



Article **Promotion of the NO-to-NO₂ Conversion of a Biofueled Diesel Engine with Nonthermal Plasma-Assisted Low-Temperature Soot Incineration of a Diesel Particulate Filter**

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Abstract: High-concentration biodiesel-diesel fuel blends are an alternative fuel widely used for compression ignition engines. However, commercial diesel engines are not designed and set up for high-concentration biodiesel-diesel fuel blends. Hence, the aim of this research was to investigate the nonthermal plasma (NTP) activities during an NOx reduction and the soot characteristics on an unmodified diesel engine (Euro V) that is fueled with various biodiesel blends with diesel under a low exhaust gas temperature (<250 °C). The experiment found that the soot composition of biodiesel fuel produces lower levels of soot when compared with diesel, in terms of both number and mass. In addition, the activation energies (Ea) of carbon oxidation under an oxygen atmosphere were found to be approximately 154.57–173.64 kJ/mol.

Keywords: nonthermal plasma; NO_x conversion; soot composition; biodiesel

1. Introduction

Compression ignition engines or diesel engines have been used extensively in the transportation sector due to the distinctive features of high-performance diesel engines, which are durable and have low fuel economies. The combustion mechanism of diesel engines is lean diffusion combustion, which leads to the limitation of the time in which the air-fuel mixture is found to be a homogenous mixture; incomplete combustion is a significant cause of the formation of particulate matter (PM). The main PM components consist of carbon in a solid state (soot) in the core and a volatile organic fraction (VOF) or soluble organic fraction (SOF), which are formed by unburned hydrocarbons (HC) and lubricant that are burned in the combustion chamber. The electrically charged carbon atoms from combustion may combine with the adjacent carbon atoms (thermionic electron capture), causing the size of the carbon to be enlarged by the carbon particles, causing a direct health hazard to humans. In addition, given the amount of soot, PM10 can enter the respiratory tract and the pleura. Therefore, it may cause inflammatory diseases of the respiratory tract. Moreover, it can be harmful to the lungs.

However, biodiesel is widely utilized in many countries, especially in those that cultivate oil crops. Biodiesel is often made from a range of feedstocks, including palm, rapeseed, jatropha, and other vegetable or animal fats. Thailand's palm oil is the most



Citation: Iamcheerangkoon, T.; Chollacoop, N.; Sawatmongkhon, B.; Wongchang, T.; Sittichompoo, S.; Chuepeng, S.; Theinnoi, K. Promotion of the NO-to-NO₂ Conversion of a Biofueled Diesel Engine with Nonthermal Plasma-Assisted Low-Temperature Soot Incineration of a Diesel Particulate Filter. *Energies* 2022, *15*, 9330. https://doi.org/10.3390/en15249330

Academic Editors: João Fernando Pereira Gomes and Constantine D. Rakopoulos

Received: 31 October 2022 Accepted: 7 December 2022 Published: 9 December 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). promising raw material for the production of biodiesel. This is because the palm oil methyl ester has much higher oxidation stability when compared to soybeans' highly saturated vegetable oil. Energy security strategies are still necessary for Thailand, a net importer of crude oil, to lessen its reliance on imported oil. As a result, Thailand announced the mandatory use of B7–B20 across the country at the beginning of 2019. Thailand is interested in biodiesel because it is homegrown and sustainable. S. K. Hoekman and C. Robbins have also demonstrated that using biodiesel lowers levels of hydrocarbons (HC), carbon monoxide (CO), and soot. Although NO_x usually increases slightly with the use of biodiesel, NO_x emissions are lower as indicated by the "biodiesel NO_x effect" [1]. Additionally, S. Jaroonjitsathian et al. showed the results of blending the biodiesel fuel component in diesel fuel for a common-rail DI engine. Low engine power output results from excessive biodiesel content, because the increased biodiesel content leads to reduced power output [2].

