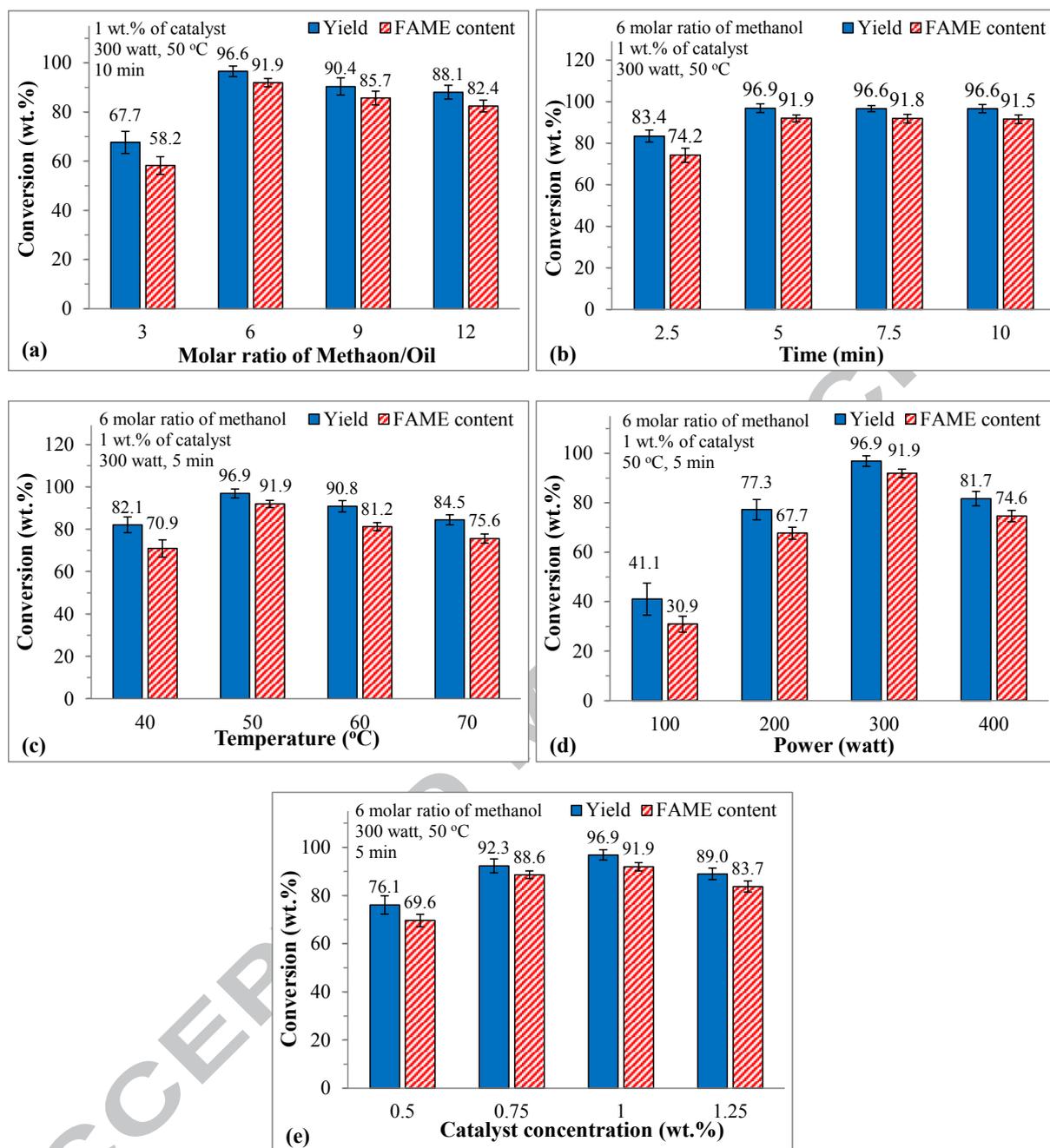


Figure 2. The effect of transesterification reaction parameters on the yield and conversion of DSO to biodiesel under ultrasonic irradiation

