Effect of Fatty Acid Profiles and Molecular Structures of Nine New Source of Biodiesel on Combustion and Emission

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ABSTRACT: The present study is an attempt to examine the effect of biodiesel chemical structure on the diesel engine combustion properties and exhaust emissions. For this purpose, nine new types of oil (second generation) are used for producing biodiesel. Also, fatty acid profiles are determined by gas chromatography. Results show that Urtica biodiesel causes the highest soot emission (0.98 vol %) and the minimum NOx emission (460 ppm). A decrease in CN increases NOx and decreases soot emission at high engine loads. The longest chain is gained via Urtica biodiesel, and the increase of carbon chain length enhances soot emission. The increase of oxygen-to-carbon (O/C) ratio also affects the soot emissions and reduces the process (the O/C ratio is 0.1087 for Urtica). The increase of long-chain biodiesel fatty acids from C18 to C24 reduces the NOx emissions (C18−C24; 97.43 wt % for Urtica); moreover, there is a direct correlation between the increased carbon chain length and the amount of enthalpy. As the amount of unsaturated acids grows (94.93 wt % unsaturated fatty acids for Urtica), the value of the output soot is enhanced. Also, the increase in hydrogen-to-carbon ratio (1.8457 molar for Urtica) decreases the soot emissions. The increase in carbon chain length and decrease in O/C affect the HC and CO emissions; therefore, Urtica biodiesel had the maximum CO and HC emission (0.036 vol % and 6.11 ppm, respectively). In addition, the reduction of fuel consumption increased the NOx emission and reduced the HC, CO, and soot emission.

1. INTRODUCTION

The energy crisis and the daily changes in the price of fossil fuels have had significant consequences in many countries. In recent decades, biofuels have been considered as an alternative for fossil fuels. Biofuels have many advantages over fossil fuels. Some of the main advantages of biofuels are that they are renewable, are highly biodegradable, have minimal toxicity, are environmentally friendly, have lower combustion emission, and have high engine performance that might improve the rural economic potential and might also be blended with petroleum-based diesel fuel in any ratios.1−3

Fatty acid methyl esters (FAMEs) are a type of fatty acid esters that are derived by transesterification of fats with methanol.1 The molecules in biodiesel are mainly FAMEs, which are normally obtained from a different source of oil through transesterification. FAMEs are generated through an alkali-catalyzed reaction between methanol and fats with bases like potassium hydroxide (KOH), sodium hydroxide (NaOH), and sodium methoxide (CH3NaO).5,6 One of the main reasons for the use of FAME in biodiesel instead of free fatty acids is to nullify any corrosion caused by free fatty acids in the production facilities, metals of engines, etc. It is mildly acidic, but, unlike its esters, it might cause cumulative corrosion over time. The structure of fatty acids affects the physical properties, exhaust emissions, etc. A sufficient knowledge of the structure of fatty acids before the selection of the desired oil indicates that biofuel results are somehow closer to our predictions. Most common fatty esters included in biodiesel are derived from palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid.5

Exhaust emissions, the heat of combustion, ignition quality, oxidative stability, viscosity, density and lubricity, and cold flow are among the important properties of biodiesel fuels. The produced biodiesel characteristics should meet D6751 standard of American Society for Testing and Materials (ASTM) or 14214 standard of European Standard Specification (EN). Instruments that examine biodiesel properties are nuclear
magnetic resonance spectroscopy, high-performance liquid chromatography, gas chromatography–mass spectroscopy, and Fourier transform infrared spectroscopy. Several studies indicated that the physical properties of biodiesel have a huge effect on emission and combustion. Kinematic viscosity, boiling point, flash point, pour point, cetane number (CN), oxidative stability, cloud point, and heating value are the most important physical properties affecting emission and combustion.10,11

The flash point is known as the temperature at which the fuel can burn in contact with the heat source. The flash point does not directly affect combustion; however, it is important over fuel transportation, storage, and handling. One of the most important properties of fuel is density because it affects pumps, injection systems, and combustion.12 The density values should be preserved at acceptable limits because of the importance of air-to-fuel ratios for combustion. High values of density result in particulate matter emissions and incomplete combustion.1 The value of viscosity is highly important to have the right performance in the CI engine. The increase of viscosity causes poor mixing, atomization, and excess penetration that affect combustion. Cloud point is the lowest temperature, at which the cloud of wax crystals is shaped when it is cooled. Compared to diesel fuels, biodiesel fuels have higher cloud point, this is an obstacle in the use of biodiesel in the cold climate situation.13,14

Biodiesel fuel emissions are carbon dioxide (CO₂), sulfur oxides (SOx), smoke, carbon monoxide (CO), and oxides of nitrogen (NOx). Many researchers have worked on reducing biodiesel emissions as one of the main concerns of current societies, which has had a significant impact on the environment and human health for aesthetics and legislative reasons.15 Carbon soot particles, water, volatile organic compounds, ashes, and metallic compounds are smoke or particulate matter (PM) components. In this regard, McCormick et al. evaluated the effect of double bonds and chain length on emissions. They have proved that the molecular structure influenced emissions, and enhancement of double bonds affected NOx/PM emissions. Moreover, decreasing the chain length led to an increase in NOx emission. They also reported that there was no significant difference between PM and NOx emissions for the ethyl and methyl esters of identical fatty acids.16