Diesel particulate filters (DPFs) are a type of after-treatment equipment for diesel engines, which lower particle emissions by up to 80% through the capture and oxidation of soot; this is undertaken by soot oxidation and trapping on the DPFs wall surface. This issue can be resolved by heating the temperature to over 550 °C, which is known as the regeneration process. Research has explained soot oxidation with O2 in terms of both temperature programming oxidation (TPO) and thermo-gravimetric analysis (TGA). P. Promhuad and B. Sawatmongkhon studied the catalytic oxidation of diesel particulate matter by using silver and ceria supported on alumina as the oxidation catalyst, which tested PM from the diesel exhaust gas in TGA. The results showed that, in the case of a pure PM, the oxidation of soot took place at temperatures of around 500–700 °C [3,4]. Similarly, X. Deng et al. studied the nano-structure of silver/ceria-zirconia as a highly active and stable catalyst for soot oxidation. They tested soot oxidation in TPO, and showed soot combustion at temperatures 450–650 °C [5]. In addition, the soot oxidation was oxidized with NO_2 at lower temperatures than with O_2 [6]. J. O. Müller et al. examined the TGA results and found that, at temperatures between 200 and 450 °C [7-10], the influence of soot oxidation through NO2 is dominant. The diesel exhaust, NO_x , mainly consists of NO and minor amounts of NO₂. Three formation processes are thought to be generally significant. First, thermal NO_x , N_2 and O_2 could be generated in conditions at high temperatures (above 1500 °C), and the rate of formation increases rapidly with the increasing temperature. Thermal NO_x was believed to be the predominant contributor to the primary source of total NO_x [11–15]. In other words, a timescale of NO_x production was comparable to the duration of combustion in a diesel engine due to the kinetics of the Zeldovich process [16]. As a result, any biodiesel impact that lengthens the amount of time the mixture spends in the cylinder or raises the temperature inside the cylinder could increase thermal NO_x . Second, prompt NO_x only occurs frequently in fuel-rich environments, where there is a surplus of hydrocarbon to react with N_2 in the combustion chamber [17] The prompt NO_x is sensitive to fuel chemistry because it relies on hydrocarbon fragments, whereas thermal NO_x is essentially indifferent to fuel chemistry (Ban-Weiss, G. A. et al.), due to high levels of unsaturated compounds. The combustion of biodiesel may produce more hydrocarbon radicals than the combustion of conventional diesel, thus leading to higher levels of NO_x formation [18]. Third, fuel NO_x , the combustion process in a diesel engine, converts fuel species containing nitrogen to NO_x. However, as both diesel fuel and biodiesel have deficient levels of natural nitrogen, this production process is typically insignificant. However, it becomes more critical with high concentrations of nitrogen-containing fuel additives.

The plasma technique is used to limit the emissions from combustion; it uses an ionized gas in which enough energy is supplied to release electrons from atoms or molecules and enable species, ions, and electrons to coexist. The percentage of atoms with lost or acquired electrons determines the degree of plasma ionization [19]. In nonthermal plasma (NTP), the electric field transfers energy to gas electrons, which collide to transfer energy to neutral species [20]. However, the system's free electrons have a temperature of more than 10,000 °C, thus promoting the required chemical changes in the exhaust gas. NTP is used

to selectively transmit the electrical energy from the input to the electrons. The oxidation processes begin when the plasma is inside the exhaust gases, and there is oxidation of NO_x, HC, CO, and soot [21,22]. Z. Wang et al. showed that the NTP system could remove NO with efficiency close to 100% in the NO/N₂ system [23]. Despite NO_x being reduced to N₂ and O₂, the plasma treatment of exhaust gases is more strongly related to NO oxidation to NO₂ [24–27]. In addition, P. Wang. et al. present a study of the influence of NTP technology on the soot emission properties of diesel PM. The results show that NTP treatment can reduce the PM combustion temperature by nearly 120 °C [28].

Thus, NTP shows the potential to improve catalyst selectivity and removal efficiency [29]. It also allows for combustion with the ability to reduce the amount of soot at low temperatures. NTP also converts NO to NO2, which can improve the efficiency of the engine exhaust treatment from biodiesel fuel applications, which approximates the engine exhaust temperature in regular operations.

