Comparative Study on the Dimethyl Ether Combustion Characteristics in Normal and Inverse Diffusion Spherical Flame Geometries

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ABSTRACT: This paper makes a comparative study on the normal diffusion flame (NDF) and inverse diffusion flame (IDF) characteristics of dimethyl ether (DME) in microgravitational spherical diffusion flame geometry by simulations with detailed fuel chemistry and a transport model. It is found that there always existed two combustion modes (i.e., hot flame and cool flame) in either NDF or IDF condition. The combustion progress of hot flames was controlled by diffusive mixing, while that of cool flames was controlled by low-temperature reacting kinetics. The cool-flame structure dynamics were far away from the chemical equilibrium. The low-temperature branching rate of DME was positively dependent on the oxygen level, while its termination rate was enhanced with the increasing temperature. Being rather distinct from the NDF counterpart, DME IDF had the oxygen-enriched combustion feature in either hot- or cool-flame condition. Furthermore, DME hot-flame extinction was induced by thermal radiative loss, while the cool-flame extinction was induced especially by the decrease of the low-temperature branching rate. Compared with hot NDFs, it would be of less effectiveness to control the hot IDF combustion process by positive measures. However, combustion in the latter configuration was much more stable than the former. In either NDF or IDF geometry, the cool-flame chemistry could help to extend the fuel flammability range considerably, and the two-reaction-zone structure of cool flame was responsible for cool-flame stability. In addition, the IDF had much better ignition performance than the NDF counterpart.

1. INTRODUCTION
The diffusion combustion systems are of great importance to power generation, and transportation and aeronautical jet engines because of its better safety, controllability, and flame stability over a much wider range of parameters as compared to the premixed/partially-premixed combustion systems,1–3 even though they are also featured with depressed heat release, high soot emission, and incomplete fuel decomposition.4,5 However, in contrast, the flames in premixed/partially-premixed configurations are superior in terms of its high thermal efficiency and ultralower emissions, including soot, NOx, and unburned hydrocarbons.6 Therefore, the practical premixed/partially-premixed combustion systems are generally assisted by a pilot diffusion jet as the external stabilization agent to improve the main flame’s stability near blowout.7 In the engineering viewpoint, the majority of diffusion combustion systems as well as the pilot diffusion jet with a small tendency to blow off are established by injecting a high-speed fuel jet into an annular, low-speed oxidizer ambient atmosphere, which is herein defined as the “normal diffusion flame (NDF)” mode. Apart from the NDF, the “inverse diffusion flame (IDF)” is another distinct kind of diffusion flame mode with an inner high-speed air jet being surrounded by annular, one or more, low-speed fuel jets in either confined or unconfined conditions.8,9 It was extensively proved by experiments and simulations that the superior advantages of premixed and nonpremixed flames can be integrated in the IDF configuration. The IDFs showed no flashback, less soot loading versus the NDFs, low emissions, and an extended range of flame flammability,10–13 and thus it has been paid growing interests in the past few years. Additionally, the IDF existed in various engineering scenarios of power generation and fire safety. For instance, in many engines or staged combustion systems, the injection of central air into annular fuel streams can help to minimize the oxidation of combustor walls;1,4,12,15 the leakage of enriched oxygen from the firefighter’s breathing equipment into an unventilated fire field would introduce a...
hazard in terms of the IDF geometry. Hence, our knowledge about the IDF combustion characteristics is of fundamental and practical importance in combustion and fire safety sciences (e.g., designing the advanced engines and high-efficiency extinguishment devices).

Existing relevant literature has indicated that the IDFs have many superior combustion and flow performances compared with NDFs. The high-momentum inner air jet could entrain the low-momentum ambient fuel or air jet efficiently and thus enhance the fuel–air mixing in the IDF configuration compared with the NDFs. The simulations performed by Kaplan and Kailasanath suggested that at the same air and fuel injection velocities, the IDFs produced less primary/initial soot particles than the corresponding NDFs because of the unfavorable temperature and stoichiometry conditions for soot inception and surface growth in IDFs. Mahesh and Mishra reported that the nonluminous, nonbuoyance, and compact jet flames can be readily established in the IDF configuration with an appropriate control of the air–fuel velocity ratio and burner aerodynamics. Sobiesiak and Wentzell experimentally compared the flame structure and characteristics in the NDF and IDF conditions, which showed that partial premixing was a feature of IDFs that depended on the nozzle geometry and flow conditions. The partial premixing degree affected the IDF stability limits, with a higher premixing level extending the range of fuel jet blowout.

Up to now, the flame appearance and structure of IDFs were studied in various configurations including coaxial IDF burner geometries and swirl IDF jet burners. Mahesh and Mishra compared the dependence of visible flame length, flame appearance, and temperature profile at various air/fuel momentum ratios on two types of coaxial IDF burner geometries, i.e., the back-step and recessed burners. It was reported that the back-step burner produced a smaller flame length, better thermal efficiency, and smaller NO\textsubscript{x} emissions as compared to the recessed type burner. Zhen et al. compared the visible flame length, temperature distribution, in-flame species concentrations, and global pollutant emission characteristics of the turbulent IDF jet flames with or without swirling stabilization. It is concluded that the swirling IDFs exhibited superior stability and emission behaviors.