The result of Takatori et al. indicated the increase of soot as well as precursor molecules over pyrolysis.17 Hellier et al. also showed the direct impact of carbon chain length on PM emissions.11,18,19 Schönborn et al. referred to the effect of double bonds on emission. They found a correlation between PM emissions and double bonds.20 Pinzi et al. concluded that the increase of chain length and unsaturation degree could enhance NOx emission. They also indicated that carbon monoxide, total hydrocarbons, soot, and volatile organic fraction emissions increased during the enhancement of hydrocarbon chain length.8

Zhu et al. showed the high influence of carbon chain length on NOx and smoke emissions. Their results indicated that the increase of chain length increased smoke and decreased NOx emissions.21 Hellier et al. showed the effect of double bonds on PM. Also, they indicated the influence of carbon chain length and saturated acid on PM emission.22 Zhang et al. investigated the effect of carbon chain length on soot and temperature flame and showed that by increasing the carbon chain length, the soot concentration is consequently increased. They also reported that the decrease of the precombustion mixing reduced the fuel oxygen content, and probably the OH-induced soot oxidation.23

In the present study, the effect of fatty acids’ chain length, double bonds, saturation and unsaturation on soot and NOx emissions, and enthalpy of combustion are examined for nine new sources of the second generation of biodiesel. Previous studies have not studied the correlation between these factors and soot and NOx emissions. The physical properties of nine different oil sources have been reported, and they have been compared with each other.

2. MATERIALS AND METHODS

2.1. Materials. Nine different oils, including Cyclamen persicum, Frutillaria persica, Lilium ledebourii, Iris meda, Viola odorata, Artemisia absinthium, Quercus, Urtica, and Carthamus tinctorius have been studied here. They are all produced by mechanical means. The preparation stage involves separating the shells and foreign matter from the grain. Thermal operations are performed to lubricate the oil inside the grain. Mechanical lubrication operations have been performed using box presses and extraction wheels, which have been prepared by Armaghan Meymand Company. Also, methanol (99%) and KOH (99%) were supplied by Aldrich Chemical Co.

2.2. Equipment and Procedures. 2.2.1. Preparation of Fuels and Analyses. In this study, transesterification was applied for biodiesel production, all of which were generated via KOH-catalyzed transesterification reaction. This procedure was performed with a 1−3 (v/v) methanol-to-oil ratio. About 2.2 g KOH was distributed and dissolved in 130 mL of methanol. Because the dissolution of KOH in methanol is a thermogenic reaction that causes alcohol to evaporate, it dissolves in a condenser during the dissolution of KOH in Erlenmeyer methanol to return the alcohol vaporized by the condensate back to the solution. When the catalyst was completely dissolved in methanol, methoxide was added to the oil. The mixture of methoxide and oil was heated for 1 h at 60 °C. The raw material was then mixed with warm distilled water for washing. The amount of water used in each stage of the rinse was twice the volume of biodiesel. After several washes, the contaminants had been completely removed, the biodiesel and the water phase were then separated by a separation funnel or centrifuge. In this way, in the biodiesel formed in the device, the water slowly enters the device through the wall at very low pressure and at a temperature of 50 °C and is stirred at a minimum speed for 2 min in a mixer. The mixture of water and biodiesel was then given time to settle. Due to the fact that the density of water is higher than that of biodiesel, the water collected at the bottom of the tank was discharged through the lower valve of the water device. This was done three times, and each time the outlet water became clearer and had less dissolved material. In the final phase, the acid value was measured.24

The flash point was measured by ASTM standard D93 with a continuously close cup flash point (CCCFP) tester employing the Grabner FLPH MiniFlash Tester (Grabner, Austria). The kinematics and dynamics of viscosities and density were specified with Stabinger Viscometer, Anton Paar, SVM3000 model (Anton Paar Co., Austria). The density was measured by ASTM standard D4052, and the viscosity was measured by ASTM standard D445. The cloud point was evaluated by s/500 model (Italian model) according to the ASTM D2500 standard. Water and sediment measurements
were done by Karl Fischer setup, metromh, 794 Basic Titritno model. Also, all biodiesel compounds generated via the transesterification process were defined by gas chromatography (GC, Cauu S80 GC model, Perkin Elmer Co.). So, 0.1 g of biodiesel and about 1 mL of a diluted solution of the internal standard were added in solvent (10 mg/mL). After shaking, the mixture was transferred to a special injection vial for gas chromatography. The internal standard used in this study was nonadecanoate, and the solvent used was heptane. After preparing the sample and injecting it into the gas chromatography machine according to EN 14103 standard, the detector responded based on the concentration of compounds in the sample. Using Total Chrome software, the chromatogram obtained from the detector responses was visible. Chromatograms included peaks corresponding to the concentration of the available compounds and soluble injected samples, methylated fatty acids, and internal standards. The area below the curve of each peak corresponds to its concentration in the sample. Finally, CN was measured by an Octan-IM device.