2. Experimental Design

2.1. Schematic Diagram of the Experimental Setup

In the experiment, we employed the system shown in Figure 1. An unmodified fourcylinder engine (engine specifications are shown in Table 1) common-rail direct injection (DI) was instrumented with a 0.1 crank angle (CA) resolution crankshaft encoder, and a pressure transducer (Kitsler 6052b1) inside cylinder head no.1. Afterwards, a Kitsler KiBox was added to monitor and record the in-cylinder pressure and heat release. This engine, which was connected to the eddy current dynamometer (AVL: EMCON 400), was used to produce different particulate samples at fixed engine-speed operating conditions at 2000 rpm, and adjusted for 3 different Indicated Mean Effective Pressures (IMEP) of 5, 6 and 7 bar (engine load operation conditions are shown in Table 2). The four different types of diesel fuel tested in this experiment were B7, B10, and B20 (blends of 7, 10, and 20 wt%, respectively, pure palm oil in low sulfur diesel) and Premium Diesel (PD) based on the reference standard fuel properties in Thailand.



Figure 1. Schematic diagram of the experimental design.

The exhausts of the engine were controlled by the back pressure valve and kept equal in all conditions. Then, the exhaust gases were taken by a vacuum pump of 10 L/min to the NTP treatment system and analyzed by an exhaust gas analyzer (TESTO 350) and an Engine Exhaust Particle Sizer spectrometer (EEPS: TSI 3090). These were installed with an adapter at the outlet of the NTP system, and all testing conditions were sampled at the same location to ensure that the number, mass, and volume were not impacted by other factors.

Table 1. Engine specifications.

Common-Rail Euro Stage V Diesel Engine			
N° of cylinder	4 cylinders, In-line		
Fuel injection	Common-rail DI		
Displacement volume (cm ³)	2499		
Bore \times Stroke (mm)	95.4 imes 87.4		
Compression ratio	18.1		
Maximum power (kW)	87 @ 1800–2200 rpm		
Maximum torque (Nm)	280 @ 1800–2200 rpm		

Table 2. Engine operation conditions.

Indicated Mean Effective Pressure: IMEP (Bar)	5	6	7
Torque (Nm)	16.3	25.2	32.6

2.2. NTP System Setup

The structure of the NTP reactor design was based on the dielectric barrier discharge (DBD) principle, and consisted of several NTP reactors to improve the exhaust gas capacity. The NTP reactor consisted of a stainless steel stud with a diameter of 10 mm as the high-voltage electrode. A stainless-steel tube was used as a reaction body around the surface of a quartz glass tube, and functioned as the ground electrode with an inner diameter of 17 mm and an effective discharge length (L = 100 mm). The discharge gap distance was fixed at 3.5 mm. An alternating current (AC) power supply (TREK 10/10B-HS) with adjustable high-voltage from 0, 2, 4, 6, 8, and 10 kV (0, 32, 128, 288, 512, and 800 watts, respectively) and a fixed frequency of 500 Hz was applied to the electrodes to generate NTP. The calculation of the power of plasma was used by the power of electric following Equation (1). "P" is the power, "V" is the voltage, and "I" is the electric current. The voltage was founded by the ratio of conversion, which is 1 V (peak to peak) input per 1000 V output. The current could be calculated according to the conversion ratio of the transformer used in the experiment, which is 1 V input per 4 mA output.

$$P = V \times I \ (W) \tag{1}$$

The discharge voltage was measured using a voltage probe (Testec TT-HVP-15HF), which could obtain an analog signal that could be digitized using an oscilloscope (KEYSIGHT DSOX 1204G).

Space Velocity (SV) was the ratio between the gas flow rate through the reactor and the effective volume of the reactor, as shown in Equation (2):

$$SV = \frac{Q_{gas}}{V_{eff}} \left(h^{-1} \right) \tag{2}$$

Hence, the SV of the plasma reactor was influenced by two factors: the gas flow rate inside the plasma reactor (Q_{gas} is the exhaust gas flow rate (m^3/h)) and the volume in the reactor (m^3), with the effective length of reactor (if the outside diameter of reactor is fixed).

