1. INTRODUCTION

With the increasing impact of fossil energy consumption and air pollution on human living environment, it is important to measure energy transformation to promote the development of renewable energy and establish an energy supply system with new and renewable energy as the main body. The energy from biomass (i.e., bioenergy) is considered to be renewable, due to the abundance of perennial bioresources, and carbon-neutral, due to their ability to reabsorb the carbon emitted from combustion of the same. The most traditional way to get energy from biomass is to direct fuel combustion. However, the biomass plant combustion has very low efficiency and a great amount of pollutant emission. As an alternative, biomass gasification, an energy conversion process including a group of complex chemical reactions wherein large organic molecules degrade into carbon monoxide, methane, hydrogen, and other flammable gases, has been regarded as an effective pathway for utilization of bioresources. The components of syngas may change according to the characteristics of biomass, the type of gasifier, the gasification fluid, and the operating parameters. Table 1 shows the main gas components of different types of biomass gasification processes in the literature. It can be noticed that the concentration of CO in rice husk gasification is high, and the gas composition ratio of CO/CH4/H2 is close to 2:1:1. In addition, CO2 and N2 account for about 15–65% in most gasification gases. As known, the thermal, chemical, and dilution effects of inert gases will have a certain impact on the combustion characteristics of hydrocarbon fuel. In this paper, the effects of different inert gas rates (0–60%) on the combustion characteristics of CO/CH4/H2 (volCO/volCH4/volH2 = 2:1:1) are numerically studied, which are based on the actual biomass gasification gas composition, for obtaining more data on the effect of inert gas on the combustion characteristics of biomass gas.

In recent years, the effects of inert gases (CO2 and N2) on the combustion characteristics of hydrocarbon fuel mixture have been studied by experiments and numerical simulations. Giurcan et al. investigated the chemical effect of CO2 replacement of N2 in air on the burning velocity of CH4 and H2 premixed flames. The numerical results showed that the chemical effect of CO2 is stronger than N2 and mainly occurs through the following reaction: CO + OH ↔ CO2 + H competes with H radicals in reactive H + O2 ↔ O + OH, thus reducing the overall reaction rate and significantly reducing the combustion speed of methane and hydrogen premixed flame. Galmiche et al. and Hu et al. studied the effects of diluents on the laminar burning velocity of methane/air mixtures. They found that the dilution effect of N2 and CO2 is the main factor to reduce the laminar burning velocity and the thermal-diffusion and chemical effects can be negligible for N2.
Burbano et al.\textsuperscript{18} Hu et al.\textsuperscript{19} and Weng et al.\textsuperscript{20} investigated the dilution effect of $N_2$/CO$_2$ on the laminar burning velocity and flame stability of $H_2$–CO–O$_2$ mixtures. It was found that, for a certain dilution fraction, the reduction in laminar burning velocity is largely independent of the equivalence ratio and fuel $H_2$–CO mole fraction. Besides, an increase in the $N_2$ and CO$_2$ dilution fractions considerably reduced the laminar burning velocity due to a decrease in heat release and an increase in heat capacity, and this effect was higher for the case of CO$_2$ due to its higher heat capacity and dissociation effects during combustion. Zhang et al.\textsuperscript{21} experimentally determined that the flame temperature profile and flame computation were conducive to analyze the effects of carbon dioxide and nitrogen dilution on methane/air flames. Results indicated that carbon dioxide addition has more significant effects on the thermal properties of flame, except for flame thickness. Mitu et al.\textsuperscript{22} studied the influence of inert gas (He, Ar, N$_2$, or CO$_2$) on the laminar burning velocity of methane–air mixtures. They found that dilution with increasing amounts of additives determines the decrease of laminar burning velocity and maximum flame temperature among all investigated compositions of the methane–air mixtures.

Although the flames of pure CH$_4$ and CO/H$_2$ syngas diluted by nitrogen and carbon dioxide have been extensively studied and the effects of nitrogen and carbon dioxide dilution on the combustion are well explored, the literature on the effects of inert gases on combustion characteristics of biomass gases is relatively scarce and the inhibition effect of inert gases on flame combustion is different. Under different inert gas concentrations, the ignition limit, flame stability, combustion heat value, and other parameters of the new tertiary CO/CH$_4$/H$_2$ mixture are not clear enough. Moreover, there is need for obtaining detailed parameters for boiler combustion and internal combustion engine operation in a biomass gasification power plant. Prevention of explosion of this new type of tertiary fuel must be considered during transportation, fuel usage, and storage. Therefore, it is quite necessary to understand the effect of inert gases on the adiabatic temperature and laminar combustion velocity of fuels.

This work aims to obtain the effects of different CO$_2$/N$_2$ contents (up to 60% in fuel volume) on combustion features of laminar premixed bio-syngas flame using ANSYS CHENKIN-PRO. The laminar burning velocities and adiabatic temperatures of $H_2$–CO/CH$_4$/CO$_2$/N$_2$/air mixtures have been numerically calculated with various equivalence ratios (0.6–1.6). The thermal-diffusion and chemical effects on the flame structure, including element species mole fraction, production rate, and net reaction speeds of main reactions, are quantitatively discussed. The mole fraction and formation mechanism of NO$_x$ and O, H, and OH active radicals under different CO$_2$/N$_2$ contents are analyzed. Besides, the sensitivity coefficient of the main reaction to the molar fraction of the active radicals is discussed.

