

Unravelling the Regulatory Role of Supercritical CO₂ in CH₄/O₂ Combustion: Linking Reaction Pathways to Performance

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Abstract:

In the context of global energy transition and net-zero emission goals, supercritical carbon dioxide (sCO₂) technology has emerged as a core solution for next-generation low-carbon energy conversion systems. However, the combustion characteristics of fuel/oxidizer in sCO₂ environments remain underexplored. To better understand the fuel performance under sCO₂ conditions, this study takes methane combustion (CH₄) as an example, employing reactive force field (ReaxFF) molecular dynamics method, to examine the combustion performance of CH₄/O₂ under varying gas blend ratios, α (the ratio of number of sCO₂ molecules to the number of CH₄ molecules). At a representative pressure of 200 atm, the results show that when a small amount of sCO₂ is introduced ($0 < \alpha \leq 1$), the consumption rate of CH₄ is markedly accelerated, as sCO₂ lowers the activation energy for CH₄ decomposition and shortens the initial decomposition time. However, when the amount of sCO₂ exceeds that of CH₄, the system exhibits an inhibitory effect on CH₄ combustion. Notably, sCO₂ addition can reduce the net formation of CO₂ in the system, contributing to emission reduction. This work elucidates the critical pathways through which sCO₂ affects CH₄ combustion reactions and intermediate product conversion. To further investigate the dependence of pressure, simulations are extended to 100 atm - 250 atm, revealing that the optimal α range varies with pressure. This study, for the first time, clarifies the mechanism by which sCO₂ concentration regulates the CH₄/O₂ combustion, provides valuable insights for optimizing combustion chamber design in sCO₂ atmospheres.

Keywords: Supercritical carbon dioxide; Methane combustion; Reactive force field; Molecular dynamics;

1 Introduction

Coal is an important resource in the global energy system and has long occupied a key position in the energy structure and power supply, especially in China [1]. However, conventional coal combustion significantly contributes to global warming, necessitating advanced technologies for cleaner energy transitions [2]. As a major greenhouse gas, carbon dioxide (CO₂) possesses inherent thermal stability and excellent physical properties [3, 4]. Extensive research has established that gaseous CO₂ consistently suppresses combustion, primarily through physical dilution and chemical interference with radical chain reactions [5, 6]. However, CO₂ in the supercritical state overcomes such inhibitory effects and exhibits unique thermophysical advantages, emerging as a promising core component for next-generation low-carbon energy conversion technologies [7]. The favourable thermodynamic properties allow CO₂ to reach a supercritical state at a relatively low critical point (31.1°C, 7.38 MPa) [8]. Compared to traditional alternatives, power generation technologies utilizing supercritical carbon dioxide (sCO₂) achieve higher thermal efficiency in the high temperature region while driving innovation in conventional energy utilization through characteristics such as compact equipment size, reduced footprint, operational flexibility, broad temperature ranges, and associated cost savings [9, 10].

The sCO₂ power cycle was initially proposed by Feher [11] and Angelino [12], and has undergone continuous theoretical development and engineering verification since being proposed [13-17]. The development of the cycle is shown in **Figure 1**. Allam cycle, as a type of semi-closed sCO₂ cycle, utilizes a direct combustion heating mode in the combustion chamber, which exhibits higher efficiency and a wide range of fuel adaptability [18]. Because of such advantages, extensive studies have focused on improving the thermal performance through multiple dimensions, including system layout [19, 20], cycle configuration [21], key process parameters [22] and equipment design [23]. However, the performance of all system-level and component-level optimizations

fundamentally depends on the combustion chamber, the core component where fuels such as syngas (H_2/CO) and methane (CH_4) mix with sCO_2 for high-pressure oxy-combustion. Furthermore, revealing the microscopic reaction mechanism of fuel combustion provides essential theoretical support for improving combustion efficiency, controlling intermediate product evolution, and ensuring system safety [24]. Consequently, a thorough understanding of combustion reactions in sCO_2 environments is of paramount importance for cycle development.

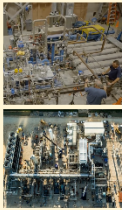
Theoretical Foundation (1968-2002)	International Situation (2011-2019)	Domestic Situation (2021...)
- Propose the cycle - Improve the cycle efficiency	- Sandia Nation Laboratory unveiled the first sCO_2 closed-cycle in the world - Net Power tested a 25MW sCO_2 power plant - France proposed a coal-fired sCO_2 cycle  (Iverson et al., 2013; White et al., 2021; Tollefson J., 2018)	- China, Xi'an Institute of Thermal Engineering - The first independently developed MW-class sCO_2 power generation test unit  (Yang et al., 2025)

Figure 1 The development of the sCO_2 power cycle.

Current research indicates that the combustion mechanism of the fuel/oxidizer system in sCO_2 environment remains limited. Relevant studies have mainly focused on syngas combustion in sCO_2 . For example, Grajales-González *et al.* [25] investigated the chemical kinetic mechanisms of syngas oxy-combustion in sCO_2 , revealing the intrinsic characteristics of the combustion process through atomic-scale simulations. But CH_4 , as a more readily available fuel, which is widely used in the semi-closed sCO_2 cycle [26], lacks well-characterized combustion behaviour in the cycle, especially regarding the reaction mechanism. Due to the chemical differences between CH_4 and syngas, existing conclusions based on syngas cannot be directly extrapolated to CH_4 combustion, resulting in a significant research gap. The theoretical deficiency restricts the mechanistic understanding and engineering optimization of CH_4 -based sCO_2 combustion system, which highlights the need for targeted investigations into the combustion characteristics and underlying reaction mechanisms of the

CH₄/O₂ system in supercritical CO₂ environments.

Therefore, to address the research gap, this study employs a reactive force field molecular dynamics (ReaxFF MD) method to systematically investigate the combustion performance of the CH₄/O₂ system in the sCO₂ atmosphere. Specifically, a gas blend ratio parameter, α , is introduced to quantitatively characterize the effect of sCO₂. By comparative analysis of the differences between CH₄/O₂ combustion reactions with and without sCO₂ over a broad range of α and operating pressures, the specific mechanism by which sCO₂ influences combustion is revealed.

2 Method

2.1 Reactive force field molecular dynamics (ReaxFF MD)

Reactive Force Field Molecular Dynamics (ReaxFF MD), developed by van Duin *et al.* [27] for hydrocarbon systems originally is a molecular dynamics technique that integrates computational efficiency and chemical process simulation capability. ReaxFF MD tracks atomic/molecular-scale particle trajectories and meets the key requirement for simulating the complex CH₄/O₂/sCO₂ combustion system in this study, as the technique is particularly suitable for modelling intermolecular reaction dynamics in large systems (≥ 1000 atoms) [28].