2.3. Engine Characteristics. In this research, a 3LD 510 model was used for a 12-hp single-cylinder diesel engine manufactured by Italian Lombardy Company. Its specifications are shown in Table 1. The dynamometer Eddy Current system would give an alert. If the temperature rises above the permissible value, the engine starts to overheating, and the probe was placed inside the embedded chamber over the exhaust outlet; then, the values were tested in the computer and soot emissions. The values measured by this device were shown in Table 2. In addition, the tests were done three times, and the P-value was around 0.05. In this study, the engine performance parameters were stated as the maximum torque. The input and boundary conditions are presented in Table 3.

| specification                  | explanations             |               |
|-------------------------------|--------------------------|---------------|
| model                         | 3LD 510                  |               |
| number of cylinders           | 1                        |               |
| bore and stroke (mm)          | 85 × 90                  |               |
| displacement (cm³)            | 510                      |               |
| aspiration                    | naturally aspirated      |               |
| cycle                         | 4 stroke                 |               |
| combustion system             | direct injection         |               |
| rotation                      | counter-clockwise (view from main PTO side) |               |
| cooling system                | air                      |               |
| fuel tank capacity (L)        | 5.3                      |               |
| oil sump capacity (L)         | 1.75                     |               |
| length (mm)                   | 466                      |               |
| width (mm)                    | 422                      |               |
| height (mm)                   | 568                      |               |
| dry weight (kg)               | 60                       |               |
| cylinder course (mm)          | 90                       |               |
| cylinder diameter (mm)        | 85                       |               |
| cylinder volume (cm³)         | 510                      |               |
| maximum power hp (3000 rpm)   | 12.2                     |               |
| maximum torque 1800 rpm (Nm)  | 33                       |               |
| compression ratio             | 17.5:1                   |               |

WE400 model from Pars Andish Innovative Company (MPA) was used to measure the torque, rotational speed, and power of the 3LD 510 diesel engine. The dynamometer is connected to the motor via the guard shaft. The guard was housed in a steel enclosure to provide safety while working with a dynamometer. The dynamometer automatically measures the torque value by applying a magnetic field and calculates the rotational speed by a magnetic sensor. After measuring these two parameters simultaneously, it calculates the motor power and presents the results in graphs or data. As the load is increased by the current passing through the coil, the amount of charge on the motor axis is measured by a force gauge connected to the dynamometer, and the dynamometer motor system is multiplied by the force at the distance of the motor gauge from the center of the dynamometer axis. The motor speed is measured by a magnetic sensor against the gear attached to the dynamometer axis. To find out the operation status of some parts of the engine, various sensors, including temperature sensors for measuring engine oil temperature, exhaust gas temperature, engine outlet water temperature, air manifold pressure, and engine fuel flow sensing sensor, are installed on the engine; in addition to these sensors, two temperature and ambient pressure sensors are also installed on the test chamber. Also, a pump was used for injecting the cooling fluid into the dynamometer. When the dynamometer’s heat is absorbed, the water is cooled by the cooling system, i.e., air conditioner and converter, and returned into the system. Sensors for controlling the dynamometer temperature were also mounted on both sides to display the instantaneous dynamometer temperature. If the temperature rises above the permissible value, the dynamometer system would give an alert. The next step was to automatically raise the engine by about 1800 rpm to report pollutants using MAHA-MGT5. This device is capable of detecting CO, CO₂, and HC values using infrared technology, as well as determining NOx values using chemical sensors; however, the focus of this study was on NOx and soot emissions. The values measured by this device were displayed using EURO System (MAHA) software. The procedure was that when the engine speed was at the desired level, the probe was placed inside the embedded chamber over the exhaust outlet; then, the values were tested in the computer system connected to the pollutant. The contaminants of biodiesels were fixed after 20 s, and the results were stored as an important point in measuring pollutants is the temperature of the engine, which is referred to as oil temperature. Oil temperature is measured by sensors located in the engine oil chamber, which should be between 60 and 100 °C. Its specifications are shown in Table 2. In addition, the tests were done three times, and the P-value was around 0.05. In this study, the engine performance parameters were stated as the maximum torque. The input and boundary conditions are presented in Table 3.

3. RESULTS AND DISCUSSION

3.1. Biodiesels’ Characteristics. In this study, the physical and chemical properties of all fuels have been investigated, and the results are shown in Table 4.

The flash point is known as the temperature at which the fuel starts burning when in contact with fire. This property is significant with regard to fuel handling, transportation, and storage. Several factors change the biodiesel flash point, with residual alcohol content being one of them. Furthermore, the flash point is influenced by the number of double bonds and the number of carbon atoms. Therefore, Urtica biodiesel had the longest carbon chain length among all biodiesel samples, in contrast to A. absinthium biodiesel. As shown in Table 4, all biodiesel fuels have a higher flash point compared to diesel fuels. The highest flash point was obtained for Urtica biodiesel (184 °C) and the lowest was achieved for A. absinthium biodiesel (166.7 °C).

