Study of Diffusion Cool Flames of Dimethyl Ether in a Counterflow Burner under a Wide Range of Pressures

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ABSTRACT: Cool flames have been studied for more than three centuries since the first observation. However, there are few achievements on the effects of the pressure on cool flames. In this work, a diffusion cool flame has been for the first time established using a counterflow configuration under a wide range of pressures. Dimethyl ether is used as the fuel because its low-temperature chemistry has been well tested. The pressure range of the experiments is from 0.05 to 0.15 MPa. The extinction limits, flame temperatures, and combustion products have been measured and simulated. In general, the reactivity of cool flames is stronger with increasing pressure. Specifically, at a fixed fuel mass fraction, the cool flame has a higher extinction strain rate, temperature, and concentration of products under higher pressure. However, the enhancement effect decreases with the increase of pressure. Interestingly, it was observed that the flame became thicker when the pressure increased. Moreover, the cool flame would deflagrate and transform to a hot flame when the pressure exceeds a certain value. The model captures the trends well but underpredicts the extinction limits and overpredicts the flame temperatures and product concentration. Path flux analyses and heat release rate analyses were carried out. It was found that the main heat release reactions are the reactions with CH$_3$OCH$_2$ radicals under low pressure, and CO prefers to form CO$_2$ indirectly through HOCHO radicals. The study advances the understanding of cool flames in a wide range of pressures and provides experimental data for the improvement of the models.

1. INTRODUCTION

Combustion is a complex process known to take place in the form of free radical chains, just as hydrocarbon produces many intermediate free radicals first and eventually CO$_2$ and H$_2$O. The type of intermediate free radicals is strongly related to the temperature.$^1$ Therefore, the combustion process at different temperatures should be discussed separately. Cool flames occur in the first stage of the combustion process of most hydrocarbons and related compounds. Their temperature is not as high as that of a hot flame, usually only around 800 K, and related to pressure and fuel characteristics. Meanwhile, the combustion process develops with a negative temperature coefficient (NTC) of reaction rate in the temperature range of the occurrence of cool flames, which makes cool flames a rather unique process.$^2$ Since Davy$^3$ first observed cool flames in 1817, more and more scholars have paid attention to cool flames due to their importance in various aspects. For example, cool flames play a key role in advanced engines due to partial or full fuel and air premixing at higher pressures.$^4$–$^6$ Specifically, Fish demonstrated that the cool flame chemistry under engine conditions was not different from that at low pressures.$^7$ Cool flames controlled the subsequent hot ignition, which most probably results from branching by intermediates generated during cool flame reactions. In addition, the timescales of low-temperature ignition are comparable at higher pressures. Moreover, the cool flame also plays a critical role in engine knocking due to the increased heat release rate as pressure increases.$^8$–$^9$ Knock rating of fuels has been rationally linked to the isomerization of peroxy radicals in cool flame reactions.$^{10}$

Dimethyl ether (DME) is regarded as a potential new fuel in the future due to a wide range of sources.$^{11}$–$^{14}$ Soot is less generated during combustion due to the absence of the carbon–carbon bond in the molecular structure. These characteristics have attracted great attention, especially using the counterflow configuration. A counterflow burner offers a well-defined, almost one-dimensional flame state, which offers a stretch quantitative study of the structure and dynamics of cool flames and is easy to diagnose.$^{15}$–$^{17}$ However, most previous studies$^{15}$–$^{17}$ have focused on the combustion characteristics of the fuels blended with DME at atmospheric pressure, which include premixed or non-
premixed combustion. Reuter et al. established neat DME-premixed cool flames using a counterflow burner and measured extinction and ignition limits quantitatively. It was seen that stable premixed cool flames can exist in a wide range of equivalent ratios and extinction rates. Especially, at low fuel mass fractions, the flammability limit of cool flames is much wider than that of hot flames. Zhao studied the coupling of the cool flame chemistry with convection–diffusion transport. It was found out that the cool flame regime is sensitive to the dilution in the flow, and the cool flame becomes dimmer under leaner conditions. The results also showed that the speeds of the neat DME-premixed cool flame are relatively low and much less sensitive to the equivalence ratio. Reuter and coworkers successfully established a self-sustaining partially cool flame in a counterflow burner with ozone. The double cool flame is observed and showed the possibility to establish both diffusion and premixed cool flames at increased fuel loading and equivalence ratios. Zhang et al. used the counterflow burner to establish the non-premixed cool flame for a mixture of DME and methane with or without ozone. It was demonstrated that methane addition to DME lowers the cool flame extinction limit at a fixed fuel mass fraction. The addition of ozone greatly increases the extinction limit of cool flames but reduces the sensitivity of the limit to the fuel mass fraction. Deng also performed an experimental study on the coupling of the NTC chemistry and transport in mixtures of DME/air. The effects of varying strains on non-premixed flame ignition were investigated and agreed with previous simulation results.