Compared with traditional force fields, ReaxFF MD introduces dynamic bond order, which eliminates the need for predefined atomic connectivity and instead calculates bond order in real time from interatomic distances, enabling dynamic descriptions of bond formation and dissociation [29]. Additionally, the polarizable charge model integrated in ReaxFF MD balances covalent and electrostatic interactions, which facilitates the revelation of synergistic mechanisms between reactive and non-reactive processes in complex chemical systems [30]. The forces on each atom are derived from the energy expression given as follows:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{tor}} + E_{\text{vdW}} + E_{\text{Coulomb}} \quad (1)$$

where E_{system} is the total energy of the system, the terms on the right-hand side of the equation

correspond to bonded energy (bond energy, over coordination energy penalty, undercoordination stability, lone-pair energy, valence angle energy, and torsion angle energy) and non-bonded energy (van der Waals and electrostatic energy), respectively. Due to the combination of the chemical reactivity of quantum chemistry and the computational efficiency of classical MD, ReaxFF MD has been widely applied in catalytic reactions [31, 32], field-assisted combustion [33-35], and the analysis of multiscale mechanisms of combustion [36-38], which further validating the applicability of the method for combustion simulations in this study.

2.2 Case set-ups

To explore the effect of supercritical CO₂ on the CH₄/O₂ combustion reaction, the study designed simulation experiments using the controlled variable method. The key fixed conditions of the experiments are as follows: the number of CH₄ molecules was set to 90, the number of O₂ molecules to 200, the reaction pressure was stabilized at 200 atm (ensuring CO₂ remains in the supercritical state under the reaction temperature), and the base reaction temperature was uniformly set to 3200 K. The reaction system was adjusted only by changing the number of sCO₂ molecules.

To quantitatively describe the degree of CO₂ participation, a gas blend ratio α was introduced as an evaluation index, which is defined as the ratio of the number of supercritical CO₂ molecules to CH₄ molecules, as shown in Equation (2).

$$\alpha = \frac{n(\text{CO}_2)}{n(\text{CH}_4)} \quad (2)$$

where $n(\text{CO}_2)$ and $n(\text{CH}_4)$ represent the number of CO₂ and CH₄ molecules, respectively. Meanwhile, a control group without sCO₂ ($\alpha = 0$) was specifically set up to compare and analyse the differences in the effect of CO₂ on the combustion reaction. The specific operating parameters of simulations are detailed in **Table 1**.

Table 1 Case setups in the present study

case	Number of molecules			α	T, K	P, atm
	CH ₄	O ₂	CO ₂			
1			0	0		
2			9	0.1		
3			18	0.2		
4	90	200	45	0.5	3200	200
5			90	1		
6			180	2		
7			450	5		
8			900	10		

In addition, supplementary simulations of temperature and pressure variations were conducted under different α conditions. For temperature variation, simulations covered $\alpha = 0, 0.1, 1$, and 5 at a constant pressure of 200 atm, with temperature ranging from 3000 K to 3800 K in increments of 200 K. For pressure variation, simulations covered $\alpha = 0, 0.1, 0.5, 1$, and 5 at a constant temperature of 3200 K, with pressure ranging from 100 atm to 250 atm in increments of 50 atm. **Table 2** and **Table 3** provide the complete set of operating parameters for each case.

Table 2 Supplementary temperature-variation simulation cases

case	Number of molecules			α	T, K	P, atm
	CH ₄	O ₂	CO ₂			
1			0	0		
2	90	200	9	0.1	3000-3800	200
3			90	1		
4			450	5		

Table 3 Supplementary pressure-variation simulation cases

case	Number of molecules			α	T, K	P, atm
	CH ₄	O ₂	CO ₂			
1			0	0		
2	90	200	9	0.1	3200	100-250
3			45	0.5		
4			90	1		
5			450	5		

To ensure data reliability and minimize random variability, five independent initial configurations of the combustion systems were constructed. All subsequent data analysis was based on a total of 195 independent simulations.

2.3 Details of simulation

The basic initial configuration of the simulation system is illustrated in **Figure 2**. For the ReaxFF molecular dynamics simulations, the PACKMOL code was used to randomly distribute CH₄, O₂, and CO₂ molecules within a cubic simulation domain [39]. Specifically, **Figure 2a** depicts the system containing only CH₄ and O₂ molecules (control group), while **Figure 2b** shows the system with CH₄, O₂, and CO₂ molecules coexisting (experimental group).

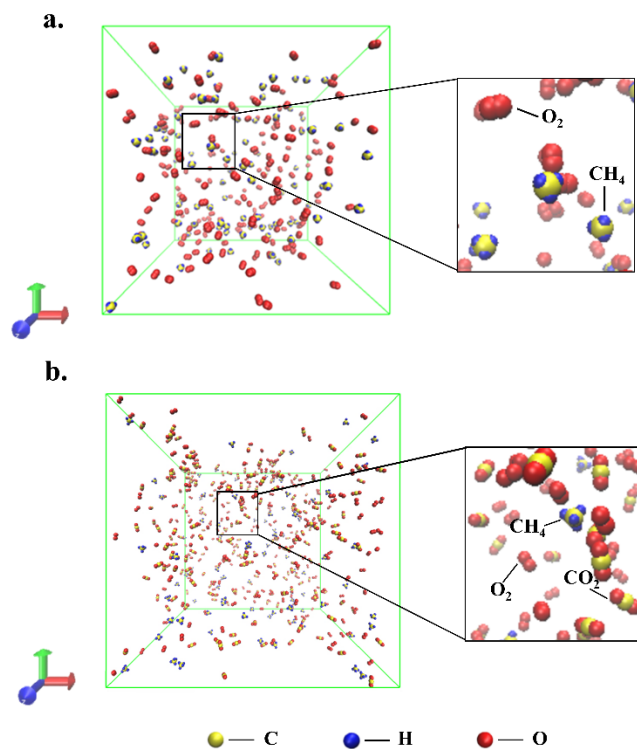


Figure 2 Basic initial configuration of the simulated case in the study a. Pure CH₄ combustion;
b. CH₄/O₂ combustion with sCO₂.

To investigate the microscopic processes of combustion reactions, this study follows the workflow shown in **Figure 3**, conducting molecular dynamics simulations via the LAMMPS platform [40]. The system utilizes the reactive C/H/O force field proposed by Chenoweth *et al.* [41], which has been successfully used to describe the initial chemical reaction events in the gas-phase oxidation of hydrocarbons at high temperatures and supercritical environment [42, 43]. Trajectory outputs are recorded every 1ps, which captures the overall reaction progress without excessive data storage [44]. All simulations are conducted under the NPT ensemble (constant particle number, pressure, and temperature) to keep sCO₂ above the critical point.

In addition, two assumptions are embedded in the simulation. One assumption is the use of periodic boundary conditions (PBCs) in all three directions. By imposing PBCs, a relatively small simulation box is assumed to represent an infinitely large, macroscopic combustion space. The practice is standard in molecular dynamics simulations because PBCs eliminate the wall effects [45]. The other assumption is that the simulation is conducted at a high temperature range. In ReaxFF MD simulations, elevated temperatures are employed to overcome inherent time-scale limitations. Selecting a higher temperature both accelerates the reaction and preserves the main reaction pathway, which is a common practice in ReaxFF MD simulations [46].

An energy stabilization protocol was implemented to prevent system instability due to high-energy configurations during the computation. First, energy minimization was performed on the system at 300 K to achieve initial energy equilibrium. Subsequently, the temperature was gradually raised to the target value under NPT constraints. Finally, continuous simulations were run at the target temperature to collect stable dynamic trajectories. After the simulations, the trajectory data were post-processed using the visualization software VMD and the path analysis tool ChemTraYzer, and were finally analysed using customized Python scripts [47, 48]. Through the post-processing, two key analyses were conducted. The first was quantifying combustion reaction patterns of CH₄/O₂ with

different fuel ratios. The second was mapping specific routes of species transformation within the system. The analyses elucidated the microscopic characteristics of the combustion process under sCO₂ influence.