Density is a prominent property of fuel since the injection system, pumps, and injectors must convert the exact adjusted amount of fuel to provide suitable combustion. The number of
Table 2. Specifications of the MAHA-MGT5 Analyzer Used in the Test

| specification | explanations |
|---------------|--------------|
| measurable gases | HC, CO, CO₂, O₂, NO (option) |
| measuring principle infrared spectrometry | HC, CO, CO₂ |
| measuring principle electrochemical detection | O₂, NO |
| warm-up time | 480 s |
| flow | 3.5 L/min |
| working pressure | 0.75−1.1 bar |
| accuracy class | O (OIML) |
| on-board voltage | 12/42 V |
| power supply | 1/N/PE 85 V/285 V 50 Hz |
| dimensions total (L × W × H) | 240 mm × 560 mm × 300 mm |
| weight | 10 kg |
| CO measurement range/measured value resolution (max) | 0−15 vol %/0.01 |
| CO₂ measurement range/measured value resolution (max) | 0−20 vol %/0.01 |
| HC measurement range/measured value resolution (max) | 0−9999 ppm/0.1 (hexane) |
| O₂, measurement range/measured value resolution (max) | 0−20 000 ppm/1 (propane) |
| λ (calculated) | 0−25 vol %/0.01 |
| NO (option), measurement range/measured value resolution (max) | 0.5−9.99/0.01 |
| − | 0−500 ppm/1 |

Table 3. Determined Initial and Boundary Conditions

| specifications | descriptions |
|---------------|-------------|
| engine speed | 1800 rpm |
| air inlet temperature | 293.15 K |
| air inlet pressure | 1 bar |
| fuel injection temperature | 330.15 K |
| cylinder head temperature | 575.15 K |
| cylinder wall temperature | 475.15 K |
| fuel injection pressure | 200 bar |
| fuel consumption Urtica | 2.1 L/h |
| fuel consumption L. ledebouri | 2.0 L/h |
| fuel consumption C. persicum | 1.9 L/h |
| fuel consumption F. persica | 1.9 L/h |
| fuel consumption Quercus | 1.8 L/h |
| fuel consumption C. tinctorius | 1.7 L/h |
| fuel consumption I. meda | 1.6 L/h |
| fuel consumption V. odorata | 1.6 L/h |
| fuel consumption A. absinthium | 1.5 L/h |

Table 4. Result of Physical and Chemical Properties of Biodiesel Sources

| biodiesel | flash point °C | density (kg/m³) | viscosity (CSt) | cloud point °C | cetane number |
|-----------|---------------|----------------|----------------|----------------|---------------|
| ASTM D93 | ASTM D40S2 | ASTM D44S | ASTM D2500 | ASTM D61S |
| C. persicum | 179.5 | 884 | 4.89 | 3 | 55 |
| F. persica | 178.8 | 883 | 4.82 | 2 | 54 |
| L. ledebouri | 182 | 885 | 4.91 | −9 | 57 |
| I. meda | 176.3 | 880 | 4.31 | −2 | 52 |
| V. odorata | 175.2 | 879 | 4.28 | −4 | 52 |
| A. absinthium | 166.7 | 875 | 4.25 | −6.5 | 51 |
| Quercus | 178.2 | 883 | 4.72 | 1 | 54 |
| Urtica | 184.9 | 887 | 5.23 | 4.5 | 58 |
| C. tinctorius | 176.8 | 882 | 4.40 | −1 | 53 |

biodiesel sources had higher density compared to that of diesel fuels.

High viscosity in the CI engine is associated with drawbacks, such as poor mixing with air, excess penetration, and poor atomization, which cause incomplete combustion. Viscosity is diminished by preheating the oil and by the transesterification process. Also, the viscosity increases with the ester chain length. Urtica biodiesel had the longest carbon chain length among all biodiesel samples in contrast to A. absinthium biodiesel.27,28 Among all viscosities achieved in this study, the highest and lowest values were gained for Urtica (5.23 CSt) and A. absinthium (4.25 CSt) samples, respectively. However, numerous studies indicated too high viscosity of biofuels compared to that of diesel fuels.29,30

Cloud point is the minimum temperature at which the cloud of wax crystals is formed when cooled. The cloud point of L. ledebouri biodiesel reached −9 °C in this work, and the highest value was obtained for Urtica, which reached 4.5 °C (Table 4). The minimum value of CN was emitted by A. absinthium (51.7), while Urtica had the highest values among all biodiesel samples.

Cetane number (cetane rating) is known as an indicator of the combustion speed and compression required for ignition. The fatty acids that can affect CN is so important, increasing the CN. The increase in carbon chain length affects CN enhancement.31 Table 4 shows that the maximum CN belongs to Urtica biodiesel, with a value of around 58, which is in contrast to that of A. absinthium biodiesel.

The results of fatty acids are shown in Table 5. The composition of fatty acid was a significant property of the biodiesel feedstock. The distribution of fatty acid composition of some oils, were aliphatic compounds by the carbon chain length of various biodiesels, ranging from C8 to C24 in the present study. As can be seen in Figure 1, the highest amount of saturated acids in C. persicum, F. persica, I. meda, V. odorata, A. absinthium, Quercus, and C. tinctorius were associated with palmitic acid (C16). The maximum amount of palmitic acid was in A. absinthium, which was about 39.55 wt %. The highest amount of unsaturated acids was related to oleic and linoleic acids. The maximum amount of oleic acids was gained by I. meda biodiesel, which was about 65.22 wt %. Finally, the double bonds influences density, the increase in which can enhance the value of the density.32 The highest value of density was achieved for Urtica biodiesel (887 kg/m³) and the lowest was obtained for A. absinthium biodiesel (875 kg/m³). All
highest amount of linoleic acids was displayed by F. persica biodiesel, which was about 53.8 wt %.