In contrast, there are few studies on the effect of pressure on cool flames, especially using the counterflow configuration. Sun et al. studied the impact of the nonequilibrium plasma on the low-pressure non-premixed flame using n-heptane and DME in a counterflow burner. It was seen that cool flames and hot flames could both exist within a nanosecond repetitive plasma discharge at 72 Torr. The cool flame could only be maintained with the help of an in situ plasma, which offers active radicals to accelerate the low-temperature chemistry. Deng measured the ignition and extinction temperatures of non-premixed DME cool flames under a high pressure of up to 5 atm. Hysteretic ignition and extinction behavior of the non-premixed cool flame was reported. The increase in ambient pressure or the oxygen concentration would promote the heat release and thus extend the hysteretic window between ignition and extinction. Non-premixed cool flames under negative pressure were not studied until 2012; Nayagam and coworkers conducted the experiments of n-heptane droplets on the International Space Station. The data of burning rates and extinction diameters were validated and found to be closer to cool flame parameters rather than to the corresponding hot flame parameters in the literature.

However, the effects of pressure on cool flames are not fully understood yet, especially on the extinction limit, flame temperature, and combustible products. Because the non-uniformities in the flow and the mixture temperature and composition invariably exist in realistic systems, the coupling between the NTC chemistry and convective–diffusive transport process needs to be considered. In this work, a counterflow configuration was used to study the diffusion cool flame of DME in a wide range of pressures, and the experimental results were compared with the simulation results. The study is conducive to a better understanding of low-temperature chemistry, improving the accuracy of the corresponding model and providing a theoretical basis for the application of dimethyl ether in a wide pressure range.

2. RESULTS AND DISCUSSION

2.1. Extinction Limits of DME Cool Flames under Different Pressures. Figure 1 shows the results of the measurements and simulations of extinction strain rates of DME diffusion cool flames under different pressures. In general, the extinction strain rates increase with the pressure. The model predicts the trend of extinction strain rates well but underpredicts overall. The gap between experimental data and simulation results decreases with the increase of pressure. In terms of the fuel mass fraction, the influence of the pressure is more significant in higher fuel mass fractions, which means that the slope of the lines in Figure 1 increases as the pressure increases. Moreover, the increase of the extinction strain rate is more obvious for the same fuel mass fraction under higher pressure. Similarly, the model captures the general trend. The gap between the simulation results and the experimental data is further reduced, which indicates that the model may perform better under higher pressures. However, it is found in the experiments that the flame becomes thinner first and then thicker within the experimental pressure range, and a higher fuel mass fraction was needed to establish a cool flame under higher pressure. This is because the cool flames of DME under high pressure are more susceptible to instabilities and low-temperature chemistry. Figure 2 compares the flames with the same strain rate but under different pressures. Moreover, consistent with the simulation results of previous scholars, the cool flames deflagrate into hot flames under elevated pressure.
The process of the transition from cool to hot flames as the pressure increases can be seen in the video, which is available in the Supporting Information.

### 2.2. Temperatures of DME Cool Flames under Different Pressures

Figure 3 compares the measured and simulated results of temperature distribution of DME cool flames with the same strain rate under different pressures.

![Figure 3](image)

**Figure 3.** Comparison of the measured (symbols) and simulated (lines) results of the temperature distribution of the DME cool flames with the same strain rate under different pressures.

simulated results of temperature distribution of DME cool flames under a wide pressure range. The experimental results indicate that the cool flame is closer to the oxidizer side under experimental pressure conditions. The temperature measurements reflect the same trend as the extinction strain rate. With the higher pressure, the flame with the same strain rate has the higher temperature. However, with the increase of the pressure, this effect is less significant. The flame temperature increases 30 K from 0.05 to 0.1 MPa but only 13 K from 0.1 to 0.15 MPa.

It is interesting that the reaction zone of the flame seems to be wider above atmospheric pressure. Unlike the simulation, the flame temperature distribution measured in the experiment gets wider when the pressure increases. This is consistent with the phenomenon of the flame regime observed in the experiment. The reasons may be that a higher pressure makes the DME molecules move more violently and the increase of the temperature intensifies this effect. On the other hand, the pressure may make the reaction area larger. It is also found out that the cool flames with an excess fuel mass fraction transform to hot flames as the pressure exceeds a certain value.

