Numerical Studies on the Action Mechanism of Combustion Intermediates and Free Radicals on Nitrogen Oxides under Oil-Water Blended Conditions

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Featured Application: Clean combustion technology of internal combustion engine and internal purification for combustion reactor.

Abstract: The action mechanism of combustion intermediates and free radicals on nitrogen oxides have been evaluated. Based on chemical reaction dynamics and modern statistical theory, the subject was investigated by means of numerical simulation. A wide water/oil ratio and a wide air/fuel ratio were also taken into account. Some main conclusions were drawn that the reaction response of H2O2 is lagged behind, with the increase of water mass fraction from 10% to 30%. The maximum generation rate is 2.77%, 5.67%, 8.38% and the maximum consumption rate is 3.55%, 6.80%, 13.01% lower than that without water. Water addition leads to decline of the maximum generation rate of NO, N2O, NO2 by 15.24%, 9.21%, 14.78% on average. Further, the saliency factor is explored in the main reaction process depending on the correlation analysis and the sensitivity analysis method. According to the degree of the significance, OH > O > H2 for NO, O > H2 > OH > HO2 for N2O, and OH > H2 > O > H2O2 > HO2 for NO2. In the case of oil-water blended, H + O2 <=> O + OH and H2O2(+M) <=> 2OH(+M) promote the generation of OH and O at the beginning of the second stage, but H + O2(+M) <=> HO2(+M), HO2 + OH <=> H2O + O2, H2O2 + OH <=> H2O + HO2 play an inhibitory role in the generation of OH and O.

Keywords: chemical reaction dynamics; oil-water blended; nitrogen oxides; Spearman rank correlation; sensitivity analysis

1. Introduction

At present, the problem of environmental pollution has attracted more and more attention, especially the problem of nitrogen oxide pollution, which has perplexed us for a long time. The generation of NOx is divided into thermal NOx, fast NOx and fuel NOx. Thermal NOx refers to nitrogen oxides produced by oxidation of N2 in the air at high temperature. The generation mechanism of the fast NOx is that a large amount of NOx is produced rapidly in the surface of the flame when the excess air coefficient is less than 1. The generation of fuel NOx depends on the nitrogen compounds in the fuel. Previous studies have demonstrated that the components of nitrogen oxides emission produced during the combustion process are mainly NO, and a small amount of NOx, N2O and so on. But NO will be reoxidized to NO2 in the air. In the control technologies of reducing nitrogen oxides emission, combustion with moderate water addition is an effective way [1,2].

Oil water emulsion and water injection are two common measures to introduce water into the combustion reaction, which is also regarded as the fuel improvement techniques. Elsanusi et al. [3]
performed a set of engine experiments at the condition of three engine speeds (1000, 2100 and 3000 rpm), three engine loads (20%, 50% and 80%), and three different levels of water concentration (5%, 10% and 15%). They concluded that the nitrogen oxides (NO\textsubscript{x}) were significantly reduced with the increase of water content in the emulsion compared to their bases. One advantage of water injection when compared with EGR is the possible reduction of NO\textsubscript{x} emissions either at low engine loads and high engine loads without a substantial increase in PM emissions [4].

Kokkulunk et al. [5] investigated the performance and efficiency of a diesel engine with a steam injection system by means of experiment and simulation. They came to the conclusion that the steam injection had a positive effect on performance and NO emissions at all speed and didn’t affect CO, CO\textsubscript{2}, and HC emissions considerably. Tesfa et al. [6] conducted an engine experiment operated with biodiesel directly injected in the cylinder and water injected in the manifold. Some conclusion was got that when the water injection rate was 3 kg/h, NO\textsubscript{x} was reduced by about 50% and this measure didn’t result in significant changes in fuel consumption. In addition, the water injection in the intake manifold had little effect on the cylinder pressure and the heat release rate [7]. Kyriakides et al. [8] performed an experimental study with gasoline-ethanol-water ternary mixtures. They pointed out that the Otto engine requires no modifications to burn E40 and E40h (10% hydrous) efficiently with advantage of NO\textsubscript{x} emissions reduction. Nag Jung Choi et al. [9,10] proposed that the combustion temperature of fuel is the most important factor that directly affecting the NO\textsubscript{x} emissions from the engine. For biodiesel, the NO\textsubscript{x} emission increases a little with increasing of biodiesel blend ratio in diesel engines fueled with biodiesel blend fuel. This could attribute to that the combustion chamber temperature of biodiesel is higher than that of diesel fuel. Because biodiesel is an oxygenated fuel.