It is concluded from the above presentation that the existing research about IDFs were almost made employing the coaxial jet configuration, which is characterized by intense flow strain and mixing across the jet boundary layer. The present work employed microgravitational spherical diffusion flame geometry to study the IDF and NDF combustion characteristics, which is attractive for the NDF/IDF comparative study for several reasons. First, the spherical diffusion flame can exclude the impact of flow strain that is inherent in, say, the jet flames or counterflow flames and enable the observation of the IDF dynamics in the pure diffusion configuration with a very broad range of a residence timescale. Second, such strainless flame has a much broadened reaction zone, wider than that formed on the jet or counterflow burner, which is very helpful to the examination on a flame structure. Third, the special burner configuration provides flexibility to select the direction of convection from fuel to oxidizer (NDF mode) or from oxidizer to fuel (IDF mode), while keeping the fuel/air composition and flow condition unchanged. Furthermore, modeling of the spherical diffusion flame is very time saving due to its one-dimensional nature, such that the majority of computational resources can be devoted to solve important physical/chemical processes that underlie the IDF phenomena.

Additionally, relevant studies have shown that for most large hydrocarbon fuels, there ubiquitously existed two temperature-dependent reaction pathways, including a high-temperature pathway (i.e., hot flame, $T > 1050$ K) and a low-temperature pathway (i.e., cool flame, $T < 750$ K). In this work, the microgravitational spherical diffusion flame geometry can provide an ideal platform for a cool flame study because the cool flame could be readily established in either NDF or IDF condition. Cool flame governed by low-temperature chemistry was first observed in 1817, which has been widely studied for many years. The definition of conventional flammability limit, which was based on hot flame, should be redefined due to the occurrence of cool flame. Additionally, low-temperature chemistry can exhibit a typical negative
temperature coefficient (NTC) behavior (i.e., fuel oxidative reactivity could be enhanced by decreasing the temperature), which was usually observed in engine knock \cite{25} and a two-stage ignition process. \cite{25} However, the study in ref \cite{25} reported that the NTC phenomenon could have only occurred within a particular temperature range. In addition, studies on low-temperature chemical kinetics are of great significance to the design of advanced engines \cite{22} (e.g., HCCI engines and RCCI engines). Hence, in this work, the low-temperature chemical kinetics of cool flames in either NDF or IDF condition were studied in detail.

Additionally, dimethyl ether (CH$_3$OCH$_3$, DME) was used as the target fuel because of its promising potential as a surrogate to substitute the traditional transportation fuels such as diesel. \cite{26} DME has a much simpler fuel structure and thus smaller chemistry mechanism size than that of other transportation alkanes like n-heptane, but it has a strong NTC chemistry subset, which enables our investigation on its cool-flame dynamics.

2. DETAILS OF THE NUMERICAL SIMULATION

2.1. Computational Model. The burner geometry that was used to establish the microgravitational spherical NDFs and IDFs is schematically shown in Figure 1. This type of burner consisted of a porous sphere burner (diameter = 1 cm), which was supported by a capillary feeding pipe, with the quiescent ambient gas surrounding it. In the NDF configuration, the heavily diluted fuel mixture (30% DME/70% Ar) is issued from the porous burner surface at an initial temperature of 300 K and velocity of 13.0 cm/s (and thus fixed thermal load) to the quiescent ambient oxidizer that is diluted by helium. The ambient temperature was fixed at 450 K, while the helium dilution varied over a wide range, from pure oxygen to pure helium, to obtain a series of DME-fed NDFs. In the IDF configuration, the helium-diluted oxygen stream (300 K) was issued from the porous burner surface to the quiescent ambient fuel domain (30% DME/70% Ar, 450 K). The helium dilution in the oxidizer mixture was varied from pure oxygen to pure helium to obtain a set of corresponding IDFs, and at the meantime, the initial oxidizer exit velocity was properly adjusted to keep its thermal load fixed and equal to that of the NDFs. All of the NDFs and IDFs were operated under a reduced pressure (0.3 atm), which helps to broaden the flame width and thus facilitate the investigations on the in-flame structure. Moreover, the ambient temperature was set to 450 K in either NDF or IDF condition. This is because microgravitational spherical diffusion flame was supported by O$_2$ diffusion flux from the right ambient boundary. Due to the restricted diffusion flux of O$_2$ supplied into the computational domain, the flame temperatures and thus reaction rates were rather depressed, and increasing the ambient temperature (450 K) can obtain a stable flame structure.

In order to get a high-fidelity combustion process of spherical diffusion flames, the present simulations were carried out using a detailed chemical reaction mechanism and a transport model. The present numerical models with the consideration of radiative heat loss were derived by an appropriately modified version of the one-dimensional PREMIX model, \cite{27} which had been widely used in the literature. The conservation equations for mass, species, and energy are written in the cartesian coordinate, as shown in eqs (1)–(3).

\begin{equation}
\frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial (\rho u r^2)}{\partial r} = 0 \tag{1}
\end{equation}

\begin{equation}
\frac{\partial Y_i}{\partial t} + \frac{u \rho}{r^2} \frac{\partial (Y_i r^2)}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \rho D_{i,i} \frac{\partial Y_i}{\partial r} \right) + \delta_i W_i \tag{2}
\end{equation}

\begin{equation}
\rho \frac{\partial T}{\partial t} + \rho \frac{u \partial T}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\lambda}{c_p} \frac{\partial T}{\partial r} \right) - \sum_{i=1}^{N} \left( \rho Y_i \omega_i \frac{\partial T}{\partial r} \right) - \sum_{i=1}^{N} (\alpha_i) W_i = \dot{q}_r \tag{3}
\end{equation}

where $r$, $t$, $T$ are the radius, time, and temperature, respectively. $\rho$, $u$, $\lambda$, and $c_p$ are the density, velocity, thermal conductivity, and specific heat of the mixture, respectively. $N$ is the total number of species involved in the system. $Y_i$, $D_{i,i}$, $\omega_i$, and $W_i$ are the mass fraction, mixture-averaged diffusivity, volumetric reaction rate, and molecular weight of species $i$, respectively. $\alpha_i$, $h_i$, and $V_i$ are the specific heat capacity, enthalpy, and diffusion velocity of species $i$, respectively. $\dot{q}_r$ is the radiative heat loss term, which was estimated using the optically thin model \cite{28} that considers major radiating species, including CO$_2$, H$_2$O, and CO.

