Experimental and Numerical Study on the Effect of NO$_2$ on n-Butanol/Biodiesel Dual-Fuel Combustion in a Compression Ignition Engine

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ABSTRACT: Nitrogen dioxide (NO$_2$) is an active species of exhaust gas recirculation gas, and it has a significant impact on the autoignition and combustion processes of fuels. This study presented a comprehensive investigation of the effect of NO$_2$ on the combustion characteristics of the n-butanol/biodiesel dual fuel. Experiments were conducted on a single-cylinder engine with 0, 100, 200, and 400 v/v ppm NO$_2$ addition at two fuel injection ratios. The findings of the experiments indicated that adding NO$_2$ resulted in an earlier start of heat release and an increase in peak in-cylinder pressure as compared to experiments where no NO$_2$ was added. The evolutions of n-butanol, biodiesel, and OH radicals were evaluated using the computational fluid dynamics software coupled with the n-butanol–biodiesel–NO$_2$ mechanism. The results revealed that when 400 v/v ppm NO$_2$ was added, the consumption of n-butanol and biodiesel occurred earlier, and the formation of OH radicals was approximately an order of magnitude higher before the biodiesel was injected. Furthermore, reaction rate and flux analyses were performed to understand the effect of NO$_2$ addition on the reaction process. When NO$_2$ was added, 35% of the HO$_2$ radicals reacted with NO which converted from NO$_2$ via the reaction NO + HO$_2$ ⇌ NO$_2$ + OH, promoting the formation of OH radicals in the reaction system. The addition of NO$_2$ can also enhance the consumption of CH$_3$ radicals via the reaction CH$_3$ + HO$_2$ ⇌ CH$_3$O + OH.

1. INTRODUCTION

Traditional spark and compression ignition (CI) engines have found it more challenging to fulfill increasingly stringent emission regulations and fuel efficiency demands. To address this, advanced combustion modes have been proposed, including homogeneous charge CI (HCCI),$^1$ premixed charge CI (PCCI),$^2$ partially premixed combustion (PPC),$^3$ and reactivity controlled CI (RCCI).$^4$ All these combustion modes utilized the exhaust gas recirculation (EGR) technique to reduce nitrogen oxides (NO$_x$) emissions. Furthermore, for various combustion modes, EGR was also used to manage the combustion phase in conjunction with other control techniques such as intake air temperature, fuel injection strategy, fuel reactivity, and so on. The effect of EGR on engine combustion can be classified into three categories:$^5$ dilution, thermal, and chemical. Early research concentrated on the dilution and thermal impact of EGR. The introduction of exhaust gas to reduce the concentration of O$_2$ in the cylinder, as well as the higher specific heat capacity of CO$_2$ and H$_2$O, was thought to lower the maximum combustion temperature when the total heat release of the fuel in the cylinder remained constant, thereby inhibiting NO$_x$ production. As the chemical kinetic mechanism of fuel combustion grew increasingly understood, the chemical effects of EGR were of considerable interest to researchers.

The active components in the EGR gas, such as NO,$^6$ formaldehyde, sulfur oxides (SO$_x$), and others, could affect the oxidation process of fuels. With a large amount of EGR, the oxygen concentration decreased, and the influence of these active components on the ignition delay and combustion process of fuels became more apparent. Jansons et al.$^6,7$ introduced formaldehyde into the intake air of a direct injection CI (DICI) engine fueled with jet propulsion fuel (JP-8) and found that the addition of formaldehyde retarded the low-temperature heat release (LTHR), prolonged ignition delay, and suppressed HCHO chemiluminescence. Kawasaki et al.$^8$ evaluated the impact of nitric oxide (NO) and nitrogen dioxide (NO$_2$) on natural gas HCCI combustion in a rapid compression expansion machine (RCEM) that was modified from a single-cylinder diesel engine. The obtained findings

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demonstrated that by adding either NO or NO₂, the autoignition was substantially accelerated, and the acute heat release was facilitated. Masurier et al. investigated the impact of adding oxidizing species including ozone, NO, and NO₂ on a single-cylinder HCCI engine fueled with iso-octane and found that all added species improved spontaneous ignition and advanced combustion phasing. Ozone was shown to have the most significant impact, whereas NO₂ had the least. Kobashi et al. found that adding NO₂ to the intake air of a DI CI engine fueled with diesel can reduce the ignition delay. The ignition delay decreased at the NO₂ concentration increased. NO₂ accelerated ignition more than NO. The addition of carbon monoxide (CO) or hydrocarbons (CH₄, C₂H₆, C₃H₈, and C₄H₈) had little effect on the ignition delay.

