

Article Effects of Carbon Chain Length on N-Alkane Counterflow Cool Flames: A Kinetic Analysis

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Abstract: An in-depth understanding of the low-temperature reactivity of hydrocarbon fuels is of practical relevance to developing advanced low-temperature combustion techniques. The present study aims to study the low-temperature chemistry of several large n-alkanes with different carbon chain lengths in counterflow cool diffusion flames by kinetic analysis. The large *n*-alkanes that were chosen are *n*-heptane (NC₇H₁₆), *n*-decane (NC₁₀H₂₂) and *n*-dodecane (NC₁₂H₂₆), which are important components of practical fuels. Firstly, the thermochemical structure of a typical cool diffusion flame is understood through its comparison with that of a hot diffusion flame. The boundary conditions, including the ozone concentration, fuel concentration and flow velocity-where cool flames can be established—are identified with a detailed chemical mechanism that evaluates the low-temperature reactivity of the investigated *n*-alkanes. The results show that the *n*-alkane with a longer carbon chain length is more reactive than the smaller one, thereby indicating the order of $NC_{12}H_{26} > NC_{10}H_{22} > NC_7H_{16}$. This trend is qualitatively similar to the findings from non-flame reactors. The reaction pathway and sensitivity analysis are performed to understand the effects of carbon chain length on the low-temperature reactivity. The contribution of an *n*-alkane with a longer carbon chain to the dehydrogenation reaction, oxidation reaction and isomerization reaction is greater than that of a smaller *n*-alkane, and abundant O and OH radicals are generated to promote the fuel low-temperature oxidation process, thereby resulting in an enhanced low-temperature reactivity. The effects of ozone addition on the low-temperature reactivity of *n*-alkanes are also highlighted. It is found that the addition of ozone could provide a large number of active O radicals, which dehydrogenate with the fuels to generate OH radicals and then promote fuel low-temperature oxidation. The present results are expected to enrich the understanding of the low-temperature characteristics of large *n*-alkanes.

Keywords: kinetic analysis; cool flames; counterflow flames; large *n*-alkanes; low-temperature reactivity

1. Introduction

In order to mitigate greenhouse gas emissions and meet the increasingly stringent emission standards, it is necessary to improve the thermal efficiency of combustion engines. Many low-temperature combustion technologies, such as advanced lean burn gasoline engines [1,2], homogeneous charge compression ignition (HCCI) [3,4], partially premixed compression ignition (PPCI) [5], and reactivity-controlled compression ignition (RCCI) [6], have been proposed in recent decades. The development of these new-concept combustion techniques depends on a deep understanding of fuel's low-temperature oxidation kinetics, which has received increasing research attention recently. Low-temperature chemistry has been proven to have a significant impact on the engine's ignition, knock and combustion



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). efficiency [7–10]. For instance, low-temperature chemistry is dominant for auto-ignition propensity, which in turn is related to the engine knock or super-knock phenomena [11–13]. Therefore, understanding the low-temperature kinetics of transportation fuels has practical significance for the development of new-concept engines.

Previous studies mainly focused on the low-temperature combustion behavior of small molecular hydrocarbon fuels, such as butane [14–17], hexane [18,19] and dimethyl ether [7,20–22]; experimental and numerical studies on their flame structure, initiation and extinction limits were carried out. However, the relevant studies on larger hydrocarbon fuels account for a large fraction of practical transportation fuels are relatively limited. Usually, longer carbon chain *n*-alkanes are more active at low-temperature conditions, which plays an important role in the first-stage ignition process [23,24]. For these reasons, several studies have been performed to understand the low-temperature kinetics of larger *n*-alkanes, such as *n*-heptane [25–29], *n*-decane [30] or *n*-dodecane [31,32], based on premixed or counterflow cool flame configurations. In these studies, the low-temperature cool flame dynamics, such as the flame propagation speed and the extinction limits, of these *n*-alkanes were covered, and the effects of additives (including NO and ozone) on the low-temperature kinetics have also attracted extensive research attention.

For instance, Won et al. [29] investigated the effects of ozone addition on the cool flame dynamics of *n*-heptane in counterflow diffusion flame configurations. It was found that the O radical produced through the decomposition of ozone dramatically shortened the induction timescale of the low-temperature chemistry in order to establish a self-sustaining cool flame. A kinetic analysis and experimental characterization of the general cool flame structure (flame temperature, main species) were provided. Brown et al. [30] and Zhou et al. [32] investigated *n*-decane and *n*-dodecane cool diffusion flames, respectively. It was also reported that the addition of ozone was beneficial and enhanced the cool diffusion flame for large *n*-alkanes (from *n*-heptane to *n*-dodecane), and investigated low-temperature oxidation behaviors through the trends of the extinction limits of cool diffusion flames.