### 2. MECHANISM AND MODEL

#### 2.1. Mechanism Validation and Computational Methods

In the research, the laminar burning velocities and adiabatic temperatures of CO/CH$_4$/H$_2$/CO$_2$/N$_2$/air mixtures were numerically simulated in CHEMKIN-PRO. A steady, adiabatic, one-dimensional freely propagating flame model was used to determine premixed laminar flame speeds by the PREMIX code.\textsuperscript{23} The models of premixed flame can solve a set of governing differential equations, such as the steady-state mass, species, and energy conservation equations. Meanwhile, the Soret effect and multicomponent transport model were taken into consideration. In the calculation process, the computational domain was set from $-2$ to $10$ cm and GRAD and CURV values were set at 0.1 to ensure that the maximum number of grids was 900, which satisfied the calculation requirement. Furthermore, this number proved sufficient in rendering the simulation as grid-independent.

One-dimensional flow with uniform inlet conditions was assumed. The governing conservation equations were reduced to the following:

**Continuity**

\[
\dot{M} = \rho u A
\]

**Energy**

\[
\frac{M}{dx} \frac{dT}{dx} - \frac{1}{c_p} \left( \frac{\lambda A}{dx} \frac{dT}{dx} \right) + \frac{A}{c_p} \sum_{k=1}^{k} \rho Y_k V_k c_{pk} \frac{dT}{dx} + \frac{A}{c_p} \sum_{k=1}^{k} \dot{\omega}_k h_k W_k + \frac{A}{\varepsilon_p} \dot{Q}_{rad} = 0
\]

**Species**

\[
\frac{M}{dx} \frac{dY_k}{dx} + \frac{A}{dx} (\rho A Y_k V_k) - A \dot{\omega}_k W_k = 0, \ (k = 1, \ldots, K_p)
\]

### Table 1. BDG Composition (Molar Fraction) from Different Biomass Sources and Conversion Processes\textsuperscript{4}

| BDGs     | CO   | CH$_4$ | H$_2$ | CO$_2$ | N$_2$ | biomass     | reaction agent | type of gasifier | ref  |
|----------|------|--------|-------|--------|-------|-------------|----------------|------------------|------|
| GG-W     | 20.67| 11.11  | 5.37  | 15.52  | 47.33 | rice husk   | air            | CFBG             | 5    |
| GG-M     | 16.67| 9.77   | 8.96  | 21.68  | 42.92 | rice husk   | air            | CFBG             | 6    |
| GG-X     | 16.9 | 9.77   | 10.01 | 20.13  | 43.19 | rice husk   | air            | BFBG             | 7    |
| GG-K     | 6.32 | 13.74  | 14.65 | 5.15   | 53.09 | mixed plastic wastes | air | TSG             | 8    |
| GG-M     | 19.25| 0.3    | 17.1  | 11.05  | 52.3  | rubber wood | steam + air    | DDG              | 9    |
| GG-M     | 32   | 0.13   | 50    | 8      | 8.87  | wood chip   | steam          | MS               | 10   |
| GG-R     | 13.99| 4.82   | 19.53 | 18.36  | 43.3  | oil palm trunk | steam + air | DDG              | 11   |
| GG-W     | 38   | 2.8    | 36    | 21     | 2.3   | cotton stalk pellets | pure O$_2$ | TSG              | 12   |
| GG-B     | 32   | 33     | 11    | 27     | 5     | almond shells | steam + O$_2$ | BFBG             | 13   |
| GG-L     | 37.65| 4.78   | 27.17 | 28.89  | 1.51  | sewage sludge | steam + O$_2$ | DDG              | 14   |

\textsuperscript{4}CFBG = circulating fluidized bed gasifier, BFBG = bubbling fluidized bed gasifier, TSG = two-stage gasifier, DDG = downdraft fixed-bed gasifier, MS = modeling and simulation.
Equation of state
\[ \rho = \frac{PW}{RT} \]  
(4)
where \( x \) represents the one-dimensional coordinates, \( M \) denotes the total mass flow rate of gas components, \( Y_k \) represents the \( k \)th species mass fraction, \( T \) represents the temperature in the \( x \) direction, \( P \) represents the pressure in the \( x \) direction, \( \rho \) means the density of the mixture, \( u \) represents the velocity of the mixed fluid in the \( x \) direction, \( W_i \) represents molecular weight of the \( k \)th species, \( R \) is the general constant of gas, \( \bar{W} \) represents the average molecular weight of the mixture, \( \lambda \) is the heat conductivity of the gas, \( \omega_k \) represents the heat capacity of the mixed gas at constant pressure, \( \gamma_k \) expresses the \( k \)th species heat capacity at constant pressure, \( \dot{\omega}_k \) is the production molar rate through the chemical reaction of the \( k \)th species, \( \dot{\omega}_k \) indicates the specific enthalpy of the \( k \)th gas, \( Q_{\text{rad}} \) expresses the radiation heat loss of mixture, and \( A \) indicates the cross-sectional area of the flow tube.