Reactor length (L) was the length of the region in which the discharge of plasma took place. This effective length was defined by the length of electrode along the gas flow. The reactor effective length determined the space velocity (SV) of the reactor and was related to the residence time of the exhaust gas in the reactor, which affected the chemical processes of the exhaust gas. Reactor Effective Volume

The effective volume of the plasma reactor was the volume inside the reactor in which the exhaust gas flows through the plasma. In this research, the stud stainless steel highvoltage electrode was located inside of a quartz tube, so its volume was considered. In addition, the quartz tube's diameter was kept constant, and, as such, the effective volume could be determined by the length of the outside electrode (the stainless steel tube used as a reaction body around the quartz tube). This was used to calculate the plasma reactor's effective volume (V_{eff}). Using a simple cylindrical volume equation to find the volume between the electrode rod (D) and the quartz tube (d), we obtained Equation (3):

$$V_{eff} = (A_{tube} - A_{eletrode}) \times L \tag{3}$$

2.3. Experimental Method

Soot was collected using a glass microfiber filter (Whatman GF/C 1.2 μ m pore size); the exhaust gases flow rate of 10 L/min through the filter for 50 L (5 min for a gas flow rate of 10 L/min). The soot components were analyzed using Thermo-gravimetric Analysis (TGA: PERKIN Elmer Pyris 1). The TGA heating program is listed in Table 3. The method was adapted from [30] which was developed to determine the amounts of moisture, volatile organic compounds, and carbon soot at their known weight loss temperatures. To prevent the breakdown of the glass fiber filter, a maximum temperature of 600 °C was set.

Temperature Program	Atmosphere
Isothermal hold at 40 $^\circ\mathrm{C}$ for 10 min.	Nitrogen 50 mL/min
Heating to 110 $^\circ C$ with a ramp rate of 10 $^\circ C/min.$	Nitrogen 50 mL/min
Isothermal hold at 110 $^\circ\mathrm{C}$ for 30 min.	Nitrogen 50 mL/min
Heating to 400 $^\circ C$ with a ramp rate of 10 $^\circ C/min.$	Nitrogen 50 mL/min
Isothermal hold at 400 $^\circ\mathrm{C}$ for 30 min.	Nitrogen 50 mL/min
Cooling to 200 $^\circ C$ with a ramp rate of 10 $^\circ C/min.$	Nitrogen 50 mL/min
Heating to 600 $^\circ C$ with a ramp rate of 10 $^\circ C/min.$	Oxygen 50 mL/min
Isothermal hold at 600 $^\circ C$ for 30 min.	Oxygen 50 mL/min
	Temperature ProgramIsothermal hold at 40 °C for 10 min.Heating to 110 °C with a ramp rate of 10 °C/min.Isothermal hold at 110 °C for 30 min.Heating to 400 °C with a ramp rate of 10 °C/min.Isothermal hold at 400 °C for 30 min.Cooling to 200 °C with a ramp rate of 10 °C/min.Heating to 600 °C with a ramp rate of 10 °C/min.Isothermal hold at 600 °C for 30 min.

Table 3. Optimized manual TGA heating programmed procedure.

3. Results and Discussion

3.1. Combustion and Emission

In-Cylinder Pressure and Heat Release Rate

This research was interested in reducing total NO_x , NO to NO_2 conversion, and soot composition from biodiesel fuel at low exhaust temperatures, which is a challenge in attempts to control pollution. The in-cylinder pressure and heat release rate were compared with the baseline for diesel, B7, B10, B20, and PD. The result shown in Figure 2 were averaged from 500 consecutive cycles; at light load conditions, the 3 selected IMEPs of 5 bar, 6 bar, and 7 bar were measured. Based on the cylinder pressure data, the combustion parameters were examined. As a result of common-rail DI with a pilot fuel injection and main injection occurring at -8 ca before TDC and 1 ca after TDC, respectively, the cylinder pressure data for all tested fuels are comparable. Only insignificant differences between all the conditions were observed. On the other hand, B10 and B20 fuels contain a larger amount of biodiesel, causing the heat release rate to lag slightly, but increasing the heat release rate in combustion, as a result of the presence of oxygen in biodiesel fuels.



Figure 2. In-cylinder pressure and heat release rate profiles.

3.2. Effect of NTP on Emissions

As the in-cylinder pressure and rate of heat release values were similar across all IMEPs, the IMEP 6 bar was selected for further testing.