Besides the flame reactors, a number of studies have been performed on the lowtemperature oxidation behavior of several other alkanes (including but not limited to *n*-butane, *n*-hexane and iso-octane) based on rapid compression machines [15,33–35], shock tubes [36,37] or flow reactors [38,39]. In those studies, the experimental and kinetic study of the ignition behavior and chemical speciation during the low-temperature oxidation process were performed and has provided the foundation for developing low-temperature combustion kinetic models for target fuels. A literature study of large *n*-alkanes such as *n*-decane and *n*-dodecane [40–42] was also performed, but most of the studies focused on the pyrolysis/oxidation process in flow reactors, while relevant investigations on the low-temperature oxidation behavior, especially in flame environments, were rather limited.

This work aims to investigate the low-temperature chemistry of large *n*-alkanes (*n*-heptane, *n*-decane and *n*-dodecane) in counterflow cool flame configurations through detailed kinetic analysis. In particular, the flame boundary conditions (such as ozone concentration, fuel concentration and flow velocity) required for establishing the counterflow cool flames (i.e., the initiation limits of cool flames) are investigated, based on which the low-temperature reactivity of these *n*-alkanes can be assessed. The effects of the carbon chain length on the fuel's low-temperature reactivity are highlighted through a detailed kinetic analysis. Nevertheless, a literature survey revealed that while several studies have investigated the cool flame dynamics of individual *n*-alkanes, very few studies have studied the effects of carbon chain length on the low-temperature behaviors of large *n*-alkanes. While Reuter et al. [24] compared the extinction limits of *n*-alkane cool diffusion flames for large *n*-alkanes at low temperatures. The present study is focused on the initiation limits of cool flames, which may provide new insights into the slow initiation chemistry of *n*-alkanes at low temperatures. The present results are expected to deepen our understanding of the low-temperature kinetics of large *n*-alkanes.

This paper is organized as follows: In Section 2, the methodology of performing the

kinetic analysis on the low-temperature kinetics is introduced. In Section 3, the thermochemical structure of a typical cool diffusion flame is presented and compared with that of a typical hot diffusion flame. Then, the initiation limits of the *n*-alkane cool flames are determined. The reaction pathway and sensitivity analysis are performed to understand the effects of the carbon chain length of *n*-alkanes and the enrichment of ozone on the low-temperature combustion behavior. The major conclusions of this work are summarized in Section 4.

2. Kinetic Analysis Method

The present numerical simulations are performed with the OPPDIF code [43]. A detailed chemical mechanism is developed based on the Polimi Mech [44,45] and consists of both low- and high-temperature kinetics, which are incorporated with the Princeton O_3 sub-mechanism from the literature [46,47]. The mechanism showed the greatest fidelity to the measurements of the cool flame extinction limits [23,48] and has been shown to capture the low-temperature oxidation behavior of large *n*-alkanes combustion, and has hence been selected for further computations. More details on the simulation process are as follows. A plug flow assumption is made for the fuel/oxidizer boundaries, and the separation distance between the fuel and oxidizer nozzle is 20 mm. A mixture-averaged formula is used to calculate the species diffusion velocity without accounting for thermal diffusion. A maximum temperature of 800 K is assigned for the flame to serve as an initial guess of the numerical solution. The grid parameters of curvature and gradient are set to 0.5 and 0.6, respectively, to ensure smoothness of the solution.

Simulations are performed to investigate the influence of various boundary conditions on the initiation limits of the tested large *n*-alkanes. It has been previously reported [14,20,29] that the establishment of stabilized counterflow cool flames is difficult to accomplish due to the slow fuel reactivity chemistry at low temperatures. However, the initiation of cool flames can be enhanced by varying the boundary conditions (such as mole fraction of fuel, the ozone concentration in the oxidizer stream, or the strain rate). It is thus necessary to study the initiation boundaries of cool flames. More importantly, the initiation limits of cool diffusion flames can be used to evaluate the low-temperature reactivity of different fuels. For instance, the introduction of ozone into the oxidizer stream is frequently used to enhance the reactivity of cool flames. The critical mole fraction of ozone needed to establish a stable cool diffusion flame can be different, depending on the chemical reactivity of the fuel. It can be expected that fuel with a stronger low-temperature reactivity will need less ozone to establish a stable cool flame. In this manner, the critical initiation limits can be used as a quantitative index for ranking the fuel's low-temperature reactivity.