$x = r - r_0$ is introduced for the sake of a later discussion, which is defined as the distance from the burner surface, where $r_0$ is the radius of the spherical burner. A sufficiently long computational domain ($x = 0$–350 mm) was designed for present simulations, which can exclude the interaction between the right ambient boundary and the inner combustion process. In addition, the modeling results demonstrated that for such a finite computational domain length, all the scalar gradients were rather small at the right ambient boundary.

The above governing equations were solved subject to the following boundary conditions:

\begin{equation}
r = r_0, \quad T = T_0, \quad Y_k(u + V_k) = u Y_{k,0} \quad (k = 1, 2, ..., K) \tag{4}
\end{equation}

\begin{equation}
r = +\infty, \quad T = T_{\infty}, \quad \text{if } (k = \text{O}_2, \text{He (for NDFs),})
\text{or } k = \text{DME, Ar (for IDFs))}, \quad Y_k = Y_{k,\infty};
\text{otherwise, } \partial Y_k / \partial r = 0 \tag{5}
\end{equation}

where the subscripts 0 and $\infty$ represent the burner surface and quiescent ambient boundary, respectively. A constant temperature $T_0$ and constant species mass flux fractions $Y_k(u + V_k)$ were specified at the spherical burner surface, as eq (4) shows. The consideration of inlet diffusion velocity ($V_k$) at the porous burner surface can ensure that the mass flux of each species into the computational domain equals its mass flux fed into the burner source. At the ambient side, mass fractions of the ambient species (including He and O$_2$ for the NDFs, or DME and Ar for the IDFs) were constrained; while that of the other species were relaxed with zero gradient, as eq (5) shows. The applicability and accuracy of the present models in the simulations of spherical diffusion flame were extensively verified in the literature. \cite{29–34}
Additionally, the governing equations were discretized on an adaptive mesh with the transient terms discretized by the forward difference scheme, the convective terms by an upwind difference scheme, and the diffusion terms by the central difference scheme. The Chemkin and Transport packages were incorporated into the code to calculate the reaction rates, thermodynamic data, and transport parameters. The Sandia’s TWOPNT package35 with the Newton’s iteration algorithm...
was used to solve the linearized algebraic equations. The Zhao’s chemical mechanism consisting of 55 species and 290 reactions was used to describe the detailed chemical kinetics of DME oxidation, and the accuracy of this detailed chemical mechanism had been well validated against the experimental data of a flow reactor, ignition delay time, pollutant emissions, laminar flame speed, etc. in the literature. Moreover, the implementation of mesh adaption was controlled by the two keywords “GRAD” and “CURV”, which means gradient and curvature of the temperature and major species profiles, respectively. Lower values of these two keywords will result in more mesh refinements. Meanwhile, the maximum number of grid points was controlled by the keyword “NTOT”. Our previous studies verified that GRAD = CURV = 0.1 and NTOT = 1000 can guarantee grid independency; hence, they were used for the present simulations.

2.2. Validation. To validate the accuracy and reliability of the computational code, a hot NDF (established at the oxygen mole fraction $X_{O_2} = 50\%$) was assumed as a reference case. The predicted results of the temperature and species CO$_2$ and O$_2$ were compared with the experimental results from ref. It is necessary to study flame structure dynamics, which could help to understand the stabilizing mechanism, pollutant emission, combustion temperature, heat production, etc. For instance, the flame mode can be identified by the combustion temperature, e.g., hot flame (its maximum temperature > 1050 K) and cool flame (its

3. RESULTS AND DISCUSSION

3.1. Comparison of the NDF and IDF DME Flame Structures. To present the flame structure behaviors, Figure 3 compares the predicted distributions of the temperature; heat release rate (HRR) as well as mole fractions of O$_2$, CH$_3$OCH$_3$, CO, H$_2$O, CO, and H$_2$O for the hot NDFs and IDFs established at oxygen mole fraction $X_{O_2} = 40\%$. The present study found that the cool flames could be readily stabilized in the NDF and IDF spherical diffusion flame geometry; Figure 4 shows the comparison of NDF/IDF cool flame structures that were established at $X_{O_2} = 20\%$. It is necessary to study flame structure dynamics, which could help to understand the stabilizing mechanism, pollutant emission, combustion temperature, heat production, etc. For instance, the flame mode can be identified by the combustion temperature, e.g., hot flame (its maximum temperature > 1050 K) and cool flame (its
maximum temperature ranges from 550 to 750 K). In the following, we will reveal the combustion features for both hot and cool flames in NDF and IDF conditions, respectively, by analyzing the flame structure in detail.

