Research on the Influences of Addition of Biodiesel on the Equilibrium Concentrations and Thermodynamic Properties of Combustion Products for Conventional Diesel Fuel

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Abstract. To deal with the increasingly stringent energy crisis and atmospheric pollution problems, biodiesel is regarded as one of the alternative biofuels with great potential for replacing the conventional diesel fuel, thus it is necessary to investigate the influences of addition of biodiesel to conventional diesel fuel on the combustion products. To this end, Jatropha biodiesel is taken as an example and under the assumption that all the combustion products are at chemical equilibrium, a system of nonlinear equations with the equilibrium concentrations of 10 combustion products as the unknown variables is constructed based on the equilibrium constant method and the numerical solutions are obtained by applying Newton-Raphson iterative method. On this basis the influences of biodiesel blending ratio on the equilibrium concentrations of the combustion products and the thermodynamic properties of burned gases mixture is investigated. The simulation results show that the addition of biodiesel does not cause significant influences on the equilibrium concentrations of combustion product, and as the three major greenhouse and poisonous gases, the relative changes of equilibrium concentration for CO\textsubscript{2}, NO and CO are less than 3.52% but with unclear trends and the influence is more significant at the “fuel rich” condition; on the other hand, the mass-based combustion products rates of CO\textsubscript{2}, NO and CO for a unity of blended fuel mass increases with blending ratio. For the thermodynamic properties of burned gases mixture, it is observed that both the constant-pressure and -volume specific heat increase slightly. The model presented here can be integrated into the engine dynamic simulation model conveniently, which lays the foundation for investigating the influence of addition of biodiesel on the engine power, economic and emission performance.

1. Introduction

With the development of the global economy, the energy crisis and air pollution problems have become increasingly serious. In order to cope with this problem, in recent years, governments and researchers in various countries have persistently sought clean and sustainable fuels in order to...
gradually replace the dominance of traditional petrochemical fuels. Among the existing alternative fuels, biofuels have attracted widespread attention from the public and the scientific community due to the renewable nature of the fuel and its potential to reduce life cycle emissions of greenhouse gases [1]. In order to promote the development of the biofuel industry, many countries have formulated corresponding policies: According to the EU Renewable Energy Directive (Directive 2009/28/EC), by 2020, at least 10% of the energy consumption in the transportation sector of each member state % comes from biofuels; the US Renewable Fuel Standard requires that by 2022, the use of biofuels should reach 36 billion gallons; in addition, some countries have formulated tax reduction policies to encourage biofuels. Planting of raw materials, production and consumption [2-3].

Among the existing biofuels, biodiesel is regarded as a type of biofuel with great potential to replace conventional diesel. Biodiesel is composed of a variety of long-chain fatty acid monoalkyl esters, which can be produced using a variety of vegetable oils or animal fats as raw materials through lipid-transfer reactions [4]. In recent years, many scholars at home and abroad have conducted extensive theoretical and experimental research on the application of biodiesel in diesel engines, mainly involving the aspects of heat release law, power performance, economic performance and emission performance [4-8]. The research results of scientific researchers show that under high load conditions, blending rapeseed biodiesel with 20% volume ratio in conventional diesel will increase the diesel specific fuel consumption rate (Brake Specific Fuel Consumption, BSFC) by 6.56%, and the braking thermal efficiency (Brake Thermal Efficiency (BTE)) decreased by 4.2%, NOx emissions increased by 8.9%, smoke emissions decreased by 53.5%, and THC and CO decreased by 30.3% and 32%, respectively [9]. Researchers have tested the emission performance of 5 types of biodiesel, including cottonseed, soybean, rapeseed, palm and waste oil biodiesel. Experimental results show that these biodiesel can reduce particulate matter (PM) emissions and reduce emissions. Between 53% and 69%, NOx increased by 10-23%. In addition, HC and CO emissions decreased due to the oxygen content of biodiesel molecules [10]. By mixing 40% volume ratio of Hutong biodiesel in conventional diesel, researchers have found that it can effectively reduce smoke, HC and CO, but NOx has increased, and BTE has increased by 2% [11]. Researchers have blended Jatropha biodiesel into conventional diesel and found that as the blending ratio increases, the BSFC of diesel engines increases, BTE decreases, and CO and HC decrease. In addition, compared to conventional diesel, pure Jatropha biodiesel is burned at that time, NOx emissions increased by 24% [12].

From the above literatures, in different studies, biodiesel has different degrees of influence on the power, economy and emission performance of diesel engines. This is mainly because the types and contents of fatty acid methyl esters in different biodiesel are different. As a result, its physical and chemical properties are also different, which will affect its combustion characteristics [13]. Overall, the advantages of biodiesel include renewability, minimal sulfur and aromatics content, high flash point, good lubricity, excellent cetane number, biodegradability, non-toxicity, and good compatibility with conventional diesel, it is more important that it can effectively reduce the emissions of PM, CO and HC pollutants without affecting the power and economic performance of diesel engines. On the other hand, the shortcomings of biodiesel, it is also not to be ignored. This includes higher NOx emissions, low energy density, poor low temperature performance and oxidation stability, high kinematic viscosity, and high production costs.

In addition to experimental research, in order to better understand the impact of biodiesel on the combustion, power, economy and emissions performance of diesel engines, and to optimize the blending ratio of biodiesel, some scholars at home and abroad have also carried out related research using numerical simulation tools. Researchers use commercial simulation software Diesel-RK to study the effect of blending palm oil biodiesel and alcohol (methanol and ethanol) on the power, combustion, and emission parameters of compression ignition engines in conventional diesel. The combustion model uses scientific research the multi-zone combustion model proposed by personnel [14-15]. Researchers have established a zero-dimensional model to study the effect of engine speed and compression ratio on braking power and BTE when burning a diesel-Jatropha biodiesel fuel. The combustion model uses the Wiebe function, but it needs to be pointed out that The model assumes that
the combustion products consist only of CO2, N2, CO2 and H2O, and that their thermal properties are only affected by temperature [16]. Researchers have given physical property prediction models for five typical fatty acid methyl esters (methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate), including boiling points and critical properties. And surface tension, etc., and based on this, 3-D CFD (Computational fluid dynamic) simulation software KIVA 4 and CHEMKIN II were used to study the effect of the blending ratio of biodiesel on diesel engine's emission performance [17-18]. Researchers have used researchers to study the effects of blending Australian Tung Tree biodiesel on diesel engine power and emissions performance [19].

Related experimental and simulation studies will undoubtedly promote the proportion of biodiesel applications. Due to the different proportions of hydrocarbons and oxygen, the blending of biodiesel in conventional diesel is bound to affect the concentration of each combustion product and the thermal properties of the burned mixture. For conventional diesel, many current studies have shown that under high temperature conditions in the cylinder, the combustion products can be considered to be in a chemical equilibrium state. Considering that the physical and chemical properties of biodiesel are similar to conventional diesel, the assumption of chemical equilibrium is therefore assumed. The same applies to the combustion products of biodiesel [13, 20-26]. In order to better understand the impact of biodiesel on the combustion, power, economy and emission performance of diesel engines, and to improve the prediction accuracy of related engine simulation models, this article will use Jatropha biodiesel as an example to construct a mixed fuel combustion method based on the equilibrium constant method. The nonlinear equations of the product equilibrium concentration were calculated using the Newton-Raphson iterative method. Based on this, the effects of the blending ratio of biodiesel on the equilibrium concentration of each combustion product and the thermodynamic properties of the burned mixture were investigated.