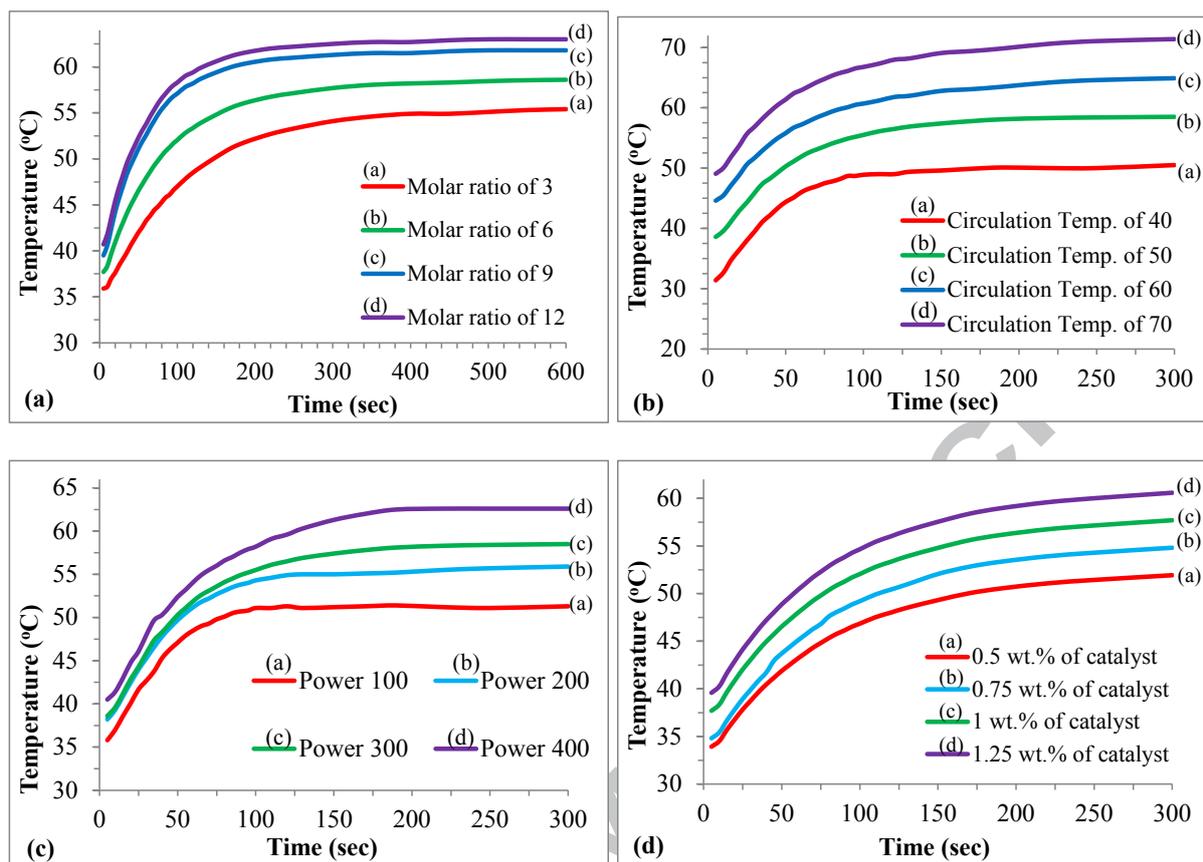


Figure 3. The effect of transesterification reaction parameters on the reaction temperature during conversion of DSO to biodiesel under ultrasonic irradiation