For either the hot NDFs or IDFs as shown in Figure 3, it is coincided with the expectation that the flame temperature, heat release rate (HRR), and production concentrations peaked at the stoichiometric location where fuel and oxygen molecules co-vanished (for the NDF and IDF, it is about 2.7 and 3.7 cm, respectively). The hot IDF had a considerably wider diameter than that of the NDF, due to the following reasons. First, the IDF configuration had a much higher burner injection velocity and thus jet momentum than the NDF configuration, in the same thermal load condition. Therefore, it is characterized by a more intense entrainment/mixing rate across the flame boundary layer, which agreed well with the previous studies.\textsuperscript{18} Second, in the current IDF flow configuration where light oxidizer was injected into the fuel ambient with heavier density, the initial jet momentum had a slower attenuation rate than that in the NDF flow field. Third, diffusive transport of the species from the ambient side into the domain controlled the overall combustion progress, in either of these two types of configurations. The combustion process was governed by the diffusion of much heavier fuel molecules in the IDF configuration versus the NDF configuration where the ambient oxygen molecules are much more diffusible. As a result, the IDFs had considerably expanded volumes than the thermal-load-equivalent NDFs.

Furthermore, Figure 3c shows that the hot flames had nearly equal partial pressures of the radiation participating species (including CO\textsubscript{2} and H\textsubscript{2}O), in either the NDF or IDF configuration. Consequently, the IDF had lower temperatures and thus HRRs than the NDF because of its expanded volume, as Figure 3a illustrates. Additionally, Figure 3d displays that the IDF had much higher emissions of unburned hydrocarbons like CO and H\textsubscript{2} than the NDF. This is because the fuel decomposition products can be completely oxidized in the NDF configuration, owing to its abundance in oxygen molecules from the ambient. While in the IDF geometry, the fuel-decomposition hydrocarbons that were generated in the flame zone would be partially diffused towards the oxygen-

Figure 5. Distributions of the HRR and mole fractions of radicals HO\textsubscript{2}, CH\textsubscript{3}OCH\textsubscript{2}, and CH\textsubscript{2}OCH\textsubscript{2}O\textsubscript{2}H for the cool (a) NDFs and (b) IDFs established at X\textsubscript{O\textsubscript{2}} = 20%, respectively.
deficient ambient side, and became the emission matter of incompletely oxidized hydrocarbons.

The comparisons of hot and cool flames structures as shown in Figures 3 and 4 demonstrate that the cool flames had a significantly wider reaction zone and thus smaller dissipative loss (longer residence time) and depressed temperatures than the hot flame, regardless if in the NDF or in the IDF flow field. The important intermediates and radicals were distributed within a much broadened area in the cool-flame condition, especially for the reactants O2 and CH3OCH3 that even did not vanish at the stoichiometric location (as Figure 4b shows), which was distinct from the hot flame condition (Figure 3b).

Therefore, it would be safe to suggest that the combustion progress of either the spherical cool NDF or IDF was kinetically controlled, rather than diffusively controlled like that in the hot flame condition. The gaseous mixtures in the cool NDFs or IDFs deviated considerably away from the equilibrium state; hence, the low-temperature chemical kinetics were most influential in the underlying dynamics of the cool-flame phenomena. In another word, stoichiometry most probably does not mean the temperature peaking. This would be the underlying reason why the location of the peaking HRR did not coincide with the location of the peaking temperature in the cool-flame condition, as shown in Figure 4a.

Additionally, being similar with the hot flame case, the low-temperature reaction zone moved to a further radius location in the IDF condition due to its larger jet momentum, in comparison with the NDF condition.

Figure 4a displays that the peak temperature was slightly higher in the IDF flow condition than in the NDF condition, although the IDF had a larger diameter. Obviously, it is irrelevant with the thermal radiative loss effect. It is because in the IDF geometry, the ambient fuel at 450 K had a larger sensible heat with its higher specific heat capacity with respect to the ambient oxygen at the same temperature in the NDF geometry. Therefore, the cool IDFs had higher temperatures than the corresponding cool NDFs. Additionally, as a further consequence, heat production in the cool IDFs was rather depressed with respect to the cool NDFs, due to the negative temperature coefficient (NTC) behavior, which states that the cool-flame reactivity and combustion intensity decreased with the increment of temperature in the low-temperature range (500–800 K). Hence, the HRR in the IDF flow field was considerably depressed than the NDF condition. Moreover, Figure 4a also demonstrates that the cool-flame HRRs were distributed in a similar manner in the NDF or IDF configuration, and more importantly, they were both bimodal, which was particularly different from the unimodal HRR profiles for the hot flames as shown in Figure 3a. The reasons for the bimodal nature of the cool-flame HRR profile will be clarified in the following.

The present study indicated a high correlation of the HRR with the HO2, CH2OCH2, and CH2OCH2O radicals for either the cool NDFs or IDFs. As shown in Figure S, these variable curves were bimodal, and the locations of the dual peaking points coincided well with each other, implying the importance of these radicals with their participating reactions in the heat production process. The HRR calculation through each reaction pathway revealed that in the cool-flame condition there existed two low-temperature heat release regions, and the employment of the local equivalence ratio (ϕlocal as expressed in eq (6) where N is the total number of species, Xi is the mole fraction of i-th species CnH2O) demonstrates that the cool flames had the feature of both premixed and nonpremixed combustion, including one located on the fuel side (rich-reaction-zone: ϕlocal > 2.8) and the other located on the oxidizer side (lean-reaction-zone: ϕlocal < 0.6). It was found that for the cool NDFs, the majority of low-temperature heat release was primarily produced from the rich-reaction-zone, while for the cool IDF, the lean-reaction-zone dominated the overall heat release.