The detailed flame conditions under numerical investigations are summarized in Table 1, which include the mole fractions of species (Fuel, N₂, O₂ and O₃), temperatures (T_F and T_O) and nozzle exit velocity (V_F and V_O). The subscripts F and O refer to the fuel and oxidizer stream, respectively. When determining the limit of a specific boundary condition at the fuel/oxidizer stream (such as the O₃ concentration), the corresponding boundary condition at the oxidizer stream is varied to determine the limit condition where cool flames can be established, while holding the other flame conditions (such as inlet temperature, fuel concentration and flow rate) unchanged. These simulation conditions are covered to perform parametric studies on the initiation limits. When performing simulations, the O₃ mole fraction is changed from 0.1 to 0.3, and the range of the fuel concentration in the fuel stream is set between 0.003–0.6, while the flow velocity is varied from 5 to 1 cm/s. Note that very few experimental studies have been performed on low-temperature cool flames and their response to varying boundary conditions. Although future experimental validation is yet to be conducted, the present simulations are expected to provide certain references for understanding the dynamics of cool diffusion flames.

Limit	Т _F (К)	V _F (cm/s)	Fuel (Mole Fraction)	N ₂ (Mole Fraction)	Т _О (К)	V _O (cm/s)	O ₃ (Mole Fraction)	O ₂ (Mole Fraction)
O_3 concentration	550	13	0.1	0.9	300	12		
Fuel concentration	550	13			300	12	0.05	0.95
Flow rate	550		0.1	0.9	300		0.05	0.95

Table 1. The flame boundary conditions of tested *n*-alkanes.

3. Results and Discussion

In the following, the thermochemical structure of a typical cool diffusion flame (for *n*-dodecane) is presented through a comparison with that of a typical hot diffusion flame. Then, the boundary conditions required to initiate a stable cool diffusion flame are numerically determined for the tested *n*-alkanes with varying carbon chain lengths. Finally, the reaction pathway and sensitivity analysis are performed to understand the effects of both ozone addition and fuel type on the low-temperature reactivity of the cool diffusion flame.

3.1. Structure of Typical Cool Diffusion Flame

Figure 1 shows the predicted thermochemical structure of a typical cool diffusion flame of *n*-dodecane, including the temperature field and the concentration profiles of the reactants (i.e., NC₁₂H₂₆, O₂, O₃) and main combustion products (i.e., CH₂O, CH₃CHO, CO, CO₂, H₂O). The cool flames are numerically obtained at boundaries of $X_F = 0.1$ (i.e., the fuel stream contains 10% NC₁₂H₂₆ balanced with N₂) and an O₃/O₂ ratio of 0.05:0.95 in the oxidizer stream. For further information, the experimental conditions of *n*-heptane cool diffusion flame established by Won et al. [24,29] can be referred to. The flow rate (initial temperature) on the fuel side and the oxidizer side are 13 cm/s (550 K) and 12 cm/s (300 K), respectively. The corresponding thermochemical structure for the *n*-dodecane hot diffusion flame is shown in Figure 2 for a cross-comparison. The flames are established at X_F = 0.2 and an O₂/N₂ ratio of 0.21:0.79 without ozone addition. The velocity and temperature boundaries at the fuel and oxidizer nozzle duct are set at 13 cm/s (550 K) and 12 cm/s (300 K), respectively.



Figure 1. Simulated structure of *n*-dodecane cool diffusion flame at boundaries of $X_F = 0.1$ and O_3/O_2 ratio of 0.05:0.95 in the oxidizer stream.



Figure 2. Simulated structure of *n*-dodecane hot diffusion flame at boundaries of $X_F = 0.2$ and O_2/N_2 ratio of 0.21:0.79 without ozone addition.