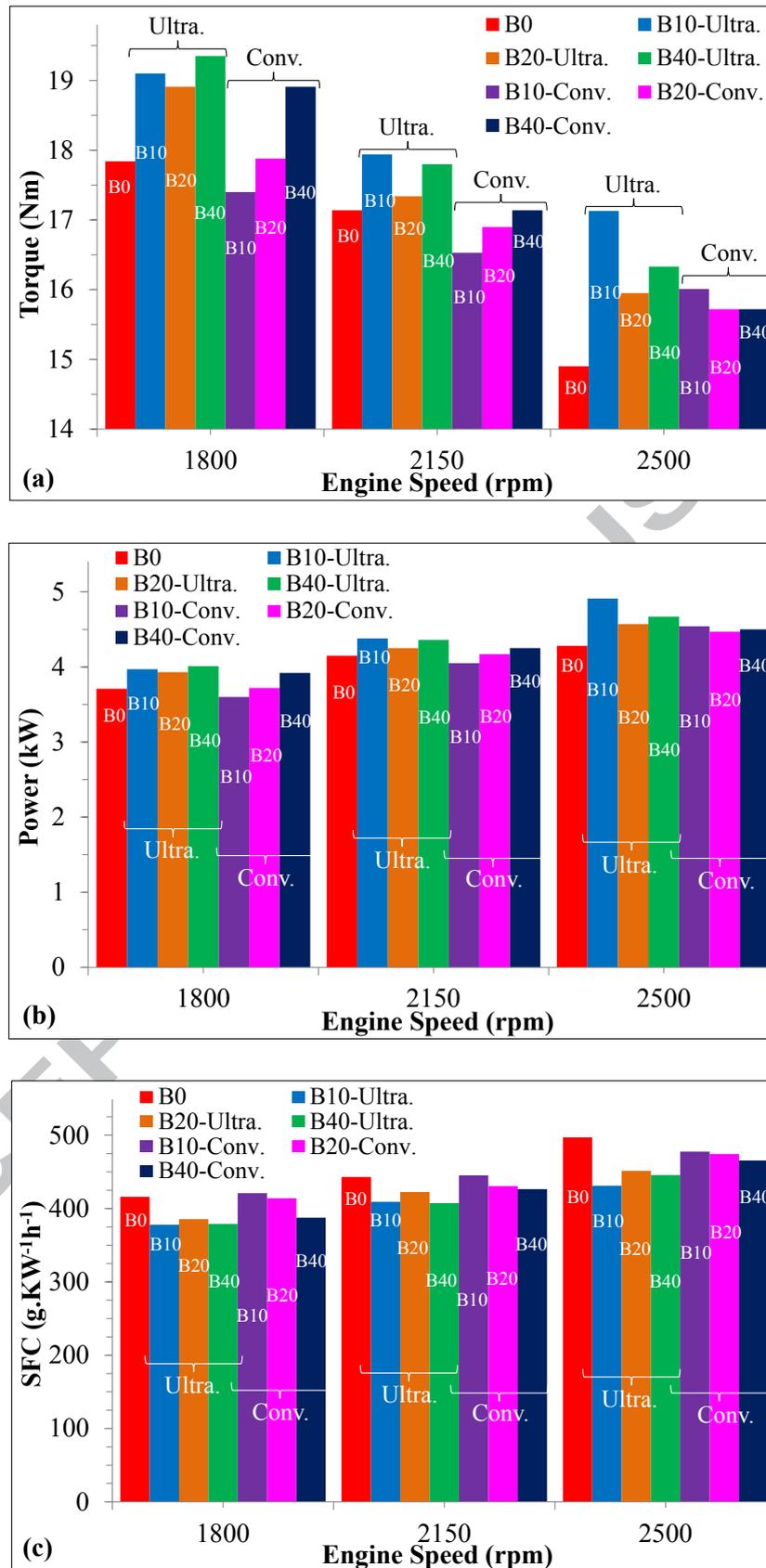


Figure 4. Effect of heating system used for biodiesel production on the (a) torque, (b) power and (c) SFC of engine fueled by various diesel-biodiesel blends worked at different engine speeds