All the references mentioned above are focused on the generation quantity of NO\textsubscript{x}, which remained at the macro and phenomenal levels. Researchers are more inclined to explain the phenomenon that water addition into the combustion chamber can inhibit the generation of nitrogen oxides based on the physical property of water. Apparently, the latent heat of vaporization of water is high (40.8 kJ/mole at 100 °C, 1 atm), after introducing water into the combustion chamber, the adiabatic flame temperature reduces due to water vaporization. And it is generally believed that the generation conditions of NO\textsubscript{x} are high temperature and oxygen enrichment. This explanation is reasonable, but not enough. Correspondingly, at the micro level, there are few studies focused on the chemical effects of water involved in the progress of NO\textsubscript{x} reduction. Namely, the related mechanism is not clear. Some experimental studies have shown that small molecules and free radicals in the period of combustion have some influence on the generation of NO\textsubscript{x} [11–13]. However, at present, most laboratories have no quantitative measurement of free radicals. Even in reference 13, planar-laser-induced fluorescence (PLIF) is used to measure the distribution of OH radical. By using planar-laser-induced fluorescence (PLIF) and laser-induced fluorescence (LIF) spectroscopy, the energy decay of incident light and fluorescence quenching will be the biggest barrier. It has a bad impact on the quantitative calibration and has a strict requirement for the output wavelength of the laser [14,15]. Experimental measurements have limitations, and therefore, numerical calculation is an alternative method.

In further microscopic research on emission problems, it is especially important for multi-level reaction analysis of reaction rate, concentration and reaction time of reaction products in chemical reaction kinetics. Hence, correlation analysis and sensitivity analysis are introduced. Correlation analysis is helpful for researchers to understand the generation and consumption process of combustion pollutants and free radicals in essence, so as to provide a theoretical basis and technical approach for effective control generation of nitrogen oxides. It is of innovative significance to study the process of NO\textsubscript{x} generation at the condition of oil-water blended with the two means above. And the coupling of correlation analysis and sensitivity analysis can greatly improve the researchers’ insight into the importance of each reaction way, thus realizing the purpose of controlling combustion [16]. Under different initial conditions and boundary circumstances, the efficiency of solving the governing equation is too low. The more parameters involved in the model, the more prominent the problem
is. Therefore, the introduction of correlation analysis and sensitivity analysis into the kinetics of elemental reaction has enriched the research means to make it possible to analyze the process of combustion [17]. The application of the coupling analysis to the generation of combustion pollutants is of great significance for analyzing the characteristics of pollutant generation, simplifying the reaction model and determining the suppression method.

In the present study, based on such realistic conditions, numerical methods enter into consideration. The valid mechanism analysis of combustion reaction process with oil-water-blended is focused. Based on correlation analysis and sensitivity analysis, the key intermediate products to control the yield of NO\textsubscript{x} in oil-water-blended condition are obtained, and the main paths are analyzed as well.

2. Experimental Method and Experimental Setup

2.1. Experimental Method

For the numerical calculation of chemical reaction dynamics, CHEMKIN [18] is a common tool, which is suitable for analyzing the chemical reaction process. Its main function is to solve a series of chemical problems involved in combustion through the analysis and calculation of the chemical reaction mechanism. Because the software package has the characteristics of reasonable structure, good reliability and easy to transplant, it has become the mainstream calculation software in the field of combustion chemistry dynamics. Some thermodynamic data are provided in the form of the NASA chemical equilibrium code, which are showed as the following Equations (1)–(6) [19]. Seven coefficients (a\textsubscript{1k} ∼ a\textsubscript{7k}) are given in a database file (e.g., therm.dat), which is provided by the mechanism file.