\[
ϕ_{\text{local}} = \frac{\sum_{i=1}^{N} [(2m + n/2)X_i]}{\sum_{i=1}^{N} (X_i)}
\]

Additionally, these two reaction zones were similar in its chemical physics and pathways. The low-temperature chain branching reactions, including reactions (R264), (R272), (R274), (R141), as well as (R31) were dominant in the heat production. In either the lean-side or rich-side HRR-peaking location of either NDFs or IDFs, the reaction (R264) that is temperature-irrelevant was always the most important for heat release. Additionally, regardless of the cool NDF or IDF, reactions (R31), (R274), and R273 were important for the rich-side HRR in decreasing order of significance following reaction (R264), while with respect to the lean-side HRR, the significance order of the reactions following reaction (R264) was (R272), (R240), and R31. This implies that the low-temperature heat production with associated chemistry and pathways would probably rely on stoichiometry, rather than the temperature.

\[
\begin{align*}
\text{HCO} + \text{O}_2 &= \text{CO} + \text{HO}_2 \\
\text{CH}_2\text{OCH}_3 + \text{OH} &= \text{CH}_3\text{OCH}_2 + \text{H}_2\text{O} \\
\text{CH}_2\text{OCH}_2\text{H} + \text{O}_2 &= \text{CH}_3\text{OCH}_2\text{O}_2 \\
\text{CH}_2\text{OCH}_2\text{O}_2\text{H} &= \text{OH} + \text{CH}_2\text{O} + \text{CH}_3\text{O} \\
\text{O}_2\text{CH}_2\text{OCH}_2\text{O}_2\text{H} &= \text{HO}_2\text{CH}_2\text{OCHO} + \text{OH}
\end{align*}
\]

By contrast, in the hot-flame condition regardless of NDF or IDF configuration, the HRR curve was always unimodal, with the ambient-side HRR peak vanished, as Figure 3a shows. The high-temperature exothermic reactions, including (R33: CH3 + H (+M) = CH4 (+M)), (R48: CH3 + O = CH2O + H), and (R29: CO + OH = CO2 + H), and the endothermic reaction (R1: H + O2 = O = O + OH) were dominated for the hot-flame heat release.

It is interesting to note that in either the hot or cool flame condition, the IDFs had the feature of enriched oxygen concentration in the preheating zone with respect to the burner surface oxygen level, as Figures 3b and 4b show. On the contrary, the preheating zone of the NDFs did not exhibit the oxygen enrichment behavior. The oxygen enrichment in the IDF configuration will be explained in the following. The reaction pathway analysis indicates that the oxygen enrichment phenomenon in the preheating zone of the IDFs was due to oxygen production through the radical HO2 in this area. More specifically, in the flame front of hot or cool IDFs, the majority of oxidized O2 molecules were converted to HO2 radical by reaction (R31), which accelerates with an increasing temperature. Then, the product HO2 was transported inwardly to the preheating zone by molecular diffusion, where HO2 radicals were reconverted to O2 molecules through reaction (R17), which is prevailing at the low-temperature condition due to its negative activation energy.
HO₂ + OH = H₂O + O₂

(R17)

It is analyzed that in the cool-flame condition, more O₂ molecules will be produced through reaction R17 because of its depressed temperatures, so the cool IDF had a larger oxygen enrichment degree in the preheating zone than the hot IDF, as Figures 3b and 4b show. The oxygen enrichment feature in the preheating zone versus the source oxygen level in the carbon element was converted to CO₂, while in the cool-flame condition, it was converted to CO. In the cool-flame condition, the IDFs had enhanced CO concentrations and a depressed CO₂ concentration, in comparison with the NDFs. This phenomenon was ascribed to the competing low-temperature reaction pathways during the fuel decomposition process, as discussed in the following.

3.2. Low-Temperature Kinetics of DME in the NDF and IDF Geometries

In this work, it was found that the low-temperature reaction pathway in the cool IDF condition was nearly consistent with that in the cool IDF condition. Figure 6 and Table 1 show the prevailing low-temperature chain branching and termination pathways in the spherical NDF/IDF geometry.

Figure 6. Low-temperature prevailing branching and termination pathways of DME in the spherical NDF/IDF geometry.

| Table 1. Prevailing Low-Temperature Chain Branching and Termination Pathways in the DME NDFs/IDFs |
|---------------------------------------------------------------|
| reaction pathway | reaction no. |
|---------------------------------------------------------------|
| branching | |
| CH₃OCH₃ + OH = CH₃CH₂O + H₂O | (R240) |
| CH₃OCH₃ + O₂ = CH₃OCH₂O₂ | (R264) |
| CH₃OCH₂O₂ = CH₃OCH₂O₂H | (R271) |
| CH₃OCH₂O₂H + O₂ = O₂CH₃CHOCH₂O₂H | (R273) |
| O₂CH₃CHOCH₂O₂H = HO₂CH₃CHOHO + OH | (R274) |
| HO₂CH₃CHOHO = OCH₃CHOHO + OH | (R275) |
| termination | |
| CH₃OCH₂O₂H = OH + CH₂O + CH₃O | (R272) |
| CH₂O + OH = HCO + H₂O | (R44) |
| HCO + O₂ = CO + H₂O | (R31) |
| HO₂ + HO₂ = H₂O₂ + O₂ | (R19) |