For the design of the EGR system in many engines, the EGR gas was cooled using an EGR cooler and then blended with fresh air before entering the cylinder. During this procedure, NO in the EGR gas was converted to NO₂. Many studies have been conducted to investigate the influence of NO₂ addition on the ignition behavior of various fuels such as hydrogen, methane, ethane, dimethyl ether, n-butane, and n-heptane. Mathieu et al. used a shock tube (ST) to evaluate the oxidation of hydrogen with three NO₂ concentrations (100, 400, and 1600 v/v ppm) at 1.0 ± 1.3, and 3 MPa, 850–1700 K, and equivalency ratios of 0.3, 0.5, and 1.0. The addition of NO₂ could promote the autoignition of H₂. The ignition delays were shown to be highly dependent on pressure and NO₂ concentration, although equivalency ratio variation had little effect on the ignition delay. Sahu et al. studied the impact of NO₂ addition (0, 200, and 400 v/v ppm) on the autoignition behavior of methane in a rapid compression machine (RCM) at 1.5 and 3.0 MPa, 900–1100 K, and equivalency ratios of 0.5, 1.0, and 2.0. The ignition delays were decreased when NO₂ was added. The promoting impact of NO₂ was discovered to increase with temperature, but the sensitizing effect was reduced at higher pressures. Deng et al. explored the NO₂-promoting effect on the ethane combustion in a shock tube at 0.12–2 MPa, 950–1700 K, and equivalency ratios of 0.5, 1.0, and 2.0. They found that adding NO₂ increased reactivity at higher pressures and lower temperatures but had a negligible impact at low pressures and higher temperatures. Zhang et al. compared the effect of NO₂ addition on the autoignition behavior of methane, ethane, and methane/ethane mixtures in a shock tube. They discovered that adding NO₂ to methane and methane/ethane mixtures reduced ignition delays significantly. However, for C₃H₆, the reduction in ignition delays was modest. The oxidation-enhancing effect of NO₂ on dimethyl ether has been studied by Ye et al. in a shock tube at 0.4 and 1 MPa, 987–1517 K, and equivalency ratios of 0.5, 1.0, and 2.0. The findings indicated that NO₂ can considerably accelerate the autoignition of DME and that it performed better at low temperatures than at high temperatures. The influence of the equivalency ratio on ignition delays became more noticeable as NO₂ concentrations increased. Wu et al. studied the effect of NO₂ on the ignition of n-butane in a shock tube at 1 and 2 MPa, 700–1200 K, and equivalency ratios of 1.0 and 2.0. The addition of trace amounts of NO₂ (500 v/v ppm) enhanced the low-temperature reactivity of n-C₄H₁₀ and reduced the ignition delays while weakening the negative temperature coefficient (NTC) behavior of n-C₄H₁₀. Shi et al. investigated the effect of NO₂ (0.5, 1%) addition on n-heptane autoignition in a shock tube at 0.2 and 1 MPa, 700–1400 K, and an equivalency ratio of 1. The findings of the experiments showed that the NO₂ effect was temperature- and NO₂-concentration dependent. At high temperatures, NO₂ can enhance n-heptane oxidation and shorten the ignition delay, but it had little impact on n-heptane autoignition around 700 K.

The use of biomass oxygenated fuels in engines can alleviate their reliance on petroleum resources while also lowering soot emissions. The most widely investigated biomass fuels included alcohols (methanol, ethanol, and n-butanol), furans (2,5-dimethylfuran and 2-methyl furan), and biodiesel. Compared to methanol and ethanol, n-butanol has a greater energy density and hydrophobicity. Biodiesel has similar physical and chemical properties as diesel; therefore, it can be utilized in compression-ignition engines without modification. Previously published work investigated the combustion and emission characteristics of a CI engine fueled with n-butanol/biodiesel dual fuel using both experiments and numerical simulations. n-Butanol was port injection, and biodiesel was injected directly into the cylinder. The n-butanol/biodiesel dual-fuel combustion was regulated by both the chemical reaction kinetics of the fuel and the in-cylinder direct injection strategy, allowing for more precise ignition timing control than HCCI, PCCI, and PPC. To lower soot emissions of the engine, it was recommended to increase the n-butanol injection ratio; nevertheless, this would result in a greater influence of the air-fuel mixture reactivity on the ignition timing. As mentioned above, the active components in the EGR gas can also affect the ignition delays and fuel combustion process of the engine. Until recently, investigations on the influence of NO₂ on fuel ignition characteristics have been limited to HCCI engines, shock tubes, and RCMs but rarely carried out on dual-fuel CI engines.

The present study aimed to investigate the effect of NO₂ on n-butanol/biodiesel dual-fuel combustion in a CI engine. Various concentrations of NO₂ were fed into the intake pipe of a single-cylinder CI engine to evaluate the changes in combustion characteristics such as pressure development and combustion phasing. Three-dimensional (3D) numerical calculation was carried out to determine the effect of NO₂ on the evolutions of fuel consumption and OH radical generation as well as to clarify the in-cylinder distribution of OH radicals. Furthermore, kinetic chemical analyses were performed to gain further insight into the role of NO₂ in fuel oxidation.

2. EXPERIMENTAL SETUP AND METHODOLOGY

2.1. Engine and Fuels. The experiments were conducted on a single-cylinder four-stroke CI engine. The engine was a single-cylinder version of a multi-cylinder marine diesel engine designed for fundamental research on high-efficiency and clean combustion. Table 1 presents the specifications of the engine. The bore and stroke are 170 and 195 mm, respectively, and the displacement is 4.43 dm³. The compression ratio is 13.5. The biodiesel is injected directly into the cylinder using a common rail system. The injector nozzle has 8 holes and a 15° spray angle.

When conducting this n-butanol/biodiesel dual-fuel combustion experiment, n-butanol was utilized for port injection, and biodiesel was used for in-cylinder direct injection. Biodiesel derived from soybean oil was employed in this investigation. Both n-butanol and soybean biodiesel were available commercially. The physical and chemical properties...
of n-butanol, biodiesel, and diesel (for comparison) are presented in Table 2.