It can be seen in Figure 1 that the maximum flame temperature of the cool diffusion flame is about 850 K, while the corresponding temperature is around 2000 K for the hot diffusion flame. In this regard, the flame temperature can serve as the criterion to determine whether the flame is cool or hot. In Figure 1, it can also be noted that the peak location of the temperature profiles is close to the center of the two nozzles, which can determine the counterflow flame position. In the cool diffusion flame, the concentration level of $NC_{12}H_{26}$ starts to decrease at a distance of z = 0.6 cm from the fuel nozzle, whereas the concentration of CH₂O and other major intermediate specials (CH₃CHO, CO, CO₂) start to increase. This indicates the occurrence of the low-temperature oxidation reaction. The kinetic analysis shows that fuel decomposition at low-temperature conditions would produce large amounts of NC₁₂-OOQOOH and NC₁₂-OQOOH through the low-temperature branching pathway, and then can form CH₂O via QOOH beta scission reactions. Therefore, CH₂O is usually regarded as a characteristic combustion product of a cool diffusion flame [11,20]. The concentration level of CH₂O is much higher in cool diffusion flames as compared to hot diffusion flames. The distribution behavior of the temperature and main species in the cool diffusion flame is found to be consistent with the previous experimental observations of Won et al. [29], although the absolute values of the temperature and species profiles may be different due to the difference in fuel type. Similar flame structures of DME and *n*-butane counterflow cool flames were also numerically observed in the literature [9,14]. It is therefore reasonable to conclude that the present kinetic model is able to describe the flame chemistry of *n*-alkane counterflow cool flames—at least at a qualitative level.

Notably different from the cool diffusion flame where there exists an overlap of fuel and oxygen across the reaction zone, the fuel and oxygen mole fraction decrease to zero without an overlap in the hot diffusion flame, as can be seen in Figure 2. This indicates that there is no fuel leakage to the oxidizer side across the reaction zone in the hot diffusion flame. In Figure 2, it is indicated that the location where the fuel and oxygen decrease to zero is consistent with the peak location of the flame temperature, and that the major combustion product of CO_2 and H_2O indicates the location of the hot flame reaction zone. Such a difference is due to the different fuel consumption pathways and reaction rates for high-temperature hot flames and low-temperature cool flames.

3.2. Initiation Limits of Cool Diffusion Flames

In this section, the results from the initiation limits of the cool diffusion flames are presented for the tested *n*-alkanes of NC_7H_{16} , $NC_{10}H_{22}$ and $NC_{12}H_{26}$; the effects of ozone concentration, fuel concentration and flow rate on the establishment of cool flames are investigated. The flame state (cool or hot) is determined by the maximum flame temperature, which determines the transition from cool flame to hot flame.

Figure 3 shows the maximum temperature distribution of large *n*-alkanes with varying carbon chain lengths in the case of different ozone concentrations. As can be seen from Figure 3, for all the tested fuels, the maximum flame temperature gradually increases with the increase in ozone concentration. When the ozone concentration is lower than the critical point, the three *n*-alkanes can establish a stable cool diffusion flame, and the flame temperature is about 900 K. However, when the ozone concentration is higher than the critical point, the three *n*-alkanes establish a stable hot diffusion flame with a flame temperature of about 2700 K. When enough ozone is added, the NTC behavior would disappear [27] and hot flames could be established. The transition from cool flame to hot flame is likely caused by the ozone decomposition, which produces enough O radicals to promote the complete oxidation of *n*-alkanes and produces the final products, CO₂ and H₂O, during the high-temperature combustion process. This critical ozone concentration can be regarded as the boundary condition where cool flames can be established. In addition, it can be concluded from Figure 3 that the critical ozone concentration required for establishing cool flames decreases with an increase in the carbon chain length of *n*alkanes. Since the introduction of ozone results in a large number of O radicals that can boost the fuel's low-temperature oxidation process [27,29,30], the fuel with a smaller limiting ozone concentration would have a stronger low-temperature reactivity. In other words, $NC_{12}H_{26}$, with its longer carbon chain, is more reactive than the smaller *n*-alkanes of $NC_{10}H_{22}$ and NC_7H_{16} during the low-temperature combustion process. This trend will be further discussed in the next section through the sensitivity analysis and reaction pathway analysis.



Figure 3. The critical point of the transition from cool flame to hot flame of *n*-alkanes with the increase of ozone concentration under the same boundary conditions of X_F and fuel/oxidizer stream flow rates.

By using increments of fuel concentration, the transition from unignited to cool flame and from cool flame to hot flame of three *n*-alkanes with varying carbon chain lengths can be observed, as shown in Figure 4—where (a) the minimum fuel concentration and (b) the maximum fuel concentration for *n*-alkanes to establish cool diffusion flames are reported. It can be seen that for *n*-alkane cool diffusion flames, the cool flame temperature tends to increase with an increase in the fuel concentration. This trend is easily understood since the increase in fuel concentration is conducive to promoting the interaction of fuel and oxidizer and the low-temperature oxidation reactions, thereby releasing more heat and thus increasing the temperature of the cool flame. Although the change in fuel mole fraction will result in different stoichiometric mixture fractions among different flames, the quantitative variation is small and is expected to impose little effect on flame dynamics. Therefore, the fuel concentration has a more significant influence on flame chemistry and the establishment of cool diffusion flame of large *n*-alkanes.