2. Diesel-biodiesel fuel combustion reaction
The combustion process of fuel in the cylinder of a diesel engine is quite complicated, involving a large number of chemical reactions and combustion products. For example, the CH4 (methane) combustion model of scientific researchers involves 40 combustion products and 207 chemical reactions [27]. Although the detailed combustion model can accurately calculate the composition and concentration of combustion products, due to the complex structure of the model, a large amount of calculation time will be consumed. In addition, the concentration of some combustion products will only be relatively large under specific combustion conditions. Significantly, and this combustion condition is almost non-existent when the diesel engine is normal. In response to this problem, many scholars have made reasonable simplifying assumptions: at temperatures below 1000 K, the combustion products can be considered to be composed of only six components: CO2, H2, N2, O2, CO and H2; under higher temperature the above combustion products will undergo a dissociation reaction to form new combustion products. Based on this, many scholars at home and abroad have proposed corresponding combustion models: researchers have considered H, O, N, OH, NO, and Ar on the basis of the above 6 components, a total of 12 combustion products [28]; researchers People ignored Ar and considered only 11 combustion products. These two types are the most widely used combustion models. On the basis of Rakopoulos, this article ignores N further, because many studies have shown that the molar concentration of N is significantly lower than other combustion products, which is mainly due to the three covalent bonds in N2 [20-21, twenty three]. Therefore, only the combustion products of CO2, H2, N2, O2, CO, H2, H, O, OH and NO are considered in this paper. Regarding the composition of air, this article ignores Ar, and believes that air consists only of O2 and N2, but this requires the molar mass of N2 to be set to 28.16kg/kmol, and the molar ratio of O2 to N2 to be set to 1: 3.773.

In the field of combustion chemistry, the molecular formula C14.4H24.9 is often used to represent conventional diesel; for biodiesel, in addition to C and H atoms, it also contains O atoms, and for biodiesel produced from different raw materials, C, H The molar ratio between O and O is also different, which is mainly determined by the type and ratio of fatty acid methyl esters in biodiesel [29].
The biodiesel used in this paper is Jatropha biodiesel. Due to its characteristics of drought resistance, barren resistance and high oil content, Jatropha curcas is the main raw material for the production of biodiesel; in addition, the cetane number of Jatropha curcas biodiesel is higher than European and American standards, and its combustion performance is close to conventional diesel, Can be directly applied to diesel engines, so this oil has also received widespread attention worldwide [30-31]. Jatropha biodiesel mainly contains four types of fatty acid methyl esters: methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate. Table 1 gives the relevant information of these four components [32]. See Table 1.

| Name             | Molecular formula | Molar mass (kg/kmol) | Parts by mass (%) | Structural formula         |
|------------------|-------------------|----------------------|-------------------|---------------------------|
| Methyl palmitate | C_{17}H_{34}O_{2} | 270                  | 14.38             | CH_{3}(CH_{2})_{14}COOCH_{3} |
| Methyl stearate  | C_{19}H_{36}O_{2} | 298                  | 7.75              | CH_{3}(CH_{2})_{16}COOCH_{3} |
| Methyl oleate    | C_{19}H_{36}O_{2} | 296                  | 41.36             | CH_{3}(CH_{2})_{17}CH=CH(CH_{2})_{2}COOCH_{3} |
| Methyl linoleate | C_{19}H_{36}O_{2} | 294                  | 34.17             | CH_{3}(CH_{2})_{17}CH=CH=CH(CH_{2})_{4}COOCH_{3} |

This paper uses the information given in Table 1, and can use C18.74H34.45O_{2} to represent the Jatropha biodiesel molecule, its molar mass is 291.33kg/kmol. This article will use D100 to represent pure conventional diesel, B100 to represent pure Jatropha biodiesel, DxxBxx to represent a mixture of conventional diesel and biodiesel fuel, for example, D95B5 means to mix biodiesel with 5% mole fraction in conventional diesel. If C_{a}H_{b}O_{c}N_{d} is used to represent the fuel mixture, the relationship between a, b, c, and d and the molar ratio \( f \) (%) is:

\[
a = 14.4(1 - f) + 18.7f \\
b = 24.9(1 - f) + 34.5f \\
c = 2f \\
d = 0
\]  

(1.1) \hspace{5cm} (1.2) \hspace{5cm} (1.3) \hspace{5cm} (1.4)

Based on the above analysis, the combustion chemical reaction equation between mixed fuel and air can be expressed as:

\[
C_{a}H_{b}O_{c}N_{d} + \frac{\alpha_{s}}{\phi} (O_{2} + 3.773N_{2}) \rightarrow n_{1}CO_{2} + n_{2}H_{2}O + n_{3}N_{2} + n_{4}O_{2} + n_{5}CO \\
+ n_{6}H_{2} + n_{7}H + n_{8}O + n_{9}OH + n_{10}NO
\]

\[
\alpha_{s} = a + b / 4 - c / 2
\]  

(2) \hspace{5cm} (3)

In the formula: \( n_{i} - n_{10} \) represents the number of moles of each combustion product per thousand moles of fuel mixture; \( \phi \) is the fuel-air equivalent ratio; \( \alpha_{s} \) is the stoichiometric air-fuel molar ratio.
If $\sum_{i=1}^{10} n_i = N$, the molar fraction $y_i$ of each combustion product can be expressed as:

$$y_i = \frac{n_i}{N}$$

(4)

In the formula: $N$ is the total number of moles of the combustion products of one thousand moles of mixed fuel.

3. Equilibrium concentration and thermal properties of combustion products of mixed fuels

3.1. Combustion product equilibrium concentration modeling method

Although the combustion process of fuel in the cylinder is affected by many factors, such as injection pressure, fuel-air equivalence ratio and injection angle, etc., when the temperature in the cylinder is high, the reaction speed of the chemical reaction involved is fast enough, the concentration of each combustion product has sufficient time to adjust to a new state, so it can be considered that the combustion products are in a chemical equilibrium state. Researchers have used the combustion model of methane and air to prove the rationality of this hypothesis. At the same time, many researchers have shown that calculating the thermodynamic properties of the burned mixture with the help of the equilibrium concentration of the combustion products can effectively improve the simulation model of the engine. Prediction accuracy [25-26, 33]. Therefore, in this article, when calculating the combustion product concentration of diesel-biodiesel blended fuels, they are considered to be in a chemical equilibrium state at all times, but it should be pointed out that this equilibrium state is affected by the temperature, pressure and fuel-air-equivalent ratio.

At present, the modeling methods for the equilibrium concentration of fuel combustion products in the literature mainly include the equilibrium constant method and the free energy minimization method for scientific researchers. The equilibrium constant method is used in this paper. The theoretical basis of the researcher's free energy minimization method is that when a chemical reaction reaches an equilibrium state under a given temperature and pressure, the researcher's free energy of all components in the system will reach a minimum. For details, please refer to [34]. This article is no longer described. The equilibrium constant method is described below.