### Table 2. Fuel Properties

| properties          | n-butanol | soybean biodiesel | diesel |
|---------------------|-----------|-------------------|--------|
| molecular formula   | C\(_{10}H_{18}O\) | C\(_{18}H_{34}O_3\) | C\(_{10}H_{21}\) |
| CAS number          | 71-36-3   | 67784-80-9        | 68334-30-5 |
| molecular weight    | 74        | 292               | 190    |
| density [kg/dm\(^3\)] | 0.81     | 0.87–0.88         | 0.83–0.85 |
| cetane number       | 25        | 48–52             | 52–55  |
| viscosity at 40 °C [m\(^2\)/s] | 2.22    | 4–4.3             | 3.35   |
| lower heating value [MJ/kg] | 33.2    | 38.4              | 42.8   |
| boiling point [°C]  | 117       | 382               | 180–370 |

### 2.2. Experiment Platform.

The engine test platform is shown in Figure 1. The NO\(_2\) in the EGR gas must be removed in the experiment in order to test the effect of NO\(_2\) on the n-butanol/biodiesel dual-fuel combustion, and then the required quantity of NO\(_2\) was fed into the intake pipe from a high-pressure gas cylinder. Consequently, a selective catalytic reduction (SCR) system was mounted on the EGR pipe to eliminate NO\(_2\). The EGR gas was blended with the intake air and entered the pressure stabilization tank. The EGR valve controlled the flow of EGR gas. After the pressure stabilization tank, NO\(_2\) from the high-pressure cylinder was introduced into the inlet pipe. A high-precision flow meter regulated the amount of NO\(_2\). For thorough mixing of NO\(_2\) and engine intake gas, a mixing tank was installed after the NO\(_2\) input location. A gas analyzer was attached to the intake pipe to determine whether the NO\(_2\) concentration in the intake air met the target value. An n-butanol injection system assembly was installed on the intake pipe, and it was used to regulate the quantity of n-butanol injected. The intake and the exhaust pressure were controlled by the pressure regulators so as to imitate those of the real multi-cylinder engine. Combustion measurement equipment from the AVL company, which included a pressure sensor, a charge amplifier, data acquisition, and indicating software, was used to determine the pressure and heat release rate in the cylinder. The specifications for measuring instruments are shown in Table 3, including their measurement range and uncertainty. Considering the minimal uncertainty of measuring instruments, the impact of measurement error on test results is negligible. The measured value of in-cylinder pressure was set to the average of 200 cycles to eliminate pressure fluctuations.

### 2.3. Experimental Methodology.

The engine ran at 1500 rpm, with an EGR rate of 30%. n-Butanol was injected into the intake pipe, and biodiesel was injected directly into the cylinder with an injection timing of \(-10^\circ\) CA ATDC. The impact of adding 0–400 v/v ppm NO\(_2\) on the ignition and combustion characteristics of the n-butanol/biodiesel dual fuel was investigated in this work. Simultaneously, two biodiesel injection ratios (denoted by R\(_{BD}\)), that is, 20 and 40%, were chosen to evaluate the influence of NO\(_2\) on the ignition characteristics of the various fuel activities. The biodiesel injection ratio was defined as the ratio of biodiesel injection energy to the overall energy of the fuels, which included port injection of n-butanol and in-cylinder injection of biodiesel. The R\(_{BD}\) can be expressed using the following equation

\[
R_{BD} = \frac{m_{BD} \times 38.4}{m_{NB} \times 38.4 + m_{NB} \times 33.2} \leq 0.5\% \text{ of measured value}
\]

where \(m_{BD}\) is the mass of biodiesel and \(m_{NB}\) is the mass of n-butanol.

The total energy of n-butanol and biodiesel injected per cycle was maintained constant throughout all test conditions, which was 240 mg of equivalent biodiesel. Equivalent biodiesel was defined as the injection mass of n-butanol converted to that of biodiesel with the same low heating value. The total mass (denoted by \(m_{\text{total}}\)) of equivalent biodiesel mass can be expressed using the following equation

\[
m_{\text{total}} = \frac{33.2}{38.4}m_{\text{NB}} + m_{\text{BD}}
\]

The intake NO\(_2\) concentrations were set at 0, 100, 200, and 400 v/v ppm. Although the EGR gas normally delivered less than 400 v/v ppm of NO\(_2\) when the engine was operating in...
actual work applications, the condition of 400 v/v ppm NO\textsubscript{2} in the intake gas was set in this study to make the effect of NO\textsubscript{2} on combustion characteristics of the engine more obvious and appreciable. Table 4 lists the engine operating conditions.

Table 4. Experimental Conditions

| items                                         | set value            |
|-----------------------------------------------|----------------------|
| engine speed [rpm]                            | 1500                 |
| EGR rate [%]                                  | 30                   |
| injection timing of biodiesel [°CA ATDC]      | −10                  |
| biodiesel injection ratios (R\textsubscript{BI}) [%] | 20, 40               |
| intake NO\textsubscript{2} concentration [v/v ppm] | 0, 100, 200, 400     |
| intake temperature [°C]                       | 35                   |
| intake pressure [MPa]                         | 0.17                 |

3. NUMERICAL MODELS

3.1. Reduced Mechanism of n-Butanol–Biodiesel–NO\textsubscript{2}. The combustion reaction kinetics of biodiesel was difficult to investigate directly due to the complexity of its components and high molecular weight. To simplify the biodiesel chemical kinetics mechanism, methyl decanoate (MD) was used as the surrogate of biodiesel. In our previous work,\textsuperscript{30} it has been demonstrated through engine bench tests that the ignition delays, combustion characteristics, and soot emissions of MD were similar to those of soybean oil methyl ester under a wide range of operating conditions. Based on the detailed chemical kinetic mechanisms of MD developed by Herbinet et al.\textsuperscript{31,32} and n-butanol developed by Sarathy et al.\textsuperscript{33} a reduced n-butanol–biodiesel dual-fuel mechanism with 157 species and 641 reactions\textsuperscript{29} was obtained using the directed relation graphs (DRG) method,\textsuperscript{34} sensitivity analysis, and reaction path analysis.