Figure 4. (a) The critical minimum fuel concentration of the transition from unignited to cool flame of *n*-alkanes. (b) The critical maximum fuel concentration of the transition from cool flame to hot flame of *n*-alkanes. The boundary conditions for O_3/O_2 ratio and fuel/oxidizer stream flow rates.

In Figure 4a, the critical point of the transition from unignited to cool flame decreases with an increase in the carbon chain length of *n*-alkanes. The critical minimum fuel concentration can be regarded as the boundary conditions where *n*-alkanes can establish cool diffusion flames. Moreover, it can be concluded from Figure 4b that with an increase in the carbon chain length of *n*-alkanes, the critical maximum fuel concentration of the transition from cool flame to hot flame decreases gradually. Compared with NC₇H₁₆ and NC₁₀H₂₂, NC₁₂H₂₆ could establish cool diffusion flames at a smaller fuel concentration. These results indicate that NC₁₂H₂₆ having a smaller limiting fuel concentration would be more reactive than the smaller *n*-alkanes of NC₇H₁₆ and NC₁₀H₂₂ during the low-temperature oxidation combustion process.

The nozzle velocity field also plays a crucial role in the establishment of *n*-alkane cool diffusion flames. Figure 5 shows the effects of flow velocity on the initiation limits of cool flames for the sake of studying the transition from cool flame to hot flame by continually varying the flow velocity of the fuel and oxidizer stream. It can be seen from Figure 5 that the temperature of the *n*-alkanes is within the cool flame temperature range (below 850 K) until the flow velocity decreases to a critical value, at which point the flame temperature suddenly increases to about 2500 K. This indicates the transition from cool flame to hot diffusion flame. In this manner, this critical flow velocity is regarded as the velocity initiation limits where *n*-alkanes could establish cool diffusion flames. Moreover, it can be concluded from Figure 5 that the critical flow velocities of *n*-alkanes with different carbon chain lengths are different. With an increase in the carbon chain length of *n*-alkanes, the critical flow velocity of the transition from cool flame to hot flame indicates an increasing trend. The critical flow velocity of $NC_{12}H_{26}$ is larger than that of NC_7H_{16} and $NC_{10}H_{22}$, which is attributed to their different low-temperature reactivities. In other words, NC12H26 having a larger limiting flow velocity is more reactive than the smaller *n*-alkanes of NC_7H_{16} and NC₁₀H₂₂ during the low-temperature combustion process.

The above conclusions about the initiation limits (ozone concentration, fuel concentration and flow velocity) for establishing the cool flames of *n*-alkanes consistently show that the *n*-alkanes with the longer carbon chains are more reactive than smaller *n*-alkanes during the low-temperature oxidation combustion process. This trend will be discussed in detail in the following section through the reaction pathway and sensitivity analysis of the *n*-alkane cool flames.

Figure 5. The critical point of the transition from cool flame to hot flame of *n*-alkanes with the decrease of flow velocity at boundaries of $X_F = 0.1$ and the O_3/O_2 ratio is 0.05:0.95.

3.3. Kinetic Analysis of the Low-Temperature Reactivity of N-Alkanes

In order to better understand the influence of carbon chain length on the low-temperature reactivity of *n*-alkanes, we performed a reaction pathway and sensitivity analysis. The concentration profiles of the important intermediate species of the three *n*-alkane cool flames were compared under identical boundary conditions. In addition, the effects of ozone addition on the fuel reactivity were investigated by comparing a cool diffusion flame and a hot diffusion flame (with a larger ozone concentration).

Figure 6 shows the reaction pathways of *n*-heptane, *n*-decane and *n*-dodecane during the low-temperature oxidation combustion process. The position of z = 8 mm, wherein the 70% fuel consumption occurs, was selected for the reaction path analysis because the position is close to the reaction zone (represented by the peaks of temperature profile); the low-temperature reaction of fuel is relatively sufficient at this stage, along with the abundance of various low-temperature intermediate species such as CH₂O and CH₃CHO and other combustion products such as H₂O and CO₂. In this manner, the important reactions that are pertinent to the low-temperature combustion of *n*-alkanes could be taken into account during the sensitivity analysis. The numerical values on the arrow represent the percentage of the individual reaction path to the consumption of the target species.