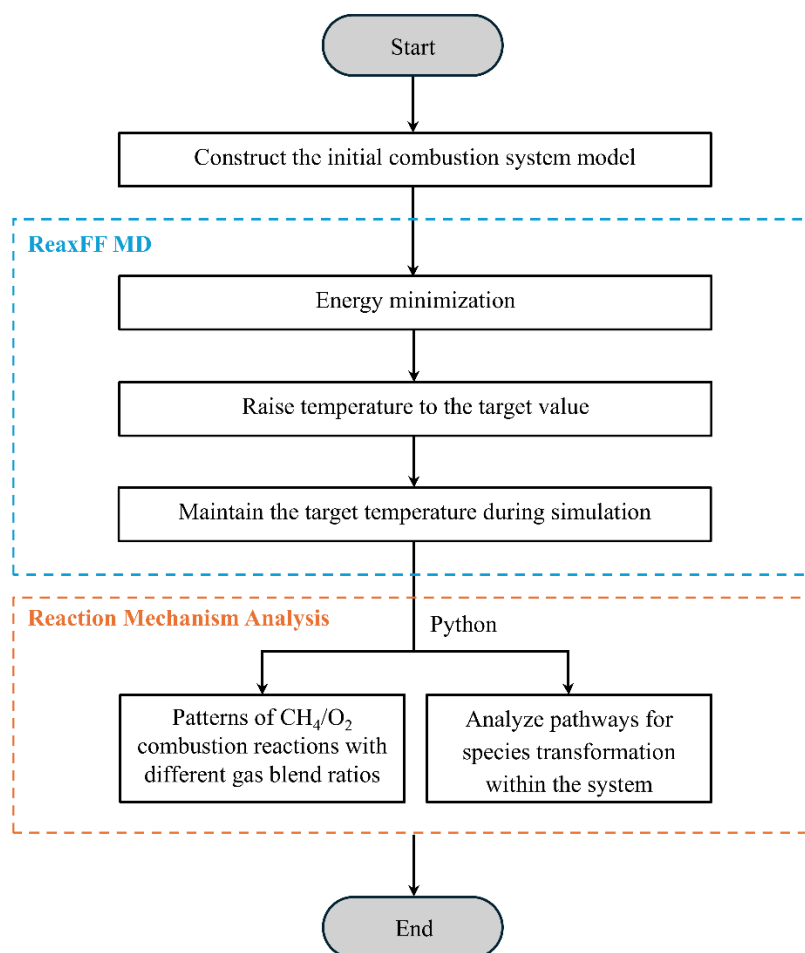


Figure 3 A flow chart of the ReaxFF MD simulation and data post-processing in the present study.

3 Results

3.1 Effects of gas blend ratio on the reactants and products at 200 atm

The influence of gas blend ratio α on the consumption of key reactants (CH₄ and O₂) in the combustion system is illustrated in **Figure 4a** and **Figure 4b**. Both figures exhibit similar trends. From an overall perspective, when the sCO₂ content is less than or equal to CH₄ ($0 < \alpha \leq 1$), the

reactant consumption rate is significantly higher than that in the system without CO₂ ($\alpha = 0$). The promoting effect reaches the peak at $\alpha = 0.1$, at which point the reactants are consumed most rapidly. In contrast, when sCO₂ content exceeds CH₄ ($\alpha > 1$), the reactant reduction rate is not only significantly lower than that in the range of $0 < \alpha \leq 1$ but also lower than that at $\alpha = 0$, indicating that excessive sCO₂ exerts an inhibitory effect on the reaction process.

Figure 4c further quantifies the specific consumption rate of CH₄. At $\alpha = 0$, the CH₄ consumption rate is approximately $4.6 \times 10^{-10} \text{ mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$. As α increases to 0.1, the rate accelerates to a maximum of $5.5 \times 10^{-10} \text{ mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$, aligning with the finding observed in **Figure 4a** and **Figure 4b**. With a further increase in sCO₂ addition, the consumption rate begins to decrease and gradually stabilizes within the range of $0.1 < \alpha \leq 1$. Nevertheless, the CH₄ consumption rate within the range remains higher than that at $\alpha = 0$, which further confirms that sCO₂ exerts a promoting effect when $0 < \alpha \leq 1$. When α exceeds 1, the CH₄ consumption rate declines sharply and maintains a stable low level ($2.9 \times 10^{-10} \text{ mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$) in the range of $1 < \alpha \leq 10$, which is far lower than that at $\alpha = 0$.

The initiation time of CH₄ molecular decomposition is shown in **Figure 4d**. At $\alpha = 0$, the average time for the first CH₄ molecule to be consumed is 126.84 ps. As the α value increases, the initiation time of CH₄ consumption occurs earlier compared to that at $\alpha = 0$. When α increases to 1, the initiation time shortens to 60.44 ps (the shortest in all α conditions), representing the most pronounced promotional effect of sCO₂ on the initiation stage. As sCO₂ continues to be added ($1 < \alpha < 10$), the initiation time of CH₄ decomposition remains shorter than that at $\alpha = 0$. Therefore, the results indicate that when $\alpha < 10$, the initiation time is consistently shorter than that in the system without CO₂, demonstrating that adding sCO₂ maintains the system in a highly active state and accelerates reaction initiation. Notably, when α is further increased to 10, the initiation time increases to 165.84 ps, slower than that at $\alpha = 0$, and at this point the inhibitory effect of excess sCO₂ dominates. The transition indicates that sCO₂ does not always exert a promoting effect on the initiation of CH₄ combustion. The trend of CH₄ decomposition initiation time differs from that of the CH₄ consumption rate. The contrast

indicates that sCO₂ exerts distinct regulatory mechanisms for the initiation stage and the continuous consumption stage of the reaction.

As shown in **Figure 4e**, H₂O, one of the products of CH₄/O₂ combustion, exhibits a generation pattern consistent with the consumption trend of reactants. In the range of $0 < \alpha \leq 1$, the amount of H₂O generation remains high. When $\alpha > 1$, the production decreases significantly. Therefore, small amounts of sCO₂ addition ($0 < \alpha \leq 1$) promote the reaction, with the strongest promoting effect observed at $\alpha = 0.1$. As α increases from 0.1 to 1, the promoting effect weakens gradually. When the sCO₂ content exceeds CH₄ ($\alpha > 1$), the effect shifts to inhibition. The results demonstrate that sCO₂ regulates the overall reaction process.

Figure 4f shows the variation of CO₂ net production under different α values. When $\alpha = 0$, no additional CO₂ is introduced into the combustion system, and the net CO₂ production is 2. As α gradually increases, net formation of CO₂ shows a continuous downward trend, decreasing from 2 at $\alpha = 0$ to -1 at $\alpha = 0.2$, and further declining to -16 at $\alpha = 10$, changing from a positive value to a negative value. Such transition indicates that the dominant direction of the reaction shifts from generating CO₂ to actively consuming CO₂ present in the system, with consumption intensity strengthening as α increases. The results demonstrate that the introduction of sCO₂ into the combustion system exerts a significant regulatory effect on CO₂ levels, effectively reducing the overall CO₂ content within the reaction environment.