\[
\frac{C^0}{R} = a_{1k} + a_{2k}T_k + a_{3k}T_k^2 + a_{4k}T_k^3 + a_{5k}T_k^4 \\
\frac{H^0}{R T_k} = a_{1k} + \frac{a_{2k}}{2}T_k + \frac{a_{3k}}{3}T_k^2 + \frac{a_{4k}}{4}T_k^3 + \frac{a_{5k}}{5}T_k^4 + \frac{a_{6k}}{T_k} \\
\frac{S^0}{R} = a_{1k}lnT_k + a_{2k}T_k + \frac{a_{3k}}{2}T_k^2 + \frac{a_{4k}}{3}T_k^3 + \frac{a_{5k}}{4}T_k^4 + a_{7k} \\
C^0_{pk} = C^0_{pk} - R \\
U^0_k = H^0_k - RT_k \\
G^0_k = H^0_k - T_kS^0_k
\]

The chemical reaction mechanism used in this paper comes from two parts. Chen et al. [20] developed a reduced mechanism, which contains 207 species and 1026 steps. The mechanism is based on five components (C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}, iC\textsubscript{5}H\textsubscript{12}, iC\textsubscript{8}H\textsubscript{18}, nC\textsubscript{5}H\textsubscript{12}, nC\textsubscript{7}H\textsubscript{16}) gasoline surrogate mechanism, which comes from Lawrence Livermore National Laboratory (LLNL) [21]. This 207-species skeletal mechanism is validated under a wide range of conditions compared to the rapid compression machine (RCM) experimental data, and it has also been mentioned or verified widely in other research [22–24]. The mixture oil in this mechanism has similar properties to local oil products in Changchun, China, so the mechanism is suitable for this study and for future research.

The NO\textsubscript{x} mechanism comes from GRI mech3.0 [25], which has been widely verified by experiments [26–28]. In order to study the effect of gasoline-water blended on NO\textsubscript{x}, this work combines the NO\textsubscript{x} mechanism in GRI mech3.0 and Chen mechanism to fulfill the research. And the composite mechanism is provided with Supplementary materials.
2.2. Experimental Setup

The research is carried out in a closed homogeneous batch reactor provided by CHEMKIN code [18]. This is a ‘Closed 0-D Reactor’, which is used to simulate constant volume combustion problems and solve the energy equation. Before running the project, some of the computing conditions need to be set up. For example, import the composite mechanism file in ‘Pre-Processing’ section and then set the solver properties. In this project, the absolute tolerance is set to $1.0 \times 10^{-20}$; the relative tolerance is set to $1.0 \times 10^{-8}$; the sensitivity absolute tolerance is set to $1.0 \times 10^{-4}$; and the sensitivity relative tolerance is set to $1.0 \times 10^{-4}$. For quantitative analysis, the water-oil mass ratio (WOMR) is defined in Equation (7). The other properties of the oil and the experimental condition are presented in Table 1.

$$r = \frac{m_{\text{water}}}{m_{\text{oil}}} \times 100\%$$  (7)

<table>
<thead>
<tr>
<th>Category</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel mixture (mol. %)</td>
<td>C$_6$H$_5$CH$_3$: 37%, iC$<em>5$H$</em>{12}$: 27%, iC$<em>8$H$</em>{18}$: 27%,</td>
</tr>
<tr>
<td></td>
<td>nC$<em>5$H$</em>{12}$: 5%, nC$<em>7$H$</em>{16}$: 4%</td>
</tr>
<tr>
<td>Dynamic viscosity (kg·m$^{-1}$·s$^{-1}$)</td>
<td>$3.1 \times 10^{-4}$ (at 25 °C, 1 atm) [29,30]</td>
</tr>
<tr>
<td>Density (kg·m$^{-3}$)</td>
<td>804 (at 25 °C, 1 atm) [29,30]</td>
</tr>
<tr>
<td>RON</td>
<td>95.4 [30,31]</td>
</tr>
<tr>
<td>MON</td>
<td>87.8 [30,32]</td>
</tr>
<tr>
<td>Oxidizer mixture (mol. %)</td>
<td>O$_2$: 21%, N$_2$: 78%, Ar: 1%</td>
</tr>
<tr>
<td>Initial condition</td>
<td>$T$: 800 K, $P$: 8 atm, $V$: 65 cm$^3$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.6, 0.8, 1, 1.2, 1.4</td>
</tr>
<tr>
<td>Water-oil mass ratio</td>
<td>0, 10%, 20%, 30%</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Two Stages Reaction Processes