As can be seen in Figure 6, the low-temperature oxidation process of three *n*-alkanes with varying carbon chain lengths all begins with the hydrogen extraction of fuels. Moreover, all three fuels, NC_NH_{2N+2} (N = 7, 10, 12), produce NC_NH_{2N+1} through a dehydrogenation reaction. Among them, more than 70% of hydrocarbon fuels react with OH in the reaction OH + NC_NH_{2N+2} \Rightarrow H₂O + NC_NH_{2N+1} to generate NC_NH_{2N+1}, and the remaining hydrocarbon fuels react with HO₂ and H to generate fuel radicals. Then, NC_NH_{2N+1} and O₂ molecules react to form the adduct, NC_NH_{2N+1} -OO, through the reaction $NC_NH_{2N+1} + O_2 \leftrightarrow NC_NH_{2N+1}$ -OO. NC_7H_{16} contributes the least to the oxidation reaction, while $NC_{10}H_{22}$ and $NC_{12}H_{26}$ contribute more to the oxidation reaction. Next, NC_N -QOOH is generated by the isomerization of NC_NH_{2N+1} -OO through the reaction NC_NH_{2N+1} -OO \leftrightarrow NC_N-QOOH. It can be concluded from the graph that *n*-alkanes with a longer carbon chain length contribute more to the isomerization reaction. NC_N-QOOH can be decomposed to generate OH and can also undergo a secondary addition reaction with O_2 to generate the peroxy-hydroperoxyalkyl radical, NC_N-OOQOOH. With an increase in the carbon chain length of n-alkanes, the contribution of NC_N-QOOH to the formation of OH radicals gradually increases, while the contribution of NC_N-QOOH to the formation of NC_N-OOQOOH indicates a decreasing trend. Then, NC_N-OOQOOH decomposes to produce OH radicals and ketohydroperoxides of NC_N-OQOOH; the contribution of NC_N-OOQOOH increases with an increase in the carbon chain length of *n*-alkanes. Finally, NC_N -OQOOH decomposes to produce OH radicals and the products, CH₃CHO and CH₂O,

and the contribution of NC_N -OQOOH increases with the increase in the carbon chain length of *n*-alkanes during the low-temperature oxidation combustion process.

Figure 6. Reaction pathways of (a) *n*-heptane, (b) *n*-decane and (c) *n*-dodecane in the low-temperature oxidation combustion process under the same boundary conditions of $X_F = 0.1$ and an O_3/O_2 ratio of 0.05:0.95.

It can be concluded that the reaction pathway of NC_NH_{2N+2} \rightarrow NC_NH_{2N+1} \rightarrow NC_NH_{2N+1}-OO \rightarrow NC_N-QOOH \rightarrow NC_N-OOQOOH \rightarrow NC_N-OQOOH \rightarrow CH₃CHO (or CH₂O or OH) is the dominant pathway for the control of the low-temperature oxidation of *n*alkane cool diffusion flames. Moreover, with an increase in the carbon chain length of *n*-alkanes, the percentage of these fuels undergoing a dehydrogenation reaction, oxidation reaction and isomerization reaction increase gradually and are associated with an increased concentration of OH radicals. The results show that the *n*-alkane with a longer carbon chain length has a stronger low-temperature reactivity. In other words, NC₁₂H₂₆ with a longer carbon chain is more reactive than the smaller *n*-alkanes of NC₇H₁₆ and NC₁₀H₂₂ during the low-temperature oxidation combustion process.

Furthermore, a sensitivity analysis of the flame temperature is performed for the cool flames produced by the three *n*-alkanes to further investigate the effect of carbon chain length on the low-temperature reactivity of *n*-alkanes. A sensitivity analysis would help to determine which reactions (and the corresponding rate parameters) are important to the heat release process (indicated by flame temperature), as represented by the sensitivity coefficient reported in Figure 7.