3.2.1. Effect of NTP on The CO-to-CO₂ Conversion

Figure 3 shows the CO and CO_2 concentrations after a high voltage was applied to the NTP reactor. It should be noted that the effective high voltage slightly increased CO and CO₂ concentrations from amounts of electrons in the discharge region to H₂O and O₂ in the exhaust gas (Equations (4) and (5)) [28]. Due to the conversion of CO into CO₂ when applying a high voltage of between 2 and 6 kV, (Equations (6)–(9)) [31], effective high voltage was seen to marginally increase CO₂. On the other hand, according to (Equations (10)–(14)), a rise in CO occurs at voltages higher than 6 kV [23].

$$e + H_2O \rightarrow OH + H + e$$
 (4)

$$e + \mathcal{O}_2 \to \mathcal{O}^* + \mathcal{O}^* + e \tag{5}$$

$$CO + OH \rightarrow CO_2 + H$$
 (6)

$$CO + O \rightarrow CO_2$$
 (7)

$$CO + O_3 \rightarrow CO_2 + O_2 \tag{8}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{9}$$

$$e + \mathrm{CO}_2 \to e + \mathrm{O}^* + \mathrm{CO} \tag{10}$$

$$e + CO \rightarrow e + O^* + C \tag{11}$$

$$CO + 2OH \rightarrow CO_2 + H_2O$$
 (12)

$$3CO + O_3 \rightarrow 3CO_2$$
 (13)

$$CO + O^* \rightarrow CO_2$$
 (14)

In addition, O radicals combined with O_2 to form O_3 (Equation (15)) and consolidated with CO and CO₂ in the exhaust gas from the reaction of the surface oxide with O_3 (Equations (16)–(21)) [28], which could represent soot oxidation in the NTP discharge. The oxidation of CO by the OH radicals is represented by Equation (22) [28].

$$O^* + O_2 \to O_3 \tag{15}$$

$$C + 2O^* \to CO_2 \tag{16}$$

$$C + 2O_3 \rightarrow CO_2 + 2O_2 \tag{18}$$

$$C + O_3 \to CO + O_2 \tag{19}$$

- $C + 2OH^* \rightarrow CO_2 + 2H^* \tag{20}$
- $C + OH^* \to CO + H^*$ (21)
- $CO + OH^* \rightarrow CO_2 + H^* \tag{22}$



Figure 3. Effect of NTP on CO and CO₂ concentrations at an engine speed of 2000 rpm and IMEP 6 bar.

3.2.2. Effect of NTP on Hydrocarbon (HC)

The hydrocarbon concentration is shown in Figure 4a, which demonstrates the effect of high voltage on HC concentrations in the different types of fuel. The results for all fuels show the reduction of the concentration of HC with increasingly high voltages. As a result of O and O₃ being the primary components of SOF in the PM, they react to create CO₂ (Equations (23) and (24)) [28]. Because of an interaction with the elevated oxidative radicals, PM's efficiency may decrease while receiving the NTP therapy.

$$HC + O_3 \rightarrow H_2O + CO_2 \tag{23}$$

$$HC + O^* \to H_2O + CO_2 \tag{24}$$



Figure 4. Effect of NTP on HC concentrations (**a**) and Oxygen concentration (**b**) at an engine speed of 2000 rpm and IMEP 6 bar.

Figure 4b depicts the oxygen content in various fuels and high voltages ranging from 0 to 10 kV. Compared to the engine out situation, the O_2 conversion changes somewhat when NTP is used at a high voltage of 2–10 kV. Due to the poor conversion of O_2 to O_3 , which occurs from the exhaust gas flow rate influencing the generation of O_3 . The formation of O_3 was low with high exhaust gas flow rates (>10 L/min), which is consistent with previous research [32].

3.2.3. Effect of NTP on NO-to-NO₂ Composition

It can be observed that the chemical reaction of NTP was able to reduce the amount of NO_x in all fuels. This corresponds to an increase in the biodiesel ratio [1], which was reduce by up to 30.32% in B10. Figure 5 shows the NO and NO₂ concentrations for the NTP system after the chemical reaction in the exhaust gas for IMEP 5, 6, and 7 bars. It shows the rise of NO₂ at high voltages of 6, 8, and 10 kV, whereby a high voltage of 8 kV was adequate to change NO completely to NO₂ in PD, B7, and B10, and effectively in B20 fuel, by 89.33%. However, the sum of NO_x is changed to N₂ according to Equations (26) and (31).