The flame speed calculator simulates a freely propagating flame at 298 K and 1 atm, the fixed-flame coordinate system was established, and the initial flow rate parameters of flue/air mixtures were set between 0.01 and 0.08 g/(cm²·s). Table 2 shows the reactants' mole fractions for the computational flames. The inert gas ratio is defined as \( X_{\text{inert}} = (n_{\text{CO}} + n_{\text{N}_2}) / 100\% \times (n_{\text{H}_2} + n_{\text{CH}_4} + n_{\text{CO}_2} + n_{\text{N}_2}) \), where the mole fractions of \( X_{\text{inert}} \) is 0, 30 and 60% in the present calculation and consistent with the proportion of inert gas in the actual gasification gas component. In addition, to make the calculation more accurate, the flue/air mixture flow rate in “C1-Inlet” of the model decreases with an increase of the proportion of inert gas.

In the present work, GRI-Mech was employed as the chemical mechanism to simulate the premixed laminar flame speed in CHEMKIN-PRO. The GRI 3.0 mechanism consists of 325 elementary chemical reactions with associated rate coefficient expressions and thermochemical parameters for the 53 species. It has been widely used in the numerical simulation of hydrocarbon fuel combustion and has been validated by a great amount of experimental data. Figure 1 shows the adiabatic temperature and laminar burning velocities for F1 and methane combustion in three widely acknowledged reaction mechanisms: GRI-Mech 3.0, USC-Mech, and San Diego-Mech. It can be seen from Figure 1 that the results of adiabatic temperature and laminar burning velocities calculated with these mechanisms are in well agreement. Furthermore, the computed methane laminar combustion velocity is also in well agreement with the experimental data from some literature works. Moreover, the optimized GRI-Mech 3.0 mechanism includes the NOx formation reaction and is hence selected.

2.2. Sensitivity Analysis. CHEMKIN-PRO sensitivity analysis is used to solve the results of flame experiments. Sensitivity analysis not only gives researchers a deep understanding of the main control parameters of the reaction process but also can be applied for uncertainty analysis, that is, characterizing the uncertainty of model output as a result of improperly known parameters. In some times, the sensitivity coefficients are often normalized expressed with eq S

\[ S_F = \frac{\alpha_i}{X_{k}^{\max}} \frac{\partial X_k}{\partial \alpha_i} \]  
(5)
where \( S_F \) denotes the sensitivity coefficient, \( \alpha_i \) means the constants of the reaction rate, and \( X_{k}^{\max} \) means the maximum species mole fraction.

2.3. Adiabatic Temperature. The adiabatic temperature was computed by gas-phase equilibrium program EQUIL. The gas-phase chemistry (chemical reactions and rate
parameters) and thermochemical data required for both are also based on GRI 3.0. In numerical simulations, the unburnt gas mixture has been assumed to be in a closed adiabatic system under constant pressure conditions.

3. RESULTS AND DISCUSSION

3.1. Adiabatic Temperature and Laminar Burning Velocity. Figure 2 shows the variation distribution of the adiabatic temperature and laminar burning velocity of different fuel components.

The proportion of inert gas increasing from 0 to 60%, the equivalence ratio corresponding to the peak adiabatic temperature decreases from 1.05 to 1 and the temperature decreases by about 478 K. Meanwhile, the laminar burning velocity is also decreased significantly and the equivalence ratio corresponding to its maximum peak value decreases from 1.25 to 1, which is decreased by about 62 cm/s.

The influence of inert additives on laminar burning velocity was assigned mostly to their ability to change the thermal properties of flammable mixtures by changing the heat capacity and subsequently the flame temperature. The simulation results of this work are similar to those reported for pure methane earlier. The increase in the concentration of inert gases dilutes the concentration of fuel, leading to a decrease in heat release and reaction rate. On the other hand, it also influences the thermal-diffusion coefficient and oxidation reaction kinetics of the mixture. As shown in Figure 2, the ability of CO₂ to affect the flame propagation speed of fuel is obviously stronger than that of N₂. According to the literature, CO₂ has a stronger chemical effect and heat capacity than N₂ and it has also been found that CO₂ is directly involved in chemical reactions through CO + OH ⇔ H + CO₂.35,38,39

3.2. Flame Structures. Figure 3 shows the flame structure profiles and production rates of the laminar-premixed flame with different components of the fuel mixture (F1, F2, F5, F6, and F9) at the equivalence ratio Φ = 1, P = 1 atm, and Tₐ = 298 K. As can be seen, the combustion reaction occurs mainly in the range of 3.92–4.02 cm. Moreover, the reaction of H₂ always takes precedence over CO and CH₄. Also, this priority becomes more pronounced as the concentration of CO₂ increases. The four main element reactions of H₂ combustion are H + O₂ ⇔ O + OH (R38), H + CH₄ ⇔ CH₃ + H₂ (R53), OH + H₂ ⇔ H + H₂O (R84), and OH + CO ⇔ H + CO₂ (R99). The sensitivities of H₂ reactions at different inert gas concentrations are shown in Figure 4. The results show that R53 and R99 mainly promote the generation of H₂ while R38 and R84 mainly promote the consumption of H₂. When the CO₂ concentration increases from 30 to 60%, the sensitivity coefficient of R38 decreases obviously, which promotes the consumption of H₂. This may be due to the reaction of CO₂ and hydrogen with reverse water gas, which consumes a certain amount of hydrogen.

In addition, the decrease in the molar fraction of CO is always slower than that of H₂ and CH₄ and may also be related to the early positive production rate. With an increase of inert gas concentration, the sensitivity of the element reaction R99, OH + CO ⇔ H + CO₂, which mainly affects the concentration of CO, becomes larger, thus reducing the consumption of CH₄.