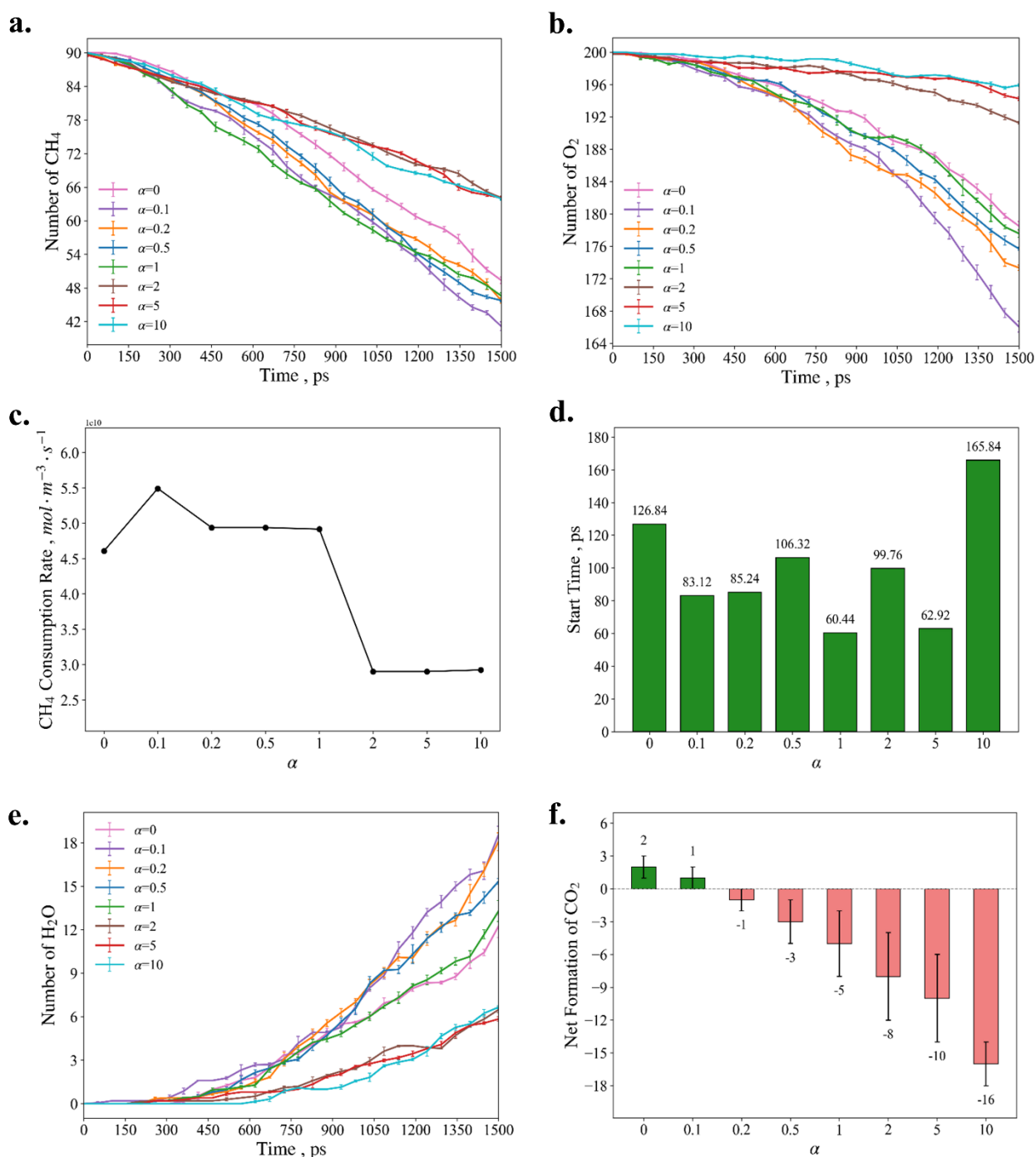


Figure 4 Effects of CO₂ on CH₄/O₂ combustion at varying gas blend ratios. a. Consumption of CH₄; b. Consumption of O₂; c. Consumption rate of CH₄; d. The average start time of CH₄ decomposition; e. H₂O formation; f. CO₂ net formation.

3.2 Effects of gas blend ratio on radicals and intermediates at 200 atm

Reaction rate closely relates to free radicals [49]. The trend of HO concentration over time during the reaction is shown in **Figure 5a**. In the early stage of the reaction (0 - 300 ps), the quantity of HO is comparable across different α conditions. As the reaction proceeds, the changes in HO quantity under different α conditions begin to exhibit differences. When $\alpha = 0$, the number of HO radicals increases slowly. Within the range of $0 < \alpha \leq 1$, HO generation rate accelerates, and the production quantity rapidly exceeds that at $\alpha = 0$, which demonstrates that a small amount of sCO₂ promotes HO formation. At $\alpha = 2$ and 5, the variation pattern of HO is similar to that at $\alpha = 0$. However, at $\alpha = 10$, HO generation exceeds that at $\alpha = 0$, with a particularly significant increase during the intermediate reaction phase (1050 ps - 1300 ps), where the amount even surpasses that in the range of $0 < \alpha \leq 1$.

To elucidate the causes of differences in HO generation under varying α conditions, **Figure 5b** illustrates the types of reaction pathways leading to HO formation. As α increases from 0 to 1, HO-generating reaction pathways increase significantly, reaching a maximum of 42 at $\alpha = 0.2$. The finding indicates that introducing a small amount of sCO₂ substantially can diversify the pathways for HO formation. When α increases to 2 and 5, the types of HO-producing reactions decrease sharply to 17 and 12, respectively, restricting HO production. At $\alpha = 10$, the types of HO-producing reactions remain low at 12, equal to that at $\alpha = 5$. Comparison with **Figure 5a** shows that the quantity of HO at $\alpha = 10$ exceeds that at $\alpha = 0$, yet **Figure 5b** reveals fewer HO generation pathways. Such phenomenon is attributed to high sCO₂ concentrations inhibiting the consumption of HO radicals, allowing HO to accumulate continuously.

Figure 5c illustrates the effect of gas blend ratio α on the number of species and elementary reactions during the reaction process. When $0 < \alpha \leq 1$, gradual addition of sCO₂ raises both the number of intermediate species and elementary reactions. Specifically, increasing α from 0 to 0.1 elevates intermediate species from 29 to 34, while elementary reactions reach a maximum near 200. As α increases to 1, although the number of intermediate species drops to 31 and the number of elementary

reactions exhibits fluctuation, the overall quantities of the two metrics remain higher than those at $\alpha = 0$. For $\alpha > 1$, intermediate species decreases to 24 - 26, below the system without sCO₂ addition. Similarly, elementary reactions also decrease compared to $0 < \alpha \leq 1$. The results indicate that modest sCO₂ addition ($0 < \alpha \leq 1$) initiates new reactions and promotes intermediate species formation, broadening reaction pathways, whereas excessive sCO₂ suppresses the processes.

Figure 5d focuses on the number of species present at the end of the simulation across different α values. At $\alpha = 0$, 16 species remain in the final state. When α reaches 0.1, the final-state species count rises to 18, reaching a peak. In addition, for $\alpha > 1$, **Figure 5d** shows that the count of final-state species stays at a relatively low level of 13 - 14. Notably, the variation trend of the final-state species count is generally consistent with that of the total number of species appearing throughout the reaction process.