As can be seen from the previous section, in order to determine the equilibrium concentration of each combustion product shown in formula (2), a total of 11 unknown variables $y_1 \sim y_{10}$ and $N$ are required to be solved, so at least 11 equations are required. The chemical reaction described by formula (2) contains four types of atoms: C, H, O, and N. According to the conservation of atoms, four linear equations can be obtained immediately:

$$C: \quad a = (y_1 + y_2) \cdot N$$

(5.1)

$$H: \quad b = (2y_2 + 2y_6 + y_7 + y_8) \cdot N$$

(5.2)

$$O: \quad c + 2\alpha / \phi = (2y_4 + 2y_2 + y_3 + y_7 + y_8 + y_9 + y_{10}) \cdot N$$

(5.3)

$$N: \quad d + 7.52 \cdot \alpha / \phi = (2y_5 + y_{10}) \cdot N$$

(5.4)

In addition, according to the definition of $y_i$ moles, it is naturally available:

$$\sum_{i=1}^{10} y_i = 1$$

(6)
In addition to the five linear equations given by equations (5) and (6), six additional equations are needed. For this purpose, six chemical dissociation reactions shown in equation (7) are used:

\[
\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}, \quad K_{p1} = \frac{y_2 p^{1/2}}{y_1^{1/2}} \\
\frac{1}{2} \text{O}_2 \rightleftharpoons \text{O}, \quad K_{p2} = \frac{y_5 p^{1/2}}{y_4^{1/2}} \\
\frac{1}{2} \text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{OH}, \quad K_{p3} = \frac{y_9}{y_4^{1/2} y_6^{1/2}} \\
\frac{1}{2} \text{O}_2 + \frac{1}{2} \text{N}_2 \rightleftharpoons \text{NO}, \quad K_{p4} = \frac{y_{10}}{y_4^{1/2} y_5^{1/2}} \\
\text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O}, \quad K_{p5} = \frac{y_2}{y_4^{1/2} y_6^{1/2}} \\
\text{CO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO}_2, \quad K_{p6} = \frac{y_1}{y_4^{1/2} y_5^{1/2}}
\]

Under the assumption that the temperature is sufficiently high, these dissociation reactions will always be in a chemical equilibrium state, that is, the forward and reverse reaction speeds are equal, so that the concentration of each combustion product remains in dynamic equilibrium. The equilibrium state of a chemical reaction is usually described by the equilibrium constant $K_p$, and $K_p$ is defined as:

\[
K_p = \sum \left( \frac{p_i}{p_0} \right)^{v_i}
\]

In the formula; $p_i$ is the partial pressure of the $i$ component; $p_0$ is the reference pressure, which can be taken as $1 \times 10^5$ Pa; $v_i$ represents the stoichiometric coefficient of the $i$ component, and stipulates that the product is positive and the reactant is negative.

According to Dalton's partial pressure law, the total pressure $p_t$ of the gas mixture is equal to the sum of the partial pressures $p_i$ of the components, and $p_i$ is equal to $p_t$ times the mole fraction $y_i$ of the $i$ component:

\[
p_i = \sum p_i \quad \text{ (9)}
\]

\[
p_i = y_i \cdot p_t \quad \text{ (10)}
\]

Therefore, formula (8) can be expressed as:

\[
K_p = \prod_i \left( \frac{p_i}{p_0} \right)^{y_i} \cdot (y_i)^{v_i}
\]

\[
K_p = \prod_i \left( \frac{p_i}{p_0} \right)^{y_i} \cdot (y_i)^{v_i}
\]
In order to make the expression of formula (11) more concise, \( p_0 \) is used to normalize \( p_r \), \( p = p_r / p_0 \). Therefore, the \( K_p \) of each chemical dissociation reaction is shown in formula (7). In order to construct six additional equations about \( y_1 \sim y_{10} \), we also need to know the specific value of \( K_p \) under a given thermal condition, which can be obtained by researchers' free energy minimization method:

\[
\ln(K_p(T)) = -\frac{\sum g_i^0(T)v_i}{RT}
\]  

(12)

In the formula: \( \bar{R} \) is the universal gas constant, 8.3143 kJ/kmolK; \( g_i^0 \) is the free energy of specific molar scientific researchers under standard conditions; \( T \) is temperature.

For the derivation of formula (12), please refer to the relevant content in Chapter 3 of the doctoral dissertation of researchers [35]. The calculation method actually used in this paper is a polynomial obtained by the researchers fitting the thermal data in the range of 600-4000 K in the JANAF data table by the least square method [36]:

\[
\log_{10} K_p(T) = A \ln(T/1000) + \frac{B}{T} + C + DT + ET^2
\]  

(13)

In the formula: \( A, B, C, D \) and \( E \) are polynomial coefficients, the specific values can refer to the literature [36], which will not be given in this article.

The calculation method of \( K_p \) shown in formula (13) has been applied by many scholars at home and abroad, such as researchers and Tang et al. [20-22, 28], which proves to some extent that formula (13) is reliable in calculating \( K_p \). Sex. Figure 1 shows the change of \( K_p \) in the six dissociation reactions in the range of 600-4000 K in formula (7). It can be seen from this figure that, in addition to the reactions represented by formulas (7.5) and (7.6), other dissociation reactions The \( K_p \) of Pb increased with the increase of \( T \), and all of them were less than 1.

![Figure 1. Changing law of equilibrium constant for each chemical dissociation reaction with temperature.](image-url)
Combining formulas (7) and (13), six additional non-linear equations are obtained, which satisfy the conditions for solving these \( y_1 \sim y_{10} \) unknown variables.

### 3.2. Solving method for combustion product equilibrium concentration

At present, \( y_1 \sim y_{10} \) and these 11 unknown quantities of 11×11 nonlinear equations have been obtained. As long as the equations can be solved, the equilibrium concentration of each combustion product under a given thermal condition can be obtained. However, for such non-linear equations, it is difficult to obtain analytical solutions in many cases, and it is usually necessary to use numerical analysis methods to find their numerical solutions [37-38]. This paper will use the Newton-Raphson iteration method to solve the system of equations.

In order to reduce the difficulty of solving the system of equations, first reduce the order of the system of equations and use formula (5.1) to remove \( N \) in formulas (5.2) to (5.4), we can get:

\[
\begin{align*}
  f_1 &= 2y_2 + 2y_8 + y_7 + y_9 - d_1y_1 - d_4y_5 = 0 \\
  f_2 &= 2y_1 + y_2 + 2y_4 + y_5 + y_9 + y_{10} - d_2y_1 - d_3y_5 = 0 \\
  f_3 &= 2y_3 + y_{10} - d_3y_1 - d_5y_5 = 0 \\
  f_4 &= \sum_{i=1}^{10} y_i - 1 = 0
\end{align*}
\]

In addition, from formula (6):

\[
f_4 = \sum_{i=1}^{10} y_i - 1 = 0
\]

Next, using the \( K_p \) expression given by formula (7), \( y_1, y_2, \) and \( y_3 \sim y_{10} \) are expressed as functions of \( y_1 \sim y_6 \), and then brought into formula (14) to get 4 about \( y_3 \sim y_6 \) Equation:

\[
f_j(y_3, y_4, y_5, y_6) = 0, \quad j = 1, 2, 3, 4
\]