NO_x removal reactions and NO–NO₂ conversion reactions:

In the first group, some of the primary and main NO_x removal reactions can be summarized as follows [33–35] in Equations (25)–(31):

$$N_2 + e \to N + N + e \tag{25}$$

$$NO + N \rightarrow N_2 + O$$
 (26)

$$O_2 + O \rightarrow O_3$$
 (27)

$$N_2 + e \to e + N_2(A) \tag{28}$$

$$N_2(A) + NO \rightarrow N_2 + N + O \tag{29}$$

$$N_2(A) + N_2O \rightarrow 2N_2 + O \tag{30}$$

$$NO_2 + N \rightarrow N_2 + O_2 \tag{31}$$

where N_2 (A) represents the N_2 metastable state.

The second group of reactions (which involves the reactions of oxidizing NO to NO_2) can be summarized as follows [34–36] in Equations (32)–(35):

$$O_2 + e \to O + O + e \tag{32}$$

- $O_2 + O \rightarrow O_3$ (34)
- $NO + O_3 \rightarrow NO_2 + O_2 \tag{35}$



Figure 5. Effect of NTP on NO and NO₂ conversion at an engine speed of 2000 rpm and IMEP 6 bar.

3.2.4. Energy Density in Converting NO to NO₂

Since the conversion rate is close to 100% at higher energy densities, as shown in Figure 6, the experiments at higher energy densities were no longer performed (high voltages more than 8 kV). Higher NO₂ concentrations are inversely proportional to NO concentrations near zero. The reason for this phenomenon is that the probability of NO collision with O and O₃ is higher in the reaction system with the increase in the NO concentration. The more likely it is that NO will convert to NO₂, the more NO will be eliminated.



Figure 6. NO, NO₂, and NOx concentrations after the plasma treatment of energy density.

3.3. Soot Composition

The results were analyzed into according to two aspects: by number and by mass. In Figure 7, turning on all conditions with the NTP system demonstrated a significant reduction in the concentration of total particulate matter. The NTP system can reduce the particulate number at every high-voltage input, with a slightly decreased rate at 2 and 4 kV, but increases the efficiency of the NTP system at the reactor's effective high-voltage inputs of 6 and 8 kV. This results in the total reduction of diesel particulate matter, with the total concentration reduced by 22.65–54.15%. This effectiveness resulted in the gradual reduction in both total mass and mean particulate size by 64.16%, as was found with the use of the NTP system with a high-voltage input of 10 kV. On the other hand, there was an increase in the ultrafine particulate matter (6.04–19.1 nm) after the plasma treatment. This occurs in every fuel due to the energy supplied being enough to disintegrate large particles into smaller particles. This ultrafine particulate matter would be harmful to human lungs; therefore, attention should be paid to this problem when using NTP technology. These phenomena could be sufficiently explained by the fact that large-scale particles were categorized as accumulating and were primarily made up of electrically conductive carbon spheres. The nearest soot patch was self selected by the high-voltage electrical plasma, which then discharged to create the plasma zone [37]. Thus, particulates in the accumulation mode reacted with the plasma and reduced. This explains why large-size particulates were effectively reduced.

The association between particle mass and the number of particulates, as shown in Figure 8, is explained by the finding that the bulk of the mass of particles is covered by particulates in the accumulation mode. However, despite Kittelson's [38] assertion that particulates in this mode comprise more than 90% of the total particle number, the data

show that particulates in the nuclei mode did not have a high particulate number. However, the increase in the ultrafine particulate matter in Figure 6 has no influence on the mass distribution. This is because the increase in mass of the ultrafine particulate matter is very slight when compared to the dN of mass distribution.



Figure 7. Effect of NTP on the particulate number distribution at an engine speed of 2000 rpm and IMEP 6 bar.



Figure 8. Effect of NTP on particulate mass distribution at an engine speed of 2000 rpm–2000_IMEP 6 bar.