Comparing **Figure 5c** and **Figure 5d**, at $\alpha = 0$, a total of 29 species is present during the reaction, while 16 remain in the final state. At $\alpha = 0.1$, 34 species emerge but only 18 remain, meaning 16 highly reactive intermediates are consumed. The consumption of the intermediates is greater than that at $\alpha = 0$. The finding indicates that small sCO₂ additions enhance consumption of reactive intermediates later in the reaction, reducing final species retention. With larger sCO₂ addition, the magnitude of the reduction in the number of species during the reaction decreases. For example, when $\alpha = 2$, only 12 highly reactive intermediates were consumed during the reaction. The result further suggests that the addition of a large amount of sCO₂ inhibits intermediate reactions, shrinking the difference between total species throughout the process and final-state species. Although small additions of sCO₂ raises reaction complexity, the conversion of intermediates into stable products is also accelerated.

Furthermore, **Figure 5e** displays the species of intermediates under different α conditions, revealing common species and unique species under various conditions. The species CH₂, CH₂O, CH₂O₂, CH₃, CH₃O, CH₃O₂, CH₄, CH₄O, CH₄O₂, CHO, CHO₂, CHO₃, CO, CO₂, H, H₂, H₂O, HO,

HO₂, O and O₂ are common to both systems with and without sCO₂ addition. When sCO₂ is added, additional common intermediates include CH, CH₅, CH₅O and CO₃. **Figure 5e** indicates that the species of intermediates involved in the reaction process change differently when the gas blend ratio α is altered. For example, CH₅O₂ and H₃O₃ are only formed under $\alpha = 0.1$ conditions. Meanwhile, CH₄O₃ is only observed under $\alpha = 1$ conditions. The species differences under varying α conditions further suggest that the presence of sCO₂ alters the reaction mechanism.

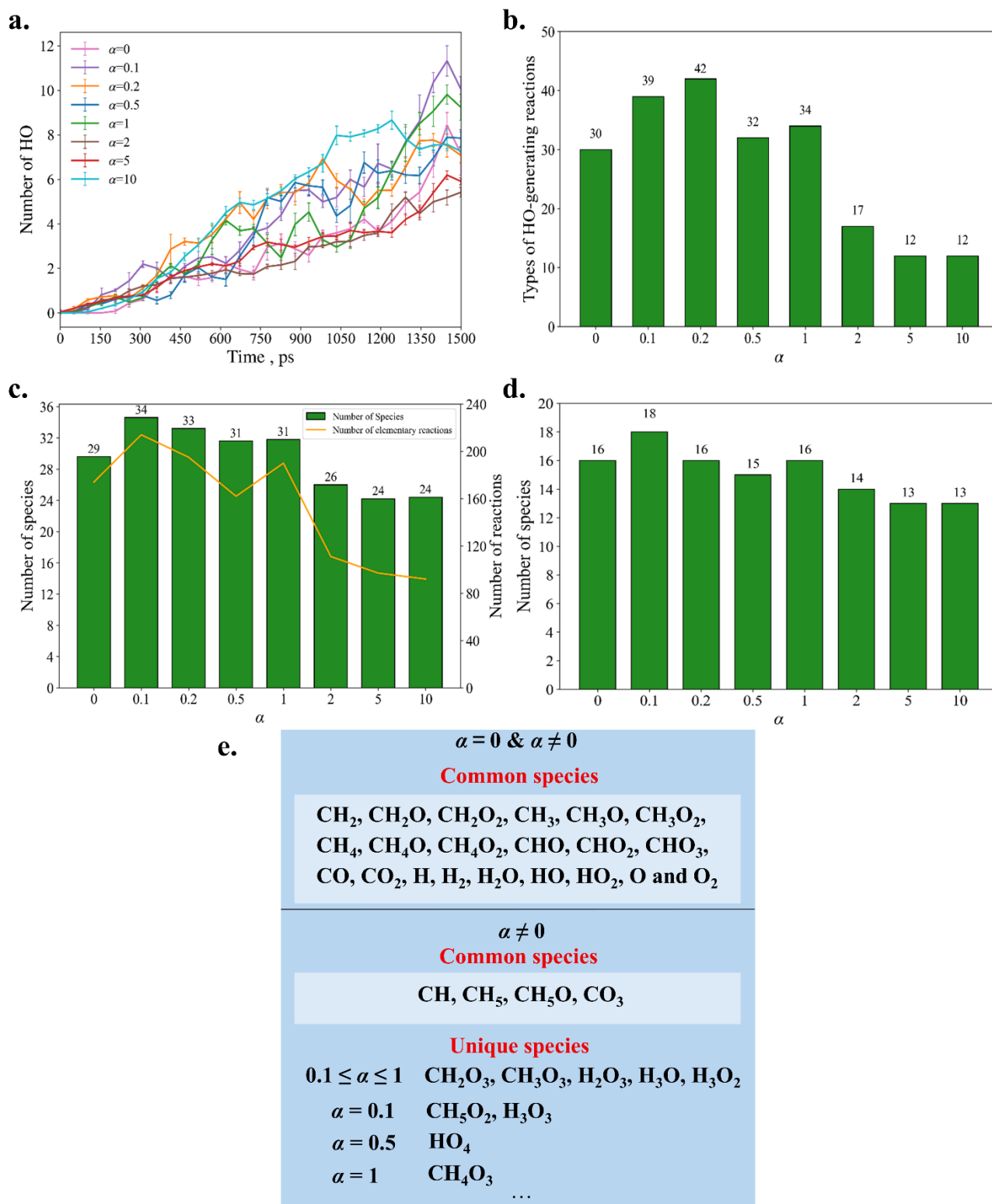


Figure 5 Effects on reaction radicals and intermediates. a. Time evolution of the number of HO radicals; b. Types of reactions generating HO radicals; c. Numbers of intermediate species throughout

the reaction; d. Number of final species at the end of the reaction; e. Comparisons of intermediates among cases at different α conditions.

3.3 Effects of gas blend ratio on the activation energy at 200 atm

In the Arrhenius equation for CH₄ decomposition reactions, the activation energy (E_a) can be calculated from the slope of the $\ln k-1/T$ curve shown in **Figure 6a**, where k represents the reaction rate constant. Activation energies for four sets of CH₄ combustion reactions, computed under the conditions of $\alpha = 0, 0.1, 1$, and 5 , are presented in **Figure 6b**.

When a small amount of sCO₂ is added ($\alpha = 0.1$), the reaction activation energy decreases and is lower than that at $\alpha = 0$. As α further increases to 1 , the activation energy rises gradually but remains lower than that in the case without sCO₂ addition. Such changes indicate that adding an appropriate amount of sCO₂ makes the reaction easier to proceed. In contrast, under high sCO₂ proportion conditions ($\alpha = 5$), E_a increases further and exceeds that at $\alpha = 0$. The finding suggests that introducing an excessive amount of sCO₂ raises the reaction activation energy, making the reaction more difficult to occur.