3.2. Soot and NOx Emissions. Table 6 shows the exhaust emission of various biodiesel sources. The difference of soot emission of Urtica biodiesel (0.98 vol %) and A. absinthium biodiesel (0.58 vol %) was around 40% and Urtica had the highest CN value among all samples. L. ledebourii biodiesel produced the highest amount of soot after Urtica, with only 0.01% difference with Urtica biodiesel. Also, there are some factors affecting soot emissions. The upper viscosity and density resulted in more smoke emissions since the great viscosity of pure biodiesel decreases the fuel atomization and promotes soot emissions. The highest viscosity and density were shown by Urtica biodiesel. Both these factors are other reasons for the increased soot emission of this biodiesel. A. absinthium biodiesel had the minimum of viscosity and density from among all biodiesel samples, that is why soot emission of this biodiesel is decreased.32,33 Another factor that affects the amount of soot emission is the amount of fuel consumption. It is such that soot emission is decreased with the reduction of fuel consumption due to more complete combustion. Therefore, the minimum fuel consumption was shown by A. absinthium biodiesel, which could decrease the amount of soot in contrast to Urtica biodiesel (Table 3). The quality of ignition is frequently influenced by CN; therefore, high CN value indicates short ignition delay, which means less fuel energy in the premixed stage and hence, lower NOx emissions throughout the premixed stage. So, the A. absinthium had NOx emission of approximately 619 ppm, with the lowest CN among all biodiesel samples (around 51). The lowest NOx emission was related to Urtica biodiesel, which has the greatest amount of CN among all samples (around 58). The difference between NOx emission values of V. odorata and A. absinthium biodiesels was just 4%, making. Figure 2 illustrates the relationship between soot and NOx. The results showed that decreasing CN results in the growth of NOx and the reduction of soot at high engine load.20,34,35 In addition, NOx formation depends on combustion duration, volumetric efficiency, and exclusively temperature ascending from high activation energy required for the reactions involved. The exhaust gas temperature has inverse an effect on NOx emissions due to the enhancement in gas flow motion and volumetric efficiency in the engine cylinder under high engine speeds, contributing faster mixing between air and fuel and shorter ignition delay.

Table 5. Analyzing Fatty Acid in Different Oil Samples

| fatty acid            | C. persicum (wt %) | F. persica (wt %) | L. ledebourii (wt %) | I. meda (wt %) | V. odorata (wt %) | A. absinthium (wt %) | Quercus (wt %) | Urtica (wt %) | C. tinctorius (wt %) |
|-----------------------|-------------------|-------------------|---------------------|----------------|------------------|---------------------|----------------|--------------|---------------------|
| caprylic, C8:0        | 0.09              | 0.03              | 0.04                | 0.03           | 0.03             | 0.03                | 0.03           | 0.03         | 0.03                |
| capric, C10:0         | 2.02              | 0.77              | 0.77                | 0.77           | 0.77             | 0.77                | 0.77           | 0.77         | 0.77                |
| lauric, C12:0         | 0.05              | 0.06              | 0.06                | 0.06           | 0.06             | 0.06                | 0.06           | 0.06         | 0.06                |
| myristic, C14:0       | 0.76              | 0.1               | 0.1                 | 0.1            | 0.1              | 0.1                 | 0.1            | 0.1          | 0.1                 |
| myristoleic, C14:1    | 1.54              | 1.54              | 1.54                | 1.54           | 1.54             | 1.54                | 1.54           | 1.54         | 1.54                |
| pentadecanoic, C15:0  | 1.06              | 0.28              | 0.28                | 0.28           | 0.28             | 0.28                | 0.28           | 0.28         | 0.28                |
| palmitic, C16:0       | 9.68              | 10.03             | 2.40                | 10.23          | 20.54            | 39.55               | 9.21           | 2.23         | 9.00                |
| palmitoleic, C16:1    | 2.02              | 1.06              | 0.45                | 1.27           | 3.41             | 7.02                | 1.11           | 0.37         | 3.02                |
| heptadecanoate, C17:0 | 5.44              | 3.30              | 1.62                | 1.64           | 4.03             | 4.20                | 3.41           | 0.37         | 2.03                |
| stearic, C18:0        | 26.54             | 19.32             | 60.93               | 65.22          | 22.12            | 26.1                | 47.12          | 5.44         | 50.23               |
| oleic, C18:1          | 53.8              | 56.17             | 19.62               | 20.52          | 38.27            | 35.38               | 32.87          | 21.13        | 28.63               |
| linoleic, C18:2       | 0.25              | 9.11              | 11.4                | 0.84           | 1.17             | 1.30                | 4.41           | 12.27        | 1.79                |
| linolenic, C18:3      | 2.64              | 1.33              | 0.79                | 0.43           | 6.53             | 0.72                | 1.11           | 0.51         | 1.30                |
| arachidic, C20:0      | 1.65              | 0.28              | 0.28                | 0.21           | 0.75             | 0.10                | 0.08           | 0.67         | 0.67                |
| gondoic, C20:1        | 0.13              | 2.23              | 2.23                | 0.13           | 0.54             | 0.13                | 0.13           | 0.13         | 0.13                |
| behenic, C22:0        | 1.5               | 0.33              | 0.54                | 0.15           | 1.72             | 7.90                | 7.90           | 7.90         | 7.90                |
| erocic, C22:1         | 0.15              | 1.72              | 7.90                | 7.90           | 7.90             | 7.90                | 7.90           | 7.90         | 7.90                |
| lignoceric, C24:0     | 0.15              | 1.72              | 7.90                | 7.90           | 7.90             | 7.90                | 7.90           | 7.90         | 7.90                |
| nervonic, C24:1       | 0.15              | 1.72              | 7.90                | 7.90           | 7.90             | 7.90                | 7.90           | 7.90         | 7.90                |
| total                 | 100               | 100               | 100                 | 100            | 100              | 100                 | 100            | 100          | 100                 |
Therefore, probably the highest rate of exhaust gas temperature belonged to Urtica biodiesel compared to other biodiesel samples.\textsuperscript{33,36} Fuel consumption can affect NOx emission. The decrease of fuel consumption increases NOx emission due to more complete combustion, which increases the heat generated by the combustion and affects NOx production. Therefore, the maximum NOx is produced by \textit{A. absinthium} biodiesel in contrast to Urtica biodiesel.