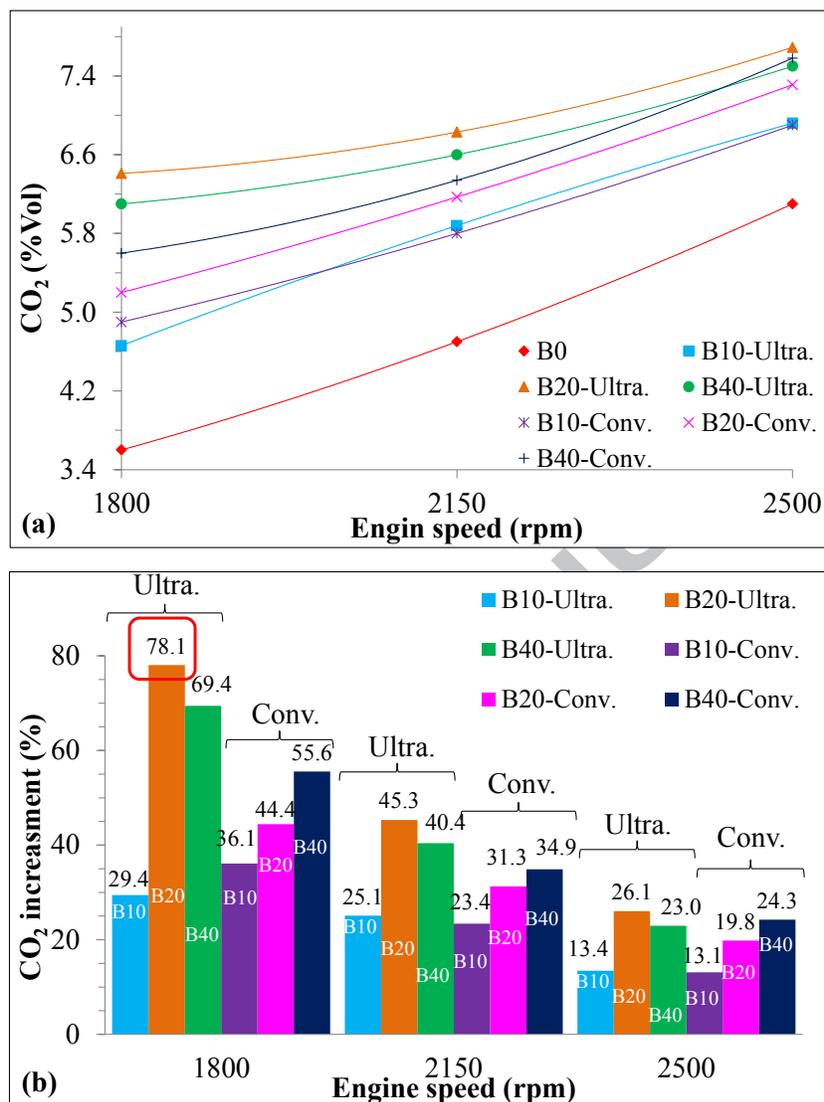


Figure 5. Effect of heating system used for biodiesel production process on CO₂ emission of engine fueled by various diesel-biodiesel blends worked at different engine speeds