The equations shown in formula (15) can be solved using the Newton-Raphson iteration method. If the solution vector of formula (15) is \( (y_3^*, y_4^*, y_5^*, y_6^*) \), the left side of the formula is Taylor-expanded at an initial solution vector \( (y_3^{(k)}, y_4^{(k)}, y_5^{(k)}, y_6^{(k)}) \) close to \( (y_3^{(l)}, y_4^{(l)}, y_5^{(l)}, y_6^{(l)}) \), and the partial differentials of the second order and above are ignored, and we get:

\[
f_j + \frac{\partial f_j}{\partial y_3} \Delta y_3 + \frac{\partial f_j}{\partial y_4} \Delta y_4 + \frac{\partial f_j}{\partial y_5} \Delta y_5 + \frac{\partial f_j}{\partial y_6} \Delta y_6 \approx 0, \quad j = 1, 2, 3, 4
\]

In the formula:

\[
\Delta y_i = y_i^* - y_i^{(l)}, \quad i = 3, 4, 5, 6
\]

Formula (16) can be expressed as a matrix equation of the form \( A_{4\times4} \cdot \Delta y_{4\times1} = B_{4\times1} \), where the coefficient matrix is a Jacobian matrix, and the matrix equation can be solved using the Gaussian elimination method, and then the solution vector of the equation is used to optimize the initial solution vector:

\[
y_i^{(k+1)} = y_i^{(k)} + \Delta y_i, \quad i = 3, 4, 5, 6
\]

Where: \( k \) is the number of iteration steps.
In this way, the value can be iterated until \( \Delta y_j / y_j^{(k+1)} \) is less than the preset accuracy threshold \( \varepsilon \). In this paper, \( \varepsilon \) is taken as 0.001, and the maximum number of iteration steps is specified as 20 steps.

For an iterative optimization process, in addition to the iterative formula, the choice of initial value also has a significant impact on the convergence of the iterative process and the convergence speed. The initial solution vector \( (y_3^{(0)}, y_4^{(0)}, y_5^{(0)}, y_6^{(0)}) \) required for the iterative process is the mole fraction of N2, O2, CO, and H2. In order to obtain these initial values, the low-temperature combustion reaction between fuel \( \text{C}_a\text{H}_b\text{O}_c\text{N}_d \) and air is used when the temperature is below 1000 K:

\[
\text{C}_a\text{H}_b\text{O}_c\text{N}_d + \frac{\alpha}{\phi}(\text{O}_2 + 3.773\text{N}_2) \rightarrow n_1\text{CO}_2 + n_2\text{H}_2\text{O} + n_3\text{N}_2 + n_4\text{O}_2 + n_5\text{CO} + n_6\text{H}_2
\]  

Conserved by the atom:

- C: \( a = (y_1 + y_3)N \)  
- H: \( b = 2(y_2 + y_6)N \)  
- O: \( c + 2\alpha / \phi = (2y_3 + y_4 + 2y_5 + y_5)N \)  
- N: \( d + \frac{\alpha}{\phi} \cdot 3.773 \cdot 2 = 2 \cdot y_1 \cdot N \)

From formulas (7.5) and (7.6), we can see that \( y_i = K_{ps}p^{1/2}y_4^{1/2}y_5 \), \( y_2 = K_{ps}p^{1/2}y_4^{1/2}y_6 \), combined with formula (19), can obtain a function about the mole fraction \( y_4 \) of O2:

\[
f(y_4) = 2 \cdot y_4N - c - 2 \cdot \frac{\alpha}{\phi} + \frac{a(2 \cdot K_{ps}p^{1/2}y_4^{1/2} + 1)}{K_{ps}p^{1/2}y_4^{1/2} + 1} + \frac{bK_{ps}p^{1/2}y_4^{1/2}}{2(K_{ps}p^{1/2}y_4^{1/2} + 1)} = 0
\]  

The above formula can be used to estimate the initial value of \( y_4 \): Assuming that the initial molar fraction of O2 in the combustion product is 100%, which is \( y_4^{(0)} = 1 \), this will obviously make \( f(y_4) \) greater than 0. Then, use formula (21) to \( y_4 \) iterates until \( f(y_4) \) is less than 0, at which point \( y_4 \) will be close to its "exact solution".

\[
y_4^{(k+1)} = y_4^{(k)} \cdot 0.1
\]  

Researchers use the results obtained from the above iterative process as initial values, and use the Newton-Raphson iterative method to obtain the "exact solution". The corresponding iterative formula is:

\[
y_4^{(k+1)} = y_4^{(k)} - \frac{f(y_4)}{f'(y_4)}
\]  

When the absolute value of the ratio of \( f(y_4)/(f'(y_4)) \) to \( y_4^{(k)} \) is less than 0.001, it can be considered that the "exact solution" of \( y_4 \) is successfully obtained. The initial values of the molar fractions of N2, CO, and H2, \( y_3 \), \( y_5 \), and \( y_6 \), can be obtained using atomic conservation:
At this point, a reasonable initial value of \( y_3 \) is obtained, which guarantees the convergence of the iterative process and the convergence speed to a certain extent. After the numerical solution of \( y_3 \) is obtained, the expression of \( K_p \) in formula (7) can be used to solve \( y_1 \), \( y_2 \) and \( y_9 \sim y_{10} \), so as to obtain the equilibrium molar fraction of each combustion product under the given thermal conditions. From the above, it can be known that for a given fuel type, \( y_1 \sim y_{10} \) is affected by the temperature, pressure and fuel-air equivalent ratio; on the other hand, \( y_1 \sim y_{10} \) will affect the thermal properties of the combustion products (constant pressure specific heat, adiabatic index and specific enthalpy, etc.), which will be discussed further below.

3.3. Thermal properties model of combustion products

For the study of engine performance simulation, establishing an accurate combustion product thermal property model is a key part to ensure the accuracy of the simulation. By comparing several constant pressure specific heat \( c_p \) and constant volume specific heat \( c_v \) models with different degrees of complexity, researchers have found that as the complexity of the \( c_p \) and \( c_v \) models increases, the calculated thermal efficiency of the standard air double cycle gradually decreases and continues to approach the real thermal efficiency of diesel engines [39]. At the same time, many studies have simplified the thermal properties of combustion products: researchers have expressed \( c_p \) and \( c_v \) as a function of temperature without considering the effect of pressure to fuel-air equivalence ratio [40]; Llamas is calculating combustion products when considering the thermal properties, the burned mixture is only composed of the five components \( O_2 \), \( N_2 \), \( CO_2 \), \( H_2O \), and \( SO_2 \), and the influence of pressure on the thermal properties is ignored [41]. These simplifications will inevitably affect the prediction accuracy of the engine performance simulation model. This is because in the high temperature environment of the engine cylinder, the combustion products will undergo chemical dissociation reactions, resulting in many additional combustion product components. At the same time, the concentration of these components is affected by temperature, influence of pressure to air-equivalent ratio. In view of this problem, based on the equilibrium concentration of the combustion products obtained, a corresponding thermodynamic model was established to investigate the effect of blending biodiesel in conventional diesel on the thermodynamic properties of the burned mixture.