Figure 1a–c are at different coordinating scales. In Figure 1a, the reaction is divided into two stages. The first stage occurs after about 1.3 ms. For the phase of low temperature oxidation, the reaction of mixed gas is exothermic, and the temperature increases from 800 K to 1000 K. H$_2$O$_2$ and HO$_2$ are mainly produced at this stage and are considered as indicator products for the two-stage reaction. Decomposition of H$_2$O$_2$, H$_2$O$_2$ + M $\leftrightarrow$ 2OH + M (#16 elementary reaction in Chen mechanism plus GRI mech3.0) happens at 6.9 ms. For the combustion reaction, the large amount of OH generation marks the start of the burning. The three-body reaction H + O$_2$ + M $\leftrightarrow$ HO$_2$ + M (#9 elementary reaction in Chen mechanism plus GRI mech3.0) is an important radical recombination step, plays an important role as a chain terminating reaction at the second explosion limit and leads to relatively long induction times at conditions near the second limit [33]. The paramount condition that the system can enter the high temperature stage after the low temperature stage is that the low temperature reaction must be able to release enough heat to increase the temperature of the system. When the temperature reaches to 1000 K, the temperature rises sharply, and the mixture enters the high temperature oxidation stage. The high temperature reaction process releases a lot of heat, which provides the conditions for NO$_x$ generation.
Figure 1. The iterative process of the intermediate products, NO\textsubscript{x} and temperature ($\lambda = 1$, WOMR = 0).
(a) Global comparison; (b) Detail comparison 1; (c) Detail comparison 2.
3.2. Intermediate Reaction Products (Small Molecules and Free Radicals) at Different WOMR

In Figure 2a, the variation of the reaction rate of H$_2$O$_2$ with different water/oil mass ratio is exhibited. Combined with Figures 1a and 2b,c, the generation of H$_2$O$_2$ occurred between 0.001 s and 0.002 s and the consumption occurred between 0.007 s and 0.008 s. When the water mass fraction increases from 10% to 30%, the response of the reaction of H$_2$O$_2$ is lagged behind, and the maximum generation rate is 2.77%, 5.67%, 8.38% lower than that without water, and the maximum consumption rate is 3.55%, 6.80%, 13.01% lower than that without water. It shows that both reaction delay and peak value decrease cause the increase of heat needed for activation reaction at the same activation energy and reaction temperature when water is introduced to inhibit the chain reaction. The existence of water plays a role in controlling the rate of the main element reaction.

![Figure 2. Reaction rate of H$_2$O$_2$ at different WOMR ($\lambda = 1$). (a) Global profile comparison; (b) Detail profile comparison 1; (c) Detail profile comparison 2.](image)

Figure 3 shows the reaction rate of H$_2$ at different WOMR. Hydrogen has the advantages of low ignition energy, high flame propagation speed, high diffusion rate and wide ignition limit [34–36]. Therefore, hydrogen addition can effectively increase combustion stability. The primary hydrogen production reaction in this mechanism is: NH + H$_2$O $\leftrightarrow$ HNO + H$_2$ (#1032 elementary reaction in Chen mechanism plus GRI mech3.0), in which the positive reaction requires very high activation energy, $E_a = 13.850$ kJ/mol. With the increase of water, the temperature of the system decreases and the generation rate of H$_2$ decreases significantly, and the reaction is pushed back. But another elementary reaction NH + NO $\leftrightarrow$ N$_2$ + OH (#1033 elementary reaction in Chen mechanism plus GRI mech3.0) mainly occurs in the reductive environment. So under this circumstance, the above two steps will result in a scramble for the NH radical. Then the final result of the effect is that the NH is oxidized by excessive H$_2$O, so the reduction process of NO is hindered, resulting in a slight increase of the yield of NO.
Figure 3. Reaction rate of H$_2$ at different WOMR ($\lambda = 1$).