The CO−C1/NO\textsubscript{2} sub-mechanism developed by Glarborg et al.\textsuperscript{35} was merged into the reduced n-butanol–biodiesel mechanism. In our previous study\textsuperscript{36} on the effect of NO\textsubscript{2} on the ignition delays of methanol using a shock tube, it was demonstrated that this sub-mechanism can accurately predict the autoignition of methanol with various NO\textsubscript{2} added concentrations. The final n-butanol–biodiesel–NO\textsubscript{2} mechanism consisted of 186 species and 723 reactions (see the Supporting Information). In order to verify the mechanism, the tests of NO\textsubscript{2} sensitization for the autoignition of n-butanol and biodiesel were conducted in a shock tube at the initial pressure of 0.6 MPa, temperatures of 1250−1550 K, and the equivalence ratio of 1. The detailed setup of the shock tube test platform is described in detail in our prior study.\textsuperscript{37,38} The SENKIN code,\textsuperscript{40} which is part of the CHEMKIN-II package,\textsuperscript{41} was used to calculate the ignition delays and species consumption rates. Figure 2 depicts a comparison of ignition delays between measurements and simulation results. As can be observed, the ignition delays calculated using this mechanism were closer to the experimental measurements.

3.2. CFD Model. The 3D CFD software AVL FIRE, coupled with the n-butanol–biodiesel–NO\textsubscript{2} reduction mechanism, was utilized to simulate the in-cylinder combustion process of the engine. The k−ε−f model\textsuperscript{42} was used to determine the turbulent motion in the combustion chamber since it was shown to be appropriate for highly compressed flows with moving boundaries. Because the Webber number was substantially larger for high-pressure injection, the Wave model\textsuperscript{43} was the most appropriate breakup model. The Dukowicz model\textsuperscript{44} was used to describe droplet heating and evaporation. For spray wall interactions, the Walljet1 model was employed, which was based on Naber’s spray/wall impingement model.\textsuperscript{45} Since the engine had a centrally mounted injector with eight injection holes, a grid of 1/8 combustion chamber was used for the computation to reduce the time required for the numerical simulation. To ensure grid independency, two grids were generated for evaluation. Figure 3 shows the two grid densities with the piston at the top dead center.

![Figure 2](http://pubs.acs.org/journal/acsodf/AOS/2022/7/24815/acsomegaj202202948/f2.png)

Figure 2. Comparison of measured ignition delays (symbols) and predictions (lines) for (a) n-butanol and (b) MD with and without NO\textsubscript{2} addition.

![Figure 3](http://pubs.acs.org/journal/acsodf/AOS/2022/7/24815/acsomegaj202202948/f3.png)

Figure 3. Computational grids: (a) 5,21,380 grids and (b) 19,62,160 grids.
temperature was set to 450 K. To determine the effect of the integration time step on the calculated result, when the calculation interval was $-20$--$60^\circ$ CA, the integration time step for basic grids was $0.05^\circ$ CA, whereas for refined grids, it was $0.02^\circ$ CA. For both grids, the integration time step in the other calculation intervals was $0.5^\circ$ CA.

To begin, the numerical results using the two grids were validated against the experimental data for cylinder pressure and heat release rate at $R_{BD} = 20\%$ with 400 v/v ppm NO$_2$ addition, as shown in Figure 4a. It can be seen that the calculated results were almost identical for both grids and agree well with the experimental data. Then, the evolutions of $n$-butanol and biodiesel were compared using the two grids under the same condition, as illustrated in Figure 3. As can be seen, the computed curves for both grids were rather close. Therefore, utilizing 521,380 computational grids with an appropriate integration time step was quite acceptable for modeling $n$-butanol/biodiesel dual-fuel combustion.

4. RESULTS AND DISCUSSION

4.1. Experimental Study on the Effect of NO$_2$ Addition on the Combustion Characteristics of the $n$-Butanol/Biodiesel Dual Fuel. This study investigated the combustion characteristics of the $n$-butanol/biodiesel dual-fuel engine with 0, 100, 200, and 400 v/v ppm NO$_2$ addition at $R_{BD} = 20$ and 40%. Figure 5 depicts a comparison of in-cylinder pressure and heat release rate profiles for various NO$_2$ concentrations. As shown in Figure 5a, for $R_{BD} = 20\%$, increasing the NO$_2$ concentration caused the beginning moment of heat release to be earlier as well as an increase in the peak heat release rate and in-cylinder pressure. The maximum cylinder pressure was 8.07 MPa without NO$_2$ addition; however, when the NO$_2$ addition concentration was increased to 400 v/v ppm, the peak in-cylinder pressure climbed to 8.74 MPa. The heat release rate curve was bimodal for $R_{BD} = 40\%$, as illustrated in Figure 5b. As the NO$_2$ concentration increased, the first heat release occurred marginally earlier, whereas the second heat release was clearly advanced, and the heat release rate peak was obviously higher. The peak in-cylinder pressure increased with increasing NO$_2$ concentration, as it did for $R_{BD} = 20\%$.