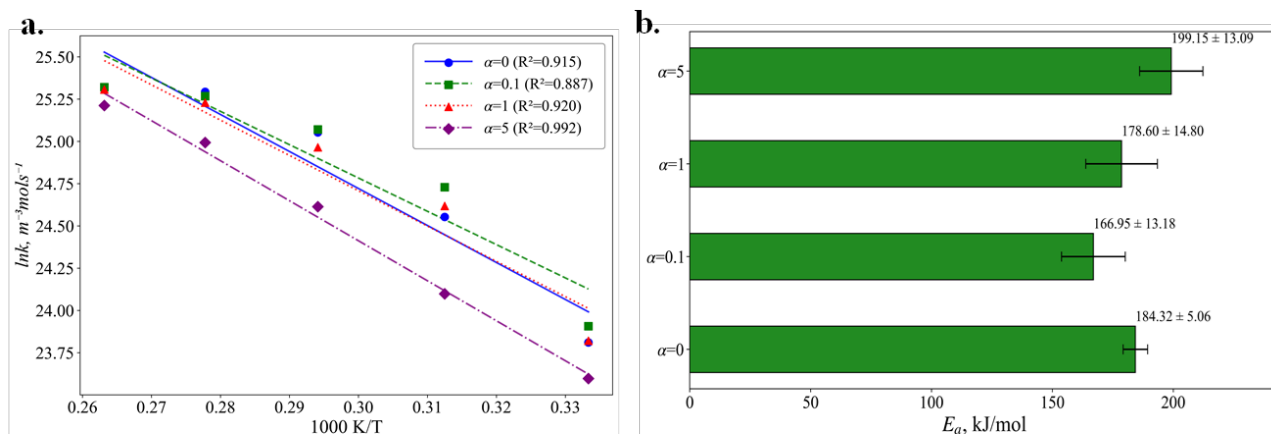


Figure 6 Activation energies for CH_4 decomposition in CH_4/O_2 combustion ($\alpha = 0$) and the combustion with added sCO_2 ($\alpha = 0.1, 0.5$ and 5). a. $\ln k$ - T curves of Arrhenius Equation. b. Activation energies obtained from the slopes of the $\ln k$ - T curves.

3.4 Effects of gas blend ratio on reaction path at 200 atm

To elucidate the impact mechanism of sCO_2 on CH_4/O_2 combustion, the analysis of reaction pathways was conducted. Examination of the reactants, products, and intermediate species revealed that the addition of a small amount of sCO_2 promotes the reaction, while excessive addition inhibits the process. Based on the finding, the gas blend ratios were divided into three groups, namely pure CH_4/O_2 combustion ($\alpha = 0$), combustion with a small amount of sCO_2 added ($0 < \alpha \leq 1$), and combustion with a large amount of sCO_2 added ($1 < \alpha \leq 10$). **Figure 7** displays the reaction pathway networks of key carbon-containing intermediates under different gas blend ratio conditions. Common and unique reaction pathways are distinguished using different colours.

To clarify the way in which sCO_2 modifies reaction pathways, **Figure 7a** first illustrates the main reaction pathway networks for $\alpha = 0$ and $0 < \alpha \leq 1$. Black arrows denote not only the reaction pathways existing at $\alpha = 0$ but also those shared within the range of $\alpha = 0$ and $0 < \alpha \leq 1$. Meanwhile, red arrows indicate the reaction pathways unique to the range of $0 < \alpha \leq 1$. The figure reveals that when the amount of added sCO_2 does not exceed CH_4 , the reaction pathways under $0 < \alpha \leq 1$ can

fully include those formed at $\alpha = 0$. Furthermore, additional new reaction pathways are formed, enriching the interconversion pathways among species during combustion. **Figure 7b** shows the network for $1 < \alpha \leq 10$, where black arrows denote the reactions still present from the $\alpha = 0$ case, and blue arrows mark specific pathways under high sCO₂ concentration. Comparing with **Figure 7a** reveals a significant reduction in black arrows, indicating that the original reaction pathways in pure methane combustion have been substantially diminished. Meanwhile, the formation of some new reactions occurs, particularly the reactions related to CO₂.

Specifically, in all three sets of combustion processes, CH₄ reacts with radicals such as H, O, and OH, and the common reaction pathways identified include CH₄→CH₃, CH₄→CH₄O, and CH₄→CH₂O. Meanwhile, the conversion pathway for CH₄ to CH₂ is present in both pure CH₄ combustion and the system with a small amount of sCO₂ added. Notably, the addition of sCO₂ induces the formation of several new reactions, including CH₄→CH₃O, CH₂O→CH₃O, CH₂O→CHO₂, and CHO₂→CHO. When the added sCO₂ content is low ($0 < \alpha \leq 1$), several unique transformation pathways emerge, including CH₂O→CHO₃, CH₂O→CH₄, CH₃→CO, and CH₂O₂→CO. The pathways for converting other substances (such as CH₃ and CH₂O) into CO have significantly increased, which can facilitate the complete oxidation of carbon-containing species. In contrast, at high sCO₂ addition levels ($1 < \alpha \leq 10$), the unique pathways observed in $0 < \alpha \leq 1$ are replaced by other new pathways, such as CH₂O→CH₃O₂ and CHO₃→CO₂. The pathway changes align with the concentration-dependent effect of sCO₂ identified earlier. When $0 < \alpha \leq 1$, the addition of sCO₂ can enrich reactive pathways to promote the material transformation. When $1 < \alpha \leq 10$, sCO₂ suppresses combustion by reducing the primary active pathways.