Figure 7 shows the elementary reactions whose rate parameters play the most important role in flame temperature during the low-temperature oxidation combustion process of the three *n*-alkanes with varying carbon chain lengths. A positive (negative) sensitivity coefficient for the elementary reaction indicates that the increase in the reaction rate will increase (reduce) the flame temperature; the larger the absolute value of the sensitivity coefficient, the stronger the influence the reaction has on the flame temperature. It can be seen from Figure 7 that the oxidation and dehydrogenation reactions have the most significant influence on the flame temperature for the cool flames of the three alkanes. In addition, with an increase in the carbon chain length of the *n*-alkanes, the sensitivity coefficient of the fuel dehydrogenation reaction OH + NC_NH_{2N+2} \Rightarrow H₂O + NC_NH_{2N+1}, oxidation reaction O₂ + NC_N-QOOH \Rightarrow NC_N-OOQOOH and decomposition reaction NC_N-OOQOOH \Rightarrow OH + NC_N-OQOOH decrease gradually. It can also be seen from Figure 7 that the sensitivity coefficient of NC₇H₁₆ in the fuel isomerization reaction NC_NH_{2N+1}-OO \Rightarrow NC_N-QOOH is larger than that of NC₁₀H₂₂ and NC₁₂H₂₆. These trends indicate that NC₇H₁₆, which has a smaller carbon chain, is less reactive than the larger *n*-alkanes of NC₁₀H₂₂ and NC₁₂H₂₆.

Figure 7. Sensitivity analysis of three *n*-alkanes with varying carbon chain lengths under the same boundary conditions of $X_F = 0.1$ and the O₃/O₂ ratio is 0.05:0.95.

From Figure 7, we can also find that the reaction involving ozone $O_3 + O_2 \Rightarrow 2O_2 + O_1$ has a strong negative sensitivity coefficient, and the sensitivity coefficient of this reaction decreases with the increase in the carbon chain length of the *n*-alkanes. It can be seen from this reaction that the addition of ozone leads to the formation of a large number of O radicals, which can react with *n*-alkanes to generate hydroxyl radicals (OH), so as to contribute to the low-temperature heat release [49] and enhance the low-temperature chemical reaction of OH radicals, NC_N-QOOH \Rightarrow OH + NC₇H₁₄O + X, which boosts low-temperature oxidation combustion, decreases with the increase in the carbon chain length of *n*-alkanes. These results indicate that NC₇H₁₆, which has more O and OH radicals participating in the fuel's dehydrogenation and oxidation reactions, has a weaker low-temperature reactivity than NC₁₀H₂₂ and NC₁₂H₂₆ during the low-temperature oxidation combustion process.

In addition, the concentration profiles of the important intermediate species of the three *n*-alkanes during the low-temperature combustion process are shown in Figures 8 and 9, which agree with the results of the above kinetic analysis. Figure 8 shows the concentration profiles of O and OH at the distance of z = 0.9-1.4 (from the fuel nozzle) where the O and OH radicals are abundant. With the increase in the carbon chain length of the *n*-alkanes, the peak positions of the O and OH radical profiles gradually move to the oxidizer side, which may indicate that the low-temperature oxidation process of NC₁₂H₂₆ starts earlier and thus is more reactive than NC₇H₁₆ and NC₁₀H₂₂. It is important to note that the peak concentration level of the O and OH radicals is quantitively similar under the same ozone concentration, which may indicate that the length of the radicals are more sensitive to ozone addition rather than the length of the carbon chain of *n*-alkanes.

Figure 8. The profiles for (**a**) O and (**b**) OH concentration of three *n*-alkane cool flames under the same boundary conditions of $X_F = 0.1$, and the O₃/O₂ ratio of 0.05:0.95.

Figure 9. The profiles for (**a**) CH₃CHO, (**b**) CH₂O and (**c**) H₂O₂ concentration of three *n*-alkane cool flames under the same boundary conditions of $X_F = 0.1$, and the O₃/O₂ ratio of 0.05:0.95.

Figure 9 shows the mole fraction profile of CH₃CHO, CH₂O and H₂O₂, which are important low-temperature combustion products with relatively high concentration levels. The results show that under the same boundary conditions, the *n*-alkanes that have longer carbon chain lengths are more readily able to generate the aforementioned low-temperature oxidation products. Given this, it is understood that the oxidation of NC₁₂H₂₆ with the longest carbon chain among the three *n*-alkanes has the largest portion of low-temperature reactions from dehydrogenation, oxidation and isomerization reactions, thus generating the most intermediate species. This also indicates that NC₁₂H₂₆ is more reactive than smaller *n*-alkanes, such as NC₇H₁₆ and NC₁₀H₂₂—as the latter two have fewer low-temperature oxidation products.