It can be seen that for $R_{BD} = 20\%$, the heat release rate had a single peak, while for $R_{BD} = 40\%$, the heat release rate showed two peaks. This was because when $R_{BD} = 20\%$, the tiny quantity of biodiesel injected into the cylinder rapidly atomized and evaporated, and when the biodiesel ignited, it was essentially consumed as premixed combustion, resulting in a single peak heat release rate. When $R_{BD} = 40\%$, because of the increased injection amount of biodiesel, part of the mixture produced during the ignition delay of biodiesel spontaneously ignited to form the first heat release, and the remaining biodiesel was burnt as diffusion combustion, resulting in the second heat release in conjunction with the combustion of $n$-butanol.

The crankshaft angle that corresponded to 10% of the cumulative heat release was regarded as the moment of ignition and was referred to as CA10. Figure 6 depicts the calculated results were almost identical for both grids and agree well with the experimental data. Then, the evolutions of $n$-butanol and biodiesel were compared using the two grids under the same condition, as illustrated in Figure 3. As can be seen, the computed curves for both grids were rather close. Therefore, utilizing 521,380 computational grids with an appropriate integration time step was quite acceptable for modeling $n$-butanol/biodiesel dual-fuel combustion.

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CA10s of various NO₂ addition concentrations of \( R_{BD} = 20 \) and 40\%\). The CA10 advanced in response to an increase in the concentration of NO₂. For \( R_{BD} = 20\% \), the CA10 was 2.3° CA ATDC without NO₂ addition, while the CA10 was advanced by 0.3, 0.7, and 1.5° crank angle with NO₂ addition concentrations of 100, 200, and 400 v/v ppm, respectively. For \( R_{BD} = 40\% \), the extent of CA10 advancement was noticeably less than it was for \( R_{BD} = 20\% \) when NO₂ was added. CA10 exhibited less advancement when the NO₂ concentrations were 100 and 200 v/v ppm, but it showed a more obvious advancement when the NO₂ concentrations were increased to 400 v/v ppm. Adding 400 v/v ppm NO₂ could advance CA10 by 0.4° as compared to no NO₂ addition. This demonstrated that when a higher proportion of biodiesel was directly injected into the cylinder, a lower NO₂ concentration (less than 200 v/v ppm) was not sensitive to the low-temperature reaction process, causing the autoignition to occur sooner.

Figure 7 illustrates the combustion durations with various NO₂ added concentrations. As can be seen, for \( R_{BD} = 20 \) and 40\%, the combustion duration decreased as the NO₂ addition concentration increased, indicating that NO₂ accelerated the combustion process. For \( R_{BD} = 20\% \), the combustion duration was 16.2° crank angle without NO₂ and 13.3° crank angle with 400 v/v ppm NO₂, a reduction of 18\%. For \( R_{BD} = 40\% \), when no NO₂ was added, the combustion duration was 19.2° crankshaft angle and practically unchanged with 100 v/v ppm NO₂ addition. However, when the NO₂ addition concentration was increased to 400 v/v ppm, the combustion duration was reduced to 16.6° crankshaft angle, a 13\% decrease. In comparison to \( R_{BD} = 40\% \), \( R_{BD} = 20\% \) had a shorter combustion duration. This was because the mixture was more homogeneous and the heat release rate was faster when the biodiesel injection volume was lower for \( R_{BD} = 20\% \). For \( R_{BD} = 40\% \), the biodiesel injection volume was larger, and the biodiesel diffusion combustion resulted in a longer combustion duration.

4.2. Numerical Simulations of the Effect of NO₂ Addition on n-Butanol/Biodiesel Dual-Fuel Combustion. The previous section indicated that adding NO₂ can considerably influence the combustion characteristics of the engine, notably at 400 v/v ppm NO₂ addition. Hence, the effect of 400 v/v ppm NO₂ addition on the processes of fuel consumption and OH radical production was evaluated employing 3D CFD simulation for \( R_{BD} = 20 \) and 40\%.

Figure 8 presented the evolutions of n-butanol, biodiesel, and OH radicals of n-butanol/biodiesel dual-fuel combustion without and with 400 v/v ppm NO₂ addition at \( R_{BD} = 20 \) and 40\%. It was found that when NO₂ was added, the beginning of biodiesel and n-butanol consumption as well as the completion of the reaction occurred earlier than when no NO₂ was added. The evolutions of the mole fraction of OH radicals in the cylinder showed that even before the biodiesel was injected, there was a modest amount of OH radical generation. The amount of OH radicals produced increased significantly when the biodiesel was injected. When biodiesel autoignited, the amount of OH radicals increased dramatically. With 400 v/v ppm NO₂ addition, the OH radical production was about an order of magnitude more than that when no NO₂ was added before 

\( -10^\circ \) CA ATDC. For \( R_{BD} = 20\% \), the crank angle corresponding to the sharp increase in OH radicals occurred 1.5° crank angle earlier with 400 v/v ppm NO₂ addition than without. For \( R_{BD} = 40\% \), this value is 0.5° crank angle.