The soot test showed that the increase of \textit{n}-alkane chain length affected soot emission. The longest chain was obtained through Urtica biodiesel, With approximately 97.43\% of Urtica, biodiesel was in the range of C18−C24, which is shown in Table 6. As can be seen, the increase in carbon chain length increased soot emission, which reached 0.98 vol \%. The \textit{L. ledebourii} biodiesel took the second place in this study with a carbon chain length of around 97.41\% and soot emission of almost 0.97 vol \%. The shortest chain length belongs to \textit{A. absinthium} biodiesel, with only 60.35\% in the range of C18−C24. So, this resulted in a decrease in the amount of soot, reaching 0.58 vol \%. This is in contrast to the previous study, which indicated that an increase in carbon chain length did not increase soot emission.\textsuperscript{25} This is because of the oxygen content, which was diminished with the increase of chain length. The higher oxygen content of fuels decreased soot precursor formation. The results showed that the maximum oxygen content was related to \textit{A. absinthium} biodiesel. The ratio of oxygen to carbon is shown in Figure 3, the highest amount of which belonged to \textit{A. absinthium} biodiesel, which was around 0.1163. \textit{V. odorata} biodiesel was in second place, with a value of 0.1160. The lowest oxygen-to-carbon ratio was seen in Urtica biodiesel. It was quite evident that a decrease in oxygen content had an inverse effect on the output soot. Also, \textit{A. absinthium} biodiesel had the highest oxygen-to-carbon ratio, which had led to a dramatic decrease in soot content. Urtica biodiesel had the lowest oxygen-to-carbon ratio, which had
increased the output soot. The increased O/C ratio reduced soot emissions.21

Table 7 shows the effect of the chain length of methyl esters on NOx emissions. Considering the presence of long-chain fatty acids in biodiesels, and comparing these values with the amount of NOx emissions after the combustion of each biodiesel, long-chain fatty acid increase from C18 to C24 in biodiesel reduced emissions. The Urtica biodiesel with the highest percentage of long-chain fatty acid (97.43%) had the lowest NOx emission among biodiesel samples, which was 460 ppm. On the other hand, the highest amount of NOx was emitted by A. absinthium biodiesel, which was around 619 ppm (with the lowest percentage of long-chain fatty acids). It was observed that NOx rises with the chain length for methyl esters of shorter hydrocarbon chain length; however, for the longer hydrocarbon chains (C18–C24), NOx emissions were reduced. Also the decrease of ignition delay, because of the greater CN of longer chain compounds, decreased NOx emissions.5,37,38 Increased oxygen-to-carbon ratio increased NOx emission. The reason for this lies in the oxygen-to-carbon ratios of biodiesel (Figure 3). The stoichiometry of the burning reaction, as well as the mechanisms of thermal NOx formation, showed that increased oxygen rate increased NOx emissions. With regard to the oxygen-to-carbon ratio and NOx emissions, the increase of the oxygen-to-carbon ratio means shorter chains and extra oxygen in the process that helps produce more NOx. So, the Urtica biodiesel with the highest amount of long-chain fatty acids had the lowest oxygen-to-carbon ratio and the lower oxygen content that reduced NOx emissions. whereas, the A. absinthium biodiesel had the highest amount of oxygen-to-carbon ratio, thus, the lowest amount of long-chain fatty acids and greater NOx emissions due to oxygen.