### 2.3. Products of DME Cool Flames under Different Pressures

Due to the detection capability of our GC system, only CO and CO$_2$ were measured at atmospheric and elevated pressures. As shown in Figure 4, the increases of pressure make the cool flames of DME produce more CO, from 1.20% (mole fraction) at 0.05 MPa to 1.35% at 0.125 MPa and then to 1.56% at 0.15 MPa. From the concentration distribution of CO, it is seen that the flame tends to move to the fuel side with the increase of pressures. Consistent with the previous study, this is related to the buoyancy of the fuel, and the buoyancy effect increases as the pressure increases. Above the atmospheric pressure, the model is closer to the experimental value with the increase of pressure. The bottom half of Figure 4 shows the distributions of CO under low pressure. The measurements of CO$_2$ are not displayed here because it only responds at the peak of 0.08 MPa when measured by GC due to the low concentration. Similarly, the increase of pressures under low pressure still has an effect on CO, from 0.63% at 0.05 MPa to 0.84% at 0.08 MPa. The position of the CO peak concentration does not change obviously, which is also related to the stability of the cool flame of DME under low pressure. The accuracy of prediction at low pressure is worse than that at elevated pressure.

### 2.4. Path Flux Analysis of DME Cool Flames under Different Pressures

It is seen that the cool flame of DME gets more active with the increase of pressure. Therefore, the path flux analyses under different pressures were carried out to understand the observed trend. Figure 5 shows the reaction pathways of DME cool flames under different pressures. DME is consumed preferentially with OH, O, and HO$_2$ radicals through H-abstraction to generate the CH$_2$OCH$_2$ radical. As the primary product, the reaction of CH$_3$OCH$_2$ largely determines the oxidation process of DME. Obviously, with the increase of pressure, the generation amount of the CH$_3$OCH$_2$ radical increases, and then, part of the CH$_3$OCH$_2$ radicals that generate formaldehyde increase. This reaction behavior of CH$_3$OCH$_2$O radicals isomerize to form hydroperoxyl alkyl radicals, CH$_3$OCH$_2$O-H. The reaction behaviors of CH$_3$OCH$_2$O radicals are another key step in the low-temperature oxidation of DME. CH$_2$OCH$_2$O-H mainly produces formaldehyde directly or indirectly in the pathways CH$_2$OCH$_2$O-H = CH$_2$O + CH$_2$O + OH and CH$_3$OCH$_2$H = C$_2$H$_4$O$_2$ + OH, C$_2$H$_4$O$_2$ = CH$_2$O + CH$_2$O$_2$.

The second oxygen addition reaction CH$_3$OCH$_2$O-H + O$_2$ = O$_2$,CH$_3$OCH$_2$O-H is favored at higher pressure. The reaction pathways of DME cool flames involve the sequence O$_2$,CH$_3$OCH$_2$O-H radical to the HO$_2$,CH$_2$OCHO radical to the OCH$_2$CHO radical, which are more active under high pressures as expected. The proportion of CH$_3$OCH$_2$O-H forming O$_2$,CH$_3$OCH$_2$O-H increases with the increasing pressure even if the total reaction rate of CH$_3$OCH$_2$H is larger under high pressures. In the process of formaldehyde formation from the sequence CH$_2$OCH$_2$O-H to OCH$_2$CHO and then to OCH$_2$OCHO, more OH radicals are produced than those directly or indirectly from CH$_3$OCH$_2$H. This makes sense that the pressure increase makes the low-temperature activity of the flame stronger. Almost all CH$_3$O undergoes H-abstraction reactions with OH, O, CH$_3$O, and HO$_2$ radicals to form HCO radicals. The HCO radical then...
reacts with oxygen to form CO. CO$_2$ has generated through CO directly or HOCHO radicals indirectly. It is not surprising that the rate of CO$_2$ production increases with increasing pressure. However, CO tends to produce HOCHO radicals rather than directly convert to CO$_2$ at 0.05 MPa. This means that the sequence CO to HOCHO to CO$_2$ is more likely to occur at lower pressures. There is one more intermediate product in the reaction process, so the amount of CO$_2$ is less, which is consistent with the phenomenon in the experiments.

Both experiments and simulations show that the temperature increases with higher pressure. As can be seen in Figure 6, the main heat release reactions under lower pressures are more related to fuel radicals. Typically, CH$_3$OCH$_3$ + OH = CH$_3$OCH$_2$ + H$_2$O and CH$_3$OCH$_2$ + O = CH$_3$OCH$_2$O$_2$ contribute more to heat release under 0.05 MPa. It implies that the flame temperature changes more greatly under lower pressures when the fuel mass fraction increases. Several detailed important low-temperature radicals and CH$_3$O path flux analyses are given to reveal the reason.