Hydroxyl radicals, which were highly reactive, can accelerate the evolution of reactants. Figure 9 shows the distribution of OH radicals in the cylinder without and with 400 v/v ppm NO₂ addition at \( R_{BD} = 20 \) and 40\%. As can be seen from Figure 9a, for \( R_{BD} = 20\% \), only minimal amounts of OH radicals were found in the biodiesel spray region at \(-7^\circ \) CA ATDC when no NO₂ was added; however, with 400 v/v ppm of NO₂ addition, a few amounts of OH radicals were generated in all areas of the combustion chamber. Minor amounts of OH radicals were produced around the biodiesel spray region without NO₂ at \(-5^\circ \) CA ATDC, but when 400 v/v ppm NO₂ was added, the OH radical concentration increased significantly. It can also be shown that with 400 v/v ppm NO₂ addition, the OH radical concentration in the biodiesel spray region was higher than that without NO₂. As the piston moved upward, the cylinder temperature increased, and the OH radical concentration in the combustion chamber further increased around the biodiesel spray region, accelerating the oxidation of n-butanol. Thus, at \(-3^\circ \) CA ATDC, the high concentration of OH radicals filled the bulk of the combustion chamber volume when 400 v/v ppm of NO₂ was added; however, without NO₂, the high concentration of OH radicals stayed localized in and around the spray region. When the cases of \( R_{BD} = 20\% \) and \( R_{BD} = 40\% \) were compared, it was
found that the amount of in-cylinder biodiesel injection increased for $R_{BD} = 40\%$, which greatly increased the amount of OH radicals generated by biodiesel during the low-temperature reaction, causing CA10 to occur earlier than in the case of $R_{BD} = 20\%$, as shown in Figure 6.

### 4.3. Chemical Kinetic Analysis

To provide further insight into the influence of NO$_2$ addition on the reaction process, the reaction rate and flux analysis for ST simulations at the initial pressure of 3 MPa and the initial temperature of 800 K were performed using the SENKIN code. The condition of the in-cylinder mixture composition with $R_{BD} = 20\%$ (Table 5) was analyzed.

Figure 10a shows the comparison with the rate of NO$_2$ consumption. It was apparent that the added NO$_2$ was consumed mainly by three types of reaction pathways: (1) NO$_2$ reacted with HO$_2$ radicals to generate HNO$_2$ via the reaction NO$_2$ + HO$_2$ $\rightleftharpoons$ HNO$_2$ + O$_2$ and HONO via the reaction NO + OH(+M) $\rightleftharpoons$ HONO(+M). (2) By undergoing the reaction CH$_3$ + NO$_2$ $\rightleftharpoons$ Table 5. Composition of the Mixture for Chemical Kinetic Analysis

| species     | w/o NO$_2$ [v/v ppm] | w/NO$_2$ [v/v ppm] |
|-------------|-----------------------|---------------------|
| MD          | 896                   | 896                 |
| n-butanol   | 9904                  | 9904                |
| NO$_2$      | 0                     | 400                 |
| N$_2$       | 7,71,400              | 7,71,000            |
| O$_2$       | 1,71,200              | 1,71,000            |
| CO$_2$      | 21,200                | 21,200              |
| H$_2$O      | 25,400                | 25,400              |

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Figure 8. Effect of 400 v/v ppm NO$_2$ addition on evolutions of n-butanol, biodiesel, and OH radicals: (a) $R_{BD} = 20\%$ and (b) $R_{BD} = 40\%$.

Figure 9. Effect of NO$_2$ on the in-cylinder distribution of OH radicals: (a) $R_{BD} = 20\%$ and (b) $R_{BD} = 40\%$. 

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CH\textsubscript{3}O + NO, the conversion of NO\textsubscript{2} to NO resulted. (3) NO\textsubscript{2} was converted to NO via the reaction NO\textsubscript{2} + H ⇌ NO + OH, while H radicals were changed to OH radicals as a result of the reaction.

Figure 10a illustrates that the reaction of NO\textsubscript{2} with CH\textsubscript{3} radicals proceeded at a fast rate. The rates of CH\textsubscript{3} radical consumption were compared to understand the extent of the influence of NO\textsubscript{2} on CH\textsubscript{3} radical consumption, as shown in Figure 10b. Without NO\textsubscript{2}, two reactions dominated CH\textsubscript{3} radical consumption, CH\textsubscript{3} + O\textsubscript{2}(+M) ⇌ CH\textsubscript{3}O\textsubscript{2}(+M) and CH\textsubscript{3} + HO\textsubscript{2} ⇌ CH\textsubscript{3}O + OH. When the reaction time was shorter than 5.5 ms, the CH\textsubscript{3} radical consumption rate via the reaction CH\textsubscript{3} + O\textsubscript{2}(+M) ⇌ CH\textsubscript{3}O\textsubscript{2}(+M) was about 1 order of magnitude more than that of CH\textsubscript{3} + HO\textsubscript{2} ⇌ CH\textsubscript{3}O + OH. When NO\textsubscript{2} was present, CH\textsubscript{3} radicals were not only consumed via the two processes mentioned above but also reacted with NO\textsubscript{2} to produce CH\textsubscript{3}O radicals via CH\textsubscript{3} + NO\textsubscript{2} ⇌ CH\textsubscript{3}O + NO. As the reaction time exceeded 4.8 ms, the rate of consumption of CH\textsubscript{3} radicals via the reaction CH\textsubscript{3} + NO\textsubscript{2} ⇌ CH\textsubscript{3}O + NO surpassed that of the other two reactions. This demonstrated that the addition of NO\textsubscript{2} had a significant effect on the rate of CH\textsubscript{3} radical consumption.