3.4. Activation Energy

The soot combustion in TGA is shown in Figure 9, which presents the percentage of weight loss and first derivative (DTG) of the TGA profile under the different temperatures and types of gas used for testing. The temperature range between room temperature and 400 °C was used for N₂ for the removal of moisture (H₂O) and to determine the soluble organic fraction (SOF), and temperatures of 400–600 °C were used to study soot combustion by O₂. The fuels under consideration were DP, B7, B10, and B20, which are shown in Figure 9a–d, respectively. In all cases, the results of DTG showed peaks of moisture around 100 °C and a peak of SOF around 150 °C to 250 °C. The soot combustion showed a peak of DTG around 400–500 °C, which presented the same peak. It can be seen from the experiment that the soot from different fuels had the same carbon composition. A summary of the soot combustion when using flowing DP, B7, B10, and B20 as fuels shows similarities in terms of both SOF composition and the type of carbon in the soot.



Figure 9. TGA spectra for the NTP of soot, before and after: all fuel_2000_IMEP 6 bar.

Figure 10 shows the TGA spectra for the soot before and after NTP at 2000 rpm and IMEP 6 bar. The percentage of weight loss in the TGA represents the quantity of soot that was released from combustion, whereby an O_2 atmosphere causes weight loss in the PM sample. Prior to the NTP treatment, the highest rate of the thermal degradation temperature for the PM samples was 495.99 °C. Following the NTP treatment at 6 and 10 kV, the temperature was reduced by 2.45% and 3.62%, respectively (483.84 °C and 478.03 °C). It was also observed that NTP could improve the activity of the low-temperature combustion of PM. This effect is primarily caused by the abundance of oxidative radicals produced

by the NTP discharge, which decreases the amount of activation energy needed for soot combustion [28]. The result of the DTG could indicate the slope of TGA spectra that present the soot oxidation activity and affect the activation energy of soot combustion. The amplitude of DTG ranges from high to low in the following order: 0 kV > 6 kV > 10 kV. This confirms the activation energy part.



Figure 10. TGA spectra for soot before and after NTP at 2000 rpm and IMEP 6 bar.

Activation Energy (Ea) to break down carbon bonds in soot. Temperature ranges from 350-600 °C were selected based on the slope of the soot weight loss [30]; moisture and VOC were not taken into consideration, as shown in Table 4. It was found that, when the high voltage was applied to the plasma at 6 and 10 kV, the Ea decreased by 4.94 and 19.07 kJ/mol (2.85 and 10.97%, respectively). As a result of NTP, the soot could be broken down more easily. The activation energy (Ea) can be calculated from Equation (36).

 $Ea (kJ/mol) = (Slope of liner plot (negative) \times Gas constant (J/mol. K))/1000$ (36)

Table 4.	Activation	Energy	(Ea).
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	High Voltage (kV)	Activation Energy (kJ/mol)
-	0	173.64
	6	168.70
-	10	154.57

4. Conclusions

NTP technology presents the advantageous possibility of enhancing NO_x and soot reduction. The chemical reaction in NTP affects the total NO_x content, and is able to effectively reduce the total NO_x in all biodiesel-diesel fuel blends. It also influences the NO-to-NO₂ oxidation. However, the amount of CO and CO₂ was only slightly increased from the reaction, and it was difficult to control, which is an interesting issue. The NTP treatment system also reduces particulate emissions, so might be used to ensure compliance with strict emission regulations. NTP reduced the activation energy for particulate

matter from combustion in all fuels. The activation energy for soot oxidation by NTP was determined using high voltages (6 and 10 kV), which reduced activation energy by 2.85 and 10.97%, respectively. The high voltage significantly reduced the measured particles' sizes, with significant reductions primarily in the range of 25.5 to 165.5 nm (the accumulation mode). However, it mainly enhanced the nuclei mode (<100 nm), when compared to the results generated without NTP. Thus, the size of the particulate matter in exhaust gas conditions depends on an optimized operating system, in order to assist NTP activities in the combustion of biodiesel-diesel fuel blends.

Author Contributions: Methodology, N.C., T.W. and S.S.; Validation, B.S.; Investigation, T.I.; Data curation, S.C.; Writing—original draft, T.I.; Writing—review & editing, K.T.; Supervision, N.C. and K.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Science, Research and Innovation Fund (NSRF), and King Mongkut's University of Technology, North Bangkok, with Contract no. KMUTNB-FF-66-19. T. Iamcheerangkoon thanks King Mongkut's University of Technology, North Bangkok, and the National Science and Technology Development Agency, Thailand. Contract No. Grad017/2563, for supporting his scholarship.

Conflicts of Interest: The authors declare no conflict of interest.

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