From Figure 4, it can be seen that with the increase of water content, the reaction rates of OH, HO$_2$, H and O decrease in varying degrees and are accompanied by the back shift of the peak value. At the same time, there is also the transfer process of material and energy between the four intermediate products. These reactions occur at the high temperature stage at the end of the first stage. Because of the high temperature, the intense reaction, the short reaction time, and the competition for the same components, there is a relationship between these reactions, forming a closed loop, as shown in Table 2. In a moment, the concentration of OH and O increases sharply, which causes the generation of many active centers. Ultimately, the activation center concentration is the key factor affecting the combustion of the fuel. This is the starting point of the second stage combustion. The concentration of OH and O decreases after some chain carrier is destroyed. Then the system reaches the steady state gradually.

Figure 4. Cont.
Figure 4. Reaction rate of OH, HO$_2$, H and O at different WOMR ($\lambda = 1$). (a) Reaction rate of OH; (b) Reaction rate of HO$_2$; (c) Reaction rate of H; (d) Reaction rate of O.
Table 2. Elementary reactions sequence in recombination mechanism.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Serial Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH} )</td>
<td>1</td>
</tr>
<tr>
<td>( \text{O} + \text{H}_2 \leftrightarrow \text{H} + \text{OH} )</td>
<td>2</td>
</tr>
<tr>
<td>( \text{OH} + \text{H}_2 \leftrightarrow \text{H} + \text{H}_2\text{O} )</td>
<td>3</td>
</tr>
<tr>
<td>( \text{O} + \text{H}_2\text{O} \leftrightarrow 2\text{OH} )</td>
<td>4</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} + \text{M} \leftrightarrow \text{H} + \text{OH} + \text{M} )</td>
<td>8</td>
</tr>
<tr>
<td>( \text{H} + \text{O}_2(\text{+M}) \leftrightarrow \text{HO}_2(\text{+M}) )</td>
<td>9</td>
</tr>
<tr>
<td>( \text{HO}_2 + \text{H} \leftrightarrow \text{H}_2 + \text{O}_2 )</td>
<td>10</td>
</tr>
<tr>
<td>( \text{HO}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{O}_2 )</td>
<td>13</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2(\text{+M}) \leftrightarrow 2\text{OH}(\text{+M}) )</td>
<td>16</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 + \text{H} \leftrightarrow \text{H}_2 + \text{HO}_2 )</td>
<td>18</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 + \text{O} \leftrightarrow \text{OH} + \text{HO}_2 )</td>
<td>19</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{HO}_2 )</td>
<td>20</td>
</tr>
</tbody>
</table>

3.3. Coupling Analysis at Water Mixing and Variable Excess Air Coefficient Conditions

Figure 5 shows the mole fraction map of free radicals corresponding to maximum rate map of production of NO, Figure 6 shows the mole fraction map of free radicals corresponding to maximum rate map of production of \( \text{N}_2\text{O} \), and Figure 7 shows the mole fraction map of free radicals corresponding to maximum rate map of production of NO\(_2\). Because the corresponding time of the maximum production rate of NO, \( \text{N}_2\text{O} \), and NO\(_2\) is very close to each other, free radicals have little change in the maps of the three groups. In these three groups of figures, because the temperature reduces obviously, the starting point of the high temperature oxidation stage is delayed, the duration of the high temperature is shorter and the generation rate of NO\(_x\) decreases, with the increase of the proportion of water in the fuel. When the water content increases by 10%, the maximum NO generation rate decreases by 15.24% on average, the maximum \( \text{N}_2\text{O} \) generation rate decreases by 9.21% on average, and the maximum NO\(_2\) generation rate decreases by 14.78% on average. In the distribution of free radicals mole fraction, H, \( \text{HO}_2 \) and \( \text{H}_2\text{O}_2 \) show obviously non-monotonicity in lambda direction, which is inconsistent with the monotonicity of NO\(_x\) generating rate map. It can be roughly estimated that the above three free radicals are not very closely related to NO\(_x\) generation. For O and OH, the mole concentration map can be observed clearly, which is consistent with the NO\(_x\) generation rate in the two-dimensional space of lambda and WOMR, in the three groups of figures. In order to further explore, the results of the above maps will be analyzed by correlation analysis and sensitivity analysis.
**Figure 5.** Mole fraction of free radicals corresponding to maximum rate of production of NO.