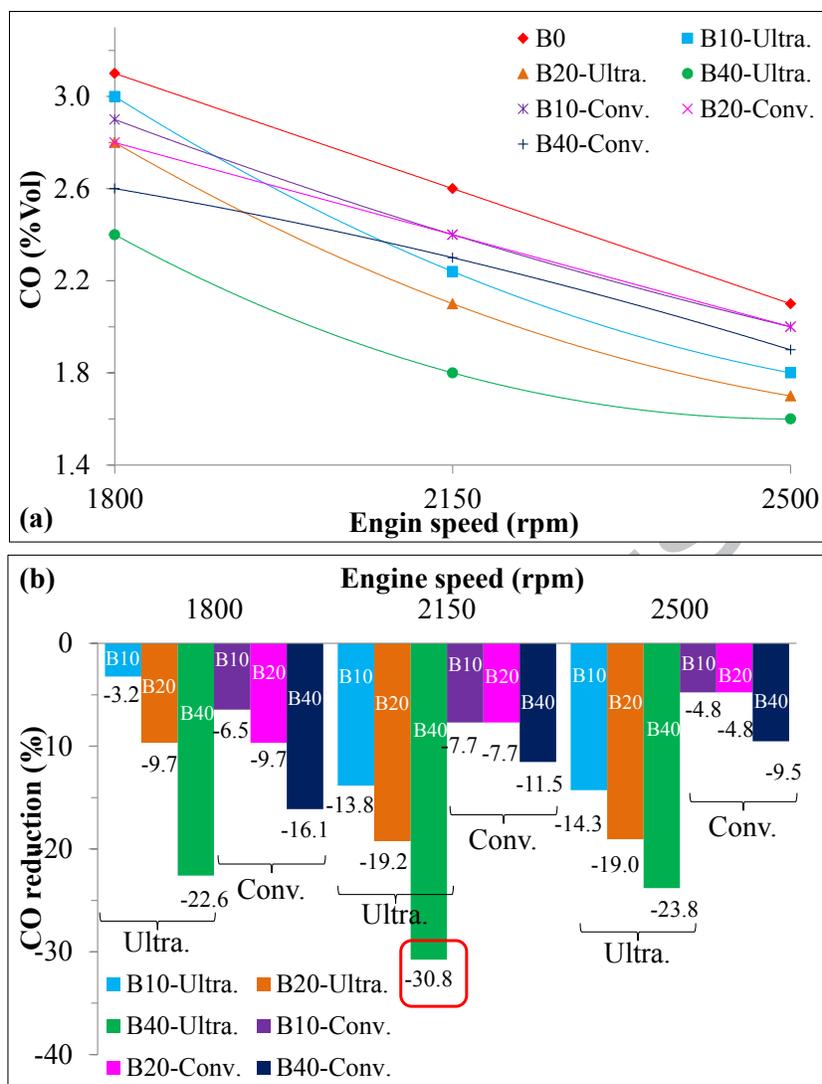


Figure 6. Effect of heating system used for biodiesel production process on CO emission of engine fueled by various diesel-biodiesel blends worked at different engine speeds