The combustion products of fuel oil are composed of multiple gas components. When calculating the thermal properties of a mixture, these gases are usually assumed to be ideal gases. Their thermal properties can be obtained by looking up tables or empirical formulas. The calculation method used in this paper is based on a large amount of experimental data, Gordon and McBride used a least squares method to fit the thermal properties of pure substances (herein referred to as NASA polynomials) [35]. After using NASA polynomials to calculate the thermal properties of each component and the molar fractions of each component by the equilibrium constant method, the thermal properties of the burned mixture can be calculated using Gibbs-Dalton's law, the corresponding molar mass \( MW \), molar specific enthalpy \( h \), Molar ratio internal energy \( u \), Molar ratio entropy \( s \) can be expressed as:

\[
y_3 = \frac{1}{2N} \left( \frac{\alpha}{\phi} \cdot 3.773 \cdot 2 + d \right) \tag{23.1}
\]

\[
y_5 = \frac{a}{N(K_{of}P^{1/2}y_4^{1/2} + 1)} \tag{23.2}
\]

\[
y_6 = \frac{b}{2N(K_{ps}P^{1/2}y_4^{1/2} + 1)} \tag{23.3}
\]
It can be known from the above formula that although each component of the mixed gas can be regarded as an ideal gas, the mixed gas is no longer an ideal gas, for example, the mixed gas \( u \) is no longer merely a function \( T \). In order to apply the ideal gas equation of state to the mixed gas, the gas constant needs to be modified:

\[
R(T, p, \phi) = \frac{\bar{R}}{MW(T, p, \phi)}
\]

(25)

Compared with the internal energy, enthalpy and entropy, the formula for calculating the specific constant pressure and specific heat \( c_p \) of the mixture is slightly different. \( c_p \) is defined as the partial derivative of the heat \( \bar{u} \) with respect to \( T \) under constant pressure conditions, that is:

\[
c_p = \left(\frac{\partial \bar{u}}{\partial T}\right)_p = \left(\frac{\partial \bar{h}}{\partial T}\right)_p
\]

(26)

According to formula (24.2), the specific enthalpy of the mixed gas can be expressed as:

\[
\bar{h} = \frac{\sum_i y_i \cdot \bar{h}_i}{MW}
\]

(27)

Putting formula (27) into (26), we get:

\[
c_p = \frac{1}{MW} \left[ \sum_i y_i \cdot c_{p,i} + \sum_i \bar{h}_i \cdot \frac{\partial y_i}{\partial T} - \frac{\bar{h}}{MW} \sum_i MW_i \cdot \frac{\partial y_i}{\partial T} \right]
\]

(28)

The second and third terms in parentheses to the right of the above equation indicate the effect of the dissociation reaction on the molar fraction of combustion products at high temperatures; however, for the "frozen" state at lower temperatures, the formula (28) can be simplified to:

\[
c_p = \frac{1}{MW} \sum_i y_i \cdot c_{p,i}
\]

(29)

It can be known from formula (28) that in order to obtain \( c_p \), it is also necessary to know the partial derivative of the mole fraction of each component in the mixed gas with respect to temperature, which
is $\frac{\partial y_j}{\partial T}$, for this purpose, the full derivative of formula (15) with respect to temperature can be taken to obtain 4 equations for $\frac{\partial y_j}{\partial y_j T}$, $\frac{\partial y_j}{\partial y_j T}$, $\frac{\partial y_j}{\partial y_j T}$, and $\frac{\partial y_j}{\partial y_j T}$:

$$\frac{\partial f_j}{\partial T} + \frac{\partial f_j}{\partial y_j} \frac{\partial y_j}{\partial T} + \frac{\partial f_j}{\partial y_j} \frac{\partial y_j}{\partial T} + \frac{\partial f_j}{\partial y_j} \frac{\partial y_j}{\partial T} = 0, \quad j=1,2,3,4$$

(30)

The solution of formula (30) is similar to that of formula (15) and will not be described in this article.

4. Model verification

Currently, there are many commercial and non-commercial software that can be used to calculate the equilibrium concentration of combustion products, such as CHEMIKIN, MATLAB software package named CHEPP developed by a well-known professor at Linköping University, Sweden, CEA, GASEQ developed by researchers at NASA Glenn Research Center As well as STANJAN developed by Stanford University researchers, these softwares have been widely used in different studies [20-21, 28, 38]. This article will verify the correctness of the results obtained by comparing the equilibrium concentrations of the combustion products obtained by using this and the CHEPP software package. The corresponding thermal conditions are $T=2250K$, $p=1bar$, and $\phi$ are 0.5, 1, 1.5, respectively. The fuel used is diesel. The comparison results are shown in Table 2. From the table, it can be known that the relative deviations of the components except NO are within 1.1%, which verifies the correctness of the mathematical model given in this paper to a certain extent. For NO, the relative deviations are 4.9914% ($\phi=0.5$), 5.3933% ($\phi=1$), and 4.7187% ($\phi=1.5$), which may be derived from this article and the theoretical basis for the calculation of the equilibrium concentration by CHEPP. The equilibrium constant method, CHEPP is the Gibbs free energy minimization method, but considering that the equilibrium concentration of NO itself is low, both do not exceed 1% and the absolute deviation does not exceed 0.04%, which explains to some extent what is given in this article. Correctness of NO equilibrium concentration. See Table 2.

| Component | This article ($\phi=0.5$) (%) | CHEPP ($\phi=0.5$) (%) | Deviation (%) | This article ($\phi=1$) (%) | CHEPP ($\phi=1$) (%) | Deviation (%) | This article ($\phi=1.5$) (%) | CHEPP ($\phi=1.5$) (%) | Deviation (%) |
|-----------|-------------------------------|------------------------|---------------|-----------------------------|-----------------------|--------------|-----------------------------|-----------------------|--------------|
| CO2       | 6.8823                        | 6.8806                 | 0.026         | 12.2955                     | 12.2892               | 0.0512       | 5.5520                      | 5.5268                 | 0.4558        |
| H2O       | 5.8922                        | 5.8914                 | 0.0142        | 11.4184                     | 11.4193               | 0.0082       | 11.0029                     | 11.0281               | 0.2288        |
| N2        | 75.9239                       | 75.9462                | 0.0293        | 73.5617                     | 73.5651               | 0.0046       | 65.8084                     | 65.8087               | 0.00004       |
| O2        | 9.5916                        | 9.6149                 | 0.2423        | 0.5905                      | 0.5970                | 0.073        | 0.00133                     | 0.00134               | 0.7885        |
| CO        | 0.1852                        | 0.1869                 | 0.0873        | 1.3336                      | 1.3396                | 0.4447       | 12.7086                     | 12.7338               | 0.1978        |
| H2        | 0.0296                        | 0.0294                 | 0.5133        | 0.2310                      | 0.2289                | 0.0002       | 4.6975                      | 4.6720                | 0.0447        |
| H         | 0.0127                        | 0.0128                 | 0.0288        | 0.0356                      | 0.0356                | 0.0006       | 0.1606                      | 0.1607                | 0.00004       |
| O         | 0.1136                        | 0.1143                 | 0.0282        | 0.0282                      | 0.0285                | 0.0003       | 0.00135                     | 0.0014                | 0.8776        |
| OH        | 0.3811                        | 0.3829                 | 0.4662        | 0.2645                      | 0.2661                | 0.0613       | 0.0565                      | 0.0569                | 0.7236        |
| NO        | 0.9877                        | 0.9408                 | 0.4914        | 0.2412                      | 0.2307                | 5.2933       | 0.0108                      | 0.0103                | 4.7187        |