**Figure 6.** Cont.
Figure 6. Mole fraction of free radicals corresponding to maximum rate of production of $N_2O$.

Figure 7. Mole fraction of free radicals corresponding to maximum rate of production of $NO_2$. 

Maximum production rate of $NO_2$
3.3.1. Correlation Analysis

In order to further explain the relative relationship between the small molecules of the free radicals and the NOx, the correlation coefficient algorithm is introduced to illustrate this problem.

Number of pairs, such as \((x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)\) are given. It is necessary to check whether the two variables, \(X\) and \(Y\), are related. The traditional Pearson product-moment correlation coefficient (PPMCC) is a measure method of the linear relationship between \(X\) and \(Y\). However, there are 2 limitations when using Pearson product-moment correlation coefficient. On one side, the data must be obtained from normal distribution in pairs. On the other side, the data are at least equidistant in logical range. Whereas the non-parameter Spearman rank correlation coefficient (SRCC) is used to measure the more generalized correlation relation (not necessarily linear).

Let \((x, y)\) be a sample from two different entire populations: \((X, Y)\) and its observation value is \((x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)\). If \(x_i\) and \(y_i\) are sorted by value individually, the new rank of \(x_i\) and \(y_i\) in the two sequential samples is recorded as \(R_{x,i}\) and \(R_{y,i}\) \((0 \leq i \leq n)\). So, \(n\) pairs of rank numbers, \((R_{x,1}, R_{y,1}), (R_{x,2}, R_{y,2}), \ldots, (R_{x,n}, R_{y,n})\) is obtained from 1 to \(n\). Generally, the Spearman rank correlation coefficient formula can be recorded as follows [37]:

\[
rs = \frac{\sum_{i=1}^{n} (R_{x,i} - \overline{R}_x)(R_{y,i} - \overline{R}_y)}{\sqrt{\sum_{i=1}^{n} (R_{x,i} - \overline{R}_x)^2 \sum_{i=1}^{n} (R_{y,i} - \overline{R}_y)^2}}
\]

\[
\overline{R}_x = \frac{1}{n} \sum_{i=1}^{n} R_{x,i}
\]

\[
\overline{R}_y = \frac{1}{n} \sum_{i=1}^{n} R_{y,i}
\]

If there is no same data in the \(X, Y\) sequence, then the mean value can be recorded as:

\[
\overline{R}_x = \overline{R}_y = \frac{n + 1}{2}
\]

So the formula of \(rs\) can be further simplified to:

\[
rs = 1 - \frac{6\sum (R_{x,i} - R_{y,i})^2}{n(n^2 - 1)}
\]

\[rs > 0\] represents positive correlation and \(rs < 0\) represents negative correlation. \(|rs|\) is more close to 1, the correlation between the samples is higher. Whereas \(|rs|\) is closer to 0, the correlation between the samples is lower. Sometimes the sample with very high correlation coefficient may also come from the uncorrelated population. In order to exclude such situation, a significance test of the correlation coefficient is needed. The Student’s \(t\) test provides the excellent ability to test the significance of \(rs\). The test formula of student’s \(t\) is as follows [38]:

\[
t = rs\sqrt{\frac{n - 2}{1 - rs^2}} \sim t(n - 2).
\]