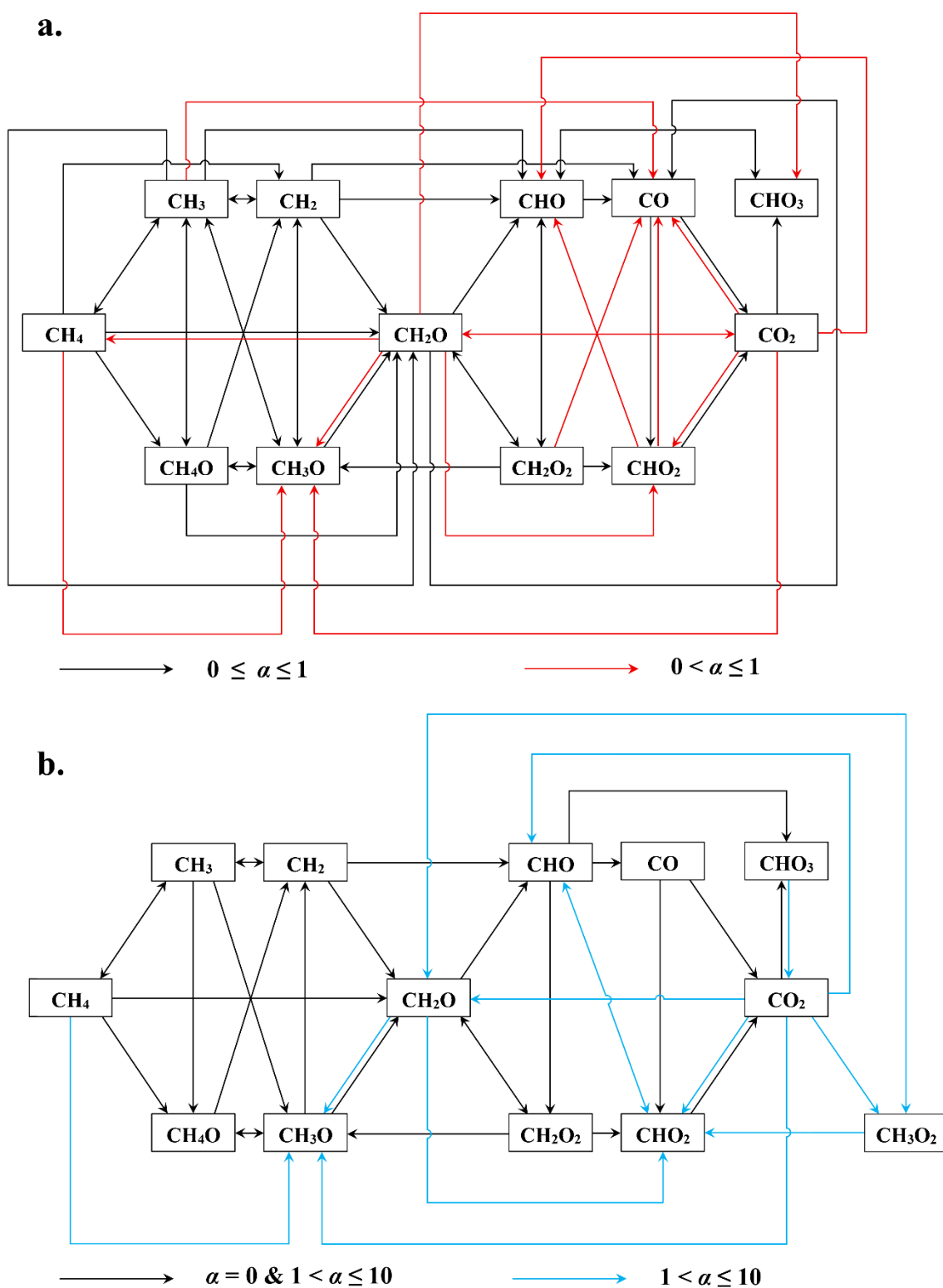


Figure 7 Reaction pathway network in different gas blend ratio conditions. a. Reaction pathway network for $\alpha = 0$ and $0 < \alpha \leq 1$; b. Reaction pathway network for $1 < \alpha \leq 10$.

To further elucidate the reaction mechanism by which CO₂ influences CH₄/O₂ combustion, **Table 4** lists the detailed reactions that CO₂ participates in. R1 (CO₂ + HO → CHO₃) takes place under all conditions. When $0 < \alpha \leq 1$, CO₂ induces reactions including R2 (CO₂ + H → CO + HO), R3 (CO₂ + O → CO₃), and R4 (CO₂ → CO + O). Specifically, R2 can generate HO radicals, which accelerate CH₄ decomposition, while R4 can produce O atoms that promote the oxidation of intermediates. These processes collectively enhance combustion by supplementing active radicals. As the α increases from 0.1 to 1, the reaction between CO₂ and intermediates gradually emerge, further facilitating the conversion among species. When α increases to 10, new reactions appear in the reaction system, such as R10 (CO₂ + O → O₂ + CO) and R11 (CO₂ + CO₂ + H → CHO₃ + CO), which compete with CH₄ for O and H and thus inhibit combustion. Additionally, with a substantial amount of CO₂ added, CO₂ can also participate in reactions to form CH₃O₂.

Throughout the combustion process, sCO₂ does not react directly with CH₄ but rather exerts influence mainly by participating in intermediate reactions, indirectly affecting the overall progress and products of the combustion reaction.

Table 4 Reaction pathways involving CO₂ under different gas blend ratios

NO.	Reaction Pathways	Ratio (α) = $\frac{n(\text{CO}_2)}{n(\text{CH}_4)}$							
		$\alpha = 0$		$0 < \alpha \leq 1$			$1 < \alpha \leq 10$		
		0	0.1	0.2	0.5	1	2	5	10
R1	CO ₂ +HO → CHO ₃	√	√	√	√	√	√	√	√
R2	CO ₂ +H → CO+HO		√	√	√	√	√	√	√
R3	CO ₂ +O → CO ₃		√	√	√	√	√	√	√
R4	CO ₂ → CO+O		√			√	√	√	√
R5	CO ₂ +H → CHO ₂			√	√	√	√	√	√
R6	CO ₂ +CH ₃ → CH ₃ O+CO				√	√	√	√	√

R7	$\text{CO}_2 + \text{CH}_2 \rightarrow \text{CH}_2\text{O} + \text{CO}$	√	√		√
R8	$\text{CO}_2 + \text{CH} \rightarrow \text{CHO} + \text{CO}$		√		√
R9	$\text{CO}_2 + \text{O}_2 \rightarrow \text{CO}_4$		√	√	√
R10	$\text{CO}_2 + \text{O} \rightarrow \text{O}_2 + \text{CO}$				√
R11	$\text{CO}_2 + \text{CO}_2 + \text{H} \rightarrow \text{CHO}_3 + \text{CO}$				√
R12	$\text{CO}_2 + \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{O}_2 + \text{CO}$				√

3.5 Effect of pressure on the optimal sCO₂ addition range

The research findings reveal that under 200 atm conditions, adding sCO₂ to the CH₄/O₂ combustion system has an optimal range where sCO₂ concentration does not exceed the CH₄ concentration. In such range, adding sCO₂ enhances combustion and reshapes oxidation pathways. To further investigate the influence of pressure on the optimal range, **Figure 8** displays the variation patterns of CH₄ consumption rates corresponding to different α conditions at pressures of 100 atm, 150 atm, 200 atm, and 250 atm.

As shown in **Figure 8**, the CH₄ consumption rate exhibits a consistent non-monotonic trend across all pressures. The CH₄ consumption rate initially rises, reaches a maximum, and then declines as α increases. The pattern confirms the existence of a pressure-specific optimal α range for maximizing CH₄ consumption. Furthermore, the result confirms the optimal α range shifts with pressure. Specifically, at 150 atm, 200 atm, and 250 atm, the optimal range for sCO₂ is $0 < \alpha \leq 1$. However, at 100 atm, when $\alpha = 1$, the CH₄ consumption rate is already slower than in systems without sCO₂, indicating a narrower optimal α range. Therefore, the optimal addition range for sCO₂ is not a fixed interval but varies with pressure.

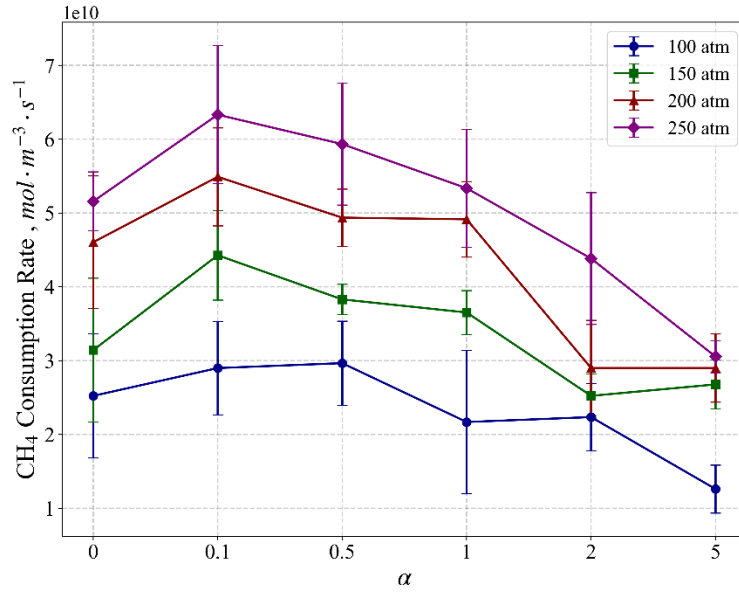


Figure 8 CH₄ consumption rates under different α conditions at varying pressures.