As an important group in low-temperature chemistry, the OH radical path flux analysis is shown in Figure 7. The main consumption way of the OH radical is the reaction CH$_3$OCH$_3$ + OH = CH$_3$OCH$_2$ + H$_2$O, which is more obvious when the pressure decreases. Figure 8 shows the path flux of the O radical, indicating that the reaction CH$_3$OCH$_3$ + O = CH$_3$OCH$_2$ + OH is the main consumption pathway of O.
radicals, tends to occur at lower pressure. Although there is still a gap in the total reaction rate, the trend makes this reaction comparable at different pressures. This is why the main reactions in heat release under low pressures are more related to fuel radicals. With the higher pressure, more CH$_2$O is produced, as shown in Figure 9. Meanwhile, over 98% of CH$_2$O reacts with O or OH radicals to produce HCO radicals. Figure 10 reveals that more than 90% HCO radicals are generated by CH$_2$O, which means that the difference of the HCO concentration becomes greater under different pressures. Almost all HCO radicals generate CO through HCO + O$_2$ = CO + HO$_2$, which confirms that this reaction has a great difference under different pressures as the dominant reaction. It is no accident that HCO + O$_2$ = CO + HO$_2$ is the main way to form the HO$_2$ radical, but its contribution is greater with the decrease of the pressure. However, it is different from the relationship between the HCO radical consumption and the pressure. This is due to the decreased flux toward the H$_2$O + OH = HO$_2$ + H$_2$O with decreasing pressure, as shown in Figure 11. Specifically, the 0.05 MPa case observes the reaction reduced by 5.4% compared to the 0.15 MPa case. This is reflected in the HRR, that is, this reaction contributes little at 0.05 MPa.

To further understand the cool flames of DME at different pressures, Figure 12 shows the distributions of the CH$_3$OCH$_2$ radical under three pressures; the rest of the species are at 0.15 MPa. Obviously, as the pressure increases, there are multiple peaks in the concentration of the CH$_3$OCH$_2$ radical, indicating the rapid response of the fuel radical under high pressures. Before the stagnation plane, the fuel goes through a low-temperature chain reaction to form CH$_3$O. At the same time, not only does the CH$_3$OCH$_2$ radical adds to oxygen to produce CH$_2$O directly but also the subsequent hydroperoxy alkyl radical pyrolysis gives the bulk of CH$_2$O, which can be seen in Figure 9. After the stagnation plane, the diffused fuel continues through low-temperature chain pathway reactions to generate low-temperature chemistry important species such as hydroperoxy peroxy alkyl radicals and ketohydroperoxide compounds.

3. CONCLUSIONS

In this study, the cool flame is for the first time established with the help of O$_3$ under both negative and elevated pressures. The diffusion cool flames of DME have been investigated on a counterflow burner from 0.05 to 0.15 MPa. The extinction strain rates, flame temperatures, and combustion products of cool flames have been measured and simulated, which indicate that the reactivity of cool flames is promoted by the increasing pressures. Moreover, it was found that the cool flames of DME turn into hot flames with excessive pressure, and this process was recorded using a camera. During the pressure increasing from 0.05 to 0.15 MPa, the flame becomes thinner first and then thicker. This phenomenon also occurs in the subsequent measurements of temperature and products. With the higher pressure, the extinction limits, flame temperatures, and concentration of products all increase in general. The HPMech-v3.3 mechanism can capture the trends well but still underpredict the extinction strain rates and overpredict the combustion products.

The main heat release reactions under lower pressures are more related to reactions with fuel radicals. A path flux analysis reveals that OH radicals prefer to react with DME under low pressures. Although the concentration of HCO radicals varies greatly due to the difference of CH$_2$O under different pressures, HCO + O$_2$ = CO + HO$_2$ is still the dominant reaction in heat release. At low pressure, CO tends to form CO$_2$ indirectly through HOCHO radicals.
4. EXPERIMENTAL SETUP AND NUMERICAL METHODS

The experimental setup in this work is a counterflow burner suitable for a wide pressure range. The schematic of the experimental system is shown in Figure 13. The distance between the two nozzles is 9.5 mm, both of which are 13 mm in diameter. The upper nozzle issues a mixture of DME and N\textsubscript{2}, which is heated to 550 ± 5 K. The bottom nozzle issues a mixture of O\textsubscript{2} and O\textsubscript{3} at 300 K. An ozone generator uses pure O\textsubscript{2} to produce O\textsubscript{3}. The O\textsubscript{3} concentration is detected using an ultraviolet ozone concentration analyzer with an accuracy of ±3% FS. The molar percentage of O\textsubscript{3} is held at 3.5%.