form O₂QOOH (i.e., O₂CH₂OCH₂O₂H), which subsequently loses one OH through reaction (R274) to form O₂Q′OOH (i.e., HO₂CH₂CHO) and then another OH through reaction (R275) to form QOOH (i.e., OCH₂CHOHO). Next, QOOH is transformed to HOCH₂OCO through the isomerization reaction (R276). Finally, HOCH₂OCO will decompose into smaller molecules and final products (such as CO and CO₂) via reactions (R277) and (R278). Since reaction (R277) characterized by a weaker activation energy was much more competitive than reaction (R278), a considerable fraction of HOCH₂OCO decomposed into CO rather than into CO₂. This explained why the CO emission was higher than CO₂ in the cool NDF/IDF condition, as Figure 4c,d shows. Additionally, the OH radical played a vital role in cool-flame chemistry, which controlled the overall supply of fuel radical R. It can be seen in Figure 6 that the prevailing low-temperature branching pathway (DME → R → RO₂ → QOOH → O₂QOOH → Q'OQ'O) consumes one OH in the beginning and produces two OHs at the end, initiated from reaction (R240) and continued by (R264), (R271), (R273), (R274), and (R275) in sequence. Moreover, the oxygen addition reactions (R264) and (R273), which were two reactions of most importance in the low-temperature decomposition process, had the temperature-irrelevant nature owing to their zero activation energy. This reveals two important findings: First, the cool-flame branching chemistry of DME was characterized by weaker temperature dependence. Second, the branching rate is highly sensitive to the oxygen concentration; it accelerates with the increment in the oxygen level considerably.

Meanwhile, there exists a competing termination pathway that starts from reaction (R272), in which QOOH is converted to two CH₂O and one OH radical. Then, the two CH₂O products can be consumed by two OH radicals and produce HCO and the product H₂O via the reaction (R44). The reaction sequence including (R272) and (R44) are the prevailing termination mechanism in the current cool-flame condition since it consumes two OHs in the beginning but produces just one OH at the end. Additionally, when the temperature is sufficiently high, the termination rate may surpass the branching rate since the termination rate becomes increasingly faster with temperature, owing to the strong activation energy of reaction (R272). This indicates that the competition of the branching rate with termination rate may be responsible for the initiation of the NTC response. In addition, the HCO radical that is produced in the termination pathways...
is oxidized to the product CO and HO₂ through reaction (R31), and the HO₂ radicals can be converted to O₂ molecules via the termination reaction (R19) in the low-temperature condition.

In summary, it is concluded that the low temperature branching-termination competition was determined by the oxygen level and temperature. The branching rate increased with the oxygen level, and termination overwhelmed at high temperatures. The present study found that in either cool NDFs or IDFs, chain branching overwhelmed termination in the fuel-lean regions, while in the fuel-rich regions the termination overwhelmed. It is analyzed that the branching chemistry in the cool IDF condition was enhanced due to its higher oxygen concentration in the main flame zone versus that in the cool NDF condition, as Figure 4b shows. As a result, the cool IDFs had much higher concentrations of H₂O and CO than the corresponding cool NDFs, since these two products were mainly produced through the branching pathway.

3.3. Flammability Limits of DME in the NDF and IDF Geometries. Figure 7 shows the S-curve of DME spherical diffusion flame in NDF and IDF configurations, respectively. For DME that includes the low-temperature chemistry subset, its S-curve consists of a stable hot-flame branch, a stable cool-flame branch, and physically unstable branches, which cannot exist in the practical experiments. It is shown that the hot IDF temperature was significantly lower than the hot NDF in the same oxygen mole fraction (X₀₂) condition. Figure 8 displays the distributions of OH radical and some typical hydrocarbons in the hot IDF that was established at X₀₂ = 40%. The high-temperature radical OH can act as an indicator of the flame front. The depression of temperature in the hot IDF condition would be caused by the existence of unburned hydrocarbons (including CO, H₂, CH₄, and C₂ species), which reserve its chemical energy in the post-flame region. However, the present simulation indicates that the thermal loss that was reserved as chemical energy of unburned hydrocarbons, in the hot IDF condition, was less than 1.0% and was kept constant over a broad range. In the near-extinction condition, the thermal loss increased just to 1.8%. Therefore, the existence of unburned hydrocarbons in the post-flame region is not the controlling factor for lower temperatures of IDFs than NDFs. It is suggested that the hot-flame extinction was induced by thermal radiation. More specifically, Figure 9 shows that the hot IDFs had a much wider flammability range than the hot NDFs (X₀₂ = 23.2–100%); hence, the IDF combustion process was more stable than the NDF combustion.

Moreover, Figure 7 also shows that the cool NDF flammability range was X₀₂ = 7.9–77.9%, and it was much broader than the cool IDFs (X₀₂ = 4.0–29.0%). The lower flammability limit of the cool IDF was smaller than that of the cool NDFs. This is because as previously discussed, the cool-flame extinction was controlled by low-temperature kinetics, and its branching rate depended considerably on the oxygen level. Therefore, the cool IDF flame which had a higher oxygen concentration in its reaction front was more stable than the NDF counterpart. It is also noted that in either NDF or IDF geometry, the cool-flame chemistry could help to extend the fuel flammability range considerably. Furthermore, compared with the hot-flame condition, in the cool-flame condition the IDFs were more sensitive with respect to X₀₂ than the NDFs. Consequently, the IDFs had much better ignition performance than the NDFs, in the same oxygen level condition.