There was a direct correlation between the increased length of the carbon chain and the amount of enthalpy. Therefore, among all samples, Urtica had the highest percentage of combustion enthalpy. The lowest amount was related to A. absinthium biodiesel. The reason is that during burning, there would be one more C–C bond and two more C–H bonds to be broken; Thus, more energy would be needed in the process of combustion. According to Table 6, the lowest energy is needed for A. absinthium biodiesel because of the smallest carbon chain length. The carbon chain length might separately affect soot emission and enthalpy of combustion and that’s why Urtica biodiesel had the highest soot emission and enthalpy from among all other samples.40,41

The effect of double bonds and unsaturation in the alkyl chain on soot and NOx emissions was also investigated and the results are shown in Table 8. As can be seen, the highest amount of unsaturated acids was observed in Urtica biodiesel (94.93%), the amount of which in L. ledebourii biodiesel was very close to Urtica biodiesel (94.91%). In our observations, there was a direct connection between the increased number of unsaturated acids and soot output. As the amount of unsaturated acids increased, the value of soot output increased either. The lowest amount of unsaturated acids was related to A. absinthium biodiesel (61.51%), which had resulted in the lowest soot content; According to Table 8, A. absinthium biodiesel had the highest amount of saturated acids, which had reduced the amount of output soot. The lowest amount of saturated fatty acids was observed in Urtica and L. ledebourii (9.44%, 10.09%). Increasing the number of unsaturated acids in samples enhanced the number of binary bonds and this raised the amount of soot output.42,43 The hydrogen-to-carbon (H/C) ratio showed the amount of saturated acids. The enhancement of this rate has an indirect effect on soot emission; Also, Figure 4 showed that the increased H/C ratio reduced soot emissions since while the fuel burns better, soot emission is reduced.

The results showed that the increase in unsaturated fatty acids influenced the amount of NOx emissions. The decrease of in-cylinder soot is a probable cause for the changes in NOx emissions among biodiesels.34,45

The amount of energy is directly related to the amount of unsaturated and saturated acids; so it has a direct impact on the amount of energy needed. Table 9 shows this amount of energy for different types of bonds.46 The presence of unsaturated acids increased the number of double bonds, which led to higher energy requirements. As can be seen, the greatest amount of energy was generated when the unsaturated acids were at their highest levels, which increased the number of double bonds. Also, when the oxygen-to-carbon ratio increased, it was observed that the highest energy amount was needed. With the reduction of oxygen-to-carbon ratio and the presence of saturated acids, the least amount of energy is needed; the reason is that due to the reduction of oxygen-to-carbon ratio and the presence of single bonds, the amount of energy decreases dramatically, which makes the amount of energy to be at its lowest level. This proves that the increase in enthalpy energy can affect soot emissions. In this regard, Urtica had the highest amount of unsaturation acid, which in contrast to A. absinthium biodiesel increased soot emission and needed the highest amount of energy.

### 3.3. CO and HC Emissions

The amount of CO emissions for different types of biodiesel is shown in Figure 5a. As can be seen, Urtica biodiesel has the maximum CO emission with a value of about 0.036 vol % (Table 10). The L. ledebourii took second place in this study with a value of about 0.034 vol %.

| Table 8. Value of Saturated and Unsaturated Fatty Acids of Different Biodiesel Sources |
|-----------------------------------------------|----------------|----------------|
| biodiesel | saturated fatty acids (wt %) | unsaturated fatty acids (wt %) | molar H/C |
| Urtica | 5.07 | 94.93 | 1.8457 |
| L. ledebourii | 5.09 | 94.91 | 1.8473 |
| C. persicum | 19.41 | 80.59 | 1.8495 |
| F. persica | 14.94 | 85.06 | 1.8221 |
| Quercus | 15.1 | 84.9 | 1.8579 |
| C. tinctiorius | 15.24 | 84.76 | 1.8685 |
| I. meda | 12.45 | 87.55 | 1.8775 |
| V. odorata | 35.74 | 64.26 | 1.8814 |
| A. absinthium | 45.32 | 54.68 | 1.9028 |

| Table 7. Value of Chain Lengths and Exhaust Emissions |
|-----------------------------------------------|----------------|----------------|
| biodiesel | C18–C24 (wt %) | molar O/C |
| Urtica | 97.43 | 0.1087 |
| L. ledebourii | 97.41 | 0.1110 |
| C. persicum | 90.32 | 0.1118 |
| F. persica | 89.97 | 0.1122 |
| Quercus | 89.02 | 0.1124 |
| C. tinctiorius | 84.65 | 0.1137 |
| I. meda | 88.92 | 0.1125 |
| V. odorata | 72.33 | 0.1160 |
| A. absinthium | 60.35 | 0.1163 |
The minimum CO emission was related to *A. absinthium* with a value of about 0.020 vol %. The reduction of CO emissions probably happened because of the oxygen, which led to easier burning at higher temperatures in the cylinder. This is proved by the higher oxygen content in the shorter carbon chain length, which contributes to a cleaner and more complete combustion. Furthermore, there are methyl esters with longer chain lengths that have higher boiling and melting points, so they are less likely to be completely vaporized and burnt, thereby enhancing CO emissions. According to Table 6, the longest chain and the minimum O/C among all biodiesel samples were obtained through Urtica biodiesel (97.43%), leading to a reverse connection between O/C and CO ratios.