5. Analysis of simulation results

As shown in Figures 2 to 4, this section first analyzes the sensitivity of the combustion product equilibrium concentrations of D100 and B100 to the fuel-air equivalence ratio, temperature, and pressure. The selected reference points are, $\phi=0.8$, $T=2000K$, $p=160bar$, the range of $\phi$ is 0.2 to 2.0, the range of $T$ is 1000 to 3000 K, and the range of $p$ is 110 bar to 200 bar. The change range of the above parameters basically covers the change range of the thermal state of the working fluid in the diesel engine cylinder during the combustion process.
Figure 2 shows the effects of radon on the equilibrium concentrations of the combustion products of D100 and B100 at T=2000K and p=160bar. As radon gradually increases from 0.2 to 2.0, the combustion will transition from "lean oil" to "rich oil" "Combustion, when \( \phi = 1 \), it is" stoichiometric "combustion. During the above changes, the equilibrium concentrations of O2, NO, OH, and O gradually decreased. However, the equilibrium concentrations of CO, H2, and H gradually increased, because the amount of oxygen available for fuel combustion gradually decreased with the increase of radon. Leading to the occurrence of incomplete combustion, in addition, the change rate of the above-mentioned seven component equilibrium concentrations is reaching a maximum. For CO2 and H2O, their equilibrium concentrations first increase with the increase of ytterbium, reach a maximum near, =1, and then decrease with the increase of ytterbium; in addition, ytterbium has a small effect on the equilibrium concentration of N2. It should be noted that due to the dissociation reaction of the combustion products, the molar fraction of O2 is not zero when \( \phi \cong 1 \), and the equilibrium concentration of CO and H is not zero when \( \phi \cong 1 \). Figure 2 only shows the simulation results of T=2000K. Although no corresponding results are given, this paper finds that as T decreases, the effect of radon on the equilibrium concentration of each combustion product will increase.

![Figure 2](image)

**Figure 2.** Sensitivity of combustion products equilibrium concentration to fuel air equivalence ratio.

Figure 3 shows the effect of T on the equilibrium concentrations of the combustion products of D100 and B100 at \( \phi = 0.8 \) and p=160bar11. As can be seen from the above, the effect of temperature on the equilibrium concentration is mainly reflected in the equilibrium of each dissociation reaction. Influence of the constant Kp. It can be seen from the figure that the effect of T on the equilibrium concentrations of N2, CO2, H2O and O2 is small. When T is increased from 1000 K to 3000 K, the relative change rates of these four components are -2.4%, -13.2%, -7.8% and -13.7%, that is to say, with the increase, their equilibrium concentration gradually decreases. For N2, its lower equilibrium concentration change rate is mainly derived from the three covalent bonds in N2 [23]. On the other hand, for CO, H2, H, O, OH and NO, their equilibrium concentrations increase significantly with increasing, and the relative change rates are 5.0826e+11%, 5.1882e+10%, 1.5854e+14%, 6.6885e+10%, 4.3446e+07%, and 1.2935e+05%, which indicates that the intensity of the chemical dissociation reaction is enhanced, but the growth rate slows down with the increase of T.
Figure 3. Sensitivity of combustion product equilibrium concentration to temperature.

Figure 4 shows the effect of the change in p (110 to 300 Bar) on the equilibrium concentrations of the combustion products of D100 and B100 at T=2000K. It can be seen from the figure that the relative change rate of the equilibrium concentrations of CO₂, H₂O, N₂, and O₂ is less than 0.04%, and that of CO, H₂, H, O, and OH is -25.83%, -25.82%, -36.12%, -25.83%, and -13.84%. The above phenomenon shows that with the increase of p, the dissociation reaction will be inhibited, so the equilibrium concentration of CO, H₂, H, O and OH will decrease, and CO₂, H₂O, N₂, and O₂ will increase slightly; in addition, By comparing with the results shown in Fig. 2 and Fig. 3, it can be found that the effect of pressure on the equilibrium concentration of combustion products is much lower. This is why only the effects of T and ϕ are considered in some combustion product thermal properties models, and Ignoring p, such as the Justi internal energy model and the Kushiyama formula for calculating the adiabatic index [42-43].

Figure 4. Sensitivity of combustion products equilibrium concentration to pressure.

Considering that CO₂, NO, and CO are the main greenhouse and harmful gas emissions of internal combustion engines, Table 3 shows that when T=2000K, p=160bar, and equal to 0.8, 1.0, and 1.2, respectively, compared with D100, B100's above relative changes in the equilibrium concentrations of
the three combustion products. It can be known from Table 3 that the blending of biodiesel in conventional diesel does affect the equilibrium concentration of CO$_2$, NO and CO, but the effect is not very obvious. Under the above thermal conditions, the maximum does not exceed 3.52%, which is mainly due to conventional diesel. Similar hydrocarbon ratios in biodiesel fuel molecules (D100: 0.578, B100: 0.544) [44]; In addition, under "rich" conditions ($\phi$=1.2), the effect of blending biodiesel on the equilibrium concentration of combustion products The effect is more obvious. For CO$_2$ as the main combustion product, whether it is "rich oil", "lean oil" or "stoichiometric" combustion, the blending of biodiesel will increase its equilibrium concentration, which is mainly due to the slightly higher biodiesel molecules. Molar ratio of hydrocarbons; however, for NO and CO, there is no obvious change law, because the equilibrium concentration of each combustion product is affected by a variety of factors, including equilibrium constant, stoichiometric fuel-air ratio, atomic conservation, and the total number of moles of combustion products. Although many studies have shown that blending biodiesel with conventional diesel can lead to increased NO emissions, it should be noted that for NO, it is difficult to reach a chemical equilibrium state because their formation process requires a long reaction time. That is, its true concentration (non-equilibrium concentration) is not equal to the equilibrium concentration. Therefore, it is necessary to use chemical kinetics theory instead of chemical equilibrium theory when calculating the true emission of NO. [35, 45-46].

Table 3. Comparison of CO$_2$, NO and CO equilibrium concentrations of biodiesel and conventional diesel.

|        | $\phi$=0.8 | $\phi$=1.0 | $\phi$=1.2 |
|--------|------------|------------|------------|
| CO$_2$ | 0.6830     | 0.4760     | 1.8512     |
| NO     | -0.8935    | -0.0190    | 3.5192     |
| CO     | 1.1375     | -0.0579    | -2.2282    |

The simulation results given above are all based on the molar blending ratio. However, in fact, the blending of biodiesel is based on the mass or volume mixing ratio in most cases [9-12]. Therefore, this article will examine the emission mass of CO$_2$, NO, and CO per one kilogram of unit fuel mixture under different mass blending conditions. To this end, the average molecular formula of the fuel mixture, the equilibrium mass fraction of the combustion products, and the combustion are calculated. The total mass of the product.

If the average molecular formula of the blended fuel is $C_\alpha H_\beta O_\gamma$, the relationship between the weight ratio of, and the mass blending ratio is:

$$ f = \frac{w_f}{MW_{BD}} / (\frac{w_f}{MW_{BD}} + \frac{1-w_f}{MW_D}) $$

$$ \alpha = N_{CD}(1-f) + N_{CBD}f $$

$$ \beta = N_{HD}(1-f) + N_{HBD}f $$

$$ \gamma = N_{OD}(1-f) + N_{OBD}f $$

In the formula: $N$ represents the number of atoms in the fuel molecule; D represents conventional diesel; BD represents biodiesel.