As noted earlier, the existence of cool-flame branch was primarily attributed to the abrupt expansion of the reaction zone in the low-temperature regime (shown in Figure 5), which caused the significant rise of the residence time. Hence, cool flames could be stably self-sustained although the reaction rates were depressed in the low-temperature condition.
Additionally, Figure 10 shows the evolvement of the cool-flame HRR on the S-curve in the space of normalized radius for NDFs and IDFs, respectively. It can be seen that when approaching the extinction tuning point on the S-curves (NDF: $X_{O_2} = 0.079$, IDF: $X_{O_2} = 0.04$), the lean-reaction-zone and rich-reaction-zone moved towards each other, and finally, these two reaction zones merged together, which resulted in a narrow reaction zone and thus the significant decrease of the residence time. Hence, the disappearance of the two-reaction-zone structure could serve as a judgment basis for the cool-flame instability.

4. CONCLUSIONS

This paper compares the DME combustion characteristics in spherical NDF and IDF configurations by numerical simulations that were performed with a detailed chemical mechanism and transport models. A broad range of oxygen mole fractions, from pure oxygen to pure inert, was considered to examine its impact on the flame dynamics. The main findings of this paper include the following:

(1) Regardless of NDF or IDF geometry, the heat release rate curve of DME in the hot-flame condition was unimodal, while that in the cool-flame condition was bimodal, with one peaking in the rich side and the other in the lean side. Additionally, the combustion progress of spherical hot NDFs or IDFs was controlled by diffusive mixing, while that of cool flames was controlled by low-temperature kinetics. Hence, the cool flames had characteristics far away from the equilibrium. Interestingly, the cool flames had the feature of double-combustion mode (i.e., premixed and nonpremixed combustion).

(2) Being rather distinct from the NDF counterpart, the DME IDFs had the combustion feature of oxygen enrichment with respect to the source oxygen level, regardless of the hot- or cool-flame condition. The oxygen-enriched characteristics associated with DME IDFs were ascribed to the $O_2$–$HO_2$ interconversion process occurring in the low-temperature preheating and high-temperature reaction front zones. The competition of low-temperature branching with termination was responsible for the distinct structure characteristics of NDFs and IDFs. The low-temperature branching rate of DME was positively dependent on the oxygen level, while its termination rate was enhanced with increasing temperature. Moreover, the low-temperature reaction pathway in the rich-reaction-zone was nearly consistent with that in the lean-reaction-zone in either cool NDF or IDF condition.

(3) The DME hot-flame extinction was induced by thermal radiation, and the cool-flame extinction was controlled especially by low-temperature branching kinetics. Compared with hot NDFs, it would be less effective to control the hot IDF combustion process by positive measures. However, combustion in the latter configurations was much more stable than the former. In either
NDF or IDF geometry, the cool-flame chemistry could help to extend the fuel flammability range considerably. The lower flammability limit of cool IDFs with a more rapid low-temperature branching rate was smaller than the cool NDFs. The IDFs had much better ignition performance than its NDF counterpart in the same oxygen level condition. In addition, the disappearance of the two-reaction-zone structure could serve as a judgment basis for the cool-flame instability.

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**Notes**
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### REFERENCES

1. Oh, J.; Noh, D. Flame characteristics of a non-premixed oxy-fuel jet in a lab-scale furnace. *Energy* 2015, 81, 328–343.
2. Lee, S.; Padilla, R.; Dunn-Rankin, D.; Pham, T.; Kwon, O. C. Extinction limits and structure of counterflow nonpremixed H2O-laden CH4/air flames. *Energy* 2015, 93, 442–450.
3. Gao, X.; Duan, F.; Lim, S. C.; Yip, M. S. NOx formation in hydrogen–methane turbulent diffusion flame under the moderate or intense low-oxygen dilution conditions. *Energy* 2013, 59, 559–569.
4. Dong, L. L.; Cheung, C. S.; Leung, C. W. Combustion optimization of a port-array inverse diffusion flame jet. *Energy* 2011, 36, 2834–2846.
5. Dong, L. L.; Cheung, C. S.; Leung, C. W. Heat transfer optimization of an impinging port-array inverse diffusion flame jet. *Energy* 2013, 49, 182–192.
6. De la Cruz-Avilá, M.; Martínez-Espinosa, E.; Polupan, G.; Vicente, W. Numerical study of the effect of jet velocity on methane-oxygen confined inverse diffusion flame in a 4 Lug-Bolt array. *Energy* 2017, 141, 1629–1649.
7. Baigmohammadi, M.; Tabejamaat, S.; Zarvandi, J. Numerical study of the behavior of methane-hydrogen/air pre-mixed flame in a micro reactor equipped with catalytic segmented bluff body. *Energy* 2015, 85, 117–144.
8. Sobiesiak, A.; Wenzell, J. C. Characteristics and structure of inverse flames of natural gas. *Proc. Combust. Inst.* 2005, 30, 743–749.
9. Choi, S.; Kim, T. Y.; Kim, H. K.; Koo, J.; Kim, J. S.; Kwon, O. C. Properties of inverse nonpremixed pure O2/CH4 coflow flames in a model combustor. *Energy* 2015, 93, 1105–1115.
10. Sze, L. K.; Cheung, C. S.; Leung, C. W. Appearance, temperature, and NOx emission of two inverse diffusion flames with different port design. *Combust. Flame* 2006, 144, 237–248.
11. Choy, Y. S.; Zhen, H. S.; Leung, C. W.; Li, H. B. Pollutant emission and noise radiation from open and impinging inverse diffusion flames. *Appl. Energy* 2012, 91, 82–89.
12. Mikofski, M. A.; Williams, T. C.; Shaddix, C. R.; Fernandez-Pello, A.; Blevins, L. G. Structure of laminar sooting inverse diffusion flames. *Combust. Flame* 2007, 149, 463–478.
13. Koth, A.; Saad, H. A comparison of the thermal and emission characteristics of co and counter swirl inverse diffusion flames. *Int. J. Therm. Sci.* 2016, 109, 362–373.
(14) De Giorgi, M.; Sciolti, A.; Ficarella, A. Application and comparison of different combustion models of high pressure LOX/CH4 jet flames. *Energies* 2014, 7, 477–497.