We now move on to understand the kinetic effects of ozone addition on the lowtemperature combustion behavior of *n*-alkanes. For the convenience of discussion, we used $NC_{12}H_{26}$ as an example. Specifically, the concentration profiles of the important intermediate species at critical ozone concentration (named as O_3 -0.18 case) and after critical ozone concentration (called as O_3 -0.19 case) are compared in Figures 10–12. It can be concluded from Figure 10 that the concentration levels of the O (a) and OH (b) radicals in case O_3 -0.19 are much higher than those in case O_3 -0.18. According to the previous conclusion in Figure 3, the amounts of O and OH radicals produced from hot flames are larger than those produced from cool flames. In general, an increase in ozone addition would lead to a sharp increase in O and OH radical concentrations during the oxidation process of NC₁₂H₂₆. The peak location of the concentration of O and OH radicals in the hot diffusion flames is close to the center of the fuel and oxidizer nozzles, meaning that they are intermediate products during the high-temperature oxidation process; however, the peak location of the concentration of O and OH radicals in the cool diffusion flames is biased towards the oxidizer side, given that most O radicals are produced by the decomposition of ozone on the oxidizer side and most OH radicals are produced by the dehydrogenation reaction (from the interaction of O and fuel) near the oxidizer side. When the O and OH radicals are moved to the fuel side, they would be consumed during the interaction with fuel, so the concentration of O and OH in the reaction zone is extremely low. These results indicate that the addition of ozone provides a large number of active O and OH radicals that can effectively enhance low-temperature reactivity.

Figure 10. The profiles for (**a**) O and (**b**) OH concentration of $NC_{12}H_{26}$ counterflow flames at the critical ozone concentration of 0.18 and after the critical ozone concentration of 0.19.

It can also be seen from Figure 11 that the concentration levels of CH₃CHO (a), CH₂O (b) and H₂O₂ (c) are much higher in case O₃-0.18 than those in case O₃-0.19. According to the previous reaction pathway analysis, H₂O₂ generated from the dehydrogenation of NC₁₂H₂₆ tends to decompose into OH radicals in order to promote the low-temperature oxidation reaction. In addition, ketohydroperoxide molecules produce a large amount of CH₃CHO and CH₂O through the low-temperature branched-chain oxidation pathway. These results indicate that CH₃CHO, CH₂O and H₂O₂ are the main products of cool diffusion flames, which are consistent with the previous studies [14,46].

Moreover, it can be concluded from Figure 12 that the concentration levels of CO (a), CO_2 (b) and H_2O (c) in case O_3 -0.18 are lower than those in case O_3 -0.19. In addition, the addition of ozone could enhance the exothermic reaction of low-temperature peroxide chemistry and improve the flame temperature. Therefore, the addition of ozone may promote the reactivity of *n*-alkanes and effectively boost the combustion of large *n*-alkanes under low-temperature conditions.

Figure 11. The profiles for (a) CH₃CHO, (b) CH₂O and (c) H_2O_2 concentration of $NC_{12}H_{26}$ counterflow flames at the critical ozone concentration of 0.18 and after the critical ozone concentration of 0.19.

Figure 12. The profiles for (**a**) CO, (**b**) CO₂ and (**c**) H_2O concentration of $NC_{12}H_{26}$ counterflow flames at the critical ozone concentration of 0.18 and after the critical ozone concentration of 0.19.

4. Conclusions

In this work, we performed a detailed kinetic study on the low-temperature oxidation kinetics of large *n*-alkanes, including *n*-heptane, *n*-decane and *n*-dodecane, in counterflow cool flame configurations by highlighting the effects of carbon chain length on the low-temperature reactivity of *n*-alkanes. The initiation limits (such as the ozone concentration in the oxidizer stream) required for the initiation of cool diffusion flames were determined, through which the low-temperature reactivity of the *n*-alkanes were compared. The results show that the *n*-alkane with a longer carbon chain is more reactive than a smaller *n*-alkane (i.e., showing the order of $NC_{12}H_{26} > NC_{10}H_{22} > NC_7H_{16}$). The reaction pathway and sensitivity analysis were performed to better understand the effect of carbon chain length on low-temperature reactivity. It was found that $NC_{12}H_{26}$ is more readily able to undergo dehydrogenation, oxidation and isomerization reactions, which produce larger amounts of O and OH radicals that can promote the fuel's low-temperature oxidation process. As a consequence, $NC_{12}H_{26}$ was more reactive than $NC_{10}H_{22}$ and NC_7H_{16} during the low-temperature combustion process.

The effects of ozone addition on the low-temperature reactivity of *n*-alkanes were also highlighted. It was found that the addition of ozone in the oxidizer stream could provide a large number of active O radicals, which tended to dehydrogenate the fuels to generate OH radicals and to promote the fuel's low-temperature oxidation reactions. The present study is expected to promote our understanding of the low-temperature chemistry of larger *n*-alkanes in flame environments.

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