The general step of the significance test for the correlation coefficient is to establish the null hypothesis that \(H_0\): \(X\) and \(Y\) are related, and the alternative hypothesis that \(H_1\): \(X\) and \(Y\) is not related. Then give the confidence level \(\alpha\). Based on \(\alpha\), find out the corresponding critical value. At the end make a comparison: if \(|t| \geq t^\alpha\), it is assumed that \(H_0\) is tenable and if \(|t| < t^\alpha\), it is assumed that \(H_1\) is tenable.
Table 3 shows the SRCC matrix of free radicals mole fraction and maximum reaction rate of NOx. Figure 8a shows that there is a close relation between the maximum production rate of NO and the mole fraction of O, OH, H2 (coefficient of SRCC, OH > O > H2). Figure 8b shows that there is a close relation between the maximum production rate of N2O and the mole fraction of O, OH, HO2, H2 (coefficient of SRCC, O > H2 > OH > HO2). Figure 8c shows that there is a close relation between the maximum production rate of NO2 and the mole fraction of O, OH, HO2, H2, H2O2 (coefficient of SRCC, OH > H2 > O > H2O2 > HO2). All results above meet a confidence level of at least 95%. Therefore, it can be considered that the above conclusions are statistically significant and correct. At the same time, it also notes that the mole content of O, OH and H2 has a very obvious common effect on the generation of nitrogen oxides (NO, N2O and NO2).

Table 3. SRCC matrix of free radicals mole fraction and maximum reaction rate of NOx.

<table>
<thead>
<tr>
<th>X</th>
<th>NO</th>
<th>H</th>
<th>O</th>
<th>OH</th>
<th>HO2</th>
<th>H2</th>
<th>H2O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>0.0075</td>
<td>0.8586</td>
<td>0.8917</td>
<td>0.0316</td>
<td>0.7789</td>
<td>0.3368</td>
<td></td>
</tr>
<tr>
<td>N2O</td>
<td>0.1474</td>
<td>0.9940</td>
<td>0.8602</td>
<td>0.7699</td>
<td>0.9383</td>
<td>0.0857</td>
<td></td>
</tr>
<tr>
<td>NO2</td>
<td>0.0887</td>
<td>0.9128</td>
<td>0.9789</td>
<td>−0.5744</td>
<td>−0.9639</td>
<td>−0.6662</td>
<td></td>
</tr>
</tbody>
</table>

Figure 8. Result of Student’s t significance test for SRCC (confidence level α = 0.05).

3.3.2. Sensitivity Analysis

In many research fields, sensitivity analysis is applied, and the reaction rate of components i is derived from mass action law:

\[
\frac{dC}{dt} = f(C; K)
\]

\[
C(0) = C_0
\]

\[
\beta_{ij}(t) = \frac{\partial C_i(t)}{\partial K_j}
\]

The higher the sensitivity, the more important the elementary reaction j to the component i. The specific sensitivity results are shown in Figure 9, corresponding to the starting point of the second stage reaction.
Figure 9. Sensitivity diagram of OH, O, HO₂, H₂ (at the time of the second stage starting point). 
(a) Normalized sensitivity of OH (b) Normalized sensitivity of O; (c) Normalized sensitivity of HO₂ 
(d) Normalized sensitivity of H₂.

The positive sensitivity coefficient indicates that the elementary reaction affects the generation of free radicals, and the negative sensitivity coefficient indicates that the elementary reaction affects the consumption of free radicals. The mutual influence increases with the absolute value of the sensitivity coefficient increases. From Figure 9, it is found that elementary reaction #1, #9, #13, #16 and #20 can promote or inhibit the generation of free radicals OH, O, HO₂ and H₂ than others, but the elementary reaction #16 is more important. At the same time, OH and O show a consistent sensitivity to different elementary reactions. HO₂ and H₂ show a consistent sensitivity to different elementary reactions. Whereas the sensitivity of OH, O and the sensitivity of HO₂, H₂ are antagonistic.

4. Conclusions

In this paper, a numerical investigation of the action mechanism of H, O, OH, HO₂, H₂ and H₂O₂ on the generation of nitrogen oxides with different air/fuel ratio and different WOMR was completed. The main conclusions are summarized as follows:

- An obvious result of two stages reaction processes is obtained by the numerical method. When the temperature reaches to 1000 K, the temperature rises sharply, and the mixture enters the high temperature oxidation stage. The rapid consumption of H₂O₂ and the rapid generation of OH indicates the generation of the flame surface.