This observation is consistent with the results of the effect of CO production rate on molar fraction proposed by Zhou et al.2

CH₄ consumption occurs mainly through the following reactions: H + CH₄ ⇔ CH₃ + H₂ (R53), OH + CH₄ ⇔ CH₃ + H₂O (R98), O + CH₄ ⇔ OH + CH₃ (R11), OH + CO ⇔ H + CO₂ (R99), and H + O₂ ⇔ O + OH (R38). When inert gas is not included, R53 plays a dominant role. However, with an increase of inert gas concentration, the sensitivity coefficient of R99 decreases obviously, and the consumption of CH₄ is much far more than that of R53.

Figure 5 presents the net reaction rates of ten main elemental reactions that were selected at different inert gas concentrations during combustion. Among them, R38 (H + O₂
O + OH) is an important chain branching reaction in the combustion process, producing a larger number of O and OH active radicals, which is of great significance to the adiabatic temperature of fuel combustion and the velocity of laminar flame propagation. As shown in Figure 5, with the addition of inert gases, the net reaction rate of each reaction is reduced by

Figure 3. Flame structure profiles and production rates of fuel mixtures with different compositions: (a, d) F1, CO2 = 0 N2 = 0; (b, e) F2, CO2 = 0 N2 = 30%; F6, CO2 = 0 N2 = 60%; and (c, f) F5, CO2 = 30% N2 = 0; F9, CO2 = 60% N2 = 0.
an order of magnitude. In addition, with the concentration of CO2 from 30 to 60%, the maximum peak of the net reaction rate of all reactions is shifted to the right, while the reaction interval is elongated, thus reducing the laminar flame speed of the fuel mixture.

3.3. Effect of Inert Gas Addition on NOx Formation. NOx have a great influence on air pollution. NOx is formed, on the one hand, by the nitrogen element in the fuel and, on the other hand, mainly by the oxidation of N2 in the air. The effects of inert gas on NOx production from CH4 combustion have been reported in previous literature works.40,41 Figure 6 shows the effects of different inert gas concentrations on the formation of NO, N2O, and NO2. As shown in the diagram, CO2 has the obvious inhibitory effect on the formation of NO but it is a promoting effect on NO2 during the combustion process. However, when the gas concentration reaches equilibrium in the whole reaction process, the molar fraction of NOx is positively correlated with the nitrogen content in the fuel component at the same concentration of the inert gas. In addition, since the molar fraction of NO is much greater than the order of magnitude of N2O and NO2, the amount of NOx in the whole reaction decreases with increasing N2 and CO2 concentrations. The results of this paper are similar to those reported by Xiang et al.42 on the effect of CO2 on the combustion of methane and NOx formation.

Figure 7 shows the production rate of the main NO reaction at different inert gas concentrations. The formation of NO is mainly through the following reaction: NNH + O ⇌ NO + OH (R208), N + OH ⇌ NO + H (R180), HNO + H ⇌ H2 + NO (R214), N + O2 ⇌ NO + O (R179), and NH + O ⇌ NO + H (R190). In general, the extended Zeldovich mechanism in the high-temperature region contains a chain reaction R178, R179, and R180 that dominates the formation of NO. However, in this paper, the element reaction R208 has a higher rate of production of NO in all working conditions. The NNH mechanism was proposed by Bozzelli et al. and verified by Harrington et al. and Hayhurst et al.43,44 At high temperatures, when the hydrogen atom is more than 0.1%, NNH is formed rapidly by the reaction of H + N2 ⇌ NNH. When the concentration of the inert gas is small, the reaction of NNH + O ⇌ NH + NO (R208) is very important for the amount of NO produced by the fuel mixture in air, as shown in Figure 5. However, with an increase of inert gas concentration, especially the concentration of CO2 from 30 to 60%, the reaction temperature and the number of H/O/OH active radicals decreased, resulting in a significant decrease in the formation rate of all reactions. Thus, the amount of NO is reduced. As shown in Figure 6, in the combustion process, as the concentration of the inert gas increases, the amount of NO2 produced increases as opposed to the result of NO. This is due to the formation of NO2 mainly through reaction HO2 + NO ⇌ NO2 + OH (R186) and consumption through reaction NO2 + H ⇌ NO + OH (R189). Meanwhile, the formation of HO2 free radicals is mainly through reaction H + O2 + M ⇌ HO2 + M (R33) at low temperatures.

3.4. Effect of Inert Gas Addition on the Formation of H, O, and OH Active Radicals. H, O, and OH active radicals play an essential role in combustion reactions.13,46–48 They exist in almost every elementary reaction including chain initial reaction, chain propagation reaction, and chain termination reaction. The reaction rate of the whole system can be directly affected by the process of impact, decomposition, reduction, and oxidation. Therefore, the effect of different inert gas concentrations on the formation of active radicals in the combustion process of CO/CH4/H2/air mixture is also analyzed in this paper. Figure 8 shows the molar fraction distribution of H, O, and OH active radicals at different inert gas concentrations. At the same time, to understand the effect of CO2/N2 on the main elements of active radicals, the sensitivity analysis of H, O, and OH active radicals under different inert gas concentrations is presented in Figure 9. As shown in Figure 8, the molar fractions of H, O, and OH decrease significantly with an increase of inert gas concentration, consistent with the expected results. Moreover, the inhibition of CO2 is significantly stronger than that of N2. The content of CO2 in pure CO/CH4/H2/air mixture increases to 30% and 60%, the maximum molar fractions of H, O and OH active radicals are almost reduced by nearly 40% and 80%, respectively. When the content of N2 increases to 30% and 60%, the maximum molar fractions of H, O and OH active radicals are almost reduced by nearly 20% and 50%, respectively.