The reaction of NO\textsubscript{2} with HO\textsubscript{2} radicals likewise had a high reaction rate, as shown in Figure 10a. To determine the influence of NO\textsubscript{2} on HO\textsubscript{2} radical consumption, the rates of HO\textsubscript{2} radical consumption were compared, as can be seen in Figure 10c. Without NO\textsubscript{2}, HO\textsubscript{2} radical consumption was dominated by HO\textsubscript{2} + HO\textsubscript{2} ⇌ H\textsubscript{2}O\textsubscript{2} + O\textsubscript{2}, which produced H\textsubscript{2}O\textsubscript{2}. When NO\textsubscript{2} was added, HO\textsubscript{2} radicals were consumed not only by the above reaction but also by the reaction NO + HO\textsubscript{2} ⇌ NO\textsubscript{2} + OH to create OH radicals. Furthermore, as noted previously, HO\textsubscript{2} radicals were consumed by the reactions NO\textsubscript{2} + HO\textsubscript{2} ⇌ HNO\textsubscript{2}O\textsubscript{2} + O\textsubscript{2} and NO\textsubscript{2} + HO\textsubscript{2} ⇌ HONO + O\textsubscript{2}. As a result, it appeared that the addition of NO\textsubscript{2}
accelerated the rate of consumption of HO_2 radicals by NO_2 and NO converted from NO_2.

The above analysis demonstrated that NO_2 was converted to NO through a series of reactions and that NO was also involved in key reactions. Figure 10d showed a comparison with the rate of NO consumption. The vast majority of NO reacted with HO_2 radicals to form NO_3 through the reaction NO + HO_2 ⇌ NO_2 + OH, which converted HO_2 radicals to OH.

Figure 10e shows the comparison with the rate of OH radical production reactions. Without NO_2, two reactions dominated the formation of OH radicals, H_2O_2(+M) ⇌ OH + OH(+M) and CH_2CHO + O_2 ⇌ CH_2O + CO + OH. With the addition of NO_2, the two reactions indicated above remain dominant in the production of OH radicals, while NO converted from NO_2 promoted the generation of OH radicals via the reaction NO + HO_2 ⇌ NO_2 + OH.

The flow analysis of the n-butanol/MD mixture without and with 400 v/v ppm NO_2 addition was performed during 50% n-butanol consumption, as shown in Figure 11. The n-butanol molecule underwent dehydrogenation at the beginning of the reaction, yielding C_4H_4OH-1 radicals and C_4H_4OH-3 radicals. The majority of the C_4H_4OH-1 radicals then reacted with O_2 to produce nC_3H_3CHO and HO_2 radicals via C_4H_4OH-1+O_2 ⇌ nC_3H_3CHO + HO_2. A small amount of C_4H_4OH-1 radicals and all of C_4H_4OH-3 radicals underwent the low-temperature reaction process, that is, RH → R* → ROO* → *QOOH → *OOQOOH → *U(OOH)_2 → ketohydroperoxides, during which HO_2 radicals were produced. In a similar vein, HO_2 radicals were produced during the low-temperature reaction process of biodiesel. Without NO_2, 91% of HO_2 radicals was consumed by the reaction HO_2 + HO_2 ⇌ H_2O_2 + O_2 to produce H_2O_2, while the remainder was consumed in reactions involving intermediate components. When NO_2 was added, 35% of the HO_2 radicals was consumed by the reaction NO + HO_2 ⇌ NO_2 + OH, which resulted in the formation of OH radicals, while 55% was consumed by the reaction HO_2 + HO_2 ⇌ H_2O_2 + O_2 to produce H_2O_2. This indicated that the addition of NO_2 during the low-temperature reaction process could promote the formation of OH radicals in the reaction system.

The macromolecular hydrocarbon intermediates were cleaved to CH_3 radicals as well as various light alkyl, alkenyl, olefin, aldehyde, and ketone intermediates as the reaction proceeded. As shown in Figure 10b, NO_2 had a significant impact on CH_3 radical consumption. Figure 11 also illustrates the reaction flow analysis of CH_3 radicals. Without NO_2, 31% of CH_3 radicals was converted to CH_3O via the reaction CH_3 + O_2(+M) ⇌ CH_3O_2(+M) and 51% of CH_3 radicals was converted to CH_3O via the reaction CH_3 + HO_2 ⇌ CH_3O + OH. With the addition of NO_2, the reaction CH_3 + O_2(+M) ⇌ CH_3O_2(+M) consumed 31% of CH_3 radicals, CH_3 + HO_2 ⇌ CH_3O + OH consumed 50%, and 21% of CH_3 radicals was converted to CH_3O by the reaction CH_3 + NO_2 ⇌ CH_3O + NO. Figure 10b shows that the rate of CH_3 radical consumption via the reaction CH_3 + NO_2 ⇌ CH_3O + NO was higher than that via the reaction CH_3 + HO_2 ⇌ CH_3O + OH indicating that the addition of NO_2 can promote the consumption of CH_3 radicals.