Meanwhile, concentric curtain flows are set to reduce the interference of ambient gases on flames through flow and heat transfer. All experiments are completed in a combustion chamber. With the help of O\textsubscript{3}, the self-sustaining cool flame of DME is established in a wide pressure range. Although the cool flame of DME is very weak, it can be captured using a digital CMOS camera (Hamamatsu C11440-36U). The temperature measurements are performed using a B-type thermocouple (Omega P30R-008). A microprobe with an inner diameter of 0.2 mm is used to collect combustion products. The products are measured using a gas chromatograph (Agilent 7890B) with an uncertainty of <5%. The strain rate is maintained at 70.6 s\textsuperscript{-1} in the process of the measurements of temperatures and combustion products.

The numerical simulations are performed using the CHEMKIN/OPPDIF code. The adaptive gradient and curvature limits are both set at 0.05 after the grid independence test. The selected DME chemical kinetic model is HPMech-v3.3 from Princeton University, which contains 130 species and 893 reactions.

1. ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01362.

- Video of DME diffusion cool flames from 0.05 to 0.15 MPa (MP4)
- Video of cool flame deflagration process (MP4)

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Notes
The authors declare no competing financial interest.

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REFERENCES
(1) Ju, Y. Understanding cool flames and warm flames. Proc. Combust. Inst. 2020, 38, 83–119.
(2) Lignola, P. G.; Reverchon, E. Cool flames. Prog. Energy Combust. Sci. 1987, 13, 75–96.
(3) Davy, H. Some new experiments and observations on the combustion of gaseous mixtures, with an account of a method of preserving a continued light in mixtures of inflammable gases and air without flame. Philos. Trans. R. Soc. London 1817, 107, 77–85.
(4) Kalghatgi, G. T.; Aramacı, S.; Arabia, S. Developments in internal combustion engines and implications for combustion science and future transport fuels. Proc. Combust. Inst. 2015, 35, 101–115.
(5) Kalghatgi, G. T.; Hildingson, L.; Harrison, A. J.; Johansson, B. Autoignition quality of gasoline fuels in partially premixed combustion in diesel engines. Proc. Combust. Inst. 2011, 33, 3015–3021.
(6) Musculus, M. P. B.; Miles, P. C.; Pickett, L. M. Conceptual models for partially premixed low-temperature diesel combustion. Prog. Energy Combust. Sci. 2013, 39, 246–283.
(7) Fish, A.; Read, I. A.; Alfeleck, W. S.; Haskell, W. W. The controlling role of cool flames in two-stage ignition. Combust. Flame 1969, 13, 39–49.
(8) Amann, M.; Alger, T.; Darius, M. The effect of EGR on low-speed pre-ignition in boosted SI engines. SAE Int. J. Engines 2011, 4, 235–245.
(9) Wang, Z.; Liu, H.; Song, T.; Qi, Y.; He, X.; Shuai, S.; Wang, J. Relationship between super-knock and pre-ignition. Int. J. Engine Res. 2015, 16, 166–180.
(10) Walsh, A. D. The knock rating of motor fuels. Symp. Int. Combust. 1963, 9, 1046–1055.
(11) Arcoumanis, C.; Bae, C.; Crookes, R.; Kinoshita, E. The potential of di-methyl ether (DME) as an alternative fuel for compression-ignition engines: A review. Fuel 2008, 87, 1014–1030.
(12) Adachi, Y.; Komoto, M.; Watanabe, I.; Ohno, Y.; Fujimoto, K. Effective utilization of remote coal through dimethyl ether synthesis. Fuel 2000, 79, 229–234.
(13) Semelsberger, T. A.; Borup, R. L.; Greene, H. L. Dimethyl ether (DME) as an alternative fuel. J. Power Sources 2006, 156, 497–511.
(14) Jin, T.; Wu, Y.; Wang, X.; Luo, K. H.; Lu, T.; Luo, K.; Fan, J. Ignition dynamics of DME/methane-air reactive mixing layer under reactivity controlled compression ignition conditions: Effects of cool flames. Appl. Energy 2019, 249, 343–354.
(15) Herrmann, F.; Jochem, B.; Oßwald, P.; Cai, L.; Petsch, H.; Kose-Höinghaus, K. Experimental and numerical low-temperature oxidation study of ethanol and dimethyl ether. Combust. Flame 2014, 161, 384–397.