The normalized logarithmic sensitivity coefficient of the H and O mole fractions with respect to the reaction rate coefficients of each elementary reaction is very similar, but it is different from that of OH, as shown in Figure 9. The chain branching/propagating reactions, H + O2 ⇌ O + OH (R38), OH + CH3 ⇌ CH2(S) + H2O (R97), OH + CO ⇌ H + CO2 (R99), HCO + M ⇌ H + CO + M (R167), O + CH2 ⇌ H + H + CO (R284), show positive sensitivity coefficients, which contribute to promote the formation of free radicals. At the same time, it can be seen from the diagram that the content of inert gas has a great effect on elemental reaction R38. When the CO2 content increases to 60%, R38 has the largest positive sensitivity coefficient and far exceeds the other flames. However, R99 always has a high positive sensitivity coefficient and is less affected by inert gas. The results indicate that R38 and R99 play an important role in the production of active free radicals and the increase of reaction rate. On the contrary, the chain termination reactions, H + O2 + M ⇌ HO2 + M (R33), H + O2 + H2O ⇌ HO2 + H2O (R35), H + O2 + N2 ⇌ HO2 + N2 (R36), H + OH + M ⇌ H2O + M (R43), H + CH2=CH(M) ⇌ CH4+(M) (R52), are constantly consuming active free radicals, diminishing the concentration of free radicals, impeding the reaction. Among them, R35 has the most...
negative sensitivity coefficient and generates a larger number of low-active \( \text{HO}_2 \) radicals and combustion products (H\(_2\)O), which affect the collision efficiency of the third body recombination and inhibit the reaction. With an increase of inert gas content, this phenomenon also becomes more obvious. In addition, it can be seen from the sensitivity coefficient of OH that when the N\(_2\) content is up to 60%, the chain termination reactions, H + O\(_2\) + H\(_2\)O \(\Leftrightarrow\) HO\(_2\) + H\(_2\)O (R35), H + O\(_2\) + N\(_2\) \(\Leftrightarrow\) HO\(_2\) + N\(_2\) (R36), H + OH + M \(\Leftrightarrow\) H\(_2\)O + M (R43), H + CH\(_3\)(+M) \(\Leftrightarrow\) CH\(_3\)(+M) (R52), 2OH(+M) \(\Leftrightarrow\) H\(_2\)O\(_2\)(+M) (R85), have a higher negative sensitivity coefficient. With an increase of N\(_2\) content, the ability of R36 and R43 to reduce free radicals was stronger than that of CO\(_2\). This may be due to the chemical effects of direct participation of N\(_2\) in the reaction.\(^{49-51}\)

Figure 5. Net reaction rates of main reactions at different inert gas concentrations: (a) F1, CO\(_2\) = 0 N\(_2\) = 0; (b) F2, CO\(_2\) = 0 N\(_2\) = 30%; (c) F6, CO\(_2\) = 0 N\(_2\) = 60%; (d) F5, CO\(_2\) = 30% N\(_2\) = 0; and (e) F9, CO\(_2\) = 60% N\(_2\) = 0.
3.4.1. H. Figure 10 shows the production rate of H active radicals under different inert gas components. As can be seen from Figure 10, the formation and consumption of H are mainly through the following reactions: OH + H2 ⇔ H + H2O (R84), OH + CO ⇔ H + CO2 (R99), O + H2 ⇔ H + OH (R3), O + CH3 ⇔ H + CH2O (R10), O + CH3 ⇔ H + H2 + CO (R284), H + O2 ⇔ O + OH (R38), H + CH4 ⇔ CH3 + H (R53), H + CH3O ⇔ HCO + H2 (R58), H + CH2 (M) ⇔ CH4 (M) (R52), and H + HO2 ⇔ 2OH (R46). Among them, R84, R99, R3, R10, and R284 have positive rates of production to promote the formation of H radical, while the others are...
negatively consumed radicals. R84 and R38 have the most positive rate of production and the most negative rate of production, respectively. Also, the production rate of each reaction also decreases with an increase of inert gas concentration in all reactions.

3.4.2. O. Figure 11 shows the production rate of O active radicals under different inert gas components. The formation and consumption of O are mainly through the following reactions: $H + O_2 \rightleftharpoons O + OH$ (R38), $O + CH_3 \rightleftharpoons H + CH_2O$ (R10), $O + H_2 \rightleftharpoons H + OH$ (R3), $O + CH_4 \rightleftharpoons OH + CH_3$ (R11), $O + CH_3 \rightleftharpoons H + H_2 + CO$ (R284), $O + CH_2O \rightleftharpoons OH + HCO$ (R15), and $2OH \rightleftharpoons O + H_2O$ (R86). R38, which has a positive rate of production, is the most important element reaction for the formation of O radicals. The other reactions have a negative production rate, among which R3 has the most negative production rate and it mainly consumes O radicals. Meanwhile, it can be seen from the diagram that the reaction of elements can convert them into H and OH radicals by consuming O radicals, which act as an intermediate. Moreover,
all production rates and consumption rates decrease with an increase of inert gas content.