The conversion relationship between the equilibrium mole fraction $y_j$ and the mass fraction $x_j$ of the $j$ combustion product is [24]:
and for gas constant gas recirculation (EGR) technology to reduce engine constant pressure and constant volume specific heat, which is also one of the reasons for using exhaust equilibrium concentration of CO equal to 0.8, 1.0 and 1.2, shown. It can be seen from the figure that with the increase of the blending ratio of biodiesel, when pressure specific heat cp and constant volume cv of the burned mixture are significantly higher than those of the other two cases. This is mainly due to the increase in the equilibrium concentration of CO and H₂O. Compared with other components, they have reached the maximum value near Φ = 1.0. As shown. It can be seen from the figure that with the increase of the blending ratio of biodiesel, when equal to 0.8, 1.0 and 1.2, c_p and c_v will increase accordingly. This is mainly due to the increase in the equilibrium concentration of CO and H₂O. Compared with other components, they have a high constant pressure and constant volume specific heat, which is also one of the reasons for using exhaust gas recirculation (EGR) technology to reduce engine nitrogen oxide emissions [47-48]; At this time, the cp and cv of the burned mixture are significantly higher than those of the other two cases. This is because the equilibrium concentration of CO₂ and H₂O has reached the maximum value near Φ=1.0. For gas constant R and adiabatic index k, as the blending ratio of biodiesel increases, R will increase and k will decrease accordingly.

Next, based on the equilibrium concentrations of the combustion products obtained, the effect of blending biodiesel on the thermal properties of the burned mixture is investigated, including constant pressure specific heat cp and constant volume specific heat cv. The results are shown in Figure 6. As shown. It can be seen from the figure that with the increase of the blending ratio of biodiesel, when equal to 0.8, 1.0 and 1.2, c_p and c_v will increase accordingly. This is mainly due to the increase in the equilibrium concentration of CO and H₂O. Compared with other components, they have a high constant pressure and constant volume specific heat, which is also one of the reasons for using exhaust gas recirculation (EGR) technology to reduce engine nitrogen oxide emissions [47-48]; At this time, the cp and cv of the burned mixture are significantly higher than those of the other two cases. This is because the equilibrium concentration of CO₂ and H₂O has reached the maximum value near Φ=1.0. For gas constant R and adiabatic index k, as the blending ratio of biodiesel increases, R will increase and k will decrease accordingly.
biodiesel in marine diesel on power, emissions and economic performance of large marine two-stroke diesel engines.

In addition to Jatropha biodiesel, this paper also tested soybean biodiesel and palm oil biodiesel, and obtained similar simulation results.

6. Conclusion
This article takes Jatropha biodiesel as the research object. Assuming that the combustion products are in a chemical equilibrium state, the equilibrium constant method and Newton-Raphson method are used to calculate the equilibrium concentration of each component of the combustion products, and on this basis, different blending ratios are examined. The effects on the thermal properties of combustion products are as follows:

(1) By comparing the equilibrium concentration results of conventional diesel combustion products obtained by using this paper and the CHEPP software package, it is found that the relative deviations of all components except NO are within 1.1%, which to some extent validates the results given in this article. The correctness of the calculated model of combustion product equilibrium concentration. This model can be easily integrated into the engine simulation model, which lays the foundation for the future use of numerical simulation technology to study the impact of blended biodiesel on engine power, emissions and economic performance; in addition, the model has a strong flexibility and scalability. By adjusting the types of reactants and products in formula (2), it can also be used to study the effects of cylinder water injection, emulsified fuel, EGR, etc. on the equilibrium concentration of combustion products and the thermal properties of the burned mixture.

(2) Blending biodiesel in conventional diesel does not have a significant impact on the equilibrium concentration of each combustion product. For the three major greenhouse gases and harmful emissions such as CO2, NO, and CO, B100 is the largest compared to D100. The rate of change does not exceed 3.52%. In addition, under "rich" conditions, the effect of blending biodiesel on the equilibrium concentration of combustion products is more obvious.

(3) With the increase of the mass blending ratio of biodiesel, the emission quality of CO2, NO, and CO has shown a downward trend to varying degrees for each kilogram of unit fuel.

(4) Blending biodiesel in conventional diesel will cause a small increase in the specific heat and constant pressure specific heat of the burned mixture, which is mainly due to the increase in the equilibrium concentration of CO2 and H2O with higher specific heat capacity.

The next work of this paper will use numerical simulation tools to study the effects of blending biodiesel in marine diesel on power, emissions and economic performance of large marine two-stroke diesel engines.
References

[1] DEMIRBAS A. Political, economic and environmental impacts of biofuels: A review [J]. Applied Energy, 2009, 86 (Supp.1): S108-S117.

[2] HOW H G, MASJUKI H H, KALAM M A, et al. An Investigation of the engine performance, emissions and combustion characteristics of coconut biodiesel in a high-pressure common-rail diesel engine [J]. Energy, 2014, 69: 749-759.

[3] SORDA G, BANSE M, KEMFERT C. An overview of biofuel policies across the world [J]. Energy Policy, 2010, 38: 6977-6988.

[4] KNOTHE G, RAZON L F. Biodiesel fuels [J]. Progress in Energy and Combustion Science. 2017; 58: 36-59.

[5] XUE J L, GRIFT T E, HANSEN A C. Effect of biodiesel on engine performances and emissions [J]. Renewable and Sustainable Energy Reviews, 2011, 15 (2): 1098-6.

[6] THANGARAJA J, Anand K, Mehta P S. Biodiesel NOx penalty and control measures – a review [J]. Renewable and Sustainable Energy Reviews, 2016, 61: 1-24.

[7] Szybist J P, Song J, Alam M, et al. Biodiesel combustion, emissions and emission control [J]. Fuel Processing Technology, 2007, 88 (7): 679-691.

[8] Hoekman S K, Robbins C. Review of the effects of biodiesel on NOx emissions [J]. Fuel Processing Technology, 2012, 96: 237-249.

[9] CAN O, OztUrk E, YUcesu H S. Combustion and exhaust emissions of canola biodiesel blends in a single cylinder DI diesel engine [J]. Renewable Energy, 2017, 109: 73-82.

[10] WU F, WANG J, CHEN W, et al. A Study on emission performance of a diesel engine fueled with five typical methyl ester biodiesel [J]. Atmospheric Environment, 2009, 43 (7): 1481-1485.

[11] Devan P K, Mahalakshmi N V. Study of the performance, emission and combustion characteristics of a diesel engine using poon oil-based fuels [J]. Fuel Processing Technology, 2009, 90 (4): 513-519.

[12] DATTA A, PALIT S, MANDAL B K. An experimental study on the performance and emission characteristics of a CI engine fuelled with Jatropha biodiesel and its blends with diesel [J]. Journal of Mechanical Science and Technology, 2014, 28 (5): 1961-1966.

[13] Yildiz M, Çeper B A. Estimation of equilibrium combustion products of diesel-biodiesel fuel blends using the developed solving process for CnHm and CαHβOγ fuel types [J]. International Journal of Automotive and Mechanical Engineering, 2017, 14 (2): 4332-4347.