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**Table 9. Different Bonds of Energy**

| bond   | bond energy (kJ/mol) |
|--------|----------------------|
| C–O    | 360                  |
| C–C    | 347                  |
| C=C    | 611                  |
| C≡O    | 799                  |

**Table 10. Exhaust Emission for Biodiesel Sources**

| biodieses | CO emissions (vol %) | HC emissions (ppm) |
|-----------|----------------------|---------------------|
| Urtica    | 0.036                | 6.11                |
| L. ledebourii | 0.034                | 6.01                |
| C. persicum | 0.031                | 5.74                |
| F. persica  | 0.029                | 5.68                |
| Quercus   | 0.027                | 5.61                |
| C. tinctorius | 0.025                | 5.57                |
| I. meda   | 0.023                | 5.51                |
| V. odorata | 0.021                | 5.49                |
| A. absinthium | 0.020                | 5.41                |

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**Figure 4.** Effect of hydrogen-to-carbon ratio on soot and NOx emissions from biofuel sources.

**Figure 5.** Amount of CO (a) and HC (b) emissions for different biodiesel sources.
The amount of HC emission for different types of biodiesels is depicted in Figure 5b. According to Table 9, with regard to the presence of long-chain fatty acids in all biodiesel samples and comparison of these values with the amount of HC emission, long-chain fatty acid increased the HC emission due to longer chain length and upper boiling point. This enhancement causes the reduction of O/C emission and an increase in the HC as well due to lower oxygen content. Therefore, Urtica biodiesel has the highest HC emission with a value of about 6.11 ppm (Table 9). The L. ledebourii biodiesel took second place in this study, with a value of about 6.01 ppm. The minimum HC emission was shown by A. absinthium biodiesel, with a value of only about 5.41 ppm. Another factor that affects the amount of CO and HC emissions is the amount of fuel consumption. It is such that emissions are declined with the reduction of fuel consumption due to more complete combustion. Therefore, the minimum fuel consumption was shown by A. absinthium biodiesel, which could diminish the amount of CO and HC in contrast to Urtica biodiesel (Table 3).

3.4. Combustion. In the present study, all biodiesel fuels were performed at 1800 rpm engine speed and full load. The in-cylinder pressure values of all biodiesel fuels subject to the crank angle (Figure 6a). The difference, which is given in figure for all biodiesel, showed that the peak pressure increases with the enhanced number of double bonds. From Table 8, the highest double bonds and carbon chain length are shown by Urtica biodiesel, and the maximum of peak pressure was achieved in contrast with A. absinthium biodiesel. Therefore, the minimum peak pressure between all biodiesel was gained by A. absinthium biodiesel due to the minimum of double bonds. Accumulated heat release (AHR) rate gives information on the combustion in the engine (Figure 6b). The AHR values enhance in parallel with the increase in in-cylinder pressure and temperature of biodiesels. The fatty acids that can affect CN is so important, increasing the CN. The increase in carbon chain length affects CN enhancement. Table 4 shows that the maximum CN belongs to Urtica biodiesel with a value of around 58, which is in contrast to that of A. absinthium biodiesel. On the other hand, the CN has a direct effect on heat release; the maximum AHR was shown by Urtica biodiesel and the minimum AHR was gained by A. absinthium biodiesel.

4. CONCLUSIONS
In the present study, the effect of the molecular structure of the samples on the soot and NOx emissions was assessed. Important results obtained in this study are as follows:

- Nine new biodiesel sources were studied in this study. They can grow in harsh conditions with no negative effect on the human food chain.
- The physical properties of biofuels showed that the highest flash point, density, viscosity, and CN were observed in Urtica biodiesel in contrast to A. absinthium biodiesel.
- The effect of carbon chain length and double bonds on flash point, density, viscosity, and CN was also approved.
- The highest amounts of soot, HC, and CO were emitted by Urtica biodiesel in contrast to the lowest amount of NOx emission.
- The reduction of CN resulted in the growth of NOx and a decrease in soot at a high engine load.
- A direct connection between carbon chain length and soot emission was shown in the study.
The increase of the O/C ratio reduced soot emissions.

The effect of long-chain fatty acids (C18–C24) on the reduction of NOx emissions was observed.

There was a direct correlation between the increased length of the carbon chain and the amount of enthalpy.

There was a direct connection between the increased number of unsaturated acids and soot output.

The increase of the H/C ratio decreased soot emissions.

The amount of energy was directly connected to the amount of unsaturated, saturated acids, and O/C ratio.

The O/C ratio and carbon chain lengths affected CO and HC emissions.

A decrease in fuel consumption increased NOx emission and reduced HC, CO, and soot emissions.

The direct effect of CN, carbon-chain length, and double bonds on pressure and accumulated heat release.

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**ABBREVIATIONS**

NOx nitrogen oxides

KOH potassium hydroxide

ASTM American Society for Testing and Materials

EN European Standard

CN cetane number

O/C oxygen-to-carbon ratio

H/C hydrogen-to-carbon ratio

HC unburned hydrocarbons

CO carbon monoxide

AHR accumulated heat release

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