(15) Xu, Z.; Duan, X.; Liu, Y.; Deng, B.; Liu, J. Spray combustion and soot formation characteristics of the acetone-butanol-ethanol/diesel blends under diesel engine-relevant conditions. *Fuel* 2020, 280, 118483.

(16) Zhang, Y.; Sunderland, P. B. Quenching limits of inverse diffusion flames with enriched oxygen. *Combust. Flame* 2015, 162, 2743–2745.

(17) Kaplan, C. R.; Kailasananth, K. Flow-field effects on soot formation in normal and inverse methane–air diffusion flames. *Combust. Flame* 2001, 124, 275–294.

(18) Mahesh, S.; Mishra, D. P. Flame stability limits and near blowout characteristics of CNG inverse jet flame. *Fuel* 2015, 153, 267–275.

(19) Mahesh, S.; Mishra, D. P. Effect of air jet momentum on the topological features of turbulent CNG inverse jet flame. *Fuel* 2019, 241, 1068–1075.

(20) Zhen, H. S.; Leung, C. W.; Cheung, C. S. Thermal and emission characteristics of a turbulent swirling inverse diffusion flame. *Int. J. Heat Mass Transf.* 2010, 53, 902–909.

(21) Ju, Y. G.; et al. Dynamics of cool flames. *Prog. Energy Combust. Sci.* 2019, 75, 100787.

(22) Deng, S.; Han, D.; Law, C. K. Ignition and extinction of strained nonpremixed cool flames at elevated pressures. *Combust. Flame* 2017, 176, 143–150.

(23) Liang, W.; Law, C. K. Extended flammability limits of n-heptane/air mixtures with cool flames. *Combust. Flame* 2017, 185, 75–81.

(24) Zhao, P.; Law, C. K. The role of global and detailed kinetics in the first-stage ignition delay in NTC-affected phenomena. *Combust. Flame* 2013, 160, 2352–2358.

(25) Wang, Z.; Liu, H.; Reitz, R. D. Knocking combustion in spark-ignition engines. *Prog. Energy Combust. Sci.* 2017, 61, 78–112.

(26) Zhang, P.; Kang, Y.; Wu, Z.; Lu, X.; Wang, Q.; Mei, L. Effect of dimethyl ether addition on soot formation dynamics of ethylene opposed-flow diffusion flames. *Ind. Eng. Chem. Res.* 2019, 58, 8370–8386.

(27) Kee, R. J., Grcar, J. F., Smooke, M. D., Miller, J. A. A Fortran program for modeling steady laminar one-dimensional premixed flames; Report No. SAND85–8240, Sandia National Laboratories, 1985.

(28) Chen, J.; Kang, Y.; Zou, Y.; Cui, K.; Zhang, P.; Liu, C.; Ma, J.; Lu, X.; Wang, Q.; Mei, L. A numerical study on near-limit extinction dynamics of dimethyl ether spherical diffusion flame. *Fuel Process. Technol.* 2019, 185, 79–90.

(29) Zhao, P.; Kang, Y.; Huang, X.; Peng, S. Study on effect of hydrogen addition on extinction dynamics of dimethyl ether spherical diffusion flame. *Int. J. Hydrogen Energy* 2020, 45, 11350–11367.

(30) Kang, Y.; Wang, Q.; Zhang, P.; Liu, C.; Lu, X.; Wang, Q. Study on flame structure and extinction mechanism of dimethyl ether spherical diffusion flames. *Energy* 2020, 193, 116786.

(31) Christiansen, E. W.; Tse, S. D.; Law, C. K. A computational study of oscillatory extinction of spherical diffusion flames. *Combust. Flame* 2003, 134, 327–337.

(32) Yoo, S. W.; Christiansen, E. W.; Law, C. K. Oscillatory extinction of spherical diffusion flames: Micro-buoyancy experiment and computation. *Proc. Combust. Inst.* 2003, 29, 29–36.

(33) Tang, S.; Chernovskiy, M. K.; Im, H. G.; Atreya, A. A computational study of spherical diffusion flames in microgravity with gas radiation Part I: Model development and validation. *Combust. Flame* 2010, 157, 118–126.

(34) Tang, S.; Im, H. G.; Atreya, A. A computational study of spherical diffusion flames in microgravity with gas radiation. Part II: Parametric studies of the diluent effects on flame extinction. *Combust. Flame* 2010, 157, 127–136.

(35) Kee, R. J.; Rupley, F. M.; Miller, J. A.; Coltrin, M. E.; Grcar, J. F.; Meeks, E.; Moffat, H. K.; Lutz, A. E.; Lewis, G. D.; Smooke, M. D. et al. *Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics*; Report No. SAND89-8009B; Sandia National Laboratories, 1989.

(36) Zhao, Z.; Chaos, M.; Kazakov, A.; Dryer, F. L. Thermal decomposition reaction and a comprehensive kinetic model of dimethylether. *Int. J. Chem. Kinet.* 2008, 40, 1–18.