[14] DATTA A, MANDAL B K. Engine performance, combustion and emission characteristics of a compression ignition engine operating on different biodiesel-alcohol blends [J]. Energy, 2017, 125: 470-483.

[15] Kulesohov A S. Use of multi-zone DI diesel spray combustion model for simulation and optimization of performance and emissions of engines with multiple injection [C]. SAE Technical Paper, 2006-01-1385, 2006.

[16] Gogoi T K, Baruah D C. A cycle simulation model for predicting the performance of a diesel engine fuelled by diesel and biodiesel blends [J]. Energy, 2010, 35 (3): 1317-1323.

[17] AN H, YANG W M, LI J. Numerical modeling on a diesel engine fueled by biodiesel-methanol blends [J]. Energy Conversion and Management, 2015, 93: 100-108.

[18] AN H, YANG W M, Maghbouli A, et al. Detailed physical properties prediction of pure methyl esters for biodiesel combustion modeling [J]. Applied Energy, 2013, 102: 647-656.

[19] Hamed N M S, Rasul M G, Harch C A. Modelling and experimental investigation of engine performance and emissions fuelled with biodiesel produced from Australian Beauty Leaf Tree [J]. Fuel, 2015, 150: 625-635.

[20] Kayadelen H K, Ust Y. Prediction of equilibrium products and thermodynamic properties in H2O injected combustion for CaHβOγHδ type fuels [J]. Fuel, 2013, 113: 389-401.

[21] Kayadelen H K. A multi-featured model for estimation of thermodynamic properties, adiabatic flame temperature and equilibrium combustion products of fuels, fuel blends, surrogates and
fuel additives [J]. Energy, 2018, 143: 241-256.

[22] Gonca G. Investigation of the influences of steam injection on the equilibrium combustion products and thermodynamic properties of bio fuels (biodiesels and alcohols) [J]. Fuel, 2015. 144: 244-258.

[23] Şanli A, Kılıçaslan İ, Çanakçı M. A comparative parametric analysis of equilibrium combustion products of gasoline, diesel, ethanol, methanol and their blends [J]. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 2014, 36 (21): 2420-2430.

[24] Eriksson L. CHEPP-A chemical equilibrium program package for Matlab [C]. SAE Technical Paper, 2004-01-1460, 2004.

[25] Rakopoulos C D, Hountalas D T, Tzanos E I, et al. A fast algorithm for calculating the composition of diesel combustion products using 11 species chemical equilibrium scheme [J]. Advances in Engineering Software, 1994, 19 (2): 109-119.

[26] Rashidi M. Calculation of equilibrium composition in combustion products [J]. Applied Thermal Engineering, 1998, 18 (3-4): 103-109.

[27] Hunter T B, Wang H, Litzinger T A, et al. The oxidation of methane at elevated pressures: experiments and modeling [J]. Combustion and Flame, 1994, 97 (2): 201-224.

[28] TANG Y Y, ZHANG J D, JIA B Z, et al. Investigation on the solution of nitric oxide emission model for diesel engine using optimization algorithms [J]. Fuel, 2018, 228: 81-91.

[29] Atabani A E, Silitonga A S, ONG H C, et al. Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions productions [J]. Renewable and Sustainable Energy Reviews, 2013, 18: 211-245.

[30] Kumar S, Chaube A, Jain S K. Sustainability issues for promotion of Jatropha biodiesel in India scenario: A review [J]. Renewable and Sustainable Energy Reviews, 2012, 16: 1089-1098.

[31] Chukwuezie O C, Nwaigwe K N, Asogwgu S N, et al. Diesel engine performance of jatropha biodiesel: A review [J]. Biofuels, 2014, 5 (4): 415-430.

[32] WANG C M. Combustion and emission characteristics of CI engine fueled with different biodiesel [D]. Dalian, Dalian University of Technology, 2014. (in Chinese)

[33] Heywood J B. Internal combustion engine fundamentals [M]. New York: McGraw-Hill, Inc., 1988.

[34] Ferguson C R, Kirkpatrick A T. Internal combustion engines: Applied Thermosciences [M]. Third Edition. Chichester: Jon Wiley & Sons Ltd, 2016.

[35] Savva N S. Development and Evaluation of a Semi–empirical Multi–zone Thermodynamic Model for the Estimation of Nitric Oxide Emissions and Formation History in Diesel Engines Using the Measured Cylinder Pressure Trace [D]. Athens: National Technical University of Athens, 2015.

[36] Olikara C, Borman G L. A computer program for calculating properties of equilibrium combustion products with some applications to I.C. engines [C]. SAE Technical Paper, 750468, 1975.

[37] XIE Z Y, ZHOU L, WANG H, et al. Application of generic algorithm in calculation of combustion equilibrium composition [J]. Chinese Journal of Energetic Materials, 2015, 23 (4): 340-345. (in Chinese).

[38] TANG Y Y. Research on the modeling methods of power engine for marine engine room simulator [D]. Dalian: Dalian Maritime University, 2018. (in Chinese)

[39] Murphy A J, Norman A J, Pazouki K, et al. Thermodynamic simulation for the investigation of marine diesel engines [J]. Ocean Engineering. 2015, 102: 117-128.

[40] Abu-Nada E, Al-Hinti I, Al-Sarkhi A, et al. Thermodynamic modeling of spark-ignition engine: Effect of temperature dependent specific heats [J]. International Communications in Heat and Mass Transfer. 2006, 33 (10): 1264-1272.

[41] Llamas X, Eriksson L. Control-oriented modeling of two-stroke diesel engines with exhaust gas recirculation for marine applications [J]. Proceedings of the Institution of Mechanical
[42] ZHANG Q F. Research on multi-point mathematical model of ship diesel propulsion plant and marine operation evaluation system [D]. Dalian: Dalian Maritime University, 2016. (in Chinese)

[43] TANG Y Y, ZHANG J D, GAN H B, et al. Development of a real-time two-stroke marine diesel engine with in-cylinder pressure prediction capability [J]. Applied Energy, 2017, 194: 55-70.

[44] Nayak S, Mishra P. Emission from a dual fuel operated diesel engine fuelled with calophyllum inophyllum biodiesel and producer gas [J]. International Journal of Automotive and Mechanical Engineering, 2017, 14 (1): 3954-3978.

[45] Finesso R, Spessa E. A real time zero-dimensional diagnostic model for the calculation of in-cylinder temperatures, HRR and nitrogen oxides in diesel engines [J]. Energy Conversion and Management, 2014, 79: 498-510.

[46] Scappin F, Stefansson S, Haglind F. Validation of a zero-dimensional model for prediction of NOx and engine performance for electronically controlled marine two-stroke diesel engines [J]. Applied Thermal Engineering, 2012, 37: 344-352.

[47] Millo F, Giacominetto P F, Bernardi M G. Analysis of different exhaust gas recirculation architectures for passenger car diesel engines [J]. Applied Energy, 2012, 98: 79-91.

[48] Hountalas D T, Mavropoulos G C, Binder K B. Effect of exhaust gas recirculation (EGR) temperature for various EGR rates on heavy duty DI diesel engine performance and emissions [J]. Energy, 2008, 33 (2): 272-283.