The reaction flow of NO_2 and NO interconversion is also depicted in Figure 11. According to Figure 10a, at the beginning of the reaction process, the added NO_2 reacted with HO_2 radicals to produce HONO via the reaction NO_2 + HO_2 ⇌ HONO + O_2 or HNO_2 via the reaction NO_2 + HO_2 ⇌ HNO_2 + O_2, and HNO_2 can be converted to HONO via the reaction HNO_2(+M) ⇌ HONO(+M). The HONO was subsequently converted to NO via the reaction NO + OH(+M) ⇌ HONO(+M). As the reaction progressed, an increasing amount of NO_2 was converted directly to NO by reacting with CH_3 radicals via the reaction CH_3 + NO_2 ⇌ CH_3O + NO. The generated NO was converted to NO_2 mainly through the reaction NO + HO_2 ⇌ NO_2 + OH.
5. CONCLUSIONS

To investigate the effects of NO\textsubscript{2} on the combustion characteristics of a CI engine fueled with n-butanol/biodiesel dual-fuel, a series of experiments and chemical kinetic simulations were carried out in this work. Experiments were conducted in a single-cylinder engine with two biodiesel injection ratios ($R_{BD} = 20$ and $40\%$). NO\textsubscript{2} was added to the engine intake pipe at concentrations of 0, 100, 200, and 400 v/v ppm. Using the 3D CFD software coupled with the n-butanol–biodiesel–NO\textsubscript{2} mechanism, the influence of 400 v/v ppm NO\textsubscript{2} addition on the evolutions of n-butanol, biodiesel, and OH radicals as well as the in-cylinder distribution of OH radicals was evaluated. Moreover, the reaction rate and flux analyses were performed to get further insight into the effect of NO\textsubscript{2} addition on the reaction process. Major conclusions of this work are as follows:

(1) The presence of increasing NO\textsubscript{2} concentrations resulted in an earlier start of heat release, a shorter duration of combustion, and an increase in peak heat release rate and in-cylinder pressure. For $R_{BD} = 20\%$, the CA10 gradually advanced as the NO\textsubscript{2} concentration increased. For $R_{BD} = 40\%$, CA10 exhibited less advancement when the NO\textsubscript{2} concentrations were 100 and 200 v/v ppm, but it showed a more obvious advancement when the NO\textsubscript{2} concentrations were increased to 400 v/v ppm. The extent of CA10 advancement for $R_{BD} = 40\%$ was noticeably less than for $R_{BD} = 20\%$ with NO\textsubscript{2} addition.

(2) When 400 v/v ppm NO\textsubscript{2} was added, the beginning of n-butanol and biodiesel consumption as well as the completion of the reaction occurred earlier than when no NO\textsubscript{2} was added. Before the biodiesel was injected, the formation of OH radicals was about an order of magnitude higher with 400 v/v ppm NO\textsubscript{2} addition than without NO\textsubscript{2}.

(3) The added NO\textsubscript{2} was mainly consumed via three reaction pathways: NO\textsubscript{2} reacted with HO\textsubscript{2} radicals to form HNO\textsubscript{2} and HONO, with CH\textsubscript{3} to promote CH\textsubscript{3} consumption, and with H radicals to produce OH radicals.

(4) The addition of NO\textsubscript{2} during the low-temperature reaction process can promote the formation of OH radicals in the reaction system. Flux analysis revealed that without NO\textsubscript{2}, 91% of HO\textsubscript{2} radicals was consumed by the reaction HO\textsubscript{2} + HO\textsubscript{2} $\rightarrow$ H\textsubscript{2}O\textsubscript{2} + O\textsubscript{2} to produce H\textsubscript{2}O\textsubscript{2}. When NO\textsubscript{2} was added, 35% of the HO\textsubscript{2} radicals was consumed by the reaction NO + HO\textsubscript{2} $\rightarrow$ NO\textsubscript{2} + OH, which resulted in the formation of OH radicals. Moreover, the rate of CH\textsubscript{3} radical consumption via the reaction CH\textsubscript{3} + NO\textsubscript{2} $\rightarrow$ CH\textsubscript{3}O + NO was higher than that via the reaction CH\textsubscript{3} + HO\textsubscript{2} $\rightarrow$ CH\textsubscript{3}O + OH, indicating that the addition of NO\textsubscript{2} can promote the consumption of CH\textsubscript{3} radicals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02948.

Reduced chemical kinetic mechanism of n-butanol–biodiesel–NO\textsubscript{2} and thermodynamic and transport data files set in CHEMKIN format (ZIP)

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X.W.: conceptualization, experimental setup and methodology, writing—original draft; F.L.: carrying out experiments, data processing, writing—review and editing; Q.Z.: numerical computation; X.L.: chemical kinetics calculation; Q.L.: writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Notes

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ABBREVIATIONSPAR

3D three-dimensional
ATDC after top dead center
CA crankshaft angle
CA10 crankshaft angle corresponding to 10% accumulative heat release rate
CFD computational fluid dynamics
CI compression ignition
DI direct injection
DICI direct injection compression
DOC diesel oxidation catalysts
DRG directed relation graphs
EGR exhaust gas recirculation
HCCI homogeneous charge compression ignition
MD methyl decanoate
NTC negative temperature coefficient
PFI port fuel injection
PPC partially premixed combustion
$R_{BD}$ biodiesel injection ratio
RCCI reactivity-controlled compression ignition
RCM rapid compression expansion
RCEM rapid compression machine

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SCR  selective catalytic reduction
ST  shock tube

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