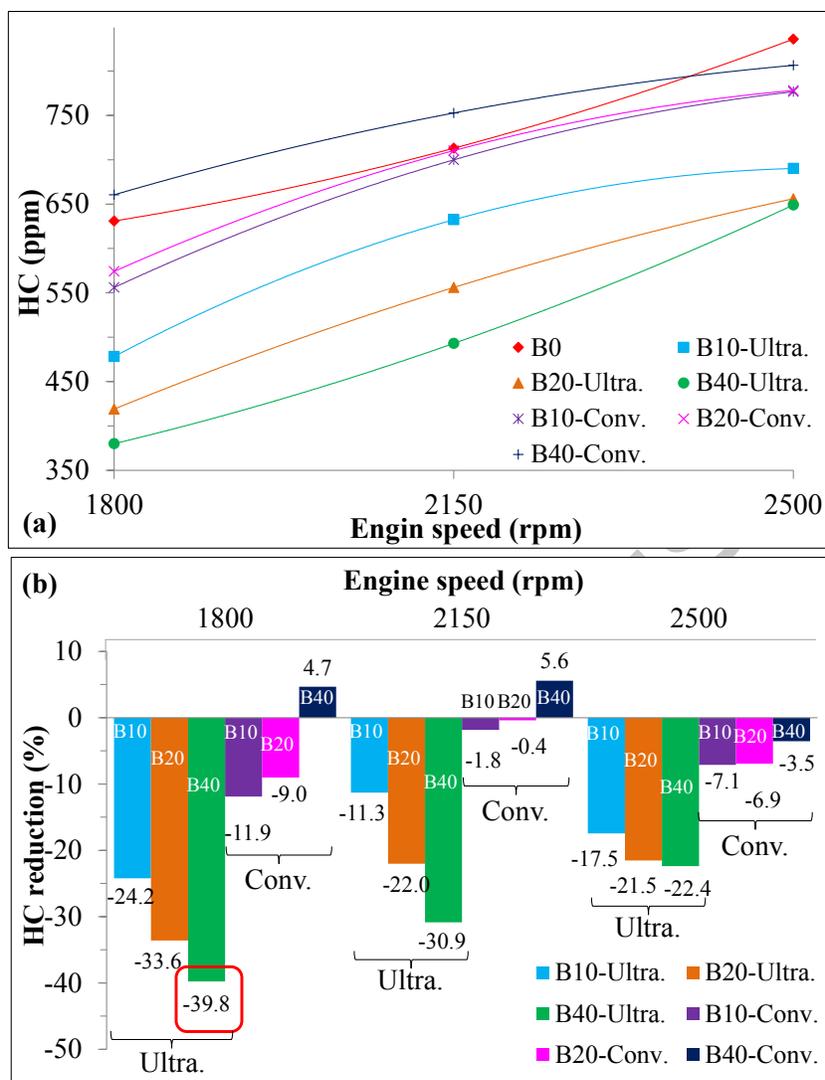


Figure 7. Effect of heating system used for biodiesel production process on HC emission of engine fueled by various diesel-biodiesel blends worked at different engine speeds

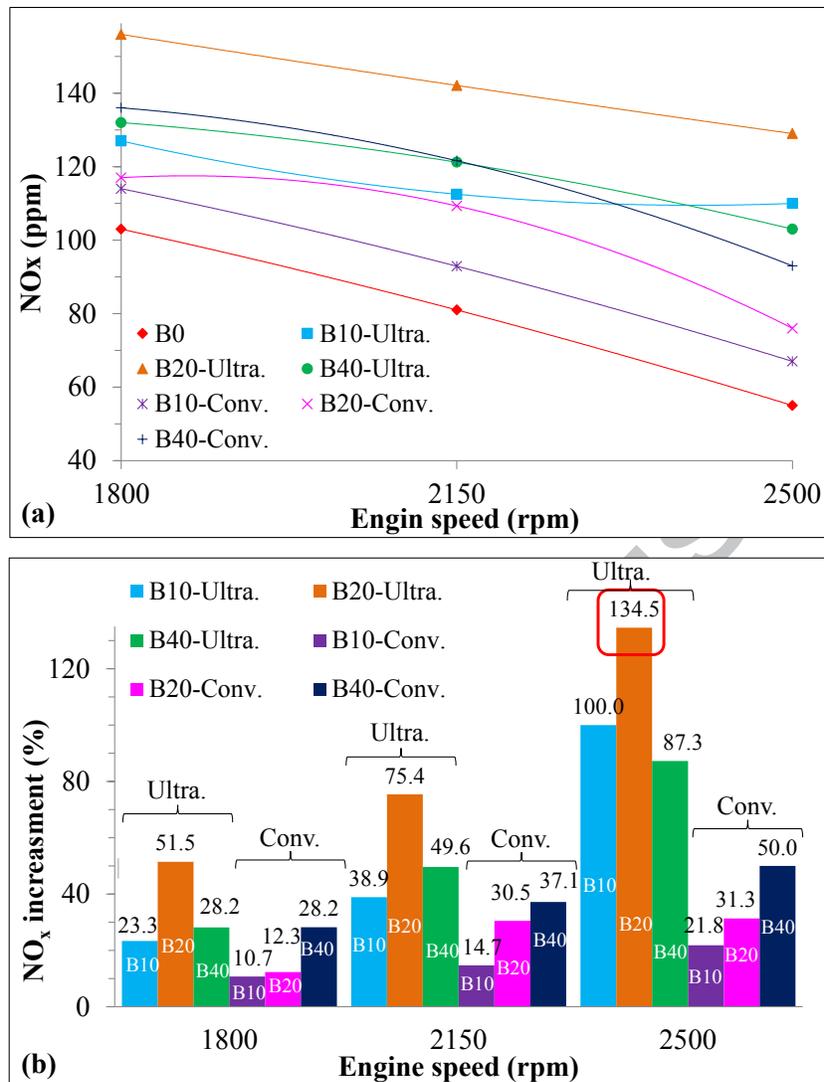


Figure 8. Effect of heating system used for biodiesel production process on NO_x emission of engine fueled by various diesel-biodiesel blends worked at different engine speeds