4. Discussion

4.1 Concentration-dependent regulatory effects of sCO₂

Based on the investigation of sCO₂ effects on CH₄/O₂ combustion conducted in the present study, the amount of sCO₂ added exhibits a distinct concentration-dependent regulatory role in the combustion process. The study confirms that at 200 atm pressure, sCO₂ exerts a promotional effect when sCO₂ addition does not exceed the content of CH₄, as the combined effect of reducing the activation energy for CH₄ decomposition, shortening the initial decomposition time of CH₄, and promoting the mutual transformation of reaction species accelerates CH₄ oxidation. In contrast, excessive sCO₂ leads to inhibitory effects on combustion. The results indicate that the addition of sCO₂ in CH₄/O₂ combustion systems exhibits an optimal range, which both accelerates the combustion reaction process and reduces the net CO₂ production in the system, reshaping the oxidation pathways. Such optimal range has not been reported in previous studies on CH₄ combustion. Furthermore, the optimal range shifts with varying pressures.

4.2 Impacts of supercritical and gaseous CO₂ on CH₄/O₂ combustion

To further elucidate the regulatory mechanism of supercritical CO₂ in combustion processes, the effects of supercritical and gaseous CO₂ on combustion reactions were compared. The present study reveals that sCO₂ at optimal concentrations can significantly enhance CH₄ oxidation rates. Specifically, the addition of an appropriate amount of sCO₂ can reduce the activation energy for CH₄ decomposition and promote the formation of intermediates and HO radicals, thereby accelerating the overall reaction. The results are consistent with previous work on sCO₂-enriched oxygenated combustion systems, which proposed that sCO₂ can form covalent intermediates with reactive species, significantly lowering energy barriers and thereby exerting a catalytic effect on combustion [50].

Such a promoting influence contrasts with the dual inhibitory mechanism exhibited by gaseous CO₂. In the gaseous state, CO₂ acts as a physical diluent, lowering the concentrations of both reactants and critical hydrocarbon intermediates, which directly lowers reaction collision frequency [5]. Chemically, gaseous CO₂ directly participates in key fundamental reactions, competing with other species for radicals, significantly decreasing the concentrations and reaction rates of key radicals such as H, O, and HO, thereby suppressing combustion [6]. Molecular simulations by Zhou *et al.* [51] further indicated that high-concentration CO₂ competes with O₂ for H radicals. The competition alters the dominant reaction of CH₄ combustion to $\text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{HO}$, reducing the main reaction rate between CH₄ and O₂ and exerting an inhibitory effect on combustion. In contrast to such inhibitory mechanism of gaseous CO₂, the promoting effect of sCO₂ observed in the present study stems from indirect involvement of sCO₂ in the reaction network. The contrasting modes of participation demonstrate that CO₂ in different states (gaseous and supercritical) engages with CH₄ combustion reactions in fundamentally different ways. Consequently, the transition to a supercritical state enables CO₂ to overcome the limitations of conventional suppression mechanisms.

4.3 Impacts of sCO₂ on CH₄ and syngas (H₂/CO) combustion

Research on supercritical CO₂ in combustion systems reveals different influences depending on fuel type. For syngas (H₂/CO) combustion, existing literature reports inhibitory effects. Grajales-González *et al.* [25] pointed out that in syngas combustion systems, increasing CO₂ concentration significantly delays ignition. However, when the main components of syngas are studied separately in supercritical H₂O/CO₂ mixtures, different results emerge. Complementary work by Fan and Lu [52] on CO oxidation revealed that high concentrations of sCO₂ suppress the formation of OH radicals, key species in chain-branching reactions. By contrast, Li *et al.* [53] studied H₂ oxidation under similar conditions and observed that sCO₂ promotes the reaction and generates additional OH radicals. The collective findings confirm that, for syngas, the effect of sCO₂ does not exhibit any concentration-dependent reversal.

In contrast to the effect in syngas combustion, the present study reveals that the role of sCO₂ in CH₄ combustion is more complex and exhibits concentration dependence. The promoting effect of sCO₂ on CH₄ oxidation at relatively low addition levels aligns with conclusions from hydrogen combustion studies [53], where sCO₂ can enhance radical generation. The results confirm that the radical-enhancing effect of sCO₂ extends from H₂ to CH₄ under supercritical conditions. However, when the amount of sCO₂ exceeds the optimal range, excessive sCO₂ competes with CH₄ for available O₂, thereby hindering the primary oxidation pathway and reducing active radical generation. Thus, such a dual role observed in CH₄ combustion is absent in syngas (H₂/CO).

5. Conclusions

The combustion in supercritical carbon dioxide (sCO₂) environments has garnered increasing attention. However, the intrinsic coupling between sCO₂ participation and CH₄/O₂ reaction kinetics remains elusive. This study, for the first time, systematically investigates the dual regulatory role of sCO₂ in CH₄/O₂ combustion by using ReaxFF molecular dynamics simulation with the gas blend

ratios ($\alpha = \text{CO}_2/\text{CH}_4$) as a key parameter. The dual regulatory mechanism fundamentally differs from the conventional diluent effect observed in syngas studies.

Specifically, at 200 atm pressure, when sCO_2 addition does not exceed the CH_4 content, the introduction of sCO_2 promotes combustion by shortening the initial decomposition time of CH_4 , reducing the CH_4 decomposition activation energy and inducing additional HO radical generation. Notably, the reduction in activation energy becomes more pronounced as α decreases, further accelerating the combustion reaction rate. However, when sCO_2 addition exceeds CH_4 content, sCO_2 exerts an inhibitory effect due to the increased reaction activation energy and reduced HO radicals. Additionally, sCO_2 influences the formation of carbon-containing products and reaction pathways of the CH_4/O_2 system, as low sCO_2 addition ($\leq \text{CH}_4$ content) enriches reaction pathways to facilitate substance mutual conversion. Beyond the kinetic modulation, the analysis of the reaction pathways reveals that sCO_2 does not directly react with CH_4 during combustion but indirectly modulates reaction processes and product formation by participating in intermediate reactions. In addition, the introduction of sCO_2 reduces the net production of CO_2 , indicating a potential pathway for lowering overall CO_2 emissions in relevant combustion systems.

The study confirms an optimal addition range for sCO_2 that ensures promotional effects on combustion. Importantly, such range is not fixed but varies with pressure. The pressure-dependent behaviour indicates that the regulatory role of sCO_2 concentration must be considered together with operating pressure in practical combustor design.

Collectively, the findings advance the fundamental mechanistic understanding of sCO_2 -assisted combustion, provide a basis for regulating combustion processes via gas blend ratios and pressure in an sCO_2 environment, and enable a synergistic enhancement of combustion efficiency along with a reduction in carbon emission intensity.

CRedit authorship contribution statement

Yuqing Liu: Writing – original draft, Investigation, Methodology, Data curation.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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