3.4.3. OH. Figure 12 shows the production rate of OH active radicals under different inert gas components. The formation and consumption of OH are mainly through the following reactions: 

\[ H + O_2 \rightarrow O + OH \text{(R38)} \]
\[ H + HO_2 \rightarrow 2OH \text{(R46)} \]
\[ O + H_2 \rightarrow H + OH \text{(R3)} \]
\[ 2OH \rightarrow O + H_2O \text{(R86)} \]
\[ O + CH_4 \rightarrow OH + CH_3 \text{(R11)} \]
\[ OH + H_2 \rightleftharpoons H + H_2O \text{(R84)} \]
\[ OH + CO \rightleftharpoons H + CO_2 \text{(R99)} \]
\[ OH + CH_3 \rightleftharpoons CH_4 + H_2O \text{(R98)} \]
\[ OH + CH_2O \rightleftharpoons HCO + H_2O \text{(R101)} \]

As shown in Figure 12, R38 and R46 mainly generate OH by consuming H radicals, while R3, R86, and R11 mainly generate OH by consuming O radicals. All of these reactions contribute to the formation of OH.
Consumption reactions are mainly through R84 and R99, which are also the main sources of H radicals. In addition, as shown in Figure 12a, when there is no inert gas, R99 has the most negative formation rate, which is main reaction of OH. With the addition of the inert gas, R84 takes precedence over R99. As the concentration of the inert gas increases, the production and consumption of the most element reaction begin to approach zero. Thus, the number of active radicals in the reaction process was reduced and the reaction was inhibited.

4. CONCLUSIONS

The influence of different N₂/CO₂ contents (up to 60% in fuel volume) on combustion features of laminar premixed biosyngas blaze with various equivalence ratios (0.6–1.6) at standard conditions was numerically studied by ANSYS CHEMKIN-PRO with the GRI-Mech 3.0 mechanism. The thermal-diffusion and chemical effects on the flame structure, including element species mole fraction, production rate and net reaction speeds, were quantitatively discussed. The mole fraction and generation mechanism of NOx and H, O, and OH active radicals under different CO₂/N₂ contents were studied. The primary results are summarized as follows:

1. In the case of various equivalence ratios, the laminar flame speed has always had a good positive correlation with adiabatic temperature and the maximum peak point shows a left shift under different CO₂/N₂ contents. The inhibition effect of CO₂ is stronger than that of N₂, which may be related to the chemical effect and heat capacity of CO₂.

2. In flame structures, the reaction of H₂ always takes precedence over CH₄ and CO, which becomes more pronounced as the concentration of CO₂ increases. The main reactions of H₂ consumption are R38 and R84, and the negative sensitivity coefficient increases with an increase of inert gas concentration. Nevertheless, the molar fraction of CO always changes more slowly than those of H₂ and CH₄. With the addition of inert gases, the net reaction rate of each reaction decreases by an order of magnitude and the maximum peak is shifted to the right, while the reaction interval is elongated, thus reducing the laminar flame speed of the fuel mixture.

3. CO₂ has the obvious inhibitory effect on the formation of NO by reducing the amount of O radicals and obstructing the conduct of the reaction NNH + O ⇌ NH + NO but promotes the formation of NO₂ mainly through reaction HO₂ + N₂O ⇌ NO₂ + OH.

4. The molar fractions of H, O, and OH decrease significantly with an increase of inert gas concentration. Moreover, the inhibition of CO₂ was significantly stronger than that of N₂. The normalized logarithmic sensitivity coefficients of the H and O mole fractions with respect to the reaction rate coefficients of each elementary reaction are very similar, but it is different from that of OH. R35, R38, and R99 are three very important reactions for the molar fractions of OH, O, and H.

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Notes
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## REFERENCES

(1) Bhattacharya, A.; Datta, A. Laminar Burning Velocity of Biomass-Derived Fuels and its Significance in Combustion Devices. In Sustainable Energy Technology and Policies; Springer, 2018; pp 359–378.
(2) Zhou, Q.; Cheung, C. S.; Leung, C. W.; Li, X.; Li, X.; Huang, Z. Effects of fuel composition and initial pressure on laminar flame speed of H2/CO/CH4 bio-syngas. Fuel 2019, 238, 149–158.
(3) Luo, X.; Wu, T.; Shi, K.; Song, M.; Rao, Y. Biomass Gasification: An Overview of Technological Barriers and Socio-Environmental Impact. In Gasification for Low-Grade Feedstock; IntechOpen, 2018; Chapter 1.
(4) Bridgwater, A. V. The technical and economic feasibility of biomass gasification for power generation. Fuel 1995, 74, 631–653.
(5) Wu, C. Z.; Yin, X. L.; Ma, L. L.; Zhou, Z. Q.; Chen, H. P. Operational characteristics of a 1.2-MW biomass gasification and power generation plant. Biotechnol. Adv. 2009, 27, 588–592.
(6) Miao, Q.; Zhu, J.; Barghi, S.; Wu, C. Z.; Yin, X. L.; Zhou, Z. Q. Modeling biomass gasification in circulating fluidized beds. Int. J. Energy Power 2013, 2, 57–63.
(7) Xiong, Q.; Yeganeh, M. M.; Yaghoubi, E.; Asadi, A.; Doranehgard, M. H.; Hong, K. Parametric investigation on biomass gasification in a fluidized bed gasifier and conceptual design of gasifier. Chem. Eng. Process. Process Intensif. 2018, 127, 271–291.
(8) Kim, J. W.; Mun, T. Y.; Kim, J.; Kim, J. S. Air gasification of mixed plastic wastes using a two-stage gasifier for the production of producer gas with low tar and a high calorific value. Fuel 2011, 90, 2266–2272.
(9) Giurcan, V.; Mitu, M.; Razus, D.; Oancea, D. Laminar Flame Propagation in Rich Ethane-Air-Inert Mixtures. Rev. Chem. 2016, 67, 1084–1089.
(10) Mehrpooya, M.; Khalili, M.; Sharifzadeh, M. M. M. Model development and energy and exergy analysis of the biomass gasification process (Based on the various biomass sources). Renewable Sustainable Energy Rev. 2018, 91, 869–887.
(11) Giurcan, V.; Mitu, M.; Movileanu, C.; Razus, D. Temperature, pressure and dilution effect on laminar burning velocity of propane-air. Rev. Roum. Chim. 2016, 61, 517–524.
(12) Wang, Z.; He, T.; Qin, J.; Wu, J.; Li, J.; Z; Liu, G.; Wu, J.; Sun, L. Gasification of biomass with oxygen-enriched air in a pilot scale two-stage gasifier. Fuel 2015, 150, 386–393.
(13) Barisoni, D.; Canneto, G.; Nanna, F.; Alonzo, E.; Braccio, G.; et al. Steam/oxygen biomass gasification at pilot scale in an internally circulating bubbling fluidized bed reactor. Fuel Process. Technol. 2016, 141, 74–81.
(14) Mitu, M.; Giurcan, V.; Razus, D.; Oancea, D. Inert Gas Influence on Propagation Velocity of Methane-air Laminar Flames. Rev. Chim. 2018, 69, 196–200.
(15) Giurcan, V.; Mitu, M.; Movileanu, C.; Razus, D.; Oancea, D. Influence of inert additives on small-scale closed vessel explosions of propane-air mixtures. Fire Saf. J. 2020, 111, No. 102939.
(16) Galmiche, B.; Halter, F.; Foucher, F.; Daguat, P. Effects of Dilution on Laminar Burning Velocity of Premixed Methane/Air Flames. Energy Fuels 2011, 25, 948–954.
(17) Hu, E.; Xue, J.; Hu, Y.; Zhang, Z.; Id, N. Numerical Study on the Effects of Diluents on the Laminar Burning Velocity of Methane/Air Mixtures. Energy Fuels 2012, 26, 4242–4252.
(18) Burbano, H. J.; Pareja, J.; Amell, A. A. Laminar burning velocities and flame stability analysis of H2/CO/air mixtures with dilution of N2 and CO2. Int. J. Hydrogen Energy 2011, 36, 3232–3242.
(19) Hu, E.; Jin, F.; Lun, P.; Xue, J.; Huang, Z.; Yang, Z. Experimental and numerical study on the effect of composition on laminar burning velocities of H2/CO/N2/CO2/air mixtures. Int. J. Hydrogen Energy 2012, 37, 18509–18519.
(20) Weng, W. B.; Wang, Z. H.; He, Y.; Whiddon, R.; Zhou, Y. J.; Li, Z. S.; Cen, K. F. Effect of N2/CO2 dilution on laminar burning velocity of H2–CO–O2 oxy-fuel premixed flame. Int. J. Hydrogen Energy 2015, 40, 1203–1211.
(21) Zhang, C.; Hu, G.; Liao, S.; Cheng, Q.; Xiang, C.; Yuan, C. Comparative study on the effects of nitrogen and carbon dioxide on methane/air flames. Energy 2016, 106, 431–442.
(22) Mitu, M.; Giurcan, V.; Razus, D.; Oancea, D. Inert gas influence on the laminar burning velocity of methane-air mixtures. J. Hazard. Mater. 2017, 321, 440–448.
(23) Kee, R. J.; Rupley, F. M.; Miller, J. A. CHEMKIN-III: A FORTRAN Chemical Kinetics Package for the Analysis of Gas-Phase Chemical and Plasma Kinetics, Sandia Report, 1989.
(24) Wang, J.; Huang, Z.; Tang, C.; Miao, H.; Wang, X. Numerical study of the effect of hydrogen addition on methane–air mixtures combustion. Int. J. Hydrogen Energy 2009, 34, 1084–1096.
(25) Smith, G. P.; Golden, D. M.; Frenklach, M.; Moriarty, N. W.; Qin, Z. GRI-Mech 3.0, 1999.
(26) Wang, H.; You, X.; Joshi, A. V.; Davis, S. G.; Laskin, A.; Egolfopoulos, F.; Law, C. K. USC Mech Version II. High-Temperature Combustion Reaction Model of H2/CO/1–C4 Compounds, 2007.
(27) Chemical-Kinetic Mechanisms for Combustion Applications, San Diego Mechanism Web Page, Mechanical and Aerospace Engineering (Combustion Research); University of California at San Diego, 2014.
(28) Liao, S. Y.; Jian, D. M.; Gao, J.; Huang, Z. H. Measurements of Markstein Numbers and Laminar Burning Velocities for Natural Gas Air Mixtures. Energy Fuels 2004, 18, 316–326.
(29) Bradley, D.; Gaskell, P. H.; Gu, X. J. Burning velocities, Markstein lengths, and flame quenching for spherical methane-air flames: a computational study. Combust. Flame 1996, 104, 176–198.
(30) Gu, X. J.; Haq, M. Z.; Laws, M.; Woolley, R. Laminar burning velocity and Markstein lengths of methane–air mixtures. Combust. Flame 2000, 121, 41–58.
(31) Gospwami, M. M.; Derks, S. S.; Coumans, K. K.; Oliveira, D. A.; Knonov, A. A.; Bastians, R. R.; Luijten, C. C.; Goey, D.; et al. The effect of elevated pressures on the laminar burning velocity of methane + air mixtures. Combust. Flame 2013, 160, 1627–1635.
(32) Pagliaro, J. L.; Linteris, G. T.; Sunderland, P. B.; Baker, P. T. Combustion inhibition and enhancement of premixed methane–air flames by halon replacements. *Combust. Flame* 2015, 162, 41–49.

(33) Turányi, T. Applications of sensitivity analysis to combustion chemistry. *Reliab. Eng. Syst. Saf.* 1997, 57, 41–48.

(34) Lutz, A. E.; Rupley, F. M.; Kee, R. J.; Reynolds, W. C.; Meeks, E. EQUIL: A CHEMKIN Implementation of STANJAN for Computing Chemical Equilibria; Reaction Design Inc., 1998.

(35) Liu, F.; Guo, H.; Smallwood, G. J. The chemical effect of CO2 replacement of N2 in air on the burning velocity of CH4 and H2 premixed flames. *Combust. Flame* 2003, 133, 495–497.

(36) Glassman, I.; Yetter, R. A.; Glumac, N. G. *Combustion*; Academic Press, 2014.

(37) Jones, A. R. Combustion physics. *Phys. Educ.* 1985, 20, 292.

(38) Hu, E.; Xue, J.; Huang, Z.; Id, N. Numerical Study on the Effects of Diluents on the Laminar Burning Velocity of Methane–Air Mixtures. *Energy Fuels* 2012, 26, 4242–4252.

(39) Galmiche, B.; Halter, F.; Foucher, F.; Dagaut, P. Effects of Dilution on Laminar Burning Velocity of Premixed Methane/Air Flames. *Energy Fuels* 2011, 25, 948–954.

(40) Konnov, A. A.; Alvarez, G. P.; Rybitskaya, I. V.; Ruyck, J. D. The Effects of Enrichment by Carbon Monoxide on Adiabatic Burning Velocity and Nitric Oxide Formation in Methane Flames. *Combust. Sci. Technol.* 2008, 181, 117–135.

(41) Lee, C. E.; Lee, S. R.; Han, J. W.; Park, J. Numerical study on effect of CO2 addition in flame structure and NOx formation of CH4-air counterflow diffusion flames. *Int. J. Energy Res.* 2001, 25, 343–354.

(42) Wu, J.; He, T.; Qin, J.; Li, J.; Zh, Z.; Liu, G.; Wu, J.; Sun, L. Gasification of biomass with oxygen-enriched air in a pilot scale two-stage gasifier. *Fuel* 2015, 150, 386–393.

(43) Bozzelli, J. W.; Dean, A. M. O + NNH: A possible new route for NOx formation in flames. *Int. J. Chem. Kinet.* 1995, 27, 1097–1109.

(44) Harrington, J. E.; Smith, G. P.; Berg, P. A.; et al. Evidence for a new no production mechanism in flames. *Symp. Combust.* 1996, 26, 2133–2138.

(45) Hayhurst, A. N.; Hutchinson, E. M. Evidence for a New Way of Producing NO via NNH in Fuel-Rich Flames at Atmospheric Pressure. *Combust. Flame* 1998, 114, 274–279.

(46) Wang, Z.; He, T.; Qin, J.; Wu, J.; Li, J.; Zh, Z.; Liu, G.; Wu, J.; Sun, L. Gasification of biomass with oxygen-enriched air in a pilot scale two-stage gasifier. *Fuel* 2015, 150, 386–393.

(47) Deng, H.; Huang, M.; Wen, X.; Chen, G.; Yao, Z.; et al. Numerical investigation of premixed methane-air flame in two-dimensional half open tube in the early stages. *Fuel* 2020, 272, 117709.

(48) Deng, H.; Yao, Z.; Chen, G.; Wen, X.; Wang, F.; Zhang, Q.; Dong, J.; Huang, M. Numerical study of the effects of laminar flame speed on flame dynamics in the early stages of flame propagation in two-dimensional half open tubes. *Int. J. Hydrogen Energy* 2021, 46, 1288–1301.

(49) Yao, Z.; Deng, H.; Dong, J.; Wen, X.; Chen, G. On explosion characteristics of premixed syngas/air mixtures with different hydrogen volume fractions and ignition positions. *Fuel* 2020, 288, No. 119619.

(50) Yao, Z.; Deng, H.; Dong, J.; Wen, X.; Zhang, Q.; et al. Effect of the Inclination Angle on Premixed Flame Dynamics in Half-Open Ducts. *ACS Omega* 2020, 5, 24906–24915.

(51) Chen, J.; Chen, G.; Zhang, A.; Deng, H.; Zheng, H.; et al. Numerical Simulation of the Effect of CH4/CO Concentration on Combustion Characteristics of Low Calorific Value Syngas. *ACS Omega* 2021, 6, 5754–5763.