- With the increase of water mass fraction, the response of the reaction of free radicals (H, O, OH, HO₂, H₂, H₂O₂) is lagged behind, meanwhile the peak value of the reaction rate decreases due to the increase of heat needed for activation reaction at the same activation energy and reaction temperature. When the water content increases 10%, the maximum generation rate of NO, N₂O, NO₂ decreases by 15.24%, 9.21%, 14.78% on average, respectively.

- According to the correlation results, maximum production rate of NO and the mole fraction of O, OH, H₂ have significant correlation relation; maximum production rate of N₂O and the mole fraction of O, OH, HO₂, H₂ have significant correlation relation; maximum production rate of NO₂ and the mole fraction of O, OH, HO₂, H₂, H₂O₂ have significant correlation relation. In contrast, OH, O and H₂ play a more significant role in the common influence of the generation of nitrogen oxides.
According to the sensitivity results, elementary reactions #1 and #16 promote the generation of OH and O at the beginning of the second stage, but elementary reaction #9, #13 and #20 have a negative effect. Meanwhile the result is just opposite for effect of HO₂ and H₂.

**Supplementary Materials:** The supplementary material contains the mechanism document used in this article. The following are available online at [http://www.mdpi.com/2076-3417/8/4/490/s1](http://www.mdpi.com/2076-3417/8/4/490/s1), mech.txt: it records the chemical reaction mechanism; thermo.txt: it records the thermodynamic parameters of the species; transport.txt: it records the transport parameters of the species.

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**Nomenclature**

- H: hydrogen atom
- O: oxygen atom
- OH: hydroxyl radical
- HO₂: hydroperoxyl radical
- H₂: hydrogen
- H₂O₂: hydrogen peroxide
- M: third body
- NOₓ: nitrogen oxides
- NO: nitric oxide
- NO₂: nitrogen dioxide
- N₂O: nitrous oxide
- EGR: exhaust gas recirculation
- PM: particle matter
- CO: carbon monoxide
- CO₂: carbon dioxide
- HC: hydrocarbon
- CA: crank angle
- PLIF: planar-laser-induced fluorescence
- LIF: laser-induced fluorescence
- LLNL: Lawrence Livermore National Laboratory
- RCM: rapid compression machine
- GRI: The Gas Research Institute
- C₆H₅CH₃: methylbenzene
- iC₅H₁₂: isopentane
- iC₈H₁₈: isoctane
- nC₅H₁₂: n-pentane
- nC₇H₁₆: n-heptane
- O₂: oxygen
- N₂: nitrogen
- Ar: argon
- λ: excess air coefficient
- WOMR: water-oil mass ratio
- PPMCC: Pearson product-moment correlation coefficient
- SRCC: Spearman rank correlation coefficient
Symbols

\( C_{0}^{pk} \) specific heat capacity at constant pressure
\( H_{0}^{k} \) enthalpy
\( S_{0}^{k} \) entropy
\( C_{0}^{vk} \) the specific heat capacity at constant volume
\( U_{0}^{k} \) internal energy
\( G_{0}^{k} \) Gibbs free energy
\( a_{1k} \sim a_{7k} \) constant column
\( r \) water-oil mass ratio
\( m_{\text{water}} \) mass of water
\( m_{\text{oil}} \) mass of oil
\( (X, Y) \) two dimension random variables
\( (x, y) \) sample of \((X, Y)\)
\( (R_{x,n}, R_{y,n}) \) rank of \((x_{n}, y_{n})\)
\( \bar{R}_{x} \) the mean value of \( R_{x} \)
\( \bar{R}_{y} \) the mean value of \( R_{y} \)
\( r_{s} \) Spearman rank correlation coefficient
\( t \) index of the significance test
\( \alpha \) confidence level
\( C \) n-dimensional vector of the concentration
\( K \) the parameter of the system, which is related to the chemical reaction rate, the activation energy and so on
\( \beta_{ij} \) the sensitivity of the component \( i \) to the reaction rate of the elementary